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INVESTIGATION OF THE PROCESSING OF DISTILLER LIQUID FOR THE PRODUCTION OF SODA ASH

Abstract

The aim of the study is to process the distiller liquid containing calcium chloride, the main waste of soda production, by treating it with natural sodium sulfate to obtain gypsum binder and sodium chloride filtrate. The filtrate after dissolving an additional amount of table salt in it and cleaning it from unwanted impurities can be used in the technology of obtaining soda ash. Sodium sulfate used in the experiments is a natural salt of the Zhaksykylysh deposit, crystallizing in the form of tenardite. A solution of distiller liquid produced by soda ash was obtained from the Sterlitamak soda plant. In order to determine the possibility of an interaction reaction of calcium chloride with sodium sulfate in the presence of impurities, the Gibbs energy was calculated. Based on the chemical composition of the distiller liquid, the required amount of natural sodium sulfate is calculated. The optimal parameters of the distiller liquid processing modes, the consumption of natural sodium sulfate in the range of 84-100% of stoichiometry, temperature and duration of the process were determined.

Keywords: soda ash production, distiller liquid, sodium sulfate, waste recycling, gypsum

INTRODUCTION

Extraction and processing of natural sodium-containing mineral salts is one of the promising areas of development of the chemical industry. The resulting products are of the greatest economic importance, for example, soda ash is one of the most popular products for the chemical, metallurgical, textile and food industries. There is still no production of soda ash in Kazakhstan. Most of the mastered production of inorganic salts is based on the use of soda ash, which must be purchased in neighboring countries, mainly from the Russian Federation. The demand of the chemical industry of the Republic of Kazakhstan for soda ash is more than 300 thousand tons per year. This determines the need to create its own soda ash production in Kazakhstan.

The following methods of soda production are used in the world industry: ammonia (Solvay method), from natural soda-containing raw materials, from nephelins and by carbonation of sodium hydroxide. Despite the rapid development of soda ash production from natural soda-containing raw materials in the 1970s, the Solvay method remains one of the main methods of obtaining soda ash to this day. The world production of soda ash per year is about 53 million tons. The share of the ammonia method from the total volume of production is approximately 80%.

The widespread use of the ammonia method of soda production in production indicates its advantages over others [1]. The raw material – sodium chloride, necessary for the production of soda by the ammonia method, is inexpensive, widespread and easily mined. The main raw material for the production of soda ash is table salt or its brine and limestone. The total reserves of table salt deposits in Kazakhstan amount to 1.3 billion tons. They are represented by various types of salt deposits: rock salt and deposited salt, as well as lake brine.

Having a number of major advantages, the production of soda ash by the ammonia method has serious disadvantages: significant consumption of energy resources and large specific investments necessary to create production, the formation of a large amount of liquid waste, the so-called distiller liquid. For 1 ton of soda ash produced, there are 9-10 m^3 of distiller liquid [2].

Currently, the problem of waste disposal of soda ash production by the ammonia method is quite acute in all countries producing soda by this method. The applied technologies of processing, utilization and use of distiller liquid solve the problem only partially, due to the large amount of waste generated. To solve this problem, we propose to use natural sodium sulfate deposited in the Kyzylorda region of the sea with large proven reserves [3-7].

MATERIALS AND METHODS

Processing and conversion of calcium chloride were studied in the time interval from 15 to 60 minutes. The best indicator of the process was considered the lowest content of calcium ions in the filtrate, which characterizes the achievement of equilibrium in the system and the maximum degree of transformation in this reaction.

The conversion rate was calculated taking into account the residual calcium content ($C(CaO_f)$, %) in the liquid phase and the total amount of calcium (CaO_{total}, g) in the initial J.

The following research methods were used in the work: chemical, thermodynamic methods of analysis, scanning electron microscopy. The processes of thermal transformation of gypsum and the regularity of hydration of its firing products, structural and textural transformations of gypsum under the influence of various temperatures were studied. In the research, a solution of distiller liquid produced by the Sterlitamak soda plant was used.

Calculations of the Gibbs energy (ΔG_T^0) were carried out using the HSC-51 complex program developed by the Finnish Metallurgical company Outokumpy using the Reaction Eguations subroutine and reference data of ΔH_T^0 and S_T^0 compounds.

The distiller liquid of soda ash production contains, in addition to calcium and sodium chlorides, carbonate, sulfate and calcium hydroxide. There is no information about the joint decomposition of these compounds by sodium sulfate and thermodynamic analysis of the reactions occurring in the literature. The reaction of calcium chloride, $MgCl_2$ and $Ca(OH)_2$ with sodium sulfate proceeds as shown in Table 1.

The evaluation of the possibility of carrying out reactions 1, 2 and 3 is performed by calculating the Gibbs energy. Based on the peculiarities of the temperature processes of the formation of a distiller liquid in soda production, changes in the Gibbs energy (ΔG_T^0) in the temperature range 293-373K are of particular interest.

Calculations of the Gibbs energy (ΔG_T^0) were carried out using the HSC-51 complex program developed by the Finnish Metallurgical company Outokumpy using the Reaction Equations subroutine and reference data of ΔH_T^0 and S_T^0 compounds. The calculated thermodynamic data of the compounds and the dependence of the Gibbs energy change (ΔG_T^0) on temperature (t) for these reactions are given in Table 1.

