

Highly Mineralized Natural Brines – Raw Material for Obtaining Magnesium Products

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Abstract

A technology for obtaining magnesium oxide from brines on the background of prevalent amount of calcium chloride is proposed. The possibility of a combined obtaining magnesium and calcium compounds in the form of magnesia and calcium chloride hexahydrate is demonstrated. It is recommended to use concentrated calcium chloride solutions for preparation of drilling fluids.

INTRODUCTION

Raw material sources for obtaining magnesium compounds

Raw material resources for obtaining magnesium compounds are manifold and widespread. Magnesium products are obtained both from solid minerals and from natural brines of lake and maritime type. Despite the fact that the hydromineral raw materials, in particular the lake brine, subterranean brines and sea waters, have lower magnesium content, they are a practically inexhaustible source [1]. Sea water and brines are widely used abroad for obtaining magnesium oxide, various kinds of magnesia, bischofite, and metallic magnesium [2].

Production of magnesium compounds is done in 29 countries of the world. In the majority of them, magnesium products are obtained from magnesite. The greatest MgO producers from magnesite are Russia and China [1]. In Russia, besides, salt formations widespread in the European part of the country are used.

The world tendency to development of magnesium production is directed to obtaining

them from sea water and natural brines. Thus, in the USA in 2000, 60% of magnesium compounds were produced from sea water (states Denver and Florida) and lake (subterranean) brines (state Utah) [1]. Industrial enterprises producing magnesium compounds from hydromineral raw materials exist in 12 countries of the world. Such countries as Japan, Israel *etc.* produce magnesium compounds only from sea water. Ukraine, Great Britain, Italy produce 45–84 % of magnesium compounds from sea waters [1].

The use of hydromineral raw materials permits first of all improving the economic indicators of production and decreasing the ecological consequences in implementation of technology: wastes and sewage that are close by their composition to sea water are discharged into the sea or pumped into subterranean horizons. Besides, the sea water, being an inexhaustible source of magnesium, makes it possible to count for an indefinitely long functioning of enterprises.

Another positive property of the hydromineral raw materials is the possibility of their comprehensive processing with the use of reagents obtained, again, from the sea water

(brine). As a rule, the sea water, subterranean and lake brines contain, besides the magnesium, such components as potassium, bromine and chlorine [3].

The great reserves of mineral raw materials in the form of subterranean brines of chloride-calcium-magnesium type concentrated in East Siberia permit speaking of enormous perspectives of obtaining magnesium-containing and other valuable products from brines in Russia [3]. The expediency of industrial-scale extraction of some or other component from natural brines can be based on hydrogeologists' recommendations [4]. In Table 1, industrial concentrations of single components and their excess in brines from various deposits of East Siberia are presented. One can see that implementation of a comprehensive technology for brines of the mentioned deposits may be efficient for extraction of lithium, magnesium, bromine, and – for some deposits – potassium, strontium and iodine.

The total mineralization of brines varies from 250 g/l (Yurubcha deposit) to 520 g/l (Znamenka deposit), the magnesium content increasing therein 3-fold (see Table 1), and that of calcium from 24.5 to 120.9 g/l. In the world practice, technologies of obtaining magnesium products from brines containing more than 5 g/l Ca^{2+} are not available [5].

Known methods of obtaining magnesium products from brines and sea waters

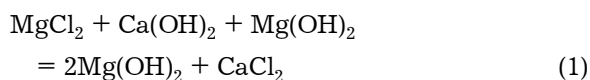
The oldest method of obtaining light kinds of magnesia consists in precipitating the basic magnesium carbonate from soluble magnesium salts ($MgCl_2$, $MgSO_4$ etc.) with soda. As the raw material natural and industrial solutions are used, *e. g.*, those formed in carnallite processing [5]. By means of calcination of basic magnesium carbonate, carbon dioxide and water are removed, and it is transformed into light kinds of magnesia (*magnesia usta*).

