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IMPROVEMENT OF EDIBLE SALT PRODUCTION BY SEPARATION OF SULPHATES FROM SALT SOLUTIONS

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Abstract. The article investigates the conditions for improving the technology of table salt by isolating sulfate ions from concentrated halite solutions using natural minerals - gypsum and anhydrite. It is confirmed by calculations that the interaction of a saline solution enriched in SO_4^{2-} after filtering table salt with anhydrite is thermodynamically favorable and is accompanied by the release of heat, while the reaction with gypsum occurs with the absorption of heat and with a lower thermodynamic probability. Experimental studies have shown that, depending on the temperature and amount of calcium-containing reagent (gypsum or anhydrite), the concentration of sulfate ions in the liquid phase can be reduced to 0.6–0.8 wt.%, which allows returning the purified solution to the cycle of evaporation and crystallization of salt. The influence of the duration of the conversion process, temperature (323–368 K) and the reagent rate on the kinetics of the formation of glauberite ($CaSO_4 \cdot Na_2SO_4$) is analyzed. It is shown that increasing the temperature intensifies the reaction due to the phase transition of gypsum into a hemihydrate with increased reactivity. X-ray phase analysis confirmed that the main product is glauberite, and with an excess of anhydrite, hemihydrate gypsum partially remains. A basic technological scheme for purifying the salt solution is proposed, which does not require the introduction of additional ions, allows avoiding supersaturation of the solution and the formation of incrustations on the equipment. In industrial conditions, the method ensures almost complete conversion of NaCl into commercial salt of the "Extra" grade. The resulting precipitate of double sulfate salt can be used as a chemical soil improver. The proposed method allows to increase the efficiency and environmental friendliness of salt production, which is especially relevant for the transformation of the salt mining industry of Ukraine.

Keywords: table salt, gypsum, anhydrite, glauberite, desulphation, brine, enthalpy, isobaric potential, X-ray phase analysis.

Introduction. Formulation of the problem

Table salt is a strategic mineral resource essential for Ukraine's food security and industrial development. Its use extends far beyond the food sector, encompassing the chemical, pulp and paper, metallurgical, and pharmaceutical industries, as well as the production of chlorine, soda ash, and paint materials. Salt is also a critical technological component in road maintenance. Prior to the full-scale Russian invasion, Ukraine consistently ranked among the top salt producers in Europe. The state-owned enterprise Artemsil played a leading role, providing more than 70% of the domestic supply of food-grade salt and exporting its products to EU and Asian markets. Ukraine possesses substantial reserves of rock salt and brines, estimated to exceed 16 billion tons. Major deposits are concentrated within the Donbas region, the Dnipro–Donets Basin, the Carpathian Foothills, Transcarpathia, and the Black Sea area. Salt production in Ukraine has a long historical trajectory, originating in the 13th century, with traditional extraction centers such as Drohobych, Solotvyno, and Henichesk well known beyond their regional contexts. In the early 21st century, the sector demonstrated a trend toward modernization: in parallel with conventional mining, underground leaching technologies and the recreational use of mine workings were actively developed.

A profound structural shift occurred after 2022, when intensive russian shelling led to the complete suspension of operations at Artemsil. The destruction of production and transport infrastructure caused a rapid decline in national salt output, resulting in temporary

shortages and a reconfiguration of supply chains. Imports from Turkey, Poland, Romania, and Egypt increasingly compensated for the domestic deficit. Despite this disruption, national demand for salt remained stable, prompting short-term market fluctuations. The industry encountered challenges related to security, logistics, and interruptions in continuous production, yet the significance of deposits in western Ukraine and Transcarpathia increased. Small private enterprises also intensified investments in the development of new extraction sites.

