

Treatment of Dried and Mixed Salts of Karaumbet in Magnesium Hydroxide Following Sodium Sulfate and Chloride Production

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Abstract:

The process of dried and mixed salt of Karaumbet in magnesium hydroxide with preparation of sodium sulfate, chloride and gypsum simultaneously has been studied. At that the following stages of mixed salts processing were conducted: removing water insoluble residue, sulphur free, cooling of sodium sulfate, deposition of magnesium hydroxide by neutralization of purified solution of sodium and magnesium chlorides using sodium hydroxide. As a result, samples of settled gypsum, sodium sulfate with high brand, purified magnesium hydroxide and sodium chloride solution. The present study chemical, X-ray imaging and thermic analysis were used.

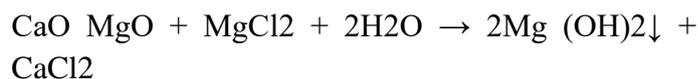
Keywords: dried mixed salts, solubilisation, deposition, filtration, mirabilite, sodium sulfate, gypsum, magnesium hydroxide, sodium chloride.

INTRODUCTION

Magnesium is belonged to number of the most widespread elements (the eighth in Earth crust and third in marine). According to INFOMINE [1], total approved reserves of magnesium salts class A+B+C1 on area of CIS makes about 6.7 billion in which MgCl₂ is 1.16 billion tonnes. Approximately 61.4 % of all supplies of magnesium is belonged to Russia, 20% - to Turkmenistan, 18.4% - to Ukraine, 0.2% - to Kazakhstan. Stocks of magnesium salts concluded in chloride (68%), sulfate (16%), mixed sulfate chloride salts (5%) and brine (11%).

The main sources of magnesia raw are the followings: magnesite (MgCO₃), dolomite (MgCO₃•CaCO₃), brucite Mg(OH)₂, carnallite (KCl•MgCl₂•6H₂O), bischofite (MgCl₂•6H₂O), kieserite (MgSO₄•H₂O), kainite (MgSO₄•KCl•3H₂O), langbeinite (2MgSO₄•K₂SO₄), epsomite (MgSO₄•7H₂O). Note that, processing of sulfate salts with NaCl along with bischofite valuable product Na₂SO₄ can be obtained. Some countries such as the USA, China, Japan, Israel, Mexico, Jordan and Western Europe Mg(OH)₂ can be produced from sea water by

mixing it with calcinated dolomite or limestone as follows:



About 15 % of magnesium is produced from sea water that consists of total magnesium producing in the world. Only 56% of magnesium world production is belonged to Japan, Holland and the USA [2]. As the main consumers of Mg(OH)₂ are metallurgical industry, refractory, electrical engineering and pulp and paper, mechanical rubber goods, building materials industry, chemical industry. Sodium sulfate has large consumption pulp and paper, glass, textile, tanning chemical and metallurgical industries too. The raw for sodium sulfate production is brine, saline deposits containing mirabilite (Na₂SO₄•10H₂O), bloedite (Na₂SO₄•MgSO₄•4H₂O), thenardite (Na₂SO₄). Such sources can be Kara-Bogaz-Gol in Turkmenistan, Kuchuk Lake in Russia, Searle Lake, mirabilite deposits, mixings of mirabilite and thenardite in Nevada, New Mexico, Texas and California States in the USA, brine and deposits of mirabilite and thenardite in Saskatchewan and