The technology of obtaining magnesium oxide from sea water which a plant of the Kaiser Refractories Co. (USA) has been using for many years [5] has been mastered. Sea water is preliminarily treated with a small amount of $Ca(OH)_2$ for separation of organic admix-

TABLE 1
Industrial concentrations of components and their content in the hydromineral raw materials of the Siberian platform

Component	Industrial concentration, g/l	Deposit		Tube "Udachnaya"		Sukhotungus		Verkholensk		Znamenka	
		Yurubcha	Excess, times	Content, mg/l	Excess, times	Content, mg/l	Excess, times	Content, mg/l	Excess, times	Content, mg/l	Excess, times
Lithium	10	50	5	150	15	222	22	237	24	415	42
Magnesium	1000	9050	9	13840	14	9500	2.5	9200	9.2	29200	29
Potassium	100	3900	39	1200	12	23100	23	27500	27	4300	43
Strontium	300	H/o	H/o	1250	4	2420	8	4400	15	620	2
Bromine	150	2350	16	4900	33	5200	35	6900	46	9300	62
Iodine	10	10	1.0	12	1.2	13	1.3	13	1.3	15	1.5

tures. After clarification (by means of settling) and filtration, the water is used for sedimentation of $\text{Mg}(\text{OH})_2$ with lime (dolomite) milk. Magnesium sedimentation with lime milk containing calcium and magnesium hydroxides goes by the reaction



According to reaction (1), when using annealed dolomite for obtaining lime-dolomite milk, the amount of magnesium hydroxide increases 2-fold.

After condensation of the pulp to the liquid/solid (l : s) phase ratio of 7, it is washed with sweet water counterflow. Washing the $\text{Mg}(\text{OH})_2$ sediment is a bottleneck in the technology, since the sediments are clarified and filtered with difficulty. Besides, their washing requires large amounts of fresh water, the losses of magnesium with wash waters being as large as 17 %. The pulp for better filtration is treated with steam whereupon it is filtered to obtain a paste containing 30 % $\text{Mg}(\text{OH})_2$. The paste is processed to obtain various commercial products: dry magnesium hydroxide (after spray drying), light magnesia (after annealing at 750–800 °C) and heavy magnesia (after annealing at 1700 °C with addition of Fe_2O_3).

At present, the lime technology of obtaining magnesium oxide from sea water and salt lake natural brine has been finished rather well and become widespread not only in the USA, but also in Great Britain, Germany, Austria, Mexico *etc.* In Russia, this technology has remained at the stage of studies and proposals [6–9]. The proposals concern mainly the use of raw materials with a low CaCl_2 content (up to 15 g/l) and brine mineralization of no higher than 60 g/l.

Obtaining magnesium hydroxide from highly mineralized brines by means of known techniques without observing special conditions results in $\text{Mg}(\text{OH})_2$ precipitation in a colloidal state, which makes its separation from the brine difficult; that is why they have not been proposed for processing of brines with high MgCl_2 and CaCl_2 content. An example of use of brines with a high MgCl_2 content, in particular natu-

ral bischofite brines, is an improved variant of the lime technology described in [10]. In the proposed technology for obtaining high-quality magnesia varieties, brines of bischofite of the Volgograd deposits and limestone (dolomite) are used. The use of dolomitized limes is preferential. After annealing and slaking, the content of CaO_{act} in the lime milk is brought to 10 %. The process of magnesium sedimentation is carried out from bischofite solution (460 g/l of MgCl_2) after its dilution by 4–5 times. The total amount of the lime-dolomite milk is 95–100 % of the reaction (1) stoichiometry. In order to improve the pulp condensation and its filtration properties, a flocculant (polyacrylamide or its substitutes, 0.25–0.50 kg/t MgO) is added to the magnesian pulp at the end of sedimentation.

Washing the condensed sediment is performed by means of repulping in water with an intermediate squeezing on the filter. The product is humid $\text{Mg}(\text{OH})_2$ paste squeezed out on the filter intended for producing different magnesia varieties: basic magnesium carbonate, dead-burned magnesia and periclase.

A side-product of the process – worked-out calcium chloride brine after pulp condensation – is proposed to be used for producing alinite cement [11].

Obtaining magnesium compounds from concentrated bischofite brines permits considering brines enriched with magnesium as a promising raw material for production of its compounds. As it was demonstrated in [10], there are techniques for improvement of crystallization of precipitated sediments: slow crystallization of $\text{Mg}(\text{OH})_2$ with maintenance of pH in the reaction zone at a level no higher than 8–10; use of dry low-active lime; energetic turbulent stirring the reacting compounds, and, finally, introducing into the solution additives, *e. g.*, polyacrylamide (PAA) [5, 10].