Recent studies highlight that the man-made and geological risks characteristic of salt deposits–including subsidence, landslides, flooding, and soil mineralization-necessitate the implementation of modern environmental standards and rational mineral resource management [1-4]. The restoration of abandoned workings, utilization of man-made brines, processing of salt sludge, and introduction of closed-loop production cycles are emerging as priority considerations for sustainable sectoral development. The current transformation of Ukraine's salt industry reflects a shift from its historically Donbas-centered structure toward the formation of new production clusters in the Carpathian and Black Sea regions. This transition requires careful assessment of the qualitative and quantitative parameters of accessible raw materials and corresponding technological optimization to ensure stable supplies of food-grade salt during wartime and throughout post-war recovery.

Analysis of recent research and publications

In the world literature, the issue of removing sulfate ions from brines and forming double sulfate salts (primarily glauberite) is considered from both the thermodynamic and kinetic sides. Classical studies by D. Fryer et al. describe the phase diagram of the Na_2SO_4–$CaSO_4$ system and the features of the formation of metastable and stable phases during cooling and crystallization, which lays the foundation for technical schemes for the interaction of Na_2SO_4 and $CaSO_4$ [5]. Separate reviews and experimental works emphasize the complexity of the kinetics of transitions between gypsum, semi-aqueous gypsum (bassantite) and anhydrite and their sensitivity to salinity and solution temperature [6]. Thermodynamic modeling and experiments by L. Shen et al. show the possibility of forming glauberite in different phase states of $CaSO_4$. Also, the stability of the double salt depends on the temperature and ionic composition of the solution, which directly affects the practical conditions for sulfate precipitation [7]. In applied engineering solutions (patents and industrial developments), both chemical methods (e.g., gypsum precipitation) and combined approaches are used to reduce sulfate content in waste or process solutions. However, these approaches often require the addition of reagents or create by-products that need to be disposed of.

Also, most publications consider laboratory experiments or model scenarios; detailed industrial cases with optimization of reagent supply and induction period control are absent [6]. Also, the role of grinding and hydrodynamics in reactors in reducing reaction time is absent - many works note this factor, but practical parameters for industrial conditions remain insufficiently studied [8]. The issues of controlling phase transitions (gypsum ↔ semi-aqueous gypsum ↔ anhydrite) in saline high-temperature environments [7, 9] and the influence of impurities on the selectivity of glauberite formation are not fully open and require further study. The issue of using glauberite sediment is also quite relevant and will require additional research into safety and long-term effects.

Unresolved or partially resolved issues identified by the analysis of sources will be addressed during the research.

The purpose of the study was to study the influence of the duration of the process, as well as the temperature and amount of gypsum on the composition of the solution.

The objectives were:

1) to study the optimal conditions of the conversion processes;

2) to confirm the conversion process and the formation of glauberite using computational and instrumental methods;

3) to propose a principle scheme for purifying a sodium chloride solution from sulfate ions.

Background of the study (thermodynamic calculations). Solutions of underground dissolution of rock salt deposits, as well as natural halite solutions are cleaned of impurities of magnesium and calcium salts and evaporated for the purpose of crystallization of table salt. Evaporation is carried out to a concentration of sulfate ions in the liquid phase of 45-55 kg/m^3 (corresponding to a SO_4^{2-} concentration of 3.7-4.6 wt. %). The liquid phase after salt filtration is disposed of at existing enterprises by various methods.

It is known [10, 11] that from concentrated solutions of sodium chloride, which contain impurities of sodium sulfate when adding calcium sulfate in the temperature range from 298 to 383 K, double sulfate salts crystallize: stable phase glauberite ($CaSO_4 \cdot Na_2SO_4$) metastable eugsterite ($CaSO_4 \cdot 2Na_2SO_4 \cdot 2H_2O$), wattevilite ($CaSO_2 \cdot Na_2SO_4 \cdot 4H_2O$), hydroglauberite ($3CaSO_4 \cdot 5Na_2SO_4 \cdot 6H_2O$), the concentration of Na_2SO_4 in the liquid phase decreases to 0.1 wt. %.

