

INVESTIGATION OF THE CONVERSION PROCESS OF CALCIUM CHLORIDE OF SODA PRODUCTION DISTILLER LIQUID IN THE PRESENCE OF MIRABILITE AND THENARDITE

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ABSTRACT

The production of soda in the world is accompanied by a large amount of hard-to-recycle liquid waste (distiller liquid) in the form of a solution of CaCl_2 and NaCl salts. To solve the problems of the soda industry, some countries of the world approach in different ways, liquid waste is drained into the seas and rivers. In some cases, distiller liquid is partially processed into calcium chloride or liquid road mixtures, building materials, etc. However, the disposal of liquid and solid waste from the soda industry does not always solve environmental problems in this region. In this regard, studies of the conversion of calcium chloride of distiller liquid using sodium sulphate of a mirabilite:thenardite mixture in various ratios have been carried out. It was found that the excess sodium sulphate and its stoichiometry lead to the jointprecipitation of calcium and sodium sulphates. In the process of conversion of calcium chloride with sodium sulphate in the ratio of natural mirabilite:thenardite = 100:0 occurs intensively due to the rapid dissolution of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. Conversion of calcium chloride at a norm of 0.92-1.0 and a temperature of 50-60°C at various ratios of mirabilite:thenardite shows that in the process of conversion of calcium chloride, the degree of conversion is reached to a maximum of ~97% and at an optimum temperature of 50 °C, the stoichiometric norm of sodium sulphate 1.0 and the duration of 60 minutes. A further increase in temperature does not affect the degree of conversion of calcium chloride.

Keywords: Production of Soda Ash, Distilled Liquid, Calcium Chloride, Mirabilite, Thenardite.

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INTRODUCTION

The production of soda is also accompanied by a large amount of hard-to-recycle liquid waste (distiller liquid) in the form of a solution of CaCl_2 and NaCl salts in a 2:1 ratio. About 17 million m^3 of such waste is generated annually at Sterlitamak JSC "Soda", which significantly pollutes the environment in the area of Sterlitamak, the Kama, Volga, and the Caspian Sea. Soda factories in Poland, Ukraine, China, and other countries face such problems.

In order to process the distiller liquid of soda production, a group of scientists from Turkey T. Çalba and E. Kavci proposed the removal of calcium sulphate from liquid waste containing calcium chloride.¹ Soda liquid wastes were reacted with chlorine gas and sulphur dioxide. During the process, calcium was precipitated as gypsum. The degree of calcium deposition in the form of gypsum was 94.44%. However, to conduct the process, it is necessary to have chlorine and gaseous sulphur dioxide near the production of soda. The scientists proposed methods for processing a distiller liquid using the salt production sludge.²

The main goal of this study was to use the main by-products of synthetic soda ash and produced evaporated salt, in particular sludge. The optimization process carried out shows that in order to obtain large crystals of gypsum with minimal moisture and impurity (for example, NaCl), it is necessary to use the waste generated in the distillation section, which has a pH of 11. A combined technology for the utilization of a distiller liquid and a method for desulphurization of combustion gases have been developed.³ The plant power plant combustion gas desulfurization process uses alkaline distillation liquid, which promotes in the absorption of acidic combustion gases, where the degree of desulphurization is 80% and the product is calcium carbonate. Scientists have developed technologies for the disposal of distiller liquid using water glass - sodium silicate.⁴ The distiller liquid is preliminarily purified from calcium carbonate and sulphate. Then a liquid glass solution is added to the resulting filtrate. The resulting colloidal solution is concentrated, calcium metasilicate precipitates. The precipitate is dried and the products wollastonite, thermorite, and xonolite of the corresponding structure are obtained. Bashkir specialists Nasyrov R.R., and Damiev R.R. propose processing of the main waste of soda ash production by the ammonia method based on the production of calcium peroxide with a basic substance content of 88.34-90.19% wt.⁵ A method of using carbonate-alkali metals in obtaining a soft mass and bleaching products by replacing sodium hydroxide is also used.⁶ However, this method is not recommended for production and clarification of some process parameters is required. Polish scientists in laboratory conditions using pure reagents studied the possibility of processing distiller sludge using 25% sulphuric acid and sodium sulphate, reducing the acidity of the solution from 11 to 3, and with slow stirring, a plate-shaped gypsum with a crystal size of 250 μm was obtained.⁷ In this direction, Bukovsky R. and other scientists proposed a combined method for distiller liquid utilization and the method of desulfurization of combustion gases, where the efficiency of the desulfurization process is 80% due to the high pH of the distiller liquid, contributing the absorption of acidic combustion gases.⁸ The economic assessment shows a reduction in the environmental costs of emissions of combustible gases and contributes to high incomes. The works are also devoted to the issues of disposal of distiller liquid. They note that in addition to economic benefits, there are significant environmental benefits due to the disposal of soda-distiller liquid.⁹⁻¹⁶ Therefore, the purpose of this research is to study the process of conversion of calcium chloride of distiller liquid of soda production in the presence of natural minerals mirabilite and thenardite.

