Investigation of Processing of Brine of Lake Karaumbet and Barsakelmes for Magnesium Hydroxide

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Abstract. The results of studies on the processing of brine from lakes Karaumbet and Barsakelmes for magnesium hydroxide from sodium and calcium hydroxide solutions purified by distillation liquid, sodium carbonate, and barium chloride are presented. Desulfation of the wound with the distiller's liquid was carried out at a CaO rate of the distiller's liquid of 100% sulfate ions. Excess calcium was precipitated with sodium carbonate, and additional purification by sulfate ions was carried out with barium chloride at a rate of 95-98% of stoichiometry. As a result, the residual content of sulfate did not exceed 0.07 % or 0.010 % in terms of calcium sulfate. The optimal technological norms of the process were established - the norm of sodium and calcium hydroxides is 100-105% of the stoichiometry, the temperature is 25°C, and the duration of the process is 120 minutes. At the same time, the filtration rate for the solution is 725.21 kg/m^2·h, and for the dry residue 75.80 kg/m^2·h. The optimum temperature for the filtration stage is 50–60°C, at which the degree of magnesium precipitation is 97.11–99.41%. The separation of the liquid and solid phases by centrifugation proceeds quite quickly in the first 6 minutes and is 91.86% of the initial amount, after 10 minutes - 95.66%, and after 15 minutes - 97.15. S:L at the same time changes from 1:8 to 1:2 and 1:1, respectively.

1 Introduction

In the world with the development of science-intensive nanotechnologies, the need for various chemical compounds is growing. In this regard, magnesium compounds, in particular magnesium hydroxide and oxide, as well as sodium sulfate, occupy a special position. In this regard, providing the industry with hydroxide, magnesium oxide, and sodium sulfate are the main areas of research for scientists around the world. Magnesium hydroxide is a raw material not only for the production of magnesium oxide but is also a product that can be processed into various magnesium salts. Therefore, providing the

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industry with hydroxide, magnesium oxide and sodium sulfate of high purity are the priority tasks facing science [1].

Today, the world pays special attention to the development of technology for obtaining pure salts of hydroxide, and magnesium oxide, with the involvement in the production of existing raw materials - brines of salt lakes, seawater, and natural deposits [2].

In terms of its abundance in nature, magnesium ranks eighth - it accounts for 2.35% of the weight of the earth's crust. The production of magnesium and its compounds is growing every year, and the areas of their application are expanding. The main consumers of magnesium compounds are the production of refractories, the construction and metallurgical industries, the production of rubber products, and other industries [3-6]. Significant amounts of magnesium compounds are processed into metallic magnesium, which is used to produce alloys with aluminum and other metals [7].

Magnesium hydroxide $Mg(OH)_2$ is a common and important magnesium compound, which is used as a flame retardant in the production of thermoplastics and polymer compositions, as a flocculant in the treatment of natural and wastewater, in the production of detergents, cosmetics, and sugar, as well as in chemical, food, pharmaceutical, and other industries [8].

The predicted growth rate of potential consumption of magnesium hydroxide averages 10% per year. Magnesium hydroxide $Mg(OH)_2$ is a colorless or white crystal with a density of 2.36 g/cm^3 having a hexagonal structure. Mohs hardness 2.5. It is practically insoluble in water and decomposes with the release of water at 350 °C. Magnesium hydroxide is the main, intermediate compound in the production of magnesium oxide and its salts [9-13].

At present, various grades or types of magnesium hydroxide are produced on an industrial scale, differing primarily in origin, specific surface area, and dispersion or granulometric composition, as well as the presence and nature of special additives that modify the surface of magnesium hydroxide particles [14-15].

Products based on natural magnesium hydroxide (brucite), as a rule, are characterized by a mass fraction of the main substance in the range of 92-95%. Their production is carried out by preparing, grinding, and fractionating the natural mineral – brucite. Commercial products based on brucite are produced and supplied both in "pure" that is, in unprocessed, crushed form, and the form of brucite grades surface-treated with special modifying additives. This method of production of magnesium hydroxide is called the "dry" method and is characterized by the fact that the quality and characteristics of the commercial product directly depend on the quality of the original mineral raw material – brucite [16].

Synthetic magnesium hydroxide is currently produced by the "wet" process, which consists of the interaction of aqueous solutions of magnesium chloride and sodium hydroxide, followed by precipitation, filtration, washing, drying, and grinding of magnesium hydroxide.