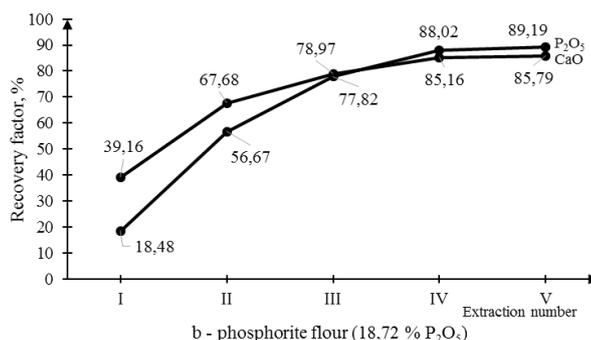
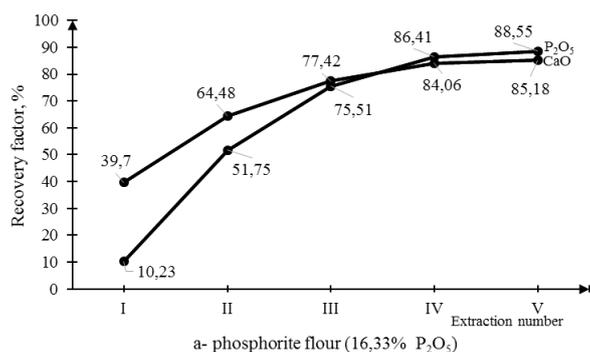
Alberta provinces in Canada, lake and underground water in India [3]. Generally sodium sulfate (thenardite) is produced by dehydration of mirabilite [4-6]. Moreover sodium sulfate is by-product of various chemical productions [7-9]. Uzbekistan has also large reserves of raw for production of magnesium and sodium salts. One of them is dried and mixed salts (DMS) from Karaumbet Lake. An approval reserve of Karaumbet Lake is estimated in 700 thousand tonnes of $MgCl_2$ or 295 thousand tonnes of MgO , but 74 thousand tonnes in brine. Additionally the reserves of magnesium salts in brine of Barsakel'mes are estimated in 2470 thousand tonnes of $MgCl_2$ or 1040 thousand tonnes of MgO [10]. For lack of promising technology of brine processing and dried mixed salts while they are not mining and treating. Therefore, the investigation directed at development of magnesium and sodium compounds technology from DMS of Karaumbet Lake is challenging. DMS can be considered as dried-up salts in lake as a result perennial expulsion of water from brine in natural conditions. Expulsion of water from brine is proceeding at present.

Object and methods DMS of Karaumbet Lake containing (weight %): Na_2SO_4 – 60.69; $NaCl$ – 18.81; $MgCl_2$ – 15.30; $MgSO_4$ – 0.42; $CaCl_2$ – 0.31; insoluble residue - 6,98; the rest – H_2O was used. As can be seen, DMS of Karaumbet Lake contents considerable quantity of mirabilite, halite and bischofite. Therefore, the processing DMS can have interest into magnesium hydroxide following sodium sulfate and chloride obtaining. Determination of CaO and MgO was conducted by volumetric complexometric method: titration with 0.05 n of Trilon B in presence fluorexon and chrome dark blue. Sodium was determined by flame photometric method. Sulfate was determined by weighting method based on sedimentation of sulfates by barium chloride in acid medium subsequent weighting of the residue. Chlorine was determined by argentometric method based on changing colour of chloride suspension of silver chloride when

interaction silver ions with potassium dichromate. Water in solid samples was determined by drying in muffle until constant mass at 100-105°C. Density of solutions and slurries were measured by pycnometer. The viscosity was determined by capillary viscometers such as VPJ-1 and VPJ-2. Measurement of the water suspension value was carried out in ion meter I-130M (Russia) with electrode system from electrodes ESL63-07, EVL-1M3.1 and TKA-7 with accurate within 0.05 of pH. Radiographic analysis was carried out on diffract meter XRD-6100 (Shimadzu, Japan). $CuK\alpha$ - emission (β - filter, Ni, current mode and voltage are 30 mA and 30 kV respectively) and constant of detector rotational velocity of 4 oC/min were used. When withdrawal of sample the camera with rotation of 30rpm/min was applied. Thermal analysis was performed on devise NETZSCH STA 409 PC/PG (Germany) in aluminium crucible at speed of heat of 2oC/min, the sample of fine grinding assay with 10-16 mg, measurement range was from 200 to 300oC. The measurements were carried out in inert condition atmosphere, in which speed of nitrogen to be 50 mL/min. Calibration of measuring systems was performed using standard set including KNO_3 , In, Bi, Sn, Zn and $CsCl$.