EXPERIMENTAL

Research Methods

The following research methods were used in this work: sedimentation, derivatographic, scanning electron microscopy, and IR spectroscopy. The processes of thermal transformation of gypsum and the regularity of hydration of products of its firing, structural and textural transformations of gypsum under the influence of various temperatures were studied.

In the studies, we used a model solution of a distiller liquid, corresponding to the composition of a distiller liquid obtained under real technological conditions in accordance with the data given in the technical regulations of the Sterlitamak soda plant. The composition of the model solution and model experiments carried out using chemically pure solutions are given below. The model composition of the distiller liquid is compiled using pure salts in wt%: CaCl_2 - 11.5; NaCl - 5.61%; $\text{Ca}(\text{OH})_2$ - 0.89; CaSO_4 - 0.25; CaCO_3 - 0.59; insoluble sediment (SiO_2)-0.03; H_2O - 81.1. In experiments, we studied the effect of different mirabilite:thenardite ratios on the degree of calcium conversion. In nature, sodium sulphate is mostly found in the form of a mixture of minerals mirabilite and thenardite. When processing soda sludge, it is possible to use sodium sulphate (Na_2SO_4), which occurs in nature as part of many minerals: thenardite Na_2SO_4 , mirabilite $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, astrakhanite $\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$, glauberite $\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$, etc. Under normal conditions, thenardite is an anhydrous and colorless rhombic crystal with a density of 2.68 g/cm^3 . When heated, it undergoes a number of polymorphic transformations, melts at 890°C. Natural thenardite and thenardite, obtained from a hot saturated solution and dried at 110°C have a structure different from that of remelted thenardite. Mirabilite $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ is a colorless prismatic crystals of monoclinic system, bitter-salty taste. The density of mirabilite is 1.464-1.481 g/cm^3 . There is also crystalline hydrate $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$. The dissolution of anhydrous sodium sulphate in water is accompanied by the release of heat due to hydration. Dissolution of mirabilite occurs with the absorption of heat spent on the

destruction of hydrate bonds. Mirabilite contains $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ -96.54%; CaO -0.81%; MgO -1.01%; Cl -0.62%; H_2O -1.02%.

RESULTS AND DISCUSSION

In experiments, the effect of different ratios of mirabilite:thenardite on the degree of calcium conversion under given conditions was investigated. The conversion of calcium chloride of distiller liquid was investigated in the presence of sodium sulphate (in the thenardite:mirabilite ratio=100:0 ÷ 0:100) in the duration interval from 15 to 60 minutes, at a temperature of 50-80 °C and a sodium sulphate stoichiometric norm of 0.92-1.0. From previous experience, increasing the temperature up to 80 °C resulted in the stable form of calcium sulphate dihydrate, which contributes to a better filtration rate of the sediment. However, a low stoichiometric norm of 0.92 indicates a lack of sodium sulphate for the conversion of calcium chloride. Therefore, the conversion process must be carried out at the sodium sulphate stoichiometric norm of 1.0 and slightly below stoichiometric. The lowest content of calcium ions in the filtrate, which characterizes the achievement of equilibrium in the system and the maximum degree of conversion in this reaction, was considered the best indicator of the process. The results of the research of optimization of the calcium chloride conversion are shown in Figs.-1 to 7.

