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, bisho-fite, 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**

<table>
<thead>
<tr>
<th>Component</th>
<th>Industrial concentration, g/l</th>
<th>Content, mg/l</th>
<th>Excess, times</th>
<th>Excess, mg/l</th>
<th>Excess, times</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium</td>
<td>10</td>
<td>9000</td>
<td>9.2</td>
<td>43000</td>
<td>43</td>
</tr>
<tr>
<td>Magnesium</td>
<td>1000</td>
<td>12310</td>
<td>23</td>
<td>275000</td>
<td>43</td>
</tr>
<tr>
<td>Potassium</td>
<td>100</td>
<td>1200</td>
<td>1.2</td>
<td>24320</td>
<td>8</td>
</tr>
<tr>
<td>Strontium</td>
<td>300</td>
<td>1250</td>
<td>4</td>
<td>24320</td>
<td>8</td>
</tr>
<tr>
<td>Bromine</td>
<td>23510</td>
<td>4000</td>
<td>13</td>
<td>4000</td>
<td>13</td>
</tr>
<tr>
<td>Iodine</td>
<td>10</td>
<td>12</td>
<td>1.3</td>
<td>12</td>
<td>1.3</td>
</tr>
</tbody>
</table>
tures. After clarification (by means of settling) and filtration, the water is used for sedimentation of Mg(OH)₂ with lime (dolomite) milk. Magnesium sedimentation with lime milk containing calcium and magnesium hydroxides goes by the reaction

\[
\text{MgCl}_2 + \text{Ca(OH)}_2 + \text{Mg(OH)}_2 = 2\text{Mg(OH)}_2 + \text{CaCl}_2 \quad (1)
\]

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 Mg(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 % Mg(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 Fe₂O₃).

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 CaCl₂ 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 Mg(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 MgCl₂ and CaCl₂ content. An example of use of brines with a high MgCl₂ content, in particular natural 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 CaOₓ in the lime milk is brought to 10 %. The process of magnesium sedimentation is carried out from bischofite solution (460 g/l of MgCl₂) 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 magnesial 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 Mg(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 Mg(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 Mg(OH)₂ from highly mineralized brines (total salt content of 350 g/l) and to obtain a product which, after
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 ($\text{CaCl}_2$, $\text{MgCl}_2$), 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: $\text{MgCl}_2$ 124, $\text{CaCl}_2$ 379, KCl 8.2, NaBr 11.5, LiCl 2.5, $\text{FeCl}_2$ 0.8, totally 526. Sedimentation of magnesium hydroxide from the brine was carried out with calcium oxide obtained from the main salts ($\text{CaCl}_2$, $\text{MgCl}_2$), 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.

**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 $\text{CaCl}_2$ was cooled to $+15^\circ C$ and lower, to negative temperatures (the brine temperature in the layer is $+25 \ldots +40^\circ C$). In Fig. 1, the crystallization polytherm and the amount of precipitated $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ sediment per 1 m$^3$ of brine depending on the temperature are presented. Thus, at $+15^\circ C$, the amount of precipitate is about 100 kg/m$^3$, while at 0 °C it is 380 kg/m$^3$. Therein, a spontaneous crystallization of calcium chloride hexahydrate takes place, and as a consequence thereof, the $\text{CaCl}_2$
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 $\text{Fe}^{2+}$ to $\text{Fe}^{3+}$ and an increase in pH from 4 to 6 was taking place, due to which sedimentation of $\text{Fe(OH)}_3$ occurred (Fig. 2). After separation of the iron admixture, the brine was used for sedimentation of $\text{Mg(OH)}_2$.

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

<table>
<thead>
<tr>
<th>Mineral</th>
<th>CaO</th>
<th>MgO</th>
<th>Admixtures of CaCO$_3$, MgCO$_3$ etc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limestone</td>
<td>89.6</td>
<td>1.6</td>
<td>8.9</td>
</tr>
<tr>
<td>Dolomite</td>
<td>53.7</td>
<td>41.2</td>
<td>5.1</td>
</tr>
</tbody>
</table>

As an addition intensifying the process of $\text{Mg(OH)}_2$ coagulation, PAA (6 mg per 1 g of magnesium hydroxide) was used. $\text{Mg(OH)}_2$ 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 $\text{Mg(OH)}_2$ 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 % $\text{Mg(OH)}_2$ content.

Humid paste was washed by a triple repulping of the sediment in water ($l : s = 3$) with
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 (l : s = 5), whereupon the pulp was carbonized. In Fig. 4, the degree of carbon dioxide binding into a bicarbonate ion according to reaction

\[
\text{Mg(OH)}_2 + 2\text{CO}_2 \rightarrow \text{Mg(HCO}_3\text{)}_2
\]

(2)

is shown. The degree of magnesium transition to solution amounts to about 95%. The degree of CO\(_2\) 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(HCO\(_3\))\(_2\) solution was separated from the sediment which contained CaCO\(_3\), MgCO\(_3\) (under-burning) 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:

\[
4\text{Mg(HCO}_3\text{)}_2 \rightarrow 3\text{MgCO}_3 \cdot \text{Mg(OH)}_2 \cdot 3\text{H}_2\text{O} + 5\text{CO}_2 \uparrow
\]

(3)

After separation of the sediment, the solution containing 0.6 g/l CaCl\(_2\) and 1.6 g/l Mg(HCO\(_3\))\(_2\) was used for Mg(OH)\(_2\) repulpation prior to carbonization. The magnesium carbonate sediment was separated from the solution, dried and annealed at 800 °C:

\[
3\text{MgCO}_3 \cdot \text{Mg(OH)}_2 \cdot 3\text{H}_2\text{O} \xrightarrow{800 \, ^\circ\text{C}} 4\text{MgO} + 3\text{CO}_2 \uparrow + 4\text{H}_2\text{O}
\]

(4)

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/cm\(^3\). 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 CaCl\(_2\)·6H\(_2\)O 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

<table>
<thead>
<tr>
<th>Component</th>
<th>Content, g/l</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I</td>
</tr>
<tr>
<td>CaCl(_2)</td>
<td>114</td>
</tr>
<tr>
<td>MgCl(_2)</td>
<td>5.4</td>
</tr>
</tbody>
</table>
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 CaCl₂·6H₂O 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 technology 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.

REFERENCES

17. N. S. Frumkin, Analiticheskaya khimiya kal’tsiya, Nauka, Moscow, 1974.