The interaction of sodium sulfate solution with calcium sulfate occurs according to the reaction equation:

$$Na_2SO_{4(solution)} + CaSO_{4(solid)} = Na_2SO_4 \cdot CaSO_{4\,(solid)} + \Delta G$$

You can choose natural gypsum or anhydrite as calcium sulfate. The thermodynamic probability of a spontaneous reaction is estimated by the change in the isobaric potential of the system according to the equations:

$$\Delta G^0_{298}\,(\text{products}) = \Delta G^0_{298}\,(\text{starting materials}) + \Delta G$$

$$\Delta G^0_{298}\,(\text{Glaub.}) = \Delta G^0_{298}\,(\text{Anh.}) + \Delta G^0_{298}\,(SO_4^{2-}) + \Delta G^0_{298}\,(Na^+) + \Delta G$$

Table 1- Value of isobaric potentials [13, 14]

№	Name	T, K	Units of measurement	Value, ΔG°_t	Value, ΔH^0_t
1.	glauberite	298.15	kJ/mol	-2598.3	-2823.20
2.	anhydrite	298.15	kJ/mol	-1322.74	-1435.07
3.	gypsum	298.15	kJ/mol	-1798.65	-2023.99
4.	SO_4^{2-}	298.15	kJ/mol	-744.33	
5.	SO_4^{2-}	323.15	kJ/mol	-730.43	-907.5
6.	SO_4^{2-}	373.15	kJ/mol	-700.07	
7.	Na^+	298.15	kJ/mol	-262.39	
8.	Na^+	323.15	kJ/mol	-264.27	
9.	Na^+	373.15	kJ/mol	-268.12	-239.7

We find the change in the isobaric potential for the reaction with anhydrite:

$$-2598.30 = -1322.74 + (-700.07) + (-268.12) + \Delta G,$$

$$\Delta G_{373.15} = -307.37 \text{ kJ/mol.}$$

Therefore, the interaction of sulfate ions of the salt solution with anhydrite at a temperature of 373.15 K is thermodynamically possible. As the temperature decreases, ΔG (SO_4^{2-}) increases, so the value of ΔG of the reaction decreases. At a temperature of 323.15 K:

$$-2598.30 = -1322.74 + (-730.43) + (-264.27) + \Delta G,$$

$$\Delta G_{323.15} = -280.86 \text{ kJ/mol.}$$

At a temperature of 298.15 K:

$$-2598.30 = -1322.74 + (-744.33) + (-262.39) + \Delta G,$$

$$\Delta G_{298.15} = -268.84 \text{ kJ/mol.}$$

Calculations show that as the temperature decreases, the probability of the reaction decreases.

We find the change in isobaric potential for gypsum:

$$\Delta G^0_{298}(\text{Glaub.}) = \Delta G^0_{298}(\text{Gyps.}) + \Delta G^0_{298}(SO_4^{2-}) + \Delta G^0_{298}(Na^+) + \Delta G$$

At a temperature of 373.15 K:

$$-2598.30 = -1798.65 + (-700.07) + (-268.12) + \Delta G,$$

$$\Delta G_{373.15} = -168.54 \text{ kJ/mol.}$$

At a temperature of 323.15 K:

$$-2598.30 = -1798.65 + (-730.43) + (-264.27) + \Delta G,$$

$$\Delta G_{323.15} = 195.05 \text{ kJ/mol;}$$

At a temperature of 298.15 K:

$$-2598.30 = -1798.65 + (-744.33) + (-262.39) + \Delta G,$$

$$\Delta G_{298.15} = 207.07 \text{ kJ/mol.}$$

Therefore, the interaction of sulfate ions of the solution with dihydrate gypsum in the temperature range of 298.15-373.15 K according to the change in the isobaric potential is not thermodynamically beneficial.

The change in the enthalpy of the reaction of sodium and sulfate ions with the formation of glauberite is determined by the equations:

$$\Delta H^0_{298}(\text{products}) = \Delta H^0_{298}(\text{starting materials}) + \Delta H$$

$$\Delta H^0_{298}(\text{Glaub.}) = \Delta H^0_{298}(\text{Gyps.}) + \Delta H^0_{298}(SO_4^{2-}) + \Delta H^0_{298}(Na^+) + \Delta H$$

We find the enthalpy change for anhydrite (numerical data from table 1):

$$-2823.2 = -1435.07 + (-907.5) + (-239.7) + \Delta H,$$

$$\Delta H = -240.93 \text{ kJ/mol.}$$

Therefore, the reaction with anhydrite occurs with the release of heat.