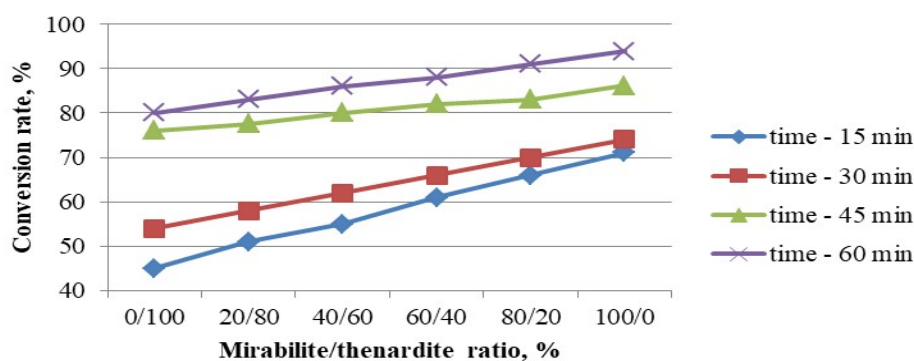


Fig.-1: Influence of Mirabilite:Thenardite Ratio on the Degree of Calcium Conversion at a Temperature of 50 °C, Stoichiometric Norm of 0.92.

Figure-1 shows that at the temperature of 50 °C and process duration of 15 minutes and sodium sulphate stoichiometric norm of 0.92 in mirabilite:thenardite ratio of 100:0, the degree of conversion is 71.01%, and at the ratio of 80:20 the degree of conversion is within 66.0% and at the norm of mirabilite:thenardite, the conversion degree is 45.00%. With an increase in duration up to 60 minutes and in a mirabilite: thenardite ratio of 100:0, the conversion degree increases to 93.98%. With a change in the ratio of mirabilite: thenardite from 80:20 to 0:100, the calcium chloride conversion degree decreases and amounts to 91.02% and 80.01%, respectively. Figure-2 shows the effect of the mirabilite:thenardite ratio on the degree of calcium conversion at the temperature of 50°C, a sodium sulphate stoichiometric norm of 1.00.

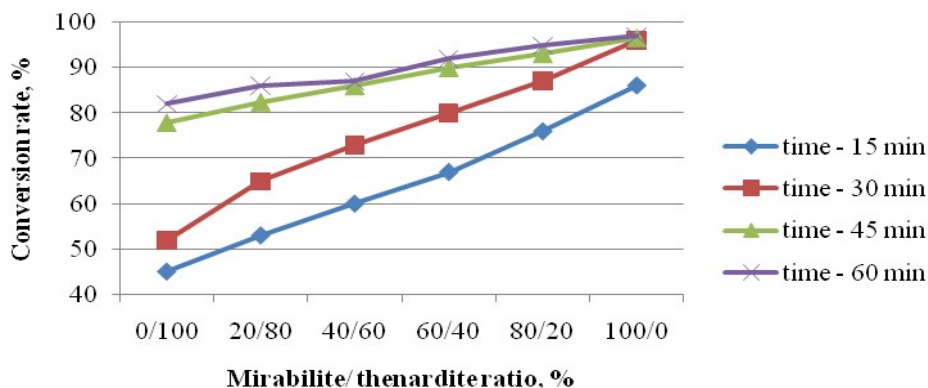


Fig.-2: Influence of Mirabilite: Thenardite Ratio on the Degree of Calcium Conversion at 50 °C, Sodium Sulphate Stoichiometric Norm of 1.00

Figure-2 shows that at a sodium sulphate stoichiometric norm of 1.00 and a temperature of 50 °C, a duration of 15 minutes in a mirabilite:thenardite ratio of 100:0, the conversion degree is 86.12%, and the conversion degree is 76.0% at an 80:20 ratio. With an increase of duration up to 60 minutes, at an mirabilite:thenardite ratio of 100:0 and 80:20 the conversion degree is 97.00% and 82.0%, respectively. By changing the ratio of mirabilite:thenardite from 80:20 to 0:100, the calcium conversion degree is reduced by 15%. The decrease in the conversion degree is associated with a higher content of crystalline thenardite in the mixture, which, during the conversion process, first dissolves in water and then enters into reactions. If the amount of mirabilite is greater in the mixture, the process proceeds faster, since it first dissolves in its own water ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) and interacts with calcium chloride even at low temperatures. With increasing temperature, an increase in the degree of calcium conversion is observed in the same ratios of mirabilite:thenardite. To research the effect of temperature on the process of calcium conversion, studies were carried out at the temperature of 60 °C and under the same conditions. Figure - 3 shows the effect of the mirabilite:thenardite ratio on the calcium conversion degree at the temperature of 60 °C, a sodium sulphate stoichiometric norm of 0.92.