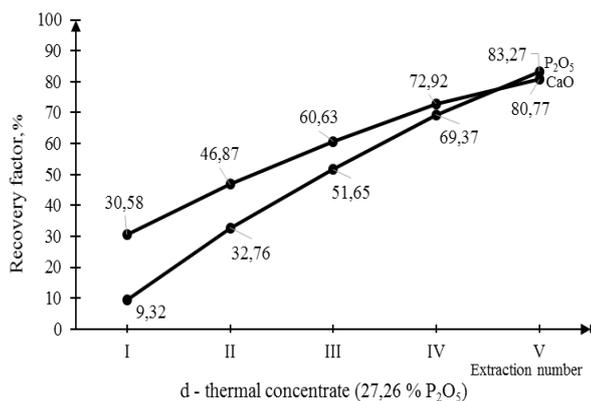
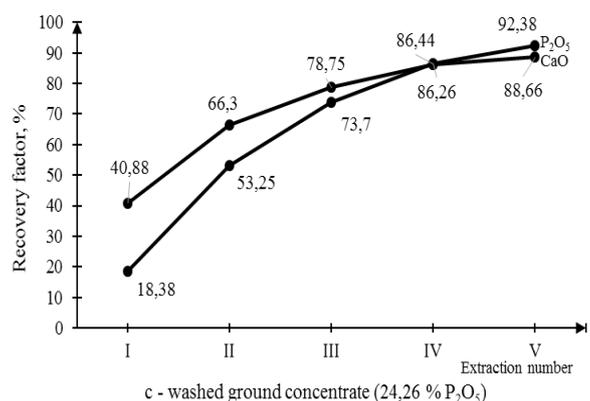
Results and discussion

To install optimal technological parameters of DMS preparation the solubility of them in water depending upon the weight ratio solid to liquid (S : L), duration and solvus temperature was studied. In Fig. 1-a the results on dissolution rate of DMS depending on the S : L at 25°C in 30 min is presented. As can be seen that the solubility of DMS in water is increasing with increase in the liquid phase in respect of the solid phase reaching 93.02% at S : L = 1 : 3. With increasing ratio of S : L from 1 : 2 to 1 : 3 the quantity of wet insoluble residue in water is decreasing from 22.63 to 4.69% in respect to total mass of the suspension.



a – Dissolution rate of DMS depending on the S : L at 25°C in 30 min.

b – Dissolution rate of DMS depending on the agitation and temperature at S : L = 1 : 3.



c – Cleaning rate of DMS suspension depending on the time and temperature of sedimentation at S : L = 1 : 3.

d – Filtration rate of thickened DMS depending on the temperature.

Fig. 1. The effect of various parameters on preparation of cleaned suspension of DMS

The data of Fig. 1-b is presenting that at S : L = 1 : 3 and 25°C each 5 min the dissolution rate of DMS of 89.25%, each 10 min – 92.4% and each 15 min – 93.02%, but at 50°C these indicates are 91.61%, 92.90 and 93.03%, which indicate that 15 min is sufficient for dissolution of DMS. In Fig. 1-c the effect of temperature and sedimentation on suspension cleaning rate of DMS at S : L = 1 : 3 is showing. Choice of sedimentation method can be explained to sedimentation insoluble particles with high rate and simplicity of settler application. From Fig. 1-c can be obviously seen that cleaning process is occurring dramatically in first 15 min, then cleaning rate is slowing down and after 30min reaching 94.59% at 20°C and 95.51% at 40; 60 and

80°C. At that optimal temperature and sedimentation can be estimated 40°C and 20 min respectively. In that case, cleaning rate of DMS suspension is no less 95%. To separate solid phase from liquid one investigation on filtration of DMS was carried out. For that thickened part of DMS, after settling, was used. The results on rate of filtration of thickened part of DMS by both slurry and filtrate against temperature is presented in Fig. 1-d. The results are showing that the higher temperature the higher filtration rate. So, with rising temperature from 20°C to 80°C the rate filtration on thickened slurry is increasing from 1028 to 2016 kg/m²·h, but on filtrate from 896 kg/m²·h to 1756 kg/m²·h. As can be seen from Fig. that 40°C is sufficient for separation of the

phases. The composition of insoluble residue based on dried mass can be shown as follows: 16.01% CaO, 1.25% MgO, 19.9% SO₃, 6.59% CO₂ and 61.33% SiO₂. It is presented mainly quartz, dolomite, calcium carbonate and sulfate.