Table 1 shows that in the temperature range of 293-373K for reactions 1 and 2, the values of ΔG_T^0 calculated using the HSC complex program have negative values, which indicates the possibility of an interaction reaction of calcium chloride with sodium sulfate to form NaCl, $CaSO_4 \cdot 2H_2O$, $MgSO_4$ and NaOH. The interaction of calcium hydroxide with sodium sulfate to form $CaSO_4 \cdot 2H_2O$ and NaOH are not possible (reaction 3), because the value of ΔG_T^0 has a positive value.

Table 1 – Change in Gibbs energy (ΔG_T^0) as a function of temperature

№	The equation of the ongoing reaction	T, K	ΔG^O_T, KJ	LogK
1	$Na_2SO_4+CaCl_2+2H_2O=2NaCl+CaSO_4{\cdot}2H_2O$	293	-72,479	12,916
		303	-71,884	12,387
		313	-71,268	11,889
		323	-70,633	11,418
		333	-69,978	10,973
		343	-69,306	10,551
		353	-68,618	10,15
		363	-67,913	9,769
		373	-67,194	9,407
2	$CaCl_2+MgCl_2+Ca(OH)_2+3Na_2SO_4+4H_2O=$ $=2CaSO_4{\cdot}2H_2O_{solid}+MgSO_4+4NaCl+2NaOH$	293	-64,473	11,489
		303	-63,346	10,916
		313	-62,177	10,372
		323	-60,97	9,856
		333	-59,725	9,365
		343	-58,446	8,898
		353	-57,135	8,452
		363	-55,791	8,026
		373	-54,418	7,618
3	$Ca(OH)_2+Na_2SO_4+2H_2O=$ $=CaSO_4{\cdot}2H_2O+2NaOH$	293	85,867	-15,301
		303	86,366	-14,883
		313	86,885	-14,494
		323	87,423	-14,132
		333	87,977	-13,795
		343	88,548	-13,48
		353	89,134	-13,185
		363	89,735	-12,908
		373	90,349	-12,648

RESULTS AND DISCUSSION

Representative samples of raw materials – natural sodium sulfate of the Southern region of Kazakhstan were previously selected for the research. Several samples were selected, the composition of which is presented in Table 2.

Table 2 - Chemical composition of natural sodium sulfate (tenardite)

Name	Salt composition of natural sodium sulfate, % in samples				
	№1	№2	№3	№4	№5
Na_2SO_4	94,18	93,98	96,80	92,19	91,82
NaCI	-	-	-	-	-
$MgSO_4$	0,40	1,875	-	0,90	1,32
$MgCI_2$	-	-	-	-	0,46
$CaSO_4$	2,465	3,859	2,07	5,12	4,42
AI_2O_3	0,283	0,24	0,321	-	0,264
SiO_2	1,596	0,375	0,675	0,90	1,47
K_2O	-	-	-	0,085	-
Fe_2O_3	0,10	-	0,071	0,221	0,121

At the initial stage, averaged natural sodium sulfate (tenardite) of the composition was taken for experiments: Na_2SO_4 – 92.95%; $CaSO_4{\cdot}2H_2O$ - 4.0%; $MgSO_4{\cdot}H_2O$ – 0.57%; Fe_2O_3– 0.09%; Al_2O_3 – 0.40%; insoluble precipitate – 1.42; moisture – less than 1.0%.

The results of the study are presented in Figures 1 and 2.

Figures 1 and 2 show changes in the degree of conversion over time, where optimal process parameters are obtained (temperature, sodium sulfate rate and the dependence of the Ca^{2+} content in the liquid phase on the time of the process).