Another example of sedimenting magnesium from highly mineralized brines is obtaining magnesium products from drainage brines of the tube “Udachnaya”. Studies demonstrated that using some of the indicated techniques, it was possible to sediment $\text{Mg}(\text{OH})_2$ from highly mineralized brines (total salt content of 350 g/l) and to obtain a product which, after

TABLE 2

Composition of the limestone used

Compound	Component				
	CaCO ₃	MgCO ₃	SiO ₂	R ₂ O ₃	*
Limestone	97.0	1.76	0.74	0.35	0.15
Dolomite	52.75	46.49	0.52	0.21	0.10

*R = Al, Fe; R¹ = Na, K.

annealing, met the GOST (All-Union State Standard) requirements of powder magnesite caustic (PMC) used for construction purposes.

The goal of the present work was the use of a new raw material – subterranean highly mineralized brines of Siberia enriched with magnesium and calcium chlorides which are badly needed in eastern regions of the country. Taking into account that calcium-magnesium chloride brines contain, apart from the main salts (CaCl₂, MgCl₂), unique amounts of bromine and lithium (see Table 1) whose extraction technologies are known [13, 14], a comprehensive development of such a raw material source will make it possible to diminish considerably the cost of the obtained products, including magnesium-containing ones [15]. It is the first time that raw materials of this type are proposed for obtaining magnesium oxide.

EXPERIMENTAL

The brine used for obtaining magnesium products had the following chemical composition, g/l: MgCl₂ 124, CaCl₂ 379, KCl 8.2, NaBr 11.5, LiCl 2.5, FeCl₂ 0.8, totally 526. Sedimentation of magnesium hydroxide from the brine was carried out with calcium oxide obtained from limestone or dolomite whose composition is presented in Table 2. Annealing of the limestone and dolomite was carried out at 900 and 850 °C to the degree of carbonate dissociation at 91 and 95 %, respectively. The brine was cooled in the cryostat at the temperatures of +15 to –25 °C.

The brine was diluted with water. For sedimentation of iron, air bubbling of the brine was performed simultaneously with dilution. Settling of the pulp was carried out in one litre cylinder. The pulp condensation degree

was estimated by the ratio of the volume of condensed pulp to the initial pulp volume.

Carbonization of Mg(OH)₂ pulp with a 5-fold amount of liquid phase (l : s = 5) was performed with balloon carbon dioxide in a system of carbonizers consisting of five Drechsel bottles in counterflow regime: CO₂ was fed to the first bottle, from the last one Mg(HCO₃)₂ solution was decanted. The degree of carbon dioxide assimilation in pulp carbonization was calculated by the ratio of carbon dioxide bound into bicarbonate ion to the total amount of CO₂ fed from the balloon to the carbonizer system.

Carbon dioxide assay was carried out by the volumetric technique based on the measurement of the volume of CO₂ released after acid treatment of the sample [16]. Magnesium, calcium and iron were assayed by complexometric methods [17, 18].

RESULTS AND DISCUSSION

According to what was told above, processing of East Siberian brines for obtaining magnesium oxide is possible only after decreasing their calcium chloride content. For this purpose, the initial brine with a calcium chloride concentration of up to 380 g/l supersaturated with CaCl₂ was cooled to +15 °C and lower, to negative temperatures (the brine temperature in the layer is +25 ...+40 °C). In Fig. 1, the crystallization polytherm and the amount of precipitated CaCl₂ · 6H₂O sediment per 1 m³ of brine depending on the temperature are presented. Thus, at +15 °C, the amount of precipitate is about 100 kg/m³, while at 0 °C it is 380 kg/m³. Therein, a spontaneous crystallization of calcium chloride hexahydrate takes place, and as a consequence thereof, the CaCl₂

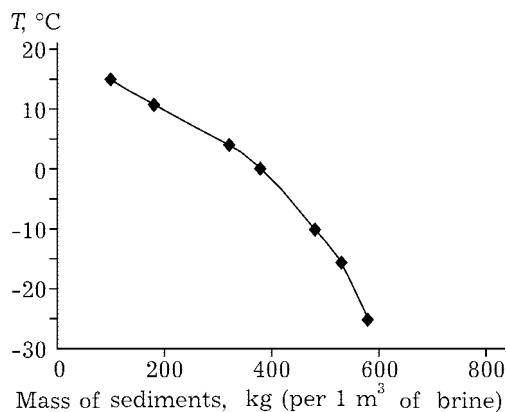


Fig. 1. Polytherm of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ crystallization during brine cooling from +15 to -25 °C.

concentration in the brine decreases to 230 g/l and lower (the total salt content being <380 g/l). The calcium chloride hexahydrate precipitated from one litre of brine was separated by filtration from the brine which was used for dilution *prior* to magnesium hydroxide sedimentation.