After removing insoluble residue in water the density of cleaned solution at S : L = 1 : 3 and 40°C of 1.1788 g/cm³, and the viscosity of 157.9 cPz (Table 1).

Table 1

Density and viscosity of cleaned solution from dried and mixed salts from Karaumbet Lake

S : L	Density, g/cm ³			Viscosity, cPz		
	20°C	40°C	60°C	20°C	40°C	60°C
1 : 2	1.1874	1.1838	1.1800	220.50	168.30	139.10
1 : 3	1.1824	1.1788	1.1751	209.17	157.91	129.94
1 : 4	1.1778	1.1741	1.1705	197.30	148.30	120.70

Thus, at optimal conditions (S : L = 1 : 3, temperature of dissolution – 25°C, agitation – 15 min, time and temperature sedimentation – 20 min and 40°C, filtration temperature 40°C) DMS with composition (mass. %): Na₂SO₄ – 18.55; NaCl – 5.82; MgCl₂ – 4.98; MgSO₄ – 0.47; CaCl₂ – 0.36; CaSO₄ – 0.08.

The following task was recovery of the mirabilite from cleaned solution. To crystallization Na₂SO₄·10H₂O DMS solution was subjected to cooling to -5 °C and at 5°C interval chemical, saline

composition, and yield of sodium sulfate was determined. In Fig. 2-a the effect of temperature on yield of sodium sulfate was presented. As can be seen that with decreasing temperature causing cooling of the solution from 20°C to 0°C yield of Na₂SO₄·10H₂O into solid phase is increasing from 11.64 to 83.61%. In that case content of NaCl; MgCl₂; MgSO₄; CaCl₂ and CaSO₄ in the liquid phase is increasing to 6.68; 5.52; 0.60; 0.43 and 0.11% respectively, but Na₂SO₄ on the contrary is decreasing to 2.51%.

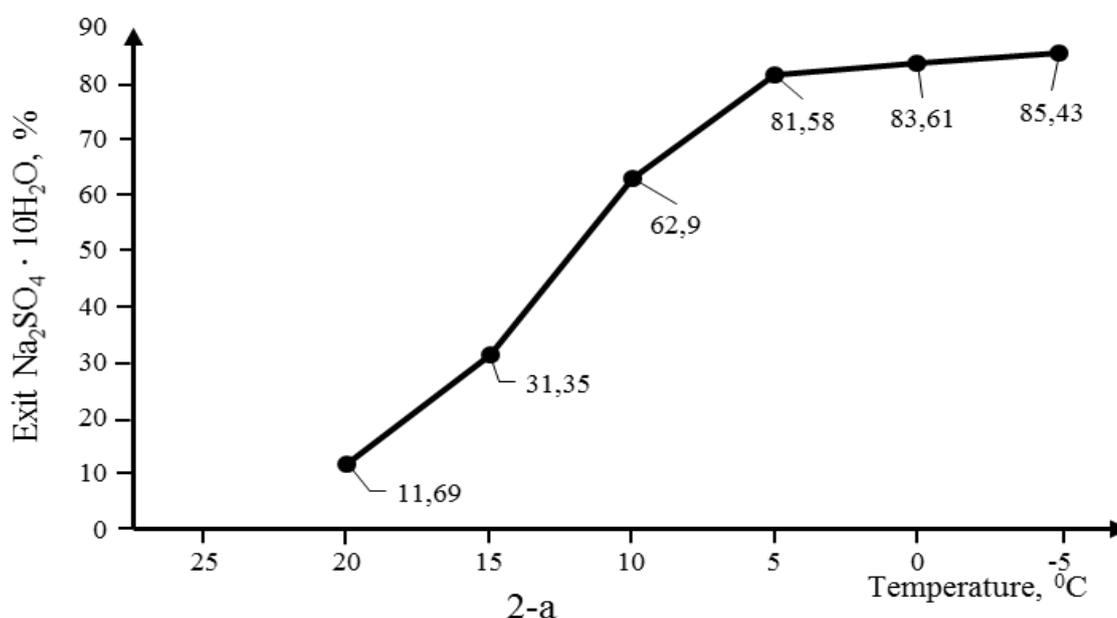


Fig. 2. Yield of Na₂SO₄·10H₂O depending on the crystallization temperature of suspension of dried and mixed salt

To separate $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ crystals obtained at 0°C the slurry having density of 1.6102 g/cm^3 was filtered out under residual pressure of 84 kPa, whose

results showed good filterability. In order to obtain anhydrous sodium sulfate derivative gram of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ was studied (Fig. 3).