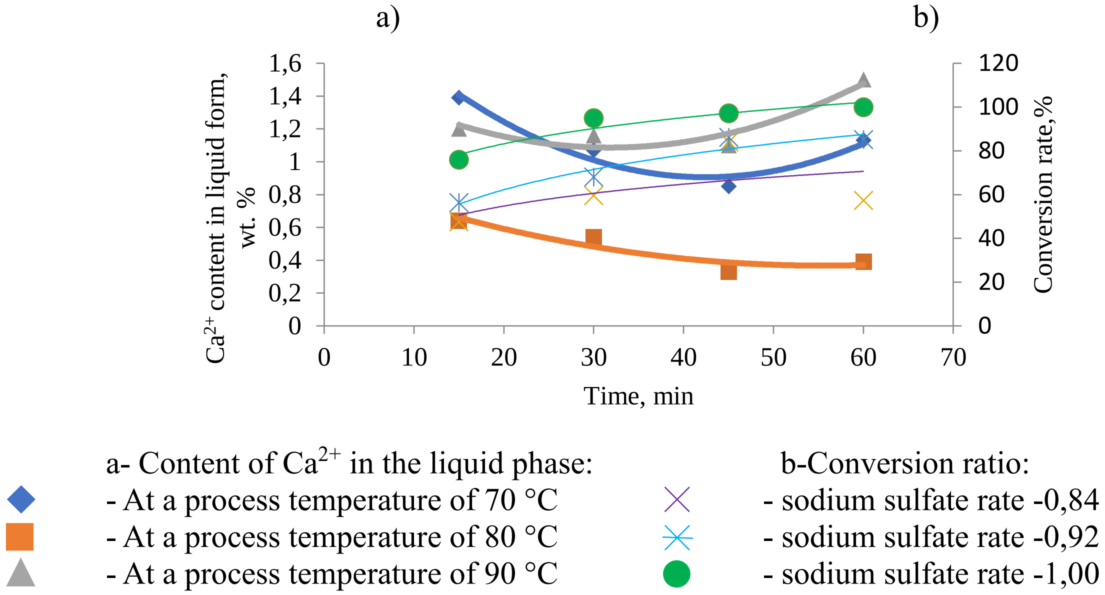


Fig.1. Dependence of the Ca^{2+} content in the liquid phase on the process time (a) and the change in the degree of conversion depending on the stoichiometry norm at 70 °C, sodium sulfate norm 0.84÷1.0 (b).

In the process of conversion of calcium chloride (Figure 1 (a)) and the use of sodium sulfate below the stoichiometric amount (84%) at a temperature of 70 °C and a time of 15-45 minutes. the content of calcium ions in sodium chloride solution decreases from 1.39% to 0.42%, increasing the norm of sodium sulfate to 1.00, the content of calcium ions in NaCI solution decreases from about 0.81% to 0.2%.

From Figure 1 (b) it can be seen that with an increase in the conversion time at a temperature of 70 °C and a sodium sulfate norm of 0.84, the conversion rate during a time of 15-45 minutes is reached from 47.54% to 84.04%, and at 60 minutes it is 57.27%. The decrease in the conversion rate may be due to the formation of $Na_2SO_4{\cdot}CaSO_4$ salt and due to the lack of calcium sulfate necessary for the decomposition of calcium chloride. At the norm of sodium sulfate 0.92 the degree of conversion within 15-45 min it is achieved from 56.3% to 86.1%. With the achievement of the time - 60 min the conversion rate is reduced to 1.0% and is 85.1%. This is due to the solubility of calcium salts and the lack of sodium sulfate, which is necessary for the decomposition of calcium chloride. With an increase in the temperature of the conversion process to 80 °C and a time of 15-45 minutes. with a sodium sulfate norm of 0.92, the conversion rate is 87.7-92.4%, and with a norm of 1.00, the conversion rate is 88.37%.

Figure 2 shows the dependence of the content of Ca^{2+} in the liquid phase on the time of the process (a) and the change in the degree of conversion of CaO at the norm of sodium sulfate -1.00, temperature 70÷90 °C (b).

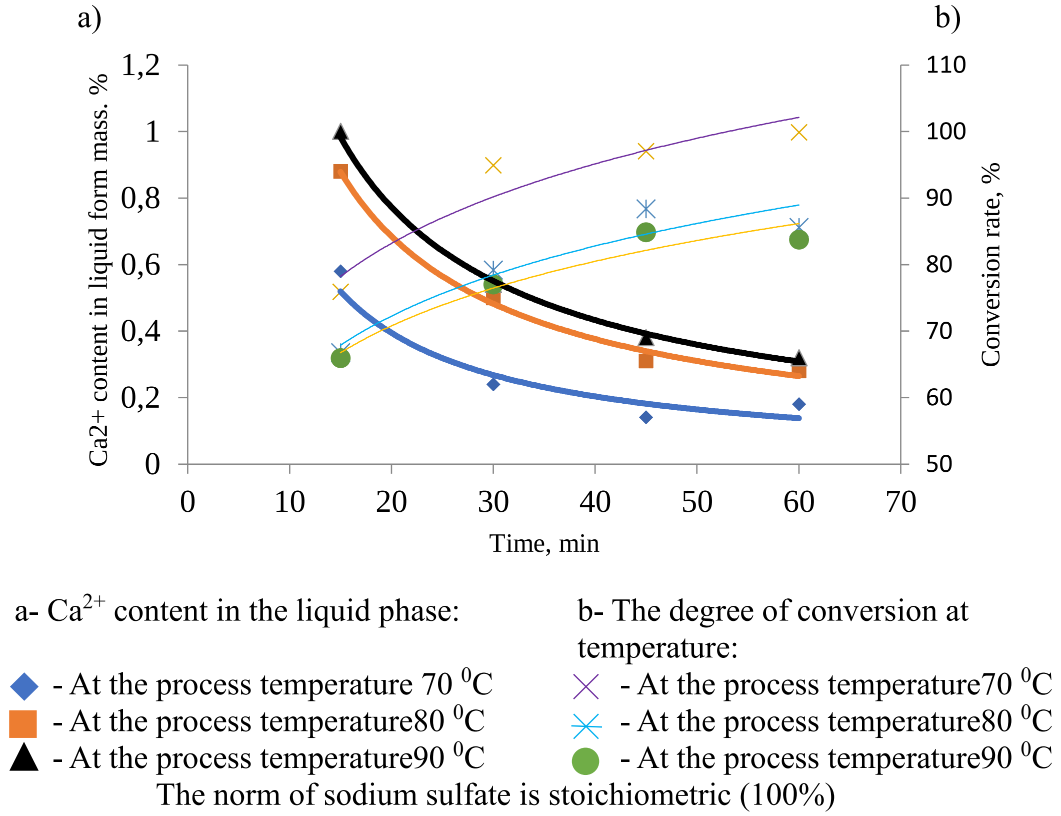


Fig.2. The dependence of the Ca^{2+} content in the liquid phase on the time of the process (a) and the change in the degree of conversion of CaO at the norm of sodium sulfate -1.00, at 70÷90^0C (b).