We find the enthalpy change for gypsum (numerical data from table 1):

$$-2823.2 = -2023.98 + (-907.5) + (-239.7) + \Delta H,$$

$$\Delta H = 347.98 \text{ kJ/mol.}$$

Research materials and methods

Analysis of the processes of conversion of sodium and sulfate ions with gypsum and crystallization of glauberite from saturated salt solutions was carried out using equilibrium diagrams of the system Na^+, Ca^{2+}, Mg^{2+}‖Cl^-, SO_4^{2-}, H_2O [10].

Therefore, the interaction of sulfate ions of the solution with dihydrate gypsum at a temperature of 373.15 K occurs with heat absorption. It can be expected that contact at a temperature of about 353 K of the solution remaining after filtering sodium chloride with natural anhydrite or gypsum will lead to its purification from sulfates. At the same time, new salts that are not present in the system are not introduced into the solution, and additional supersaturation of the solution and incrustation of the hot surfaces of the evaporators are not created. The double sulfate salt is filtered, and the sulfate-free filtrate is returned to the process for evaporation.

A solution for research was prepared:

10 dm^3 of a solution purified from impurities of magnesium and calcium salts by the soda-caustic method [5, 6], with a density of 1203 g/dm^3, was saturated with SO_4^{2-} ions by adding 820 g of anhydrous Na_2SO_4 (pure for analysis of 99.5% Na_2SO_4), stirred for 4 hours at a temperature of 301 K, kept for 12 hours, settled and filtered. The density of the obtained solution was 1243 g/dm^3, composition, wt. %: Mg^{2+} 0.00; Ca^{2+} 0.01; Na^+ 11.13; Cl^- 13.85; SO_4^{2-} 4.52; H_2O 70.49.

Single crystals of natural gypsum and anhydrite were used for deposition. They were crushed to a particle size of less than 0.25 mm. The composition of natural gypsum, mass. %: Mg^{2+} 0.45; Ca^{2+} 23.12; Cl^- 0.45; SO_4^{2-} 55.62; H_2O 20.36. Composition of natural anhydrite, mass %: Mg^{2+} 0.14; Ca^{2+} 29.17; Cl^- 0.38; SO_4^{2-} 70.05; H_2O 0.26.

The amount of sulfate mineral for precipitation was calculated according to equation of the reaction of the interaction of sodium sulfate solution and crystalline calcium mineral with the formation of glauberite. Research on the process of separating sulfates from halite solution was carried out under isothermal conditions. For the experiment, 0.5 dm^3 of salt solution containing sulfate ions was taken, heated to the temperature of the experiment, and a weight of the natural mineral gypsum or anhydrite was added with

constant stirring with a stirrer. The influence of the duration of the process, as well as the temperature and amount of gypsum on the composition of the solution was studied. The suspension was stirred in isothermal conditions with an accuracy of ±1 K and the liquid phases were periodically filtered for analysis. The analysis was carried out on the content of Mg^{2+} and Ca^{2+} ions complexonometrically; Cl^- - by mercurimetric, SO_4^{2-} - by weight methods. The concentration of Na^+ was determined by the difference of double equivalents of cations and anions.

To determine the phase composition and crystal structure of a glauberite sample obtained after the interaction of sodium sulfate with gypsum (anhydrite) X-ray phase analysis (XRD) was performed. The measurements were performed on a diffractometer using Cu-Kα1 radiation (λ = 1.5406 Å) in the angle range 2θ = 10–70°.

