

Статья поступила в редакцию: 02.09.2026

Статья принята к публикации: 07.09.2026

Статья опубликована: 28.09.2026

УДК 661.86+553.65+338.2

DOI: 10.32743/UniTech.2026.150.9.23381

Processing of calcium nitrate solutions generated during nitric acid treatment of Central Kyzylkum phosphorites

Sultonov Bokhodir Elbekovich

doctor of Technical Sciences, Associate Professor

Namangan State University

Republic of Uzbekistan, Namangan

E-mail: bse-chemist-68@mail.ru

Giyasidinov Abduaziz Lutfidinovich

PhD, Associate Professor

Department of Chemical Engineering Namangan State Technical University

Republic of Uzbekistan, Namangan

Переработка растворов нитрата кальция, образующихся при азотнокислотной обработке фосфоритов Центральных Кызылкумов

Султонов Боходир Элбекович

д-р техн. наук, проф.

Наманганский государственный университет

Республика Узбекистан, г. Наманган

Гиясидинов Абдуазиз Лутфидинович

PhD, доц.

кафедры Химическая инженерия, Наманганский государственный технический университет

Республика Узбекистан, г. Наманган

Abstract

This study aimed to evaluate the processing of calcium nitrate solutions generated during nitric acid treatment of Central Kyzylkum phosphorites by cooling crystallization and evaporative concentration, and to determine technologically rational operating conditions for calcium nitrate recovery and concentration. A representative process solution containing 24.40 wt.% $\text{Ca}(\text{NO}_3)_2$ was used. The methodology comprised material-balance calculations based on 1000 g of the initial solution, stepwise cooling from +20 to -20 °C at 5 °C intervals, and evaporative concentration at

Библиографическое описание: Султонов Б.Э., Гиясидинов А.Л. Переработка растворов нитрата кальция, образующихся при азотнокислотной обработке фосфоритов Центральных Кызылкумов // Universum: технические науки : электрон. научн. журн. 2026. 9(150). URL: <https://7universum.com/ru/tech/archive/item/23381>

For citation: Sultonov B.E., Giyasidinov A.L. Processing of calcium nitrate solutions generated during nitric acid treatment of central kyzylkum phosphorites // Universum: Technical Sciences : electronic scientific journal. 2026. No. 9(150). Available at: <https://7universum.com/ru/tech/archive/item/23381>

atmospheric pressure. During cooling, the calculated recovery of calcium nitrate into the crystalline phase increased as temperature decreased. Between 0 and -15 °C, recovery rose from 59.74 to 94.21 %. Further cooling to -20 °C increased recovery only to 95.04 %, corresponding to an additional 2.03 g of $\text{Ca}(\text{NO}_3)_2$ equivalent per 1000 g of initial solution; therefore, cooling below -15 °C was considered economically inefficient under the investigated conditions. During evaporation, removal of 531.58 g of water increased the $\text{Ca}(\text{NO}_3)_2$ concentration from 24.40 to 52.09 wt.%, while approximately 37 wt.% was identified as a technologically relevant intermediate concentration for subsequent conversion processes. The results indicate that cooling crystallization and evaporative concentration are complementary processing routes for obtaining calcium nitrate-containing crystalline products or concentrated solutions. These approaches promote more complete utilization of calcium and nitrate nitrogen during nitric acid processing of Central Kyzylkum phosphate raw materials.

Аннотация

Целью настоящего исследования являлась оценка переработки растворов нитрата кальция, образующихся при азотнокислотной обработке фосфоритов Центральных Кызылкумов, методами охлаждающей кристаллизации и выпарного концентрирования, а также определение технологически рациональных условий извлечения и концентрирования нитрата кальция. В качестве исходного технологического раствора использовали репрезентативный раствор, содержащий 24.40 мас.% $\text{Ca}(\text{NO}_3)_2$. Методология включала материально-балансовые расчеты на основе 1000 г исходного раствора, ступенчатое охлаждение от +20 до -20 °C с интервалом 5 °C и выпарное концентрирование при атмосферном давлении. В процессе охлаждения расчетная степень извлечения нитрата кальция в кристаллическую фазу возрастала по мере снижения температуры. В интервале от 0 до -15 °C степень извлечения увеличилась с 59.74 до 94.21 %. Дальнейшее охлаждение до -20 °C повысило степень извлечения лишь до 95.04 %, что соответствовало дополнительному извлечению 2,03 г $\text{Ca}(\text{NO}_3)_2$ в пересчете на 1000 г исходного раствора; поэтому охлаждение ниже -15 °C в исследованных условиях было признано экономически неэффективным. В процессе выпаривания удаление 531.58 г воды позволило повысить концентрацию $\text{Ca}(\text{NO}_3)_2$ с 24.40 до 52.09 мас.%, при этом концентрация около 37 мас.% была определена как технологически значимый промежуточный уровень для последующих процессов конверсии. Полученные результаты показывают, что охлаждающая кристаллизация и выпарное концентрирование являются взаимодополняющими технологическими направлениями для получения кальций-нитратсодержащих кристаллических продуктов или концентрированных растворов. Применение данных подходов способствует более полному использованию кальция и нитратного азота при азотнокислотной переработке фосфатного сырья Центральных Кызылкумов.