In Uzbekistan, there is no production of magnesium hydroxide and oxide, despite the existing natural deposits of magnesium salts in the form of intercrystalline brine, dry mixed salts (DMS), and dolomite. So in the Aral Sea region, in the lakes, Karaumbet and Barsakelmes, huge deposits of chloride-sulfate salts of sodium and magnesium are concentrated in the form of intercrystalline brine and DMS.

The industrial reserves of the Karaumbet deposit are halite salts of 2032.57 thousand tons, of which 1943.93 thousand tons of sodium chloride and 4009 thousand tons of dry mixed salts, of which 754 thousand tons of sodium chloride, 2452 thousand tons of sodium sulfate, 613 thousand tons of magnesium chloride and the remaining 4.74% are associated components (Table 1).

The reserves of intercrystalline brine in Lake Karaumbet are 1506.3 thousand tons, of which 504.07 thousand tons are halite salts and 1002.23 thousand tons are a mixture of salts - chloride and magnesium sulfate.

Table 1. Reserves of dry mixed salts Karaumbet.

Category	Sum salt, thousand tons	NaCl, thousand tons	Average content, %	Na_2SO_4, thousand tons	Average content, %	$MgCl_2$, thousand tons	Average content, %
IN	1196	201	16.82	746	62.35	194	16.18
$From_1$	2813	553	19.64	1706	60.60	419	14.90
$B+C_1$	4009	754	18.8	2452	61.15	613	15.28

The content of the main components in the Karaumbet brine averages (wt.%): $MgSO_4$ - 5.46; $MgCI_2$ - 5.45; NaCI - 18.36; H_2O – 70. The reserves of $MgCI_2$ in brine are 87.5 thousand tons. The total reserves of $MgCI_2$ in brine and dry mixed salts of Karaumbet are 700 thousand tons.

Salt reserves in the solid phase of the Barsakelmes deposit are approved in the amount of 131,053 thousand tons with an average content of 96.32% sodium chloride.

The brine of Lake Barsakelmes is mainly represented by sodium chloride, magnesium chloride and magnesium sulfate, the average content of which is: NaCI - 25%, $MgCI_2$ - 2.3% and $MgSO_4$ - 2.42 %. The reserves of magnesium salts in brine are estimated on average more than 1 million tons in terms of MgO [17-18].

2 Materials and methods

To obtain magnesium hydroxide, we used the brine of the Karaumbet and Barsakelmes lakes, distillery liquid, the compositions of which are given in Table 2.

Table 2. Chemical and salt compositions of the initial brine of lakes Karaumbet and Barsakelmes and distiller liquid.

Names	Chemical composition, wt. %					Salt composition, wt. %			
	Na^+	Mg^{2+}	Ca^{2+}	C^{l-}	SO_4^{2-}	$MgCl_2$	NaCl	$CaCl_2$	$MgSO_4$
Rapa Karaumbet	8.08	3.15	0.018	17.67	5.41	6.98	20.55	0.05	6.78
Rapa Barsakelmes	10.25	1.33	0.011	18.13	2.13	4.09	23.08	0.03	2.67
Distiller liquid	2.18	0.007	3.03	8.74	0.03	0.028	5.54	8.41	0.04

Studies on the production of magnesium hydroxide were carried out from purified brine solutions from lakes Karaumbet and Barsakelmes [19]. To do this, the solutions and brine of the Karaumbet and Barsakelmes lakes were subjected to desulfurization with a distiller liquid at a rate of 100% CaO of the distiller liquid for sulfate ions and further purification with sodium carbonate and barium chloride at a rate of 95-98% of the stoichiometry for sulfate ions. The compositions of the brine solutions of the Karaumbet and Barsakelmes lakes used for the precipitation of magnesium hydroxide are shown in Table 3.

Table 3. Composition of solutions of purified brine.

No.	Names	Chemical composition, wt. %					Salt composition, wt. %			
		Na^+	Mg^{2+}	Ca^{2+}	C^{l-}	SO_4^{2-}	$MgC1_2$	NaC_1	$CaSO_4$	$CaCl_2$
1	Purified brine Karaumbet	7.09	2.29	0.12	10.93	0.06	8.98	18.02	0.009	0.35
2	Purified brine Barsakelmes	9.61	1.37	0.13	18.84	0.07	5.37	24.45	0.010	0.36

Experiments on the precipitation of magnesium hydroxide from purified solutions of the brine of lakes Karaumbet and Barsakelmes were carried out at a temperature of 25 °C, with constant stirring for 10 minutes and the duration of the settling process for 120 minutes. Purified lake brine, sodium and calcium hydroxides were used to obtain magnesium hydroxide [20].