Results of the research and their discussion

It was visually observed that after pouring anhydrite or gypsum into the heated solution, the suspension noticeably thickens after 3-4 minutes. This indicates oversaturation of the system by the reaction product (induction period). In a continuous production process, the calcium reagent will be fed into the reacting suspension and there will be almost no sudden thickening. The obtained results of the influence of the duration of interaction of the solution and crushed minerals on the composition of the liquid phase at different temperatures are shown in Fig. 1, and Fig. 2.

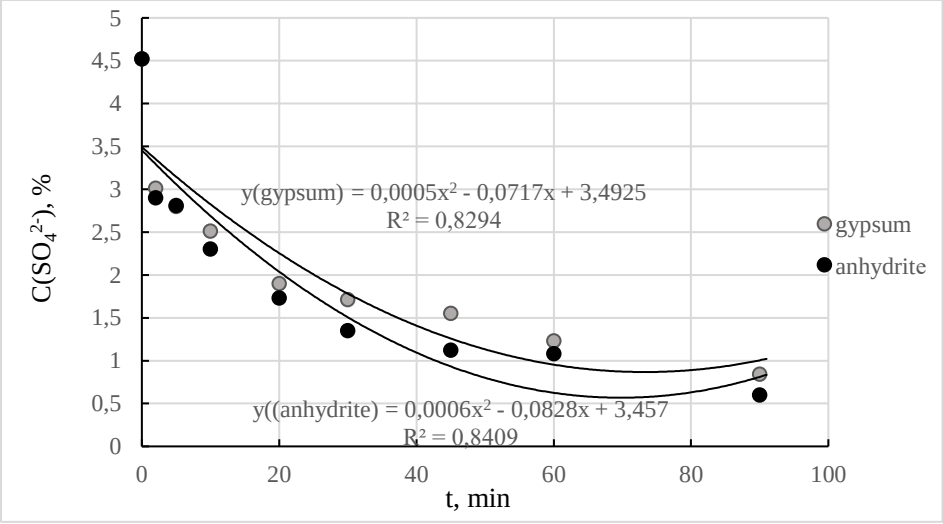

Fig. 1. Change in the concentration of SO_4^{2-} in the liquid phase for different durations of the conversion process (at 353 K).

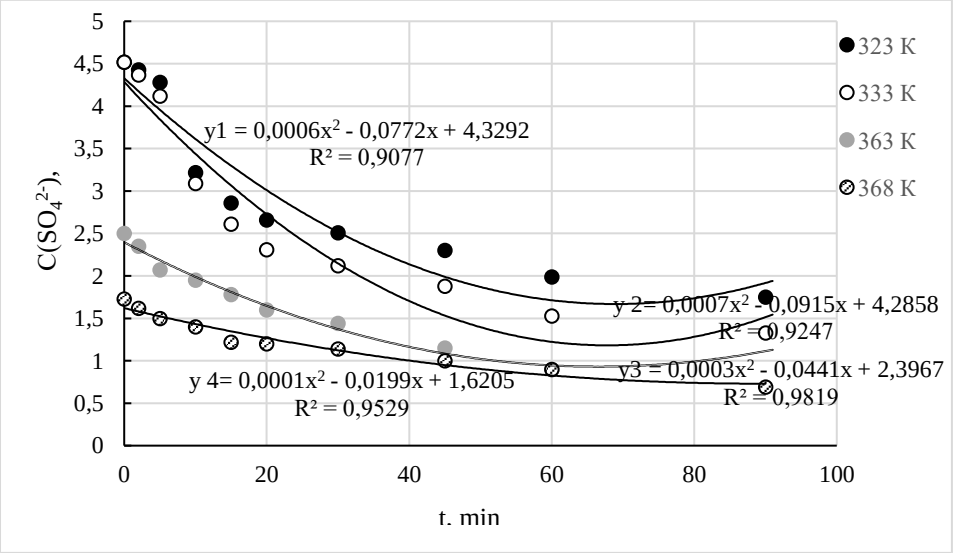

Fig. 2. Changes in the concentration of SO_4^{2-} in the liquid phase for different durations of the conversion process and at different temperatures (323, 333, 363, 368 K).