Keywords: Central Kyzylkum phosphorites, nitric acid processing, calcium nitrate, cooling crystallization, evaporative concentration, material balance, nitrogen–calcium fertilizer, resource utilization.

Ключевые слова: фосфориты Центральных Кызылкумов, азотнокислотная переработка, нитрат кальция, охлаждающая кристаллизация, выпарное концентрирование, материальный баланс, азотно-кальциевое удобрение, комплексное использование ресурсов.

Introduction

Phosphate rock is the principal mineral raw material used for the production of phosphoric acid and phosphate fertilizers. Its technological behavior during chemical processing is determined not only by the phosphorus content but also by the mineralogical and chemical composition of the accompanying components. Calcium is generally the dominant non-phosphorus constituent, while magnesium, iron, aluminum, fluorine, silica, carbonates, and other components may also occur in significant amounts. These constituents affect acid consumption, dissolution behavior, phase separation, filtration, and ultimately the composition and quality of the resulting products [1]. Consequently, the efficient processing of phosphate raw materials increasingly requires an integrated approach aimed not only at phosphorus recovery but also at the rational utilization of other valuable components of the feedstock. This consideration is particularly relevant to the phosphate resources of the Central Kyzylkum region. Along with conventional phosphate raw materials, mining, beneficiation, and thermal processing operations generate mineralized mass and phosphorite slurry characterized by relatively low phosphorus contents and high proportions of calcium- and carbonate-containing components. Recent studies have demonstrated that such Central Kyzylkum phosphate materials can be involved in nitric-acid-based processing and converted into phosphorus-containing fertilizer products [2,3]. These findings indicate that low-grade and off-specification phosphate materials should not necessarily be regarded solely as waste streams, but may represent secondary mineral resources suitable for further chemical processing. The selection of the acid used for phosphate-rock decomposition strongly influences the subsequent distribution of calcium within the technological system. In the conventional sulfuric acid route, calcium originating from the phosphate mineral matrix is predominantly separated as calcium sulfate, producing phosphogypsum as the major solid by-product of wet-process phosphoric acid production [4]. Although various approaches for phosphogypsum utilization have been proposed, its large-scale generation and the presence of residual phosphorus, fluorine, trace metals, and other impurities continue to complicate its comprehensive utilization [4]. Nitric acid processing provides a fundamentally different pathway because calcium released during phosphate-rock decomposition remains largely in the liquid phase in the form of soluble calcium nitrate rather than being precipitated as calcium sulfate [5,6]. This difference creates an opportunity to recover calcium and nitrogen as useful products within an integrated phosphate-processing scheme. Previous investigations of Central Kyzylkum phosphorites have demonstrated the feasibility of nitric acid treatment for producing phosphorus-containing fertilizers and fertilizer precipitates. In particular, mineralized mass from Central Kyzylkum has been processed with nitric acid to obtain phosphorus fertilizer products, and physicochemical characterization has confirmed substantial changes in the mineral and elemental composition of the material after treatment [2]. More recent work has also shown that mineralized mass and slurry phosphorite generated during thermal processing can be treated with nitric acid to produce activated nitrogen–phosphate fertilizer materials [3]. These studies provide an important technological basis for the nitric-acid processing of Central Kyzylkum

phosphate resources. However, their principal emphasis has been placed on phosphate conversion and the properties of the resulting solid fertilizer products rather than on the subsequent recovery and utilization of the calcium nitrate-containing liquid phase.