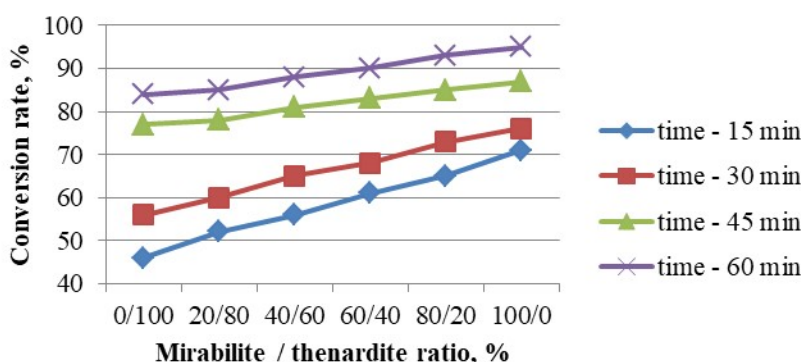


Fig.-3: Influence of Mirabilite:Thenardite Ratio on the Degree of Calcium Conversion at the Temperature of 60 °C, a Sulphate Stoichiometric Norm of 0.92

Figure-3 shows that at the temperature of 60 °C and process duration of 15 minutes and in a mirabilite:thenardite ratio of 100:0, a sodium sulphate stoichiometric norm of 0.92 and 1.00, the conversion degree is 71.0% and 84.0%, respectively, and at ratio of 80:20, the degree of conversion gradually decreases and is 65.0% and 77.0%. With an increase in the duration of the process to 60 minutes, the degree of conversion increases. When the mirabilite:thenardite ratio of 80:20 and 0:100, the degree of calcium conversion is 93.00% and 84%, respectively. The decrease in the degree of conversion is associated with a higher content of the thenardite in the mixture, which initially dissolves during the conversion and then enters into reactions. When the amount of mirabilite is greater in the mixture, usually it first dissolves in its own water ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) and interacts with calcium chloride at the temperature of 50-60 °C. The optimal parameters of the calcium conversion process are the temperature of 60 °C and the process duration of 45-60 minutes, a sodium sulphate norm of 1.0, and a mirabilite:thenardite ratio of 80:20. In order to increase the degree of calcium conversion and the formation of calcium sulphate dehydrate crystals, the experiments were carried out at the temperature of 80 °C. Moreover, in the following experiments at the temperature of 80 °C, the sodium sulphate norm was chosen 1.0. The results of the experiment are shown in Fig.-4.

Figure-4 shows that at a sodium sulphate norm of 1.0 and the temperature of 80 °C and a time of 15 minutes at a mirabilite:thenardite ratio of 100:0 and 80:20, the degree of calcium conversion is 86.03% and 82.00%, respectively. With an increase in the process duration of 45-60 minutes, the conversion degree is reached 95-97%. The higher the mirabilite content, the higher the degree of calcium conversion. Optimization of the calcium chloride conversion process shows the lowest and the highest area of the degree of conversion (Figs.-5 to 7). From Fig.-5(a, b) it can be seen that on the three-dimensional surface of the graph (indicated by the red stripe) at a mirabilite:thenardite ratio equal to 80:20 and at the temperature of 50 °C and the duration of 60 minutes, the degree of conversion of calcium chloride reaches 93%. Figure-5 (c, d) shows that at a sodium sulphate stoichiometric norm of 1.0, at the temperature

of 50 °C and a duration of 45 minutes, on the three-dimensional surface of the graph (indicated by a red stripe) the highest degree of conversion of calcium chloride is observed more than 93%.