From Figure 2 (b) it can be seen that the highest degree of conversion is achieved at a temperature of 70 °C and 45 minutes of 97.02%, at 80 °C - 88.37%, at 90 °C-84.85%. A decrease in the degree of conversion with an increase in temperature (90 °C and above) is associated with the transition of dihydrate to calcium sulfate semihydrate, which binds sodium sulfate salts in the form of $Na_2SO_4 \cdot CaSO_4 \cdot 0{,}5H_2O$ and passes into the solid phase. Thus, the maximum achieved content of Ca^{2+} in this case does not exceed 1.05÷1.61% (Figure 2, b) whereas with the stoichiometric norm of sodium sulfate at 70°C, it is 0.14÷0.18% Ca^{2+}. The conversion rate of calcium chloride is 96.89÷97.02%. Moreover, as already noted above, temperature plays a key role in facilitating the dissolution of sodium sulfate, hence the course of the reaction and the precipitation of more calcium ions when obtaining a saturated sodium chloride solution. Based on the kinetic study carried out on a laboratory installation, the duration of the conversion process was determined to be 45 minutes, ensuring a minimum content of calcium ions in the filtrate at temperatures of 70-90 °C and the norm of sodium sulfate 100% of stoichiometry. The composition of the liquid phase, depending on the norm of sodium sulfate at a conversion temperature of 70 °C, is shown in Table 3.

The effect of the norm of sodium sulfate on the degree of conversion of calcium chloride contained in the distiller liquid was studied at an optimal process duration of 45 minutes (Figures 3 and 4).

Table 3 - Norms of sodium sulfate for conversion rates of calcium chloride. Conversion temperature - 70 °C

№	Time min	Norm Na_2SO_4 (N), %	Content in the liquid phase, mass.%							Molar ratio $\frac{Ca^{2+}}{SO_4^{2-}}$	Conversion rate, %
			Ca^{2+}	SO_4^{2-}	Na^+	Cl^-	Mg^{2+}	Fe^{3+}	Al^{3+}		
1	45	84	0,420	0,30	4,91	7,01	0,002	0.003	0.004	3,36	80,04
2	45	92	0,128	0,64	6,03	7,13	0,001	0.002	0,002	0,49	86,10
3	45	100	0.142	0.68	7.52	8.32	-	0.001	0.001	0.38	97.02
4	45	108	0,09	1,58	6,76	7,19	-	-	-	0,14	95,60
5	45	127	0,06	2,72	6,05	6,15	-	-	-	0,20	95,52

It can be seen from Table 3 and Figure 3 that with an increase in the sodium sulfate consumption rate from 84 to 127%, the CaO content in the liquid phase decreases from 0.42 to 0.06%, respectively. This is due to a large excess of sulfate ions (an increase from 0.30% to 2.72% at N=127%). Under these conditions, calcium chloride is almost completely converted into calcium sulfate in the form of a precipitate, and calcium remains in the solution within the limits of the solubility of $CaCO_4$ (Ca^{2+}- 0.06%). However, such a large excess of sulfate ions in the form of dissolved sodium sulfate in a solution of sodium chloride is highly undesirable, because when using filtrate in the production of soda ash, the presence of sulfate ions in the brine leads to the formation of inlays on the walls of carbonation columns, which requires frequent stops of the main equipment, in addition to the washing column, as well as the distillation column for washing.

It follows from Table 3 that an increase in the norm of sodium sulfate from 84% to 100% leads to a 3-fold decrease in the content of calcium ions in the liquid phase, from 0.42 to 0.142% (with sediment repulpation to 0.07%) and, accordingly, to a sharp increase in the degree of conversion from 80.04% to 97.02%. At a rate of 108%, the content of calcium ions decreases to 0.09%, i.e. by 40% rel. A further increase in the norm of sodium sulfate in excess of stoichiometric, i.e. the conversion in the sulfate mode does not significantly affect the content of calcium ions in the filtrate (0.06%). At the same time, the degree of conversion practically does not change, even there is a slight decrease in this indicator by 0.5% rel. (Figure 3). At the same time, this leads to an increase in the content of sulfate ions to almost 3%, which can cause problems with possible encrustation of the distillation separation equipment with crystallizing gypsum, as well as with increased consumption of precipitators at the brine purification stage.

At the same time, a more dilute solution of sodium chloride (6.15% Cl^- and 6.05% Na^+) is also formed, requiring an increased consumption of table salt for its saturation or coolant consumption for evaporation of the filtrate to a solution concentration close to saturation. Based on the data obtained, it is recommended to carry out the process of distiller liquid processing at the stoichiometric (100%) norm of sodium sulfate, where the degree of conversion of calcium chloride reaches the highest value and the lowest content of impurities in the filtrate Ca, Mg, Fe, Al.

The effect of the process temperature on the composition of the filtrate and the degree of conversion was studied at an optimal rate of 100% sodium sulfate. The results are shown in Table 5 and Figure 5.