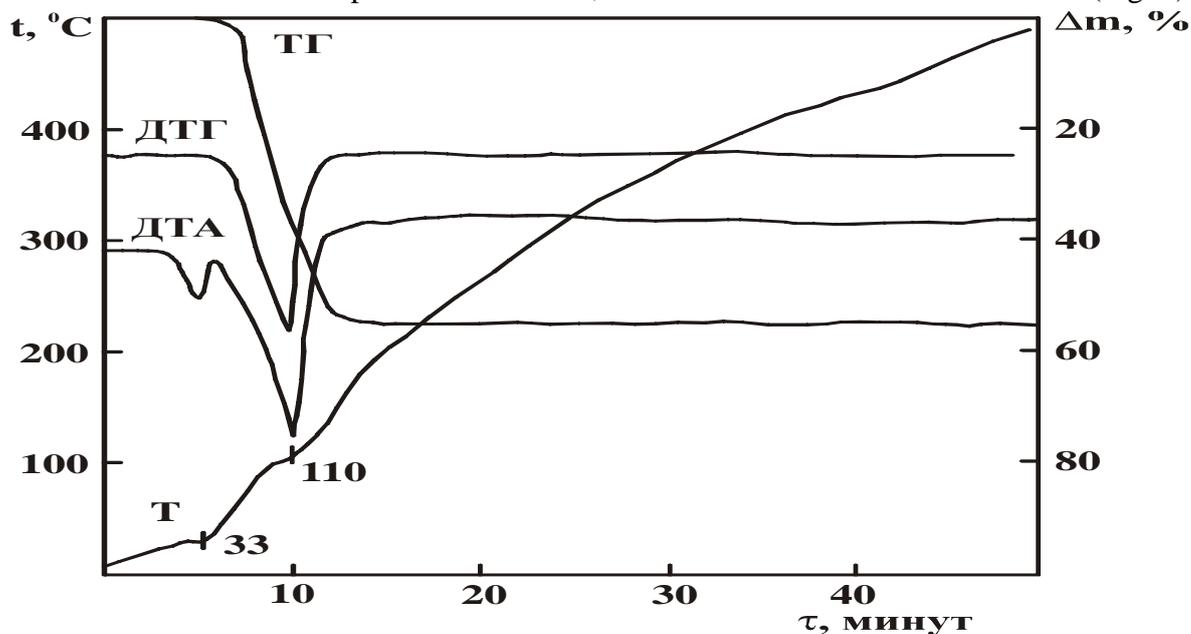


Fig. 3. Derivative gram of mirabilite

According to results of thermic analysis mirabilite is incongruent melting in own crystallization water that complying endothermic effect on derivate gram of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ at 33°C . At that saturated solution of sodium sulfate is formed. Beginning with 70°C removing water and boiling of solution at high $101-102^\circ\text{C}$ can be occurred. Intensive removing water from solution can be observed at range of $101-113^\circ\text{C}$. Full water extraction and formation of Na_2SO_4 takes place at heating to $200-205^\circ\text{C}$. On derivative gram the starting process of water extraction from $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ is corresponding

endothermic effect at 110°C . The mass loss of sample is 55.1%. Based on results of thermic studies of remained mirabilite was dried at 200°C and the product with Na_2SO_4 containing no less than 99.4% fitting high grade was obtained. The sample of sodium sulfate (thenardite) was studied by radiographical method. On the diffractograms of sodium sulfate some reflexes, d , equalled to 4.64; 3.83; 3.17; 3.07; 2.78; 2.64; 2.32; 1.86; 1.68; 1.66; 1.55 \AA (Fig. 4) are the most intensive. After separating mirabilite at 0°C the solution is remaining with composition (weight %): $\text{Na}_2\text{SO}_4 - 2.51$; $\text{NaCl} - 6.68$; $\text{MgCl}_2 - 5.52$; $\text{MgSO}_4 - 0.60$; $\text{CaCl}_2 - 0.43$; $\text{CaSO}_4 - 0.11$.