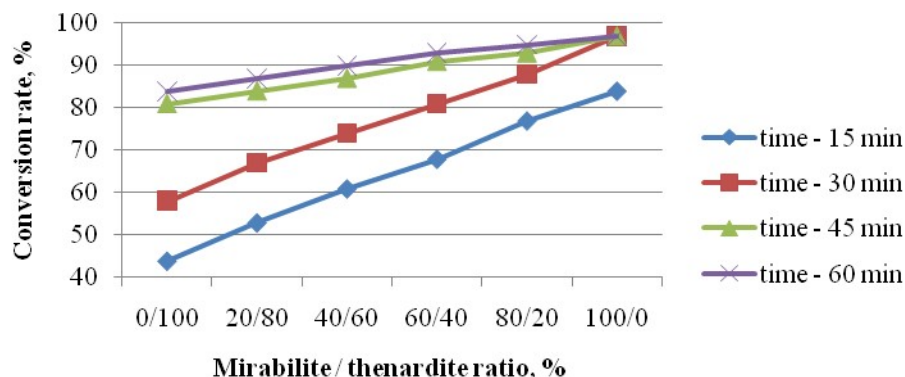
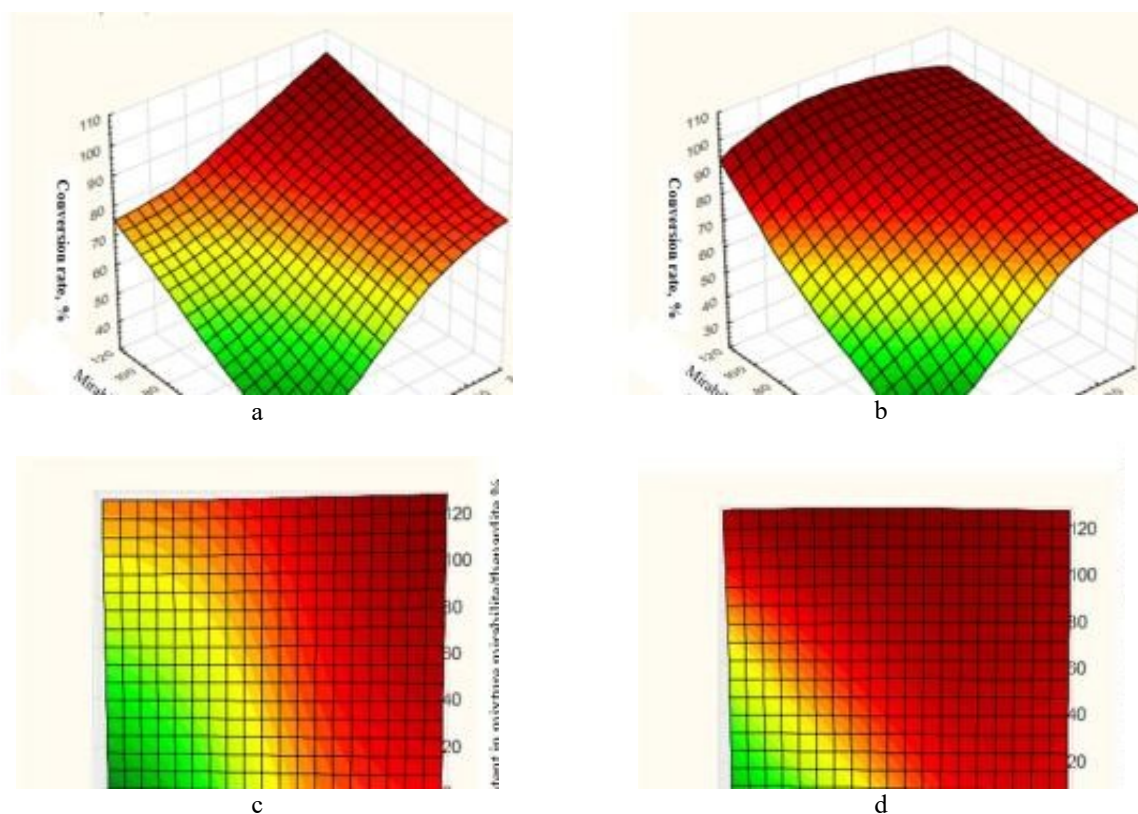


Fig.-4: Influence of Mirabilite: Thenardite Ratio on the Degree of Calcium Conversion at the Temperature of 60 °C, a Sodium Sulphate Stoichiometric Norm of 1.00