As can be seen from the obtained results, when the solution interacts with gypsum at a temperature of 353 K, with a gypsum ratio of 100%, the concentration of SO_4^{2-} in the liquid phase gradually decreases to 1.82% in 10 min, 1.71% in 30 min, 1.23% in 60 min, 0.84% in 90 min. For anhydrite at a rate of 125%, 1.72 were obtained, respectively; 1.35; 1.08 and 0.60% SO_4^{2-}. During the interaction of the solution with gypsum, crystallization water is released and the solution becomes larger, so the concentration of SO_4^{2-} for the same time is somewhat lower.

The obtained results of the influence of the duration of interaction of the solution and crushed minerals on the composition of the liquid phase at different temperatures are shown in Figure 2. As can be seen from the obtained results, during the interaction of the solution with gypsum at a temperature of 353 K, with a gypsum norm of 100%, there is a gradual decrease in the concentration of SO_4^{2-} in the liquid phase to 1.82% in 10 min, 1.71% in 30 min, 1.23 in 60 min and 0.84% in 90 min. In Figure 2 also shows the influence of the duration of interaction of gypsum with a sulfate solution at temperatures of 323, 333, 363 and 368 K. As can be seen from the given data, at a temperature of 323 K, the decrease in SO_4^{2-} concentration occurs more slowly and its lowest value in 60 min is only 2.40%. At a temperature of 333 K, the concentration of SO_4^{2-} decreases more intensively and after 60 min it is 1.65%. At temperatures of 363 and 368 K, the concentration of SO_4^{2-} decreases to less than 1.0%. At temperatures above 333 K, the reaction with gypsum is more intense. This is explained by the phase transition of gypsum into hemihydrate, renewal of the reactive surface and increase in its reactivity. Therefore, in industrial conditions, when solutions are evaporated in multi-body vacuum evaporation units and the product salt is removed from the body at a temperature of 353-358 K, at which the highest yield of pure salt is achieved [10], or during evaporation in a single-body apparatus with a turbocompressor, when the temperature of the solutions high, for sulfate binding solutions can be taken directly from the process.

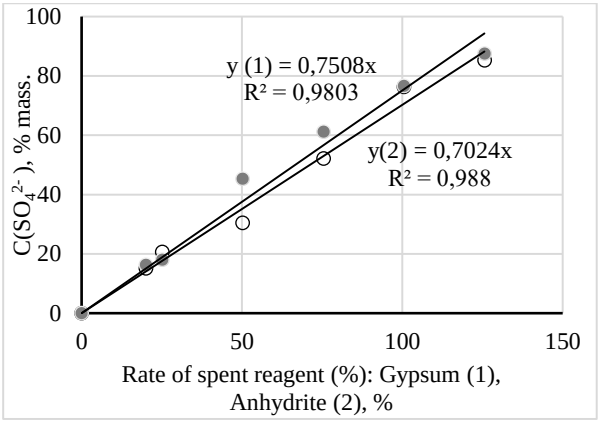

Fig. 3. Dependence of the rate of gypsum and anhydrite on the degree of precipitation of SO_4^{2-} ions from the solution into glauberite

In Figure 3 shows the results of studies of the effect of gypsum and anhydrite on the degree of precipitation of SO_4^{2-} from the solution into glauberite. The latter was calculated as the difference between the amount of SO_4^{2-} in the initial solution and the solution for the current time to the amount of SO_4^{2-} in the initial solution. As can be seen from the above data, for gypsum and anhydrite, the degrees of SO_4^{2-} release are practically the same. Characteristically, they are significantly smaller than the calcium reagent norm. This is explained by the fact that particles of calcium reagents with a size of 0.25 mm do not have time to react during heterogeneous reactions.