In comprehensive processing, a partial (approximately 1.5-fold) dilution of the brine is achieved when bromine and lithium are extracted [15]. In the course of studies, an approximately 2-fold dilution was made with fresh water. Therein, magnesium chloride content amounted to about 60 g/l, and the total mineralization 220 g/l. Simultaneously to dilution and aeration of the brine, oxidation of iron Fe^{2+} to Fe^{3+} and an increase in pH from 4 to 6 was taking place, due to which sedimentation of $\text{Fe}(\text{OH})_3$ occurred (Fig. 2). After separation of the iron admixture, the brine was used for sedimentation of $\text{Mg}(\text{OH})_2$.

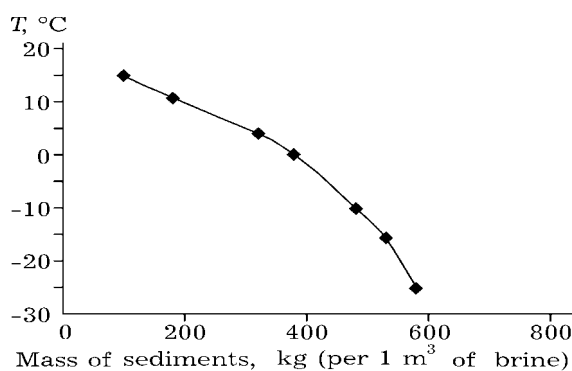


Fig. 2. Decrease in iron concentration in 2-fold dilution of the brine with fresh water and increase in brine pH from 4 to 6.

For sedimentation of magnesium, lime or lime-dolomite milk ($\text{CaO}_{\text{act}} = 10\%$) obtained after extinguishing of CaO (MgO) formed in annealing limestone or dolomite was used. Herein below, the composition of phases obtained after annealing the limestone and the dolomite is presented, %:

Mineral	CaO	MgO	Admixtures of CaCO_3 , MgCO_3 etc.
Limestone	89.6	1.6	8.9
Dolomite	53.7	41.2	5.1

As an addition intensifying the process of $\text{Mg}(\text{OH})_2$ coagulation, PAA (6 mg per 1 g of magnesium hydroxide) was used. $\text{Mg}(\text{OH})_2$ sediment condensation curves are presented in Fig. 3. It is shown that when using diluted brines, and in the presence of carbonate admixtures in the sediment (underburning), the pulp condensation was as high as 40 % of the initial volume.

The presence of carbonate admixtures in the precipitating mixture makes it possible to improve the sedimentation properties of the precipitate and to increase the condensation rate (cf. curves 1 and 3 in Fig. 3). The best results of sedimentation of $\text{Mg}(\text{OH})_2$ from diluted brines were obtained when using lime-dolomite milk with an about 5 % underburning (see Fig. 3, curve 5). Condensed pulp was squeezed on a vacuum filter to obtain paste with a 40–50 % $\text{Mg}(\text{OH})_2$ content.

Humid paste was washed by a triple repulping of the sediment in water (1 : s = 3) with

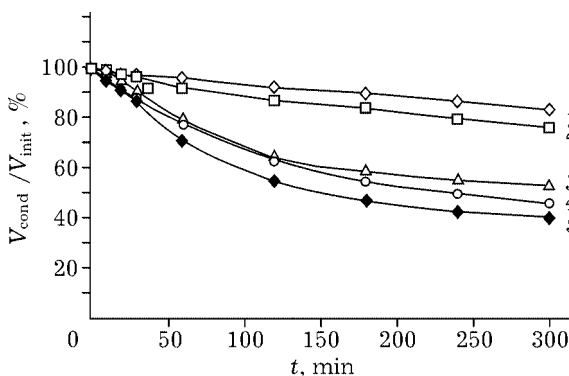


Fig. 3. Curves of condensation of magnesium hydroxide sediment whose precipitation was carried out from the initial (1, 2) and 2-fold diluted (3–5) brine using lime (1–3) and lime-dolomite (4, 5) milk in the presence of (2, 5) or without, PAA addition.