The calcium nitrate solution formed during nitric acid processing represents a potentially valuable intermediate stream because it contains both calcium and nitrate nitrogen. The management of calcium nitrate is also an important technological issue in other nitric-acid-based phosphate-processing schemes, where its presence and separation can significantly influence downstream product quality and process configuration [6]. From a physicochemical standpoint, aqueous calcium nitrate systems exhibit strongly temperature- and concentration-dependent solid–liquid and vapor–liquid equilibria [7]. Therefore, water removal and temperature control can be used to modify the concentration state of the solution and promote the formation of calcium nitrate-containing crystalline phases. The feasibility of recovering calcium nitrate crystals from concentrated aqueous solutions has also been demonstrated using crystallization-based separation approaches [8]. These findings suggest that calcium nitrate-containing process liquors may be treated not only through chemical conversion but also through physical concentration and crystallization routes.

Despite the established potential of nitric acid for processing Central Kyzylkum phosphorites, comparatively little attention has been given to the direct treatment of the resulting calcium nitrate solutions by cooling crystallization and evaporative concentration. Evaluation of these routes is important for determining whether the calcium nitrate-containing liquid phase can be transformed into a concentrated or crystalline product suitable for further processing or fertilizer-related applications while simultaneously improving the overall utilization of calcium and nitrogen within the technological system.

Accordingly, the aim of the present study was to evaluate the processing of calcium nitrate solutions generated during nitric acid treatment of Central Kyzylkum phosphorites using two technological approaches: cooling crystallization and evaporative concentration. The study examined the effect of temperature on calcium nitrate recovery from solution and evaluated the material balance of progressive water removal during evaporation. On this basis, technological options for obtaining calcium nitrate-containing crystalline products and concentrated solutions intended for further processing or potential use as nitrogen–calcium fertilizer materials were assessed.

2. Materials and Methods

Calcium nitrate-containing process solutions

The calcium nitrate-containing solutions used in this study were obtained as the liquid phase generated during nitric acid processing of Central Kyzylkum phosphorite materials. In the preceding technological stage, the phosphate raw material was treated with nitric acid, after which the resulting nitrocalcium phosphate slurry was neutralized and separated into solid and liquid phases. The solid phase represented the phosphorus-containing fertilizer product, whereas the filtrate contained calcium predominantly in the form of soluble calcium nitrate.

Four representative filtrates obtained under different nitric acid consumption conditions and solid-phase separation modes were considered. The nitric acid dosage corresponded to 100 or 105 % of the stoichiometric requirement calculated with respect to dicalcium phosphate formation. The principal characteristics of the resulting calcium nitrate-containing solutions are summarized in Table 1.

Table 1.

Composition of calcium nitrate-containing solutions generated during nitric acid processing of Central Kyzylkum phosphorites

Processing condition	Nitric acid dosage, % of stoichiometric requirement	Water-soluble CaO, wt. %	N, wt. %	Equivalent $\text{Ca}(\text{NO}_3)_2$ concentration, wt. %
Without preliminary removal of insoluble residue	100	8.33	6.21	24.40
Without preliminary removal of insoluble residue	105	8.49	6.28	24.86
After removal of insoluble residue	100	8.39	6.24	24.57
After removal of insoluble residue	105	8.52	6.30	24.95

The solutions contained approximately 24.40-24.95 wt.% $\text{Ca}(\text{NO}_3)_2$ equivalent, indicating relatively small differences among the investigated process conditions. The detailed cooling and evaporation calculations presented in this study were based on the solution containing 24.40 wt.% $\text{Ca}(\text{NO}_3)_2$ equivalent, corresponding to a water-soluble CaO content of 8.33 wt.%.

Cooling crystallization

The calcium nitrate solution was cooled stepwise to evaluate the effect of temperature on calcium nitrate recovery from the liquid phase. The solution was cooled from +20 °C to -20 °C in 5 °C increments. The temperatures investigated were +20, +15, +10, +5, 0, -5, -10, -15, and -20 °C.

Material-balance calculations were based on 1000 g of the initial solution containing 24.40 wt.% $\text{Ca}(\text{NO}_3)_2$, equivalent to 244.0 g of $\text{Ca}(\text{NO}_3)_2$. At each temperature, we determined the amounts of calcium nitrate transferred to the crystalline phase and remaining in the mother liquor from the material balance.