From the data in Table 4 and Figure 4, it can be seen that with an increase in temperature from 70 °C to 95 °C, the content of Ca^{2+} ions in the solution practically does not change and is in the range of 0.13-0.16%, Fe^{3+} and Al^{3+} impurities are stable in the range of 0.001-0.003% and practically does not affect the degree of conversion calcium. The rest of the admixture of Ca, Mg, Fe, Al and insoluble precipitate passes into the precipitate in place of calcium sulfate.

Maintaining a "zero" or sulfate regime ensures a minimum content of calcium ions and impurities in the filtrate, and hence the maximum degree of transformation.

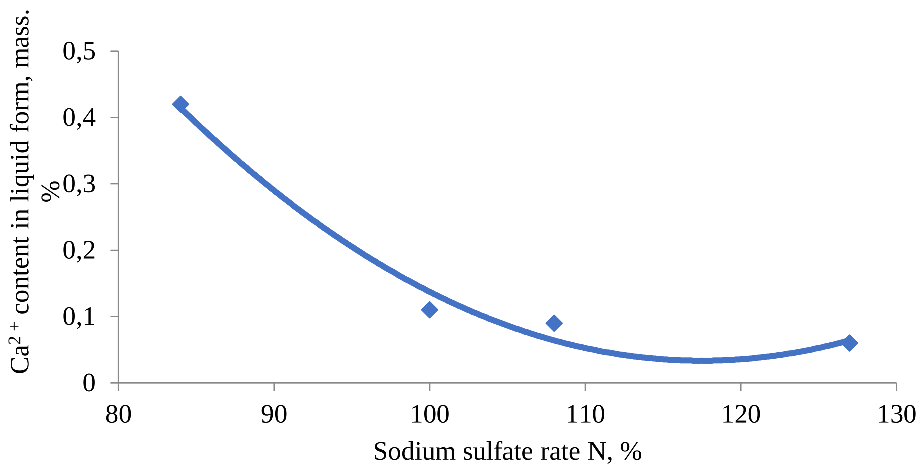


Fig.3.Dependence of Ca^{2+} content in the liquid phase on the norm of sodium sulfate

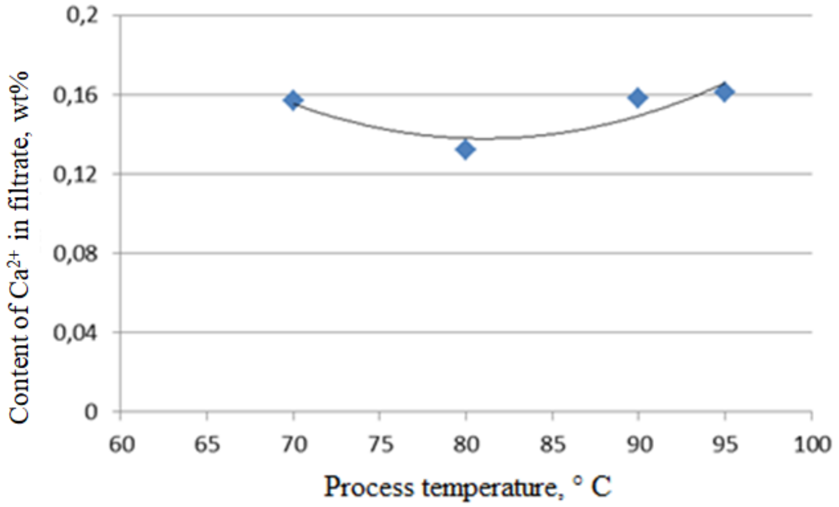


Fig. 4. Dependence of the Ca^{2+} content in the filtrate on the process temperature. Sodium sulfate rate is 100%.

Table 4. Influence of the process temperature on the conversion rates of calcium chloride

№	t, °C	Content in the filtrate, mass.%							Molar ratio $\frac{Ca^{2+}}{SO_4^{2-}}$	Conversion rate, %
		Ca^{2+}	SO_4^{2-}	Mg^{2+}	Na^{+}	Cl^{-}	Fe^{3+}	Al^{3+}		
1	70	0,157	0.71	0,002	6,97	9,57	0,002	0,003	0,51	97,0
2	80	0,132	1,02	0,001	8,41	9,39	0,002	0,002	0,45	94,6
3	90	0,158	0,79	0,001	5,93	7,39	0,001	0,001	0,24	96,4
4	95	0,161	0,12	-	7,36	10,1	0,001	0,001	7,6	93,6

Table 5 shows the composition of the precipitate obtained in the temperature range of 70-95°C and the duration of the process of 45 minutes. The precipitate consists mainly of CaO and SO_4^{2-} in the form of a calcium sulfate compound. In addition, the sediment contains impurities of MgO 0,131÷0,141%, Fe_2O_3 0,61÷0,76%, Al_2O_3 0,71÷0,89%, SiO_2 0,08÷0,09%. These impurities come with sodium sulfate and do not interact with calcium chloride. During the conversion of calcium, metal oxides precipitate together with calcium sulfate and do not affect the degree of conversion of calcium chloride.