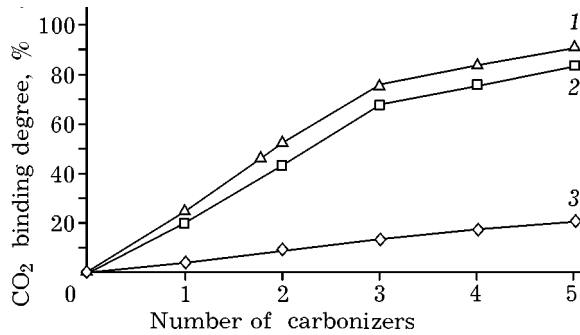
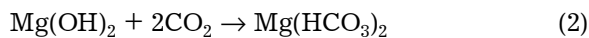


Fig. 4. Dependence of the degree of CO₂ binding on the number of carbonizers and on the rate of CO₂ feeding, g/l: 1 (1), 3 (2), 40 (3).

subsequent washing and squeezing on the filter. The wash water composition is shown in Table 3. Such a washing regime makes it possible to wash away about 90 % of salts at the stage of the first washing and to use the wash waters of stages II–IV for counterflow washing of Mg(OH)₂ sediments, using fresh water only at the fourth washing carried out on the filter.

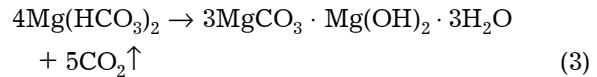
The washed Mg(OH)₂ sediment was used for obtaining magnesium carbonate, for which the sediment was repulped in water (1 : s = 5), whereupon the pulp was carbonized. In Fig. 4, the degree of carbon dioxide binding into a bicarbonate ion according to reaction



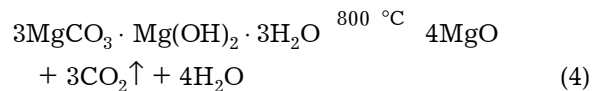
is shown. The degree of magnesium transition to solution amounts to about 95 %. The degree of CO₂ assimilation depends on the rate of its feeding and is as high as 89 % at the rate of 1–3 l/h.

After completing the carbonization process, Mg(HCO₃)₂ solution was separated from the sediment which contained CaCO₃, MgCO₃ (underburning) and a part of magnesium hydroxide that did not participate in the interaction. The magnesium bicarbonate solution was heated to

60 °C during which magnesium carbonate was precipitated:



After separation of the sediment, the solution containing 0.6 g/l CaCl₂ and 1.6 g/l Mg(HCO₃)₂ was used for Mg(OH)₂ repulping prior to carbonization. The magnesium carbonate sediment was separated from the solution, dried and annealed at 800 °C:



The active magnesium oxide obtained had the following composition, % mass: MgO 93.7, CaO 0.5, losses in annealing – 5.8. The product met the GOST 1216–87 requirements of powder magnesite caustic PMC-90. Magnesium oxide of such composition permits obtaining in its dead – annealing to 1600 °C a periclase powder in which the MgO content is above 97 % (GOST 13236–93).

The solution, after sedimentation of magnesium, enriched with calcium chloride, was used for dissolving the crystals of calcium chloride hexahydrate to obtain a heavy salt solution with the density of 1.28 g/cm³. Brines of such composition, after addition a polymer that gives the solution antifiltration and film-forming properties, may be used for hole drilling. When there are stratal waters saturated with calcium and magnesium salts, which is characteristic of regions of the Siberian platform, such drilling fluids contribute to conservation of the natural water-salt balance. According to specialists' conclusion, a brine strengthened with CaCl₂ · 6H₂O crystalline hydrate may be used as a dispersion medium for low-clay drilling fluids applied in drilling for petroleum and gas [19].

TABLE 3

Composition of wash waters

Component	Content, g/l			
	I	II	III	IV
CaCl ₂	114	16.4	5.6	1.9
MgCl ₂	5.4	0.5	0.24	0.20