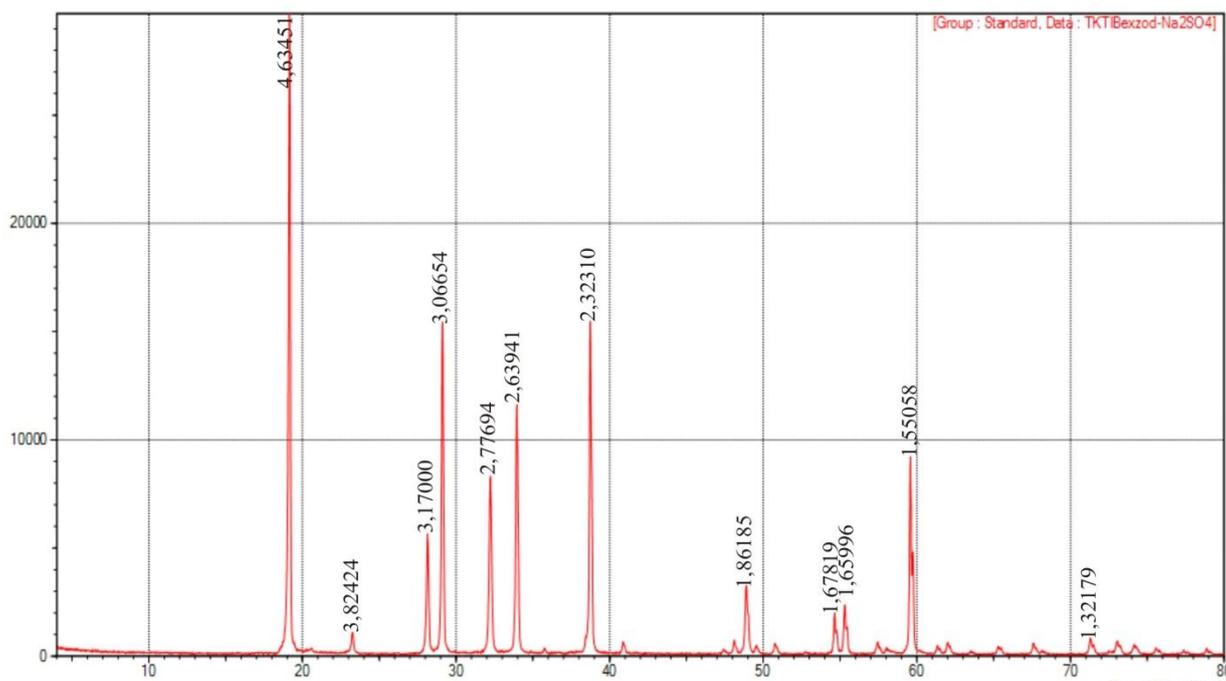
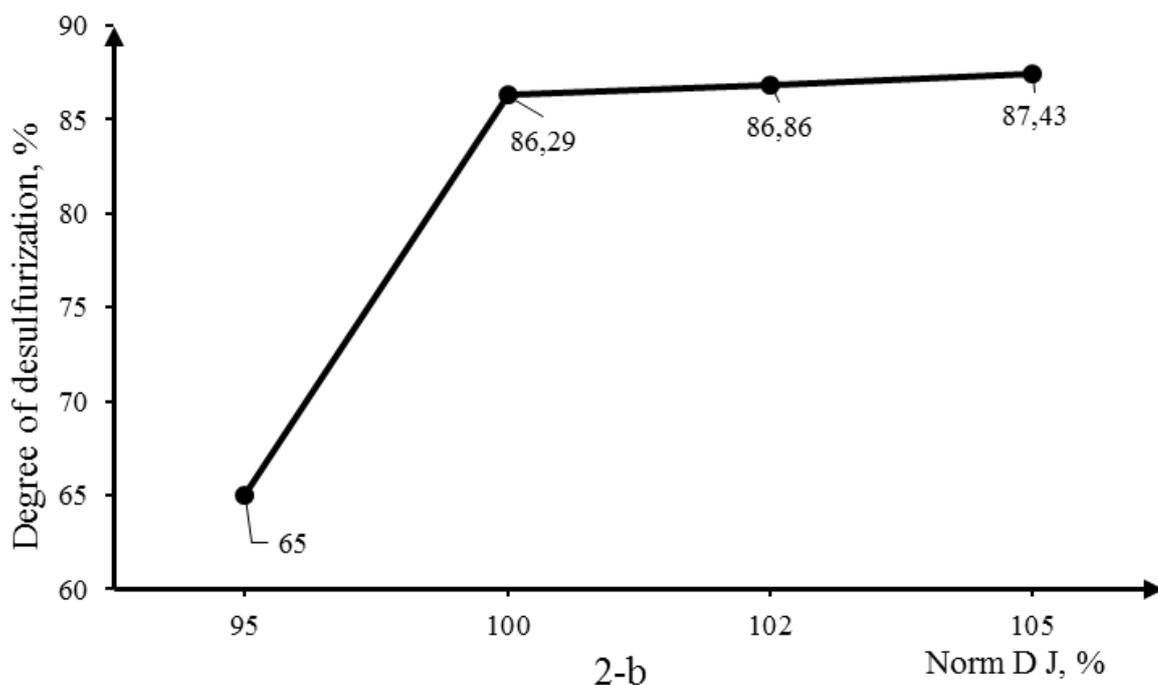