Quantities transferred to the solid phase are reported as $\text{Ca}(\text{NO}_3)_2$ equivalent on an anhydrous-salt basis. No specific hydrate composition was assigned because independent phase characterization of the crystalline product was not available.

Evaporative concentration

The calcium nitrate solution was also concentrated by evaporation at atmospheric pressure. The initial solution contained 24.40 wt.% $\text{Ca}(\text{NO}_3)_2$ and 75.60 wt.% water.

For the material-balance calculations, we considered 1000 g of the initial solution, corresponding to 244.0 g of $\text{Ca}(\text{NO}_3)_2$ and 756.0 g of water. During progressive evaporation, calcium nitrate was treated as the nonvolatile dissolved component, and the decrease in solution mass was attributed to water removal.

At each concentration stage, we calculated the residual solution mass, the amount of evaporated water, the calcium nitrate concentration, and the amount of water remaining in the solution. The evaporation process was evaluated up to a $\text{Ca}(\text{NO}_3)_2$ concentration of approximately 52 wt.%.

Material-balance evaluation

Material-balance calculations evaluated both processing routes. For cooling crystallization, the initial calcium nitrate content was distributed between the crystalline phase and the mother liquor. For evaporative concentration, we evaluated the progressive removal of water and the resulting increase in calcium nitrate concentration.

All concentrations and mass-flow values were reported on a mass basis. Because the original dataset did not report replicate measurements or statistical variability, the results were treated as technological and material-balance data, with no inferential statistical analysis.

3. Results and Discussion

Effect of cooling temperature on calcium nitrate recovery

The effect of temperature on the distribution of calcium nitrate between the crystalline phase and the residual mother liquor was evaluated over the range from +20 to -20 °C. The results, calculated based on 1000 g of the initial solution containing 24.40 wt.% $\text{Ca}(\text{NO}_3)_2$ are presented in Table 2.

Table 2.

Effect of cooling temperature on the material balance of calcium nitrate recovery

Temperature, °C	$\text{Ca}(\text{NO}_3)_2$ Transferred to the crystalline phase, % of initial amount	$\text{Ca}(\text{NO}_3)_2$ in the crystalline phase, g	$\text{Ca}(\text{NO}_3)_2$ remaining in the mother liquor, % of initial amount	$\text{Ca}(\text{NO}_3)_2$ remaining in the mother liquor, g
+20	25.27	61.66	74.73	182.34
+15	31.02	75.69	68.98	168.31
+10	36.77	89.72	63.23	154.28
+5	48.26	117.75	51.74	126.25
0	59.74	145.77	40.26	98.23
-5	71.23	173.80	28.77	70.20
-10	82.72	201.84	17.28	42.16
-15	94.21	229.87	5.79	14.13
-20	95.04	231.90	4.96	12.10

As shown in Table 2, lowering the temperature progressively increased the calculated recovery of calcium nitrate into the crystalline phase. At +20 °C, 25.27 % of the initial $\text{Ca}(\text{NO}_3)_2$ equivalent was in the crystalline fraction, whereas cooling to 0 °C increased this value to 59.74 %. Further cooling produced a more pronounced recovery: 71.23 % at -5 °C, 82.72 % at -10 °C, and 94.21 % at -15 °C.

For a 1000 g initial solution, the starting amount of $\text{Ca}(\text{NO}_3)_2$ was 244.0 g. At $-15\text{ }^\circ\text{C}$, 229.87 g of $\text{Ca}(\text{NO}_3)_2$ equivalent was transferred to the crystalline phase, leaving only 14.13 g in the mother liquor. When the temperature was further decreased to $-20\text{ }^\circ\text{C}$, the calculated amount transferred to the crystalline phase increased only to 231.90 g, leaving 12.10 g in the liquid phase.

An important feature of the temperature dependence is the diminishing incremental recovery observed below $-15\text{ }^\circ\text{C}$. Cooling from -10 to $-15\text{ }^\circ\text{C}$ increased calcium nitrate recovery by 11.49 percentage points, whereas a further decrease from -15 to $-20\text{ }^\circ\text{C}$ increased recovery by only 0.83 percentage points, corresponding to an additional 2.03 g of $\text{Ca}(\text{NO}_3)_2$ equivalent per 1000 g of initial solution. Thus, within the investigated temperature range, most of the achievable recovery had already been attained at $-15\text{ }^\circ\text{C}$.