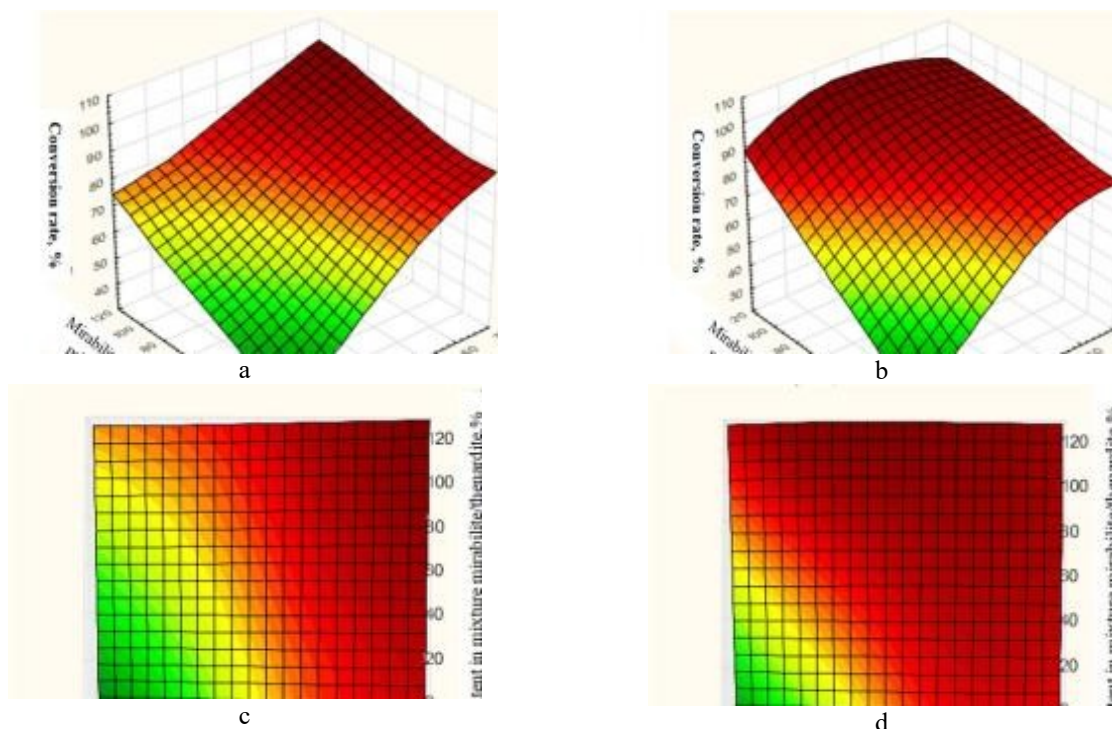


a, b - three-dimensional view, c, d - plane view

Fig.-5: Dependence of the Degree of Conversion on Time At the Temperature of 50 °C, Stoichiometric Norm of Sulphate (Mirabilite:Thenardite) (a, b) equal to 0.92 and (c, d) equal to 1.0