Fig. 4. XRD of sodium sulfate sodium.

In view of that residual content of sulfate ions the solution was subjected to post-treatment off sulfates by distiller liquid – waste of soda production containing (weight %): Na^+ – 2.18; Mg^{2+} – 0.007; Ca^{2+} – 3.03; Cl^- – 8.74; SO_4^{2-} – 0.03. It was shown that with increasing rate of distiller liquid from 95 to 105% for CaSO_4 formation in solution SO_4^{2-} is decreased from 1.75% to 0.24%. At that the free sulfurization rate is increased from 65.14 to 87.43% (Fig. 5). The resulting sodium sulfate is removed from the suspension by filtration. In sulfate free solution

contents (weight %): NaCl – 8.84, MgCl_2 – 6.39, CaSO_4 – 0.34, CaCl_2 – 0.86, Na_2SO_4 – absent.

Further the processing the solution into magnesium hydroxide those was subjected to neutralization using NaOH . The precipitation of $\text{Mg}(\text{OH})_2$ was carried out at 25°C in 10 min and constant agitation. It was established that when neutralization of the solution by NaOH to $\text{pH} = 10.5-11$ the maximal sedimentation rate of $\text{Mg}(\text{OH})_2$ ($K_{\text{precipitation}} = 99\%$) is occurred. Recovered precipitate was separated from the slurry by centrifugation and then dried at 100°C until constant weight.



2-b

Fig. 5. Sulfate free rate of sodium and magnesium chlorides solutions.

X-ray was used in order to identify the chemical analysis of $Mg(OH)_2$. From Fig.6 can be seen that on the radiograph intensive peaks of 4.79; 2.72; 2.36;

1.9; 1.57; 1.49; 1.37 and 1.31\AA , specified for magnesium hydroxide were highlighted.