3 Results and Discussion

The amount of sodium and calcium hydroxides required for the precipitation of magnesium ions was determined based on the following reactions:

$$Mg^{2+} + 2NaOH = Mg(OH)_2 \downarrow + 2Na^{+} \quad (1)$$

$$+ Ca(OH)_2 = Mg(OH)_2\downarrow + Ca^{+2} \quad (2)$$

The precipitant rate varied from 95 to 110% for the formation of Mg $(OH)_2$.

Data on the precipitation of magnesium hydroxide by sodium and calcium hydroxides are given in Tables 4 and 5.

Table 4. Influence of the sodium hydroxide rate on the degree of precipitation of magnesium hydroxide and the composition of the liquid phase.

Norm NaOH, %	The composition of the liquid phase, wt. %					The degree of precipitation, $Mg(OH)_2$,%
	Na^{+}	Ca^{2+}	Mg^{2+}	C^{1-}	SO_4^{2-}	
95	9.73	0.37	0.57	15.88	0.18	75.12
100	10.04	0.37	0.04	16.03	0.18	98.16
105	10.23	0.37	0.01	15.98	0.18	99.41
110	10.42	0.37	0.01	15.92	0.18	99.53

$\gamma_{Mg^{2+}}$ – the degree of precipitation of magnesium ions, which is calculated by the formula:

$$\gamma_{Mg^{2+}} = \frac{m_{raw} \times \omega_{raw} — m_{cons} \times \omega_{cons}}{m_{raw} \times \omega_{raw}}, \quad (3)$$

Where m_{raw} *and* m_{cons} - respectively, the mass of the original brine and brine after separation of magnesium hydroxide, $\omega_{raw,}$ and ω_{cons} - respectively, the concentration of magnesium ions in the original brine and brine after separation of magnesium hydroxide (g/100 g of solution). As can be seen from the tables, the optimal amount of sodium and calcium hydroxides required for the precipitation of magnesium hydroxide are the norms of 100-105% of stoichiometry. At the same time, the degree of magnesium precipitation is 98.16-99.41% during precipitation with sodium hydroxide (Table 4) and 97.11-98.15% during precipitation with calcium hydroxide (Table 5). Reducing the rate of sodium and calcium hydroxides below 100% leads to a decrease in the degree of precipitation of magnesium hydroxide to 72.14 and 75.12%, respectively.

Thus, the optimal rate of sodium and calcium hydroxides in the production of magnesium hydroxide is 100-105% of the stoichiometry, and the duration of the settling process is 120 minutes at a temperature of 25°C. This produces magnesium hydroxide, which contains Mg^{2+}-31.31%, $C1^{-}$-3.52%, SO_4^{2-}-0.04%, H_2O-19.98%.

Table 5. Influence of the rate of calcium hydroxide on the degree of sedimentation of magnesium hydroxide and the composition of the liquid phase.

Norm $Ca(OH)_2$, %	The composition of the liquid phase, wt. %					The degree of precipitation, $Mg(OH)_2$, %
	Na^+	Ca^{2+}	Mg^{2+}	$C1^-$	SO_4^{2-}	
95	5.56	4.03	0.64	15.94	0.18	72.14
100	5.62	4.26	0.07	16.11	0.17	97.11
105	5.61	4.44	0.04	16.06	0.16	98.15
110	5.59	4.62	0.03	16.01	0.14	98.87

Figure 1 shows data on the filtration rate of magnesium hydroxide pulp.The analysis shows that at a sodium hydroxide rate of 105% and a temperature of 25°C, the filtration rate of magnesium hydroxide in solution and the dry residue is 725.21 and 75.80 kg/m^2 h, respectively.

As the temperature of the pulp increases, the filtration rate increases, which is explained by a decrease in its viscosity. So, at a temperature of 20°C, the filtration rate for the solution and the dry residue is 625-725 kg/m^2 h and 40-60 kg/m^2 h and 1700-1900 and 180-222 kg/m^2 h at temperature 60°C.