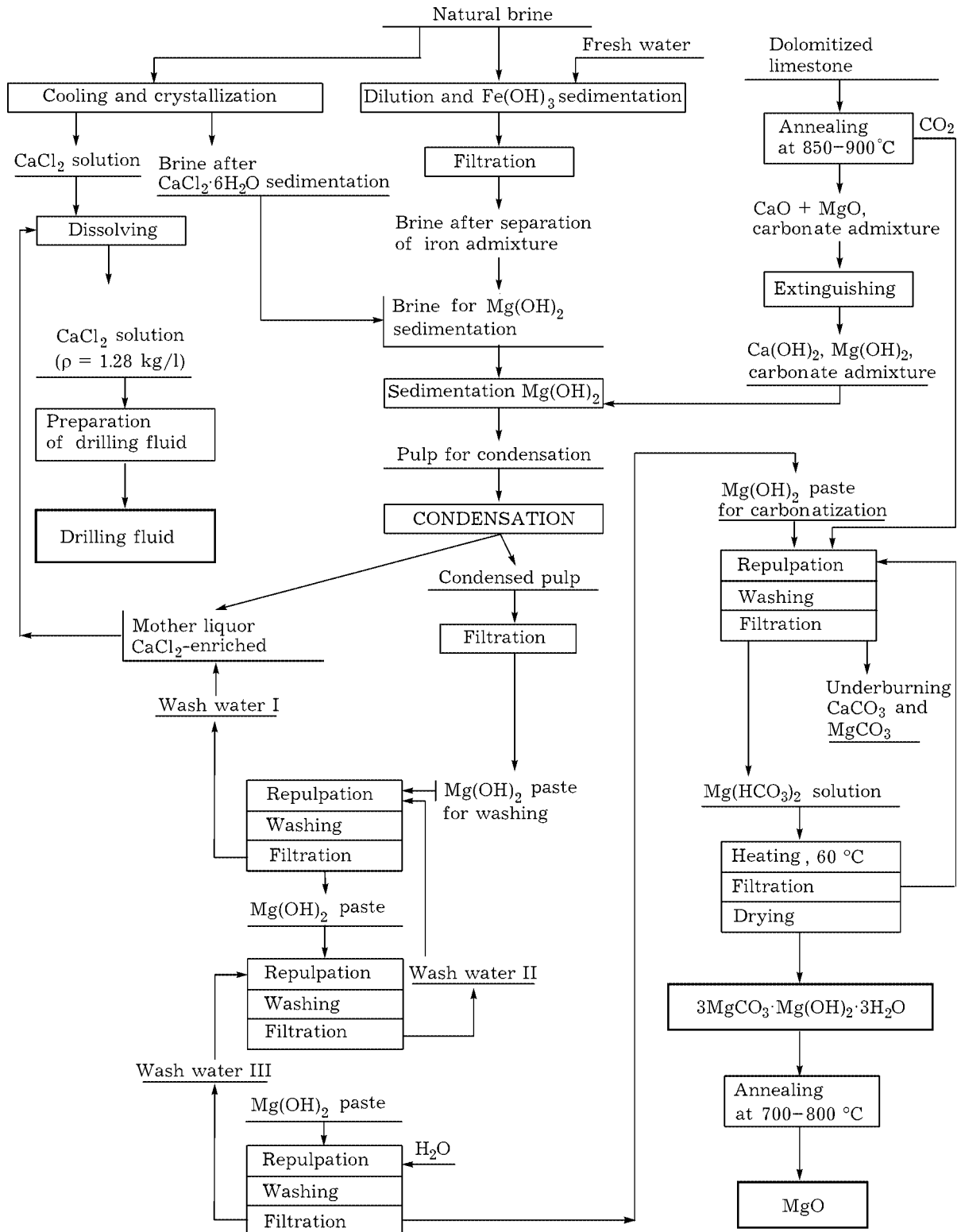


Fig. 5. Technological scheme of obtaining magnesium oxide from a highly mineralized brine.

On the basis of the studies, a technology for obtaining magnesium oxide from highly mineralized brines has been developed (Fig. 5) [20].

Advantages of this technology are as follows:

- Possibility of involving highly mineralized brines of calcium-magnesium chloride type in the raw material balance for obtaining magnesium-containing products.

- Possibility of decreasing the calcium chloride content of the brine *prior* to magnesium sedimentation by means of spontaneous crystallization of calcium chloride hexahydrate.

- Decrease in iron content by 25–30 times in the brine dilution due to the change of brine pH from 4 to 6.

- Utilization of the carbon dioxide formed during limestone annealing and magnesium carbonate degradation within the framework of the technology to be implemented, which decreases, apart from the technological load, the ecological consequences.

- Use of brines enriched with calcium chloride after sedimentation of magnesium hydroxide for dissolving $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ crystals and obtaining heavy salt solutions applied for preparation of drilling fluids.

- Increase in utilization of salt components of the brine.

CONCLUSION

In this way, the proposed technology makes it possible to obtain high-quality magnesium-containing products: magnesium carbonate, powder magnesite caustic, periclase powders, and, as by-products, drilling fluids necessary for drilling for petroleum and gas. The tech-

nology can be implemented both within the framework of a comprehensive scheme of processing highly mineralized brines for obtaining lithium, magnesium and bromine compounds, and as an independent production for obtaining magnesium- and calcium-containing products.

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