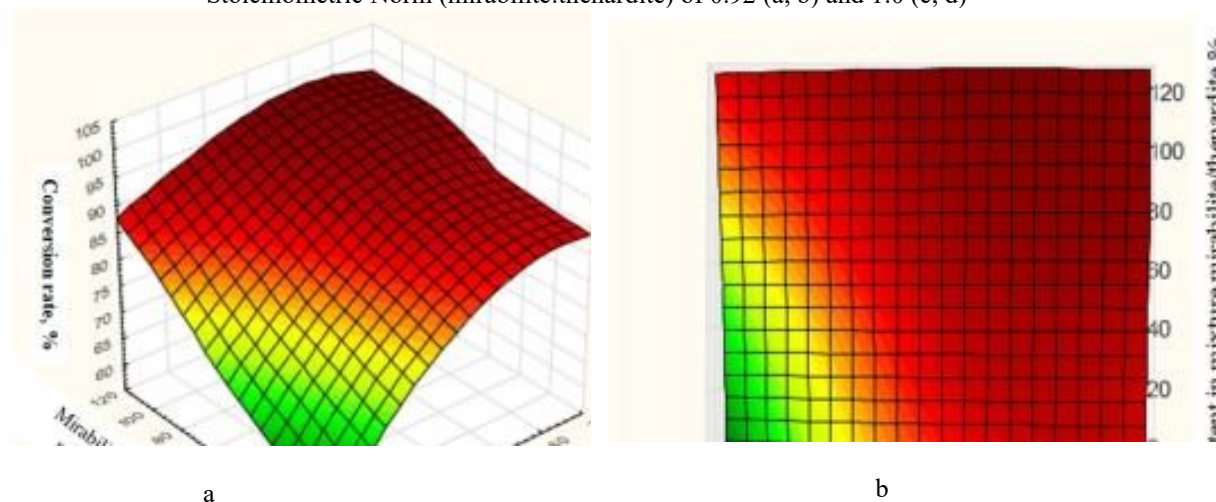
Figure-6 shows that at a sodium sulphate norm of 0.92, at the temperature of 60 °C and a time of 60 minutes, the highest conversion degree is reached up to 93%, at sodium sulphate rate of 1.0, the conversion degree is 95%. Figure-7 shows that at the temperature of 80 °C and a duration of 60 minutes, a sodium sulphate norm of 1.0, and a mirabilite:thenardite ratio of 80:20, the highest conversion degree of calcium chloride is 97%. Optimization of the calcium chloride conversion process at the stoichiometric norm of 0.92-1.0 and temperatures of 50-80 °C at various ratios of mirabilite:thenardite were conducted and the results of researches shows that the conversion degree of calcium chloride is achieved up to a maximum of ~97% at an optimum temperature of 80 °C, sodium sulphate norm of 1.0 and 45-60 minutes.

During the conversion of calcium chloride with sodium sulphate, a precipitate of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is formed in the form of crystals and SEM micrograph of calcium sulphate precipitate is shown in Fig.-8.



a, b - three-dimensional view, c, d - plane view

Fig.-6: Dependence of the Degree of Conversion on the duration at the Temperature of 60 °C, Sulphate Stoichiometric Norm (mirabilite:thenardite) of 0.92 (a, b) and 1.0 (c, d)



a - three-dimensional view, b - plane view

Fig.-7: Dependence of the Degree of Conversion on the duration at the Temperature of 80 °C, Sulphate Stoichiometric Norm of 1.0 (mirabilite:thenardite)

The size and shape of the crystals can be clearly seen in the SEM micrographs (Fig.-8). The average crystal size and specific surface area were determined using an FSKh-6 scanning photosedimentograph. A sedimentation analysis of calcium sulphate precipitates obtained under optimal conversion conditions of distiller liquid was performed. As follows from Fig.-8, calcium sulphate crystallizes during the conversion at 80 °C mainly in the form of medium-square particles in the form of elongated gypsum prisms in the form of the so-called "dovetails", in most of the hemihydrate needle crystals, located in the

spaces between the prisms, as well as partially lamellar forms of calcium sulphate crystals. Such crystals, formed at 80°C, have a larger size - the root-mean-square particle diameter is 71.56-119.01 microns (Figure-8, a), but the crystals have a thickness of 6.40-22.77 microns (Figure-8, b). Experimental researches have confirmed the presence of a mixture of CaSO_4 and Na_2SO_4 salts and a small amount of impurities in the precipitate. After thorough washing of the sediment with hot water from sodium sulphate, sodium chloride, and soluble impurities, the content of calcium sulphate can reach at least 98%, depending on the degree of washing of the solid phase.