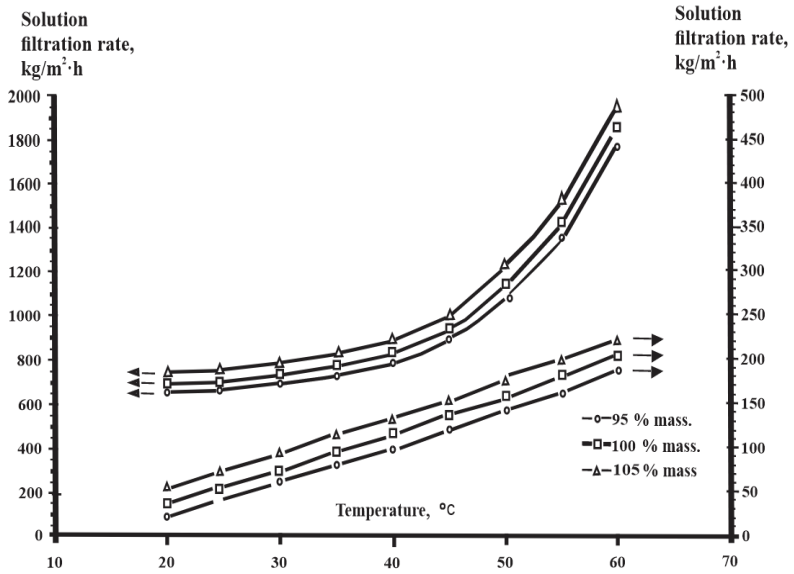

Fig. 1. Influence of sodium hydroxide rate and temperature on filtration rate.

It follows from the data that to ensure the maximum pulp filtration rate, the process must be carried out at higher temperatures. The optimum temperature is 50-60°C. But such an indicator (195-222 kg/m^2 h) is not acceptable from a technological point of view. Therefore, studies on the separation of magnesium hydroxide precipitate from the liquid phase were carried out by centrifugation.

Due to the high intensity of the centrifugation process for phase separation under laboratory conditions, the influence of the centrifugation time on the S:L ratio in the thickened part was studied (Figure 2).

Phase separation by centrifugation proceeds quite quickly. The most intense occurs in the first 6 minutes. For example, thickening after 6 minutes is 91.86% of the original

amount or S:L=1:8, after 10 minutes 95.66% and S:L=1:2, and after 15 minutes 97.15% and S:L=1:1, respectively.

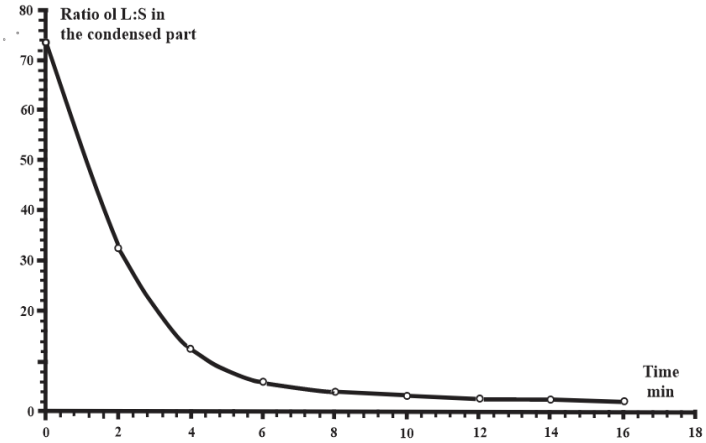

Fig.2. Influence of centrifugation time on the ratio S:L in the thickened part.

Thus, the studies carried out have shown that centrifugation is an acceptable method for separating the magnesium hydroxide precipitate.

4 Conclusion

The conducted studies have shown the fundamental possibility of obtaining magnesium hydroxide from purified distillery liquid, sodium carbonate, and barium chloride of the brine of Karaumbet and Barsakelmes lakes by precipitation with sodium and calcium hydroxides.

To obtain dry mixed salts purified from accompanying impurities, it is necessary to dissolve them in water at L:S = 1:3, temperature 50°C for 10 minutes. The settling process proceeds very quickly and after 30 minutes reaches a value of 95%. Filtration of thickened sludge on the pulp is over 1028 kg/m^2 h at 20°C. Purification of sulfates from a solution of dry mixed salts is carried out by cooling to a temperature of 0-5°C, followed by post-treatment with a distiller's liquid. Precipitation of mirabilite is well filtered.

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