Table 5. Composition of the precipitate obtained during the conversion of calcium chloride

№	t, °C	Content in the filtrate, mass.%										Conversion rate, %
		CaO	SO_4^{2-}	MgO	Na_2O	Cl	CO_2	Fe_2O_3	Al_2O_3	SiO_2	H_2O	
1	70	35,24	61,08	0,131	0,56	0,16	1,03	0,61	0,72	0,08	0,39	97,0
2	80	36,76	59,02	0,135	0,82	0,31	1,04	0,75	0,86	0,09	0,22	94,6
3	90	35,18	61,19	0,140	0,54	0,17	1,04	0,62	0,71	0,08	0,37	96,4
4	95	37,04	58,94	0,141	0,62	0,24	1,04	0,76	0,89	0,08	0,24	93,6

In the recommended temperature range of 70-90°C optimum temperature is 70 °C, which is due to the conversion process in a more stable mode, which excludes the phase transition of semihydrate into gypsum. This in turn ensures the formation of large homogeneous gypsum crystals. The choice of the optimal temperature regime is directly related to the filtering properties of the resulting suspension. To ensure the maximum degree of conversion of calcium chloride, the process must be carried out in a stoichiometric ratio of 100%, a temperature of 70 °C and a process duration of 45 minutes.

To assess the effect of the reaction conditions set during the preparation of gypsum, experiments were carried out, including a number of experiments. The influence of parameters such as temperature, duration of the reaction and stoichiometric ratio between the added amount of tenardite and the Ca+ present in the model liquid was evaluated.

The experiment was planned using the STATISTICA-10 program. 3-level Box-Benken plans were chosen as a model.

To assess the effect of the reaction conditions set during the preparation of gypsum, an experiment was conducted, including a number of experiments. The influence of parameters such as temperature, reaction time and stoichiometric ratio between the added amount of tenardite was evaluated (Table 6).

Table 6. Correlation with factors

Name	Time, min	Temperature, ^{0}C	The norm of sodium sulfate
Lower level (-1)	15	50	0,84
Average level (0)	30	70	0,92
Upper level (+1)	60	90	1,0

To determine the influence of individual factors, a correlation analysis was carried out and correlation coefficients were determined between the degree of conversion and individual factors, as well as between the degree of conversion and inter-factor interactions (Table 7).

Table 7. Correlation with factors

Parameters	Correlation coefficient
τ (time)	0,102361108
τ^2	0,254467727
t (temperature)	0,0383546826
t^2	0,362349174
μ (norm of sodium sulfate)	0,367237891
μ^2	0,228491011
τ*t	-0,0816034867

Table 7 continuation

$\tau * t^2$	-0,0612537286
$\tau^2 * t$	-0,123086963
$\tau^2 * t^2$	-0,12734025
$\tau * \mu$	0,162604734
$\tau * \mu^2$	0,111033249
$\tau^2 * \mu$	-0,123029012
$\tau^2 * \mu^2$	-0,0549711065
$t * \mu$	-0,33474493
$t * \mu^2$	0,277988776
$t^2 * \mu$	-0,484640428
$t^2 * \mu^2$	-0,0138180566

As can be seen from Table 7, weak and very weak correlations dominate. There are no strong correlations between the degree of conversion and individual factors.

For a visual assessment of the change in the degree of conversion with varying values of individual factors, graphs of the dependence of the degree of conversion on one factor with two other constants were constructed. Figures 5 and 6 show the dependence of the degree of conversion on temperature, time and the norm of sodium sulfate 0.84-1.00.

From Figure 5 it can be seen that the conversion rate of sodium sulfate 0.84 and 0.92 in the temperature range of 50÷80 °C increases to a maximum and is 40.9÷94.6%.

At the norm of sodium sulfate 1.0, the degree of conversion with an increase in temperature from 50°C to 90°C reaches up to 81.1-97.00% (Figure 6).

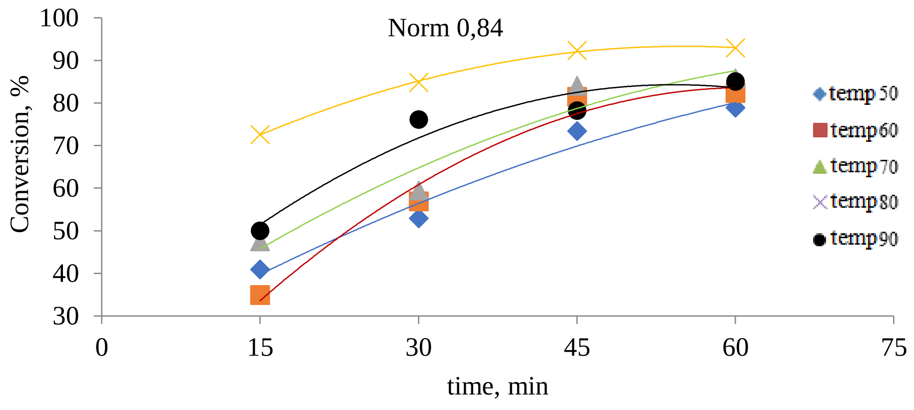
To determine the type of mathematical model describing the dependence of the calcium conversion value on the temperature and reaction time, and the stoichiometric norm of the added sodium sulfate, the regression coefficients of the equations indicated on the graphs were analyzed. The functions for the regression coefficients are listed below.