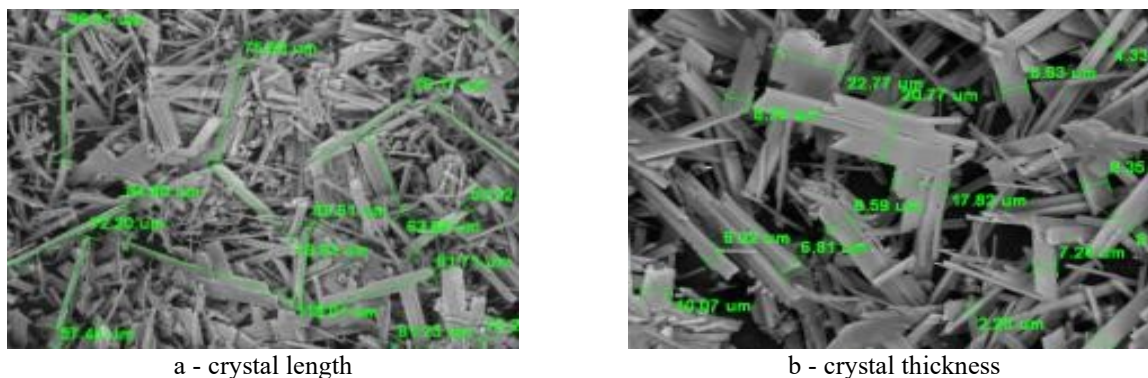


Fig.-8: Micrograph of the Washed $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ Precipitate Obtained at 80 °C with an Increase of 500 Times



Fig.-9: DTA of Gypsum Obtained at the Temperature of 80 °C and a Sodium Sulphate Stoichiometric Norm of 1.0 On the derivatograms of precipitate (Fig.-9), obtained at the temperature of 80 °C, an endothermic effect is observed at 146-170 °C, associated with gypsum dehydration. Figure-10 shows an X-ray diffraction pattern of gypsum obtained at 80 °C.

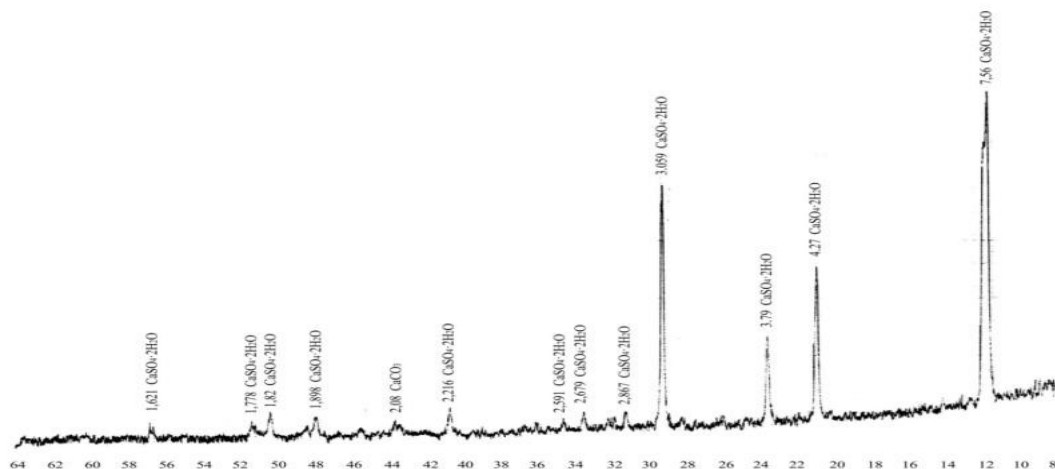


Fig.-10: X-ray diffraction Analysis of Gypsum Dihydrate Obtained at the Temperature of 70 °C

The X-ray diffraction pattern (Fig.-10) of the precipitate confirms the presence of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystal hydrate with characteristic diffraction maxima $d = 1.62; 1.77; 1.82; 1.89; 2.21; 2.59; 2.67; 2.86; 3.05; 3.79; 4.27; 7.56 \text{ \AA}$ and CaCO_3 with characteristic diffraction maximum $d=2.08 \text{ \AA}$.

CONCLUSION

It has been established that an excess of sodium sulphate and its stoichiometry lead to the joint precipitation of calcium and sodium sulphates. In the process of calcium chloride conversion with sodium sulphate in the ratio of natural mirabilite:thenardite=100:0, it proceeds faster due to the rapid dissolution of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. Thus, the conversion of calcium chloride at the stoichiometric norm of 0.92-1.0 and a temperature of 50-60 °C at various ratios of mirabilite: thenardite show that in the process of conversion of calcium chloride, the degree of conversion is reached to a maximum of ~97% and at an optimum temperature of 50 °C, sodium sulphate norm of 1.0 and duration of 60 minutes. A further increase in temperature does not affect the calcium chloride conversion degree.

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