The observed temperature dependence is consistent with the strong influence of temperature on solid–liquid equilibria in the $\text{Ca}(\text{NO}_3)_2\text{--H}_2\text{O}$ system [7]. However, because calcium nitrate can form hydrated crystalline phases in aqueous systems, the solid-phase quantities in the present study are expressed as $\text{Ca}(\text{NO}_3)_2$ equivalents on an anhydrous-salt basis rather than assigned to a specific calcium nitrate hydrate. Identifying the exact crystalline phase would require independent structural or thermal characterization.

From a technological and economic standpoint, cooling the solution below $-15\text{ }^\circ\text{C}$ was considered inefficient under the investigated conditions. Lowering the temperature from -15 to $-20\text{ }^\circ\text{C}$ increased calcium nitrate recovery by only 0.83 percentage points, equivalent to an additional 2.03 g of $\text{Ca}(\text{NO}_3)_2$ per 1000 g of the initial solution. This limited increase in product recovery does not justify the additional cooling requirement. Therefore, the temperature range from 0 to $-15\text{ }^\circ\text{C}$ is a rational operating range for calcium nitrate crystallization, providing a recovery of 59.74–94.21 %.

Evaporative concentration of calcium nitrate solutions

A second processing route involved concentrating the calcium nitrate solution by evaporation at atmospheric pressure. The initial solution mass was 1000.0 g and contained 24.40 wt.% $\text{Ca}(\text{NO}_3)_2$, corresponding to 244.0 g of calcium nitrate and 756.0 g of water. During evaporation, water was progressively removed while calcium nitrate remained in the liquid phase, causing a continuous decrease in total solution mass and a corresponding increase in $\text{Ca}(\text{NO}_3)_2$ concentration.

Table 3.

Material balance of evaporative concentration of the calcium nitrate solution

Stage	Solution mass, g	Cumulative evaporated water, g	$\text{Ca}(\text{NO}_3)_2$ concentration, wt. %	Water content, wt. %	Water remaining, g
Initial	1000.0	-	24.40	75.60	756.0
1	781.8	218.2	31.21	68.79	537.8
2	712.0	288.0	34.27	65.73	468.0
3	659.1	340.9	37.02	62.98	415.1
4	572.23	427.77	42.64	57.36	328.23
5	551.29	448.71	44.26	55.74	307.29
6	528.14	471.86	46.20	53.80	284.14
7	506.33	493.67	48.19	51.81	262.33
8	487.90	512.10	50.01	49.99	243.90

Stage	Solution mass, g	Cumulative evaporated water, g	Ca(NO ₃) ₂ concentration, wt. %	Water content, wt. %	Water remaining, g
9	468.42	531.58	52.09	47.91	224.42

As shown in Table 3, progressive evaporation systematically increased the calcium nitrate concentration. After removing 218. 20 g of water, the solution mass decreased to 781.80 80 g, and the Ca(NO₃)₂ concentration rose from 24. 24.40 to 31. 21 wt. %. Further evaporation reduced the solution mass to 659.10 10 g, at which point the calcium nitrate concentration reached 37. 02 wt. %.

Continued water removal produced progressively more concentrated calcium nitrate solutions. At a residual solution mass of 506.33 g, 33 g, the Ca(NO₃)₂ concentration reached 48. 19 wt. %, whereas at 487.90 90 g, it reached approximately 50 wt. %. At the final investigated stage, the solution mass decreased to 468.42 42 g, and the calcium nitrate concentration increased to 52. 09 wt. %.

Overall, 531.58 g 58 g of water was removed from the initial 756.00 g, corresponding to approximately 70.33% of the initial water content. The remaining concentrated solution contained 224.42 g of water together with the initial 244.00 g of calcium nitrate. The complete mass balance was therefore preserved throughout the calculation.

The results show that evaporation directly increases calcium nitrate concentration without introducing additional chemical reagents. In contrast to cooling crystallization, which transfers calcium nitrate into a solid phase, evaporative concentration retains calcium nitrate in the liquid phase while reducing water content. Consequently, the two approaches serve different technological purposes: cooling crystallization may be used when recovery of a crystalline calcium nitrate-containing product is required, whereas evaporation may be preferred when a concentrated liquid calcium nitrate stream is desired for subsequent processing or direct fertilizer-related applications.