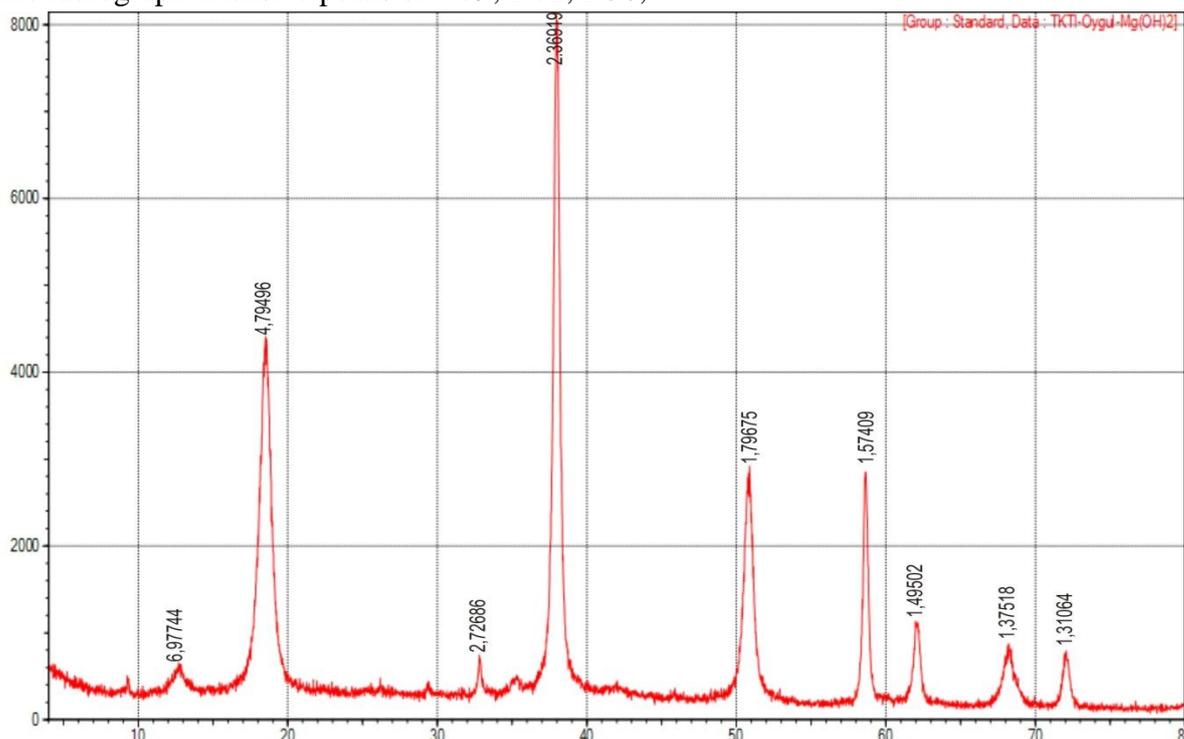


Fig. 6. XRD of magnesium hydroxide.

The composition and physicochemical behaviours of magnesium hydroxide synthesized are presented in

Table 2. After stage of the synthesis the sodium chloride solution is remaining that can be as raw for soda production by Solvay.

Table 2
Physicochemical behaviours of magnesium hydroxide synthesized

Name	Magnesium hydroxide
Mass fraction of Mg ²⁺ , %	39.14
Mass fraction of MgO, %	64.91
Mass fraction of Mg(OH) ₂ , %	93.90
Mass fraction of Ca ²⁺ , %	Absent
Mass fraction of iron based on ferric oxide, %	0.012
Mass fraction of insoluble residue in hydrochloric acid, %	0.01
Mass fraction of sulfates, %	0.05
Residue on the sieve with No 014K	0.04
Apparent density, g/cm ³	0.30

CONCLUSIONS

Thus, during the investigation of processing dried and mixed salt from Karaumbet Lake the following tasks were performed and optimal conditions were found out:

At S : L = 1 : 3 and 25oC in 15 min solubility of DMS in water reached of 93.02%;

At temperature and settling duration equal to 40oC and 20 min cleaning rate of DMS suspension makes no less than 95% and acceptable filtration rate of 1176.84 kg/m²•h, as a result solution of DMS can be purified out maximally from insoluble in water residue;

When cooling cleaned solution of DMS to 0oC Na₂SO₄•10H₂O is obtained with yield of 83.61%;

When tempering Na₂SO₄•10H₂O to 200oC the product containing Na₂SO₄ no less than 99.4% fitting high grade is prepared;

When sulfate free process of remained quantity of DMS solution with 100% distiller liquid to form

CaSO₄ content of SO-24 is decreased from 1.75% to 0.24%;

When neutralization of sulphur free by NaOH to pH = 10.5-11 precipitation rate Mg(OH)₂ equal to 99%.

XRD and thermogravimetry were used to identify the phase composition of synthesized compounds.

Thus, based on scientific and founded data conducted studies allowed to prepare magnesium hydroxide from the dried and mixed salts from Karaumbet Lake following calcium sulfate precipitated (gypsum) and, sodium sulfate and salt table solution.

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