The X-ray pattern of the reaction products is shown in Figure 4, Figure 5, which shows that during the reaction with anhydrite, the reaction product is glauberite

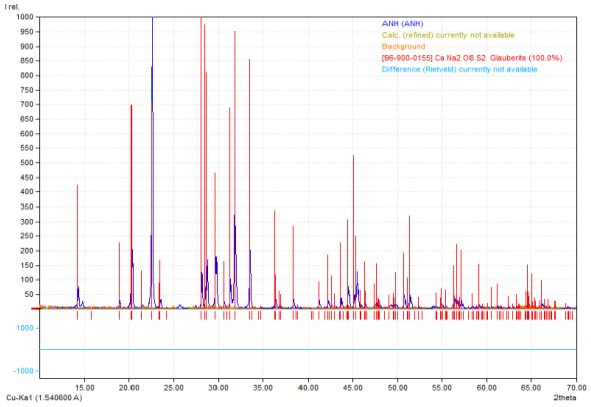

Fig. 4. Conversion products of sodium sulfate with anhydrite (according to the results of X-ray phase analysis)

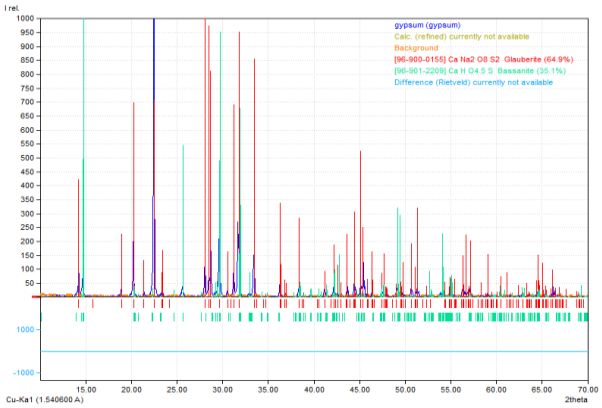

Fig. 5. Conversion products of sodium sulfate with gypsum (according to the results of X-ray phase analysis).

In the reaction with an excess of gypsum, the reaction product is also glauberite and part of semi-aqueous gypsum (Figure 5). This makes it possible to conclude that the interaction of both gypsum and anhydrite at a temperature of 253 K proceeds with a phase transition into semi-aqueous gypsum, which then interacts with sodium sulfate in the solution and may be one of the factors affecting the delay of the reaction in a periodic process.

In industrial processes, these reactions should be carried out in a mill, where better grinding can be achieved and by adding a calcium reagent to the suspension, where the reaction product is already present, and the process will be completed in 20-25 minutes. After filtering, double salt (glauberite) can be used for chemical land reclamation. The amount of double salt sediment for the production capacity of 100 thousand tonnes of salt per year will be about 2.0-2.1 thousand tonnes per year in terms of dry salt.

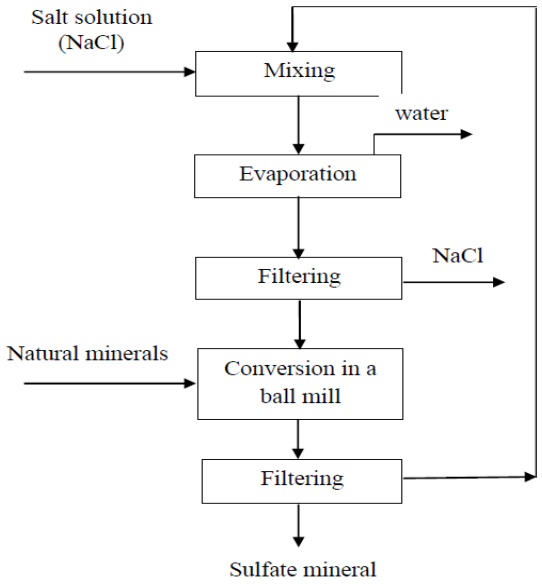

Fig. 6. Schematic diagram of purification of sodium chloride solution from sulfates.

The implementation of the method is carried out according to the block diagram shown in Figure 6 solution of sodium chloride after evaporation, crystallization and filtration of table salt, which contains 3.7-4.6% SO_4^{2-} impurities, with a temperature of 333-373 K is mixed with crushed (1) natural gypsum (3). The suspension, after stirring for 0.5-2.0 hours, is settled (4) and filtered (6). The sediment is removed from the process, and the filtrate is submitted to reagent purification (5) from impurities and further to evaporation (7). The evaporated salt suspension is thickened (8) and filtered (9). Salt is removed as a product after filtration.