A particularly relevant concentration level was reached at approximately 37 wt.% Ca(NO₃)₂, corresponding to a residual solution mass of 659.10 g after removal of 340.90 g of water. Previous investigations of calcium nitrate solutions generated during nitric acid processing of Central Kyzylkum phosphorites identified a Ca(NO₃)₂ concentration of approximately 37 wt.% as a suitable condition for subsequent conversion with ammonium carbonate to ammonium nitrate and calcium carbonate [9-10]. Therefore, concentrating the initial 24.40 wt.% solution to at least approximately 37 wt.% may provide a technologically suitable intermediate stream for subsequent conversion. Further evaporation in the present study increased the Ca(NO₃)₂ concentration to 52.09 wt.%, indicating that the final concentration can be adjusted according to the intended downstream processing route.

Comparative technological assessment of cooling crystallization and evaporative concentration

The results for the two investigated processing routes indicate that cooling crystallization and evaporative concentration can serve different technological purposes in treating calcium nitrate-containing solutions generated during nitric acid processing of Central Kyzylkum phosphorites.

Cooling crystallization provides a direct route for transferring calcium nitrate from the liquid phase into a solid crystalline fraction. Within the investigated temperature range, the calculated recovery increased continuously as the temperature decreased. Cooling from 0 to -15 °C increased

recovery from 59.74 to 94.21 %, while further cooling to -20 °C yielded only a small additional increase to 95.04 %. Thus, the interval of 0 to -15 °C can be regarded as the rational operating range for calcium nitrate recovery under the investigated conditions. The limited increase of only 0.83 percentage points between -15 and -20 °C indicates that deeper cooling provides little additional product recovery while requiring more intensive refrigeration.

Evaporative concentration operates on a different technological principle. Rather than transferring calcium nitrate to a solid phase, evaporation retains the dissolved salt in the liquid phase while progressively removing water. Starting from a solution containing 24.40 wt.% $\text{Ca}(\text{NO}_3)_2$, the concentration increased to 37.02 wt.% after removing 340.90 g of water and reached 52.09 wt.% at the final investigated stage. Overall, 531.58 g of water, corresponding to approximately 70.3 % of the initial water content, was removed from 1000 g of the starting solution.

A concentration of approximately 37 wt.% $\text{Ca}(\text{NO}_3)_2$ is technologically relevant because previous studies of calcium nitrate solutions derived from Central Kyzylkum phosphorites identified this range as suitable for subsequent conversion to ammonium nitrate and calcium carbonate [9]. Related work has also demonstrated the feasibility of converting calcium nitrate solutions obtained from Kyzylkum phosphate raw materials with ammonium carbonate [10]. Therefore, evaporative concentration to approximately 37 wt.% may be a practical intermediate step when subsequent chemical conversion is intended. From a process-selection perspective, cooling crystallization may be preferred when the objective is to recover calcium nitrate as a solid, whereas evaporative concentration is more suitable when a concentrated liquid stream is required for subsequent conversion or potential fertilizer application. The two routes should therefore not be regarded as mutually exclusive alternatives. Instead, they represent complementary processing options that can be selected based on the desired final product and downstream technological requirements. Overall, both approaches lead to more complete utilization of the calcium and nitrogen in the liquid phase formed during nitric acid processing of Central Kyzylkum phosphorites. Their application reduces the need to treat the calcium nitrate-containing filtrate as a residual process stream and supports more integrated utilization of the mineral raw material.

Conclusions

The study demonstrated the technological feasibility of processing calcium nitrate solutions generated during nitric acid treatment of Central Kyzylkum phosphorites by cooling crystallization and evaporative concentration.

Cooling of the initial 24.40 wt.% $\text{Ca}(\text{NO}_3)_2$ solution from +20 to -15 °C progressively increased the calculated calcium nitrate recovery into the crystalline phase from 25.27 to 94.21 %. Further cooling to -20 °C increased the recovery only slightly, to 95.04 %, corresponding to an additional 2.03 g of $\text{Ca}(\text{NO}_3)_2$ equivalent per 1000 g of the initial solution. Therefore, the temperature range from 0 to -15 °C was identified as the rational operating range for calcium nitrate crystallization, while further cooling to -20 °C was considered economically inefficient because of the limited additional recovery. Evaporative concentration provided an alternative route for retaining calcium nitrate in the liquid phase while removing water. Starting from 1000 g of solution containing 24.40 wt.% $\text{Ca}(\text{NO}_3)_2$, removal of 531.58 g of water increased the calcium nitrate