For the case of the stoichiometric norm argument of the added sodium sulfate:

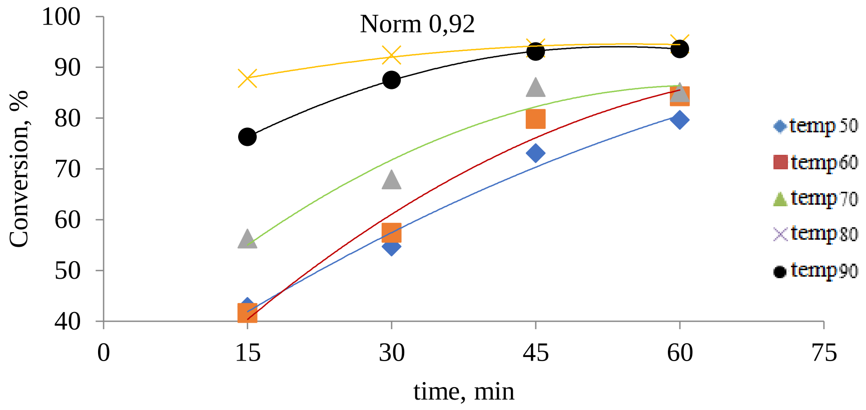
$$a_1 = 8263{,}802 - 39{,}622 \cdot \tau - 1{,}902 \cdot \tau^2 - 52{,}709 \cdot t - 1{,}075 \cdot t^2 + 2{,}219 \cdot \tau \cdot t,$$

$$a_2 = -2953{,}34 + 50{,}15 \cdot \tau + 3{,}7 \cdot \tau^2 - 192{,}92 \cdot t + 3{,}72 \cdot t^2 - 3{,}99 \cdot \tau \cdot t,$$

$$a_3 = -4854{,}89 - 9{,}23 \cdot \tau - 1{,}81 \cdot \tau^2 + 236{,}33 \cdot t - 2{,}59 \cdot t^2 + 1{,}78 \cdot \tau \cdot t,$$



a)



b)

Fig.5– The dependence of the degree of conversion on time at constant rates of sodium sulfate 0.84 (a) and 0.92 (b) and a temperature of 50÷90 °C

For the case of the reaction time argument:

$$a_1 = -1{,}97 + 0{,}02 \cdot t - 0{,}0005 \cdot t^2 + 2{,}469 \cdot \mu - 0{,}823 \cdot \mu^2 - 0{,}012 \cdot \mu \cdot t,$$
$$a_2 = 149{,}374 - 1{,}882 \cdot t + 0{,}005 \cdot t^2 - 154{,}041 \cdot \mu + 37{,}297 \cdot \mu^2 + 1{,}092 \cdot \mu \cdot t,$$
$$a_3 = -4112{,}94 + 61{,}02 \cdot t - 0{,}2 \cdot t^2 + 3672{,}99 \cdot \mu - 716{,}78 \cdot \mu^2 - 30{,}03 \cdot \mu \cdot t,$$

For the case of the temperature argument:

$$a_1 = -2{,}988 + 3{,}513 \cdot \mu - 1{,}07 \cdot \mu^2 + 0{,}022 \cdot \tau - 0{,}00028 \cdot \tau^2 - 0{,}004 \cdot \mu \cdot \tau,$$
$$a_2 = 386{,}997 - 344{,}594 \cdot \mu + 47{,}122 \cdot \mu^2 - 3{,}829 \cdot \tau + 0{,}047 \cdot \tau^2 - 0{,}618 \cdot \mu \cdot \tau,$$
$$a_3 = -12257{,}4 + 6304{,}7 \cdot \mu + 2343{,}5 \cdot \mu^2 + 161{,}5 \cdot \tau - 1{,}9 \cdot \tau^2 + 23 \cdot \mu \cdot \tau,$$

where a_1 is the coefficient for the squared argument; a_2 is the coefficient for the argument in the first degree; a_3 is the free term.

To select the optimal dependence, the deviations of experimental data from those predicted by each model were compared.

For the three cases presented, the smallest deviation of the predicted values from the experimental ones is observed if the reaction time is taken as an argument. Thus, a mathematical model is chosen:

$$N = (-1{,}97 + 0{,}02 \cdot t - 0{,}00005 \cdot t^2 + 2{,}469 \cdot \mu - 0{,}823 \cdot \mu^2 - 0{,}012 \cdot \mu \cdot t) \cdot \tau^2$$
$$+(149{,}374 - 1{,}882 \cdot t + 0{,}005 \cdot t^2 - 154{,}041 \cdot \mu + 37{,}297 \cdot \mu^2 + 1{,}092 \cdot \mu \cdot t) \cdot \tau$$
$$+(-4112{,}94 + 61{,}02 \cdot t - 0{,}2 \cdot t^2 + 3672{,}99 \cdot \mu - 716{,}78 \cdot \mu^2 - 30{,}03 \cdot \mu \cdot t)$$