According to the above method, the sodium chloride of the underground leaching solutions completely, minus mechanical losses, turns into a commercial product - salt of the "Extra" grade. Separation of sulfates from solutions of table salt production in the form of the specified minerals is of interest for industrial production.

Conclusion

The thermodynamic potential of the interaction of the solution after evaporation and salt separation with natural anhydrite occurs with heat release, the isobaric potential of the reaction at a temperature of 353 K ΔG = - 307.37 kJ/mol, and with natural gypsum occurs with heat absorption and ΔG = 168.54 kJ/mol.

Mixing the sulfate-enriched solution after filtering table salt with gypsum or anhydrite makes it possible to reduce the concentration of SO_4^{2-} to 0.6-0.8 % and return the purified solution to evaporation and salt crystallization. The interaction of gypsum and anhydrite with solution sulfates at a temperature of 353 K is accompanied by a phase transition of the reagents into semi-aqueous gypsum.

X-ray phase analysis of the reaction products showed that the reaction products are glauberite, and the excess of anhydrite remains the unreacted part of semi-aqueous gypsum.

The new method of cleaning solutions from sulfates is easy to implement, does not require the introduction of additional ions that are not present in the initial solution and does not create supersaturation of the solution with salts that cause encrustation of hot surfaces, and the separated precipitate of double sulfate salt can be used as a chemical soil improver. According to this method, all the sodium chloride of the underground leaching solution, with the exception of mechanical losses, turns into a commercial product - salt "Extra".

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ВДОСКОНАЛЕННЯ ВИРОБНИЦТВА ХАРЧОВОЇ СОЛІ ШЛЯХОМ ВИДІЛЕННЯ СУЛЬФАТІВ ІЗ СОЛЬОВИХ РОЗЧИНІВ

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Анотація. У статті досліджено умови вдосконалення технології харчової солі шляхом виділення сульфат-іонів із концентрованих галітових розчинів за допомогою природних мінералів – гіпсу та ангідриту. Підтверджено розрахунками, що взаємодія сольового розчину, збагаченого SO_4^{2-} після фільтрування кухонної солі, з ангідритом є термодинамічно вигідною та супроводжується виділенням теплоти, тоді як реакція з гіпсом відбувається з поглинанням теплоти та з меншою термодинамічною ймовірністю. Експериментальними дослідженнями доведено, що залежно від температури та кількості кальцієвмісного реагенту (гіпсу або ангідриту) концентрацію сульфат-іонів у рідкій фазі можна знизити до 0,6–0,8 мас. %, що дозволяє повертати очищений розчин у цикл випарювання та кристалізації солі. Проаналізовано вплив тривалості процесу конверсії, температури (323–368 К) і норми реагенту на кінетику утворення глауберіту ($CaSO_4 \cdot Na_2SO_4$). Показано, що підвищення температури інтенсифікує реакцію через фазовий перехід гіпсу в напівгідрат із підвищеною реакційною здатністю. Рентгенофазовий аналіз підтвердив, що основним продуктом є глауберит, а при надлишку ангідриту частково залишається півводний гіпс. Запропоновано принципову технологічну схему очищення сольового розчину, яка не потребує введення додаткових іонів, дозволяє уникати пересичення розчину та утворення інкрустацій на обладнанні. У промислових умовах спосіб забезпечує практично повний перехід NaCl у товарну сіль сорту «Екстра». Отриманий осад подвійної сульфатної солі може бути використаний як хімічний меліоратор ґрунтів. Запропонований спосіб дозволяє підвищити ефективність і екологічність виробництва солі, що є особливо актуальним для трансформації солевидобувної галузі України

Ключові слова: харчова сіль, гіпс, ангідрит, глауберит, обезсульфачення, сольовий розчин, ентальпія, ізобарний потенціал, Х-променевий фазовий аналіз.