concentration to 52.09 wt.%. This process removed approximately 70.3 % of the initial water content. A $\text{Ca}(\text{NO}_3)_2$ concentration of approximately 37 wt.% was reached after removal of 340.90 g of water and represents a technologically relevant intermediate level for subsequent conversion processes reported for calcium nitrate solutions derived from Central Kyzylkum phosphorites. Further evaporation to concentrations above 50 wt.% provides additional flexibility depending on the intended downstream use. Overall, cooling crystallization and evaporative concentration represent complementary processing routes. The first is suitable for recovering calcium nitrate as a crystalline product, whereas the second provides concentrated calcium nitrate solutions for subsequent chemical conversion or potential nitrogen–calcium fertilizer applications. The proposed approaches improve the utilization of calcium and nitrate nitrogen contained in the liquid phase and contribute to a more integrated processing scheme for Central Kyzylkum phosphate raw materials.

References

1. Ryszko U., Rusek P., Kołodziej D. Quality of phosphate rocks from various deposits used in wet phosphoric acid and P-fertilizer production // *Materials*. – 2023. – Vol. 16, No. 2. – Art. 793. – DOI: 10.3390/ma16020793.
2. Giasidinov A.L., Sultonov B.E., Dormeshkin O. Study on the composition of phosphorus fertilizers obtained on the basis of Kizilkum phosphorites and nitric acid // *Journal of Chemical Technology and Metallurgy*. – 2023. – Vol. 58, No. 2. – P. 347–352.
3. Kholmatov D.S., Rasulov A.A. Treatment of phosphate waste generated during thermal processing of phosphorites of the Central Kyzylkum // *Obogashchenie Rud.* – 2024. – No. 4. – P. 1–8. – DOI: 10.17580/or.2024.04.06.
4. Akfas F., Elghali A., Aboulaich A., Munoz M., Benzaazoua M., Bodinier J.L. Exploring the potential reuse of phosphogypsum: a waste or a resource? // *Science of the Total Environment*. – 2024. – Vol. 908. – Art. 168196. – DOI: 10.1016/j.scitotenv.2023.168196.
5. Wang B., Zhou Z., Xu D., Wu J., Yang X., Zhang Z., Yan Z. A new enrichment method of medium–low grade phosphate ore with high silicon content // *Minerals Engineering*. – 2022. – Vol. 181. – Art. 107548. – DOI: 10.1016/j.mineng.2022.107548.
6. Xu C., Zhang M., Su J., Peng X., Kong X., Luo Y., Sun G. Removal of calcium from phosphoric acid produced by the nitric acid process using solvent extraction with TCHDGA and stripping with water // *Hydrometallurgy*. – 2024. – Vol. 229. – Art. 106379. – DOI: 10.1016/j.hydromet.2024.106379.
7. Novikov A.A., Dzuban A.V., Kovalenko N.A., Uspenskaya I.A. Thermodynamic properties and phase equilibria in the $\text{H}_2\text{O}-\text{Ca}(\text{NO}_3)_2$ system // *Journal of Chemical & Engineering Data*. – 2021. – Vol. 66, No. 5. – P. 1839–1855. – DOI: 10.1021/acs.jced.1c00102.
8. Nasiraei M., Mousavi S.M., Saljoughi E., Kiani S., Razmgar K. Production of calcium nitrate crystals via membrane distillation crystallization using polyvinylidene fluoride/sorbitan trioleate membranes // *Advanced Powder Technology*. – 2021. – Vol. 32, No. 5. – P. 1463–1471. – DOI: 10.1016/j.apt.2021.02.043.

-
9. Dekhkanov Z.K., Seytnazarov A.R., Namazov Sh.S., Beglov B.M. Conversion of calcium nitrate as a by-product of chemical beneficiation of Central Kyzylkum phosphorites // *Khimicheskaya Promyshlennost*. – 2013. – Vol. 90, No. 2. – P. 87–92.
 10. Allamuratova A.J., Erkaev A.U., Reymov A.M. Conversion of calcium nitrate solution obtained from Kyzylkum phosphorite with ammonium carbonate // *Chemical Science International Journal*. – 2016. – Vol. 16, No. 4. – P. 1–6. – DOI: 10.9734/ACSJ/2016/28146.