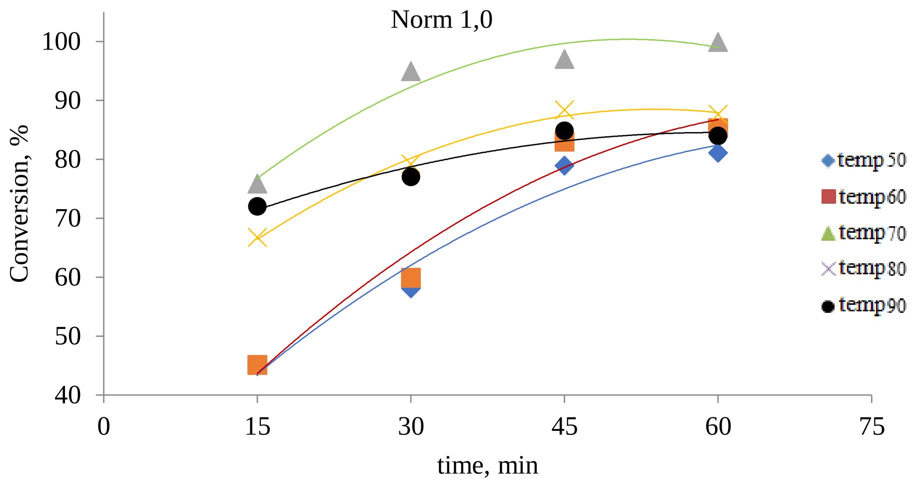


Figure 6. The dependence of the degree of conversion on time at a norm of 1.0 sodium sulfate and a temperature of 50÷90 °C.

For this dependence, the value of the Fisher criterion F_{exp}=2.31 was calculated. This value is greater than the theoretical value F_{teor}=1.93. This indicates the significance of the chosen dependence.

When studying the extremum points of this model, it was found that they lie at a considerable distance from the studied range. In this regard, optimal parameters should be chosen based on experimental data, as well as model predictions at these points.

CONCLUSION

According to the experimental data obtained, taken for mathematical processing, it is deduced that the highest value of the conversion rate is achieved at the following optimal parameters: τ=45 min; t=70 ^{0}C; μ=1.0. At this point, in addition to the highest conversion value, the smallest deviation of the predicted value from the experimentally obtained value is also observed.

The mathematical processing carried out allows us to anticipate the nature of these dependencies and use them in the operational regulation of process parameters in real production conditions.

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СОДА КҮЛІН АЛУ ҮШІН ДИСТИЛЛЯТОР СҰЙЫҚТЫҒЫН ӨҢДЕУДІ ЗЕРТТЕУ

Түйін

Зерттеудің мақсаты-құрамында сода өндірісінің негізгі қалдықтары болып табылатын кальций хлориді бар дистиллятор сұйықтығын табиғи натрий сульфатымен өңдеп, гипс байланыстырғыш пен натрий хлориді фильтратын алу. Ас тұзының қосымша мөлшерін ерітіп, оны қажетсіз қоспалардан тазартқаннан кейін фильтратты сода күлін алу технологиясында қолдануға болады. Тәжірибелерде қолданылатын натрий сульфаты-тенардит түрінде кристалданатын Жақсықылыш кен орнының табиғи тұзы. Стерлитамак сода зауытынан сода күлі шығаратын дистиллятор сұйықтығының ерітіндісі алынды. Қоспалар болған кезде кальций хлоридінің натрий сульфатымен әрекеттесу реакциясының мүмкіндігін анықтау үшін Гиббс энергиясы есептелді. Дистиллятор сұйықтығының химиялық құрамы негізінде табиғи натрий сульфатының қажетті мөлшері есептеледі. Дистиллятор сұйықтығын өңдеу режимдерінің оңтайлы параметрлері, стехиометрияның 84-100% диапазонында табиғи натрий сульфатын тұтыну, процестің температурасы мен ұзақтығы анықталды.

Кілттік сөздер: сода күлін өндіру, дистиллятор сұйықтығы, натрий сульфаты, қалдықтарды қайта өңдеу, гипс

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ИССЛЕДОВАНИЕ ПРОЦЕССА ПЕРЕРАБОТКИ ДИСТИЛЛЯЦИОННОЙ ЖИДКОСТИ ДЛЯ ПРОИЗВОДСТВА КАЛЬЦИНИРОВАННОЙ СОДЫ

Аннотация

Целью исследования является переработка дистилляционной жидкости, содержащей хлорид кальция, основного отхода содового производства, путем ее обработки природным сульфатом натрия с получением гипсового вяжущего и фильтрата хлорида натрия. Фильтрат после растворения в нем дополнительного количества поваренной соли и очистки его от нежелательных примесей может быть использован в технологии получения кальцинированной соды. Сульфат натрия, используемый в экспериментах, представляет собой природную соль месторождения Жаксыкылыш, кристаллизующуюся в виде тенардита. На Стерлитамакском содовом заводе был получен раствор для дистилляции кальцинированной соды. Для определения возможности реакции взаимодействия хлорида кальция с сульфатом натрия в присутствии примесей была рассчитана энергия Гиббса. Исходя из химического состава дистилляционной жидкости, рассчитывается необходимое количество природного сульфата натрия. Определены оптимальные параметры режимов обработки дистилляционной жидкости, расход природного сульфата натрия в диапазоне 84-100% от стехиометрии, температура и продолжительность процесса.

Ключевые слова: производство кальцинированной соды, дистилляционная жидкость, сульфат натрия, переработка отходов, гипс