Magnesia Binders from Natural Highly Mineralized Multicomponent Brines

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Abstract—The economic efficiency of obtaining magnesium-containing products (magnesium oxide and magnesium chloride) from multicomponent brines of calcium chloride, magnesium chloride, and mixed types is shown. Based on the obtained products, a highly active magnesia binder and a water-resistant composite binder are obtained.

Key words: brine, magnesium oxide, bischofite, magnesia binder, composite magnesia binder, economic efficiency.

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INTRODUCTION

The main component of magnesia binders and composite magnesia binders is active magnesium oxide (caustic magnesite), which in most industrial cases is obtained during the roasting of magnesite mineral, MgCO\textsubscript{3}. However, in recent years, increasingly larger attention has been attracted to the obtainment of magnesium-containing products from seawater and natural brines. In this case, the primary product is chemically deposited magnesium hydroxide and/or hydromagnesite 3MgCO\textsubscript{3} \cdot Mg(OH)\textsubscript{2} \cdot 3H\textsubscript{2}O \cite{1–3}. After the calcination of the mentioned products (at 500–800\textdegree C), magnesium oxide is obtained.

The advantage of hydromineral raw materials compared to mining ore (magnesite, brucite, dolomite) are the following:

(i) a lower calcination temperature of the starting raw materials;

(ii) the finely dispersed state of the forming magnesium oxide and, as a consequence, high reaction ability of the material under its tempering with magnesium salts and during its hydration hardening;

(iii) the possibility of obtaining a tempering agent from the same raw material (the solution of magnesium chloride);

(iv) the exclusion of technogeneous wastes polluting the environment (wastes of solutions of inorganic salts are discharged into the basins or pumped into underground bedrock);

(v) the improvement of the environmental characteristics of production.

In addition, hydromineral raw materials are a highly efficient source of magnesium, which allows for the orientation to the prolonged functioning of the enterprise \cite{4}.

The magnesia binders are applied for the production of xylolite and fibrolite, magnesia light concretes, plasters, heat-insulating materials, drilling agents and grouting mortars, dry building mixtures, and other composites.

Upon tempering the active MgO by the concentrated solution of magnesium chloride, during hydration and hardening, the formation of preferentially crystal hydrates of magnesium salts, namely, 3MgO \cdot MgCl\textsubscript{2} \cdot nH\textsubscript{2}O and 5MgO \cdot MgCl\textsubscript{2} \cdot nH\textsubscript{2}O, takes place, which provides a rapid increase in the strength up to high values in the early times of hardening.

The purpose of this report is to analyze the application of natural multicomponent brines of different types for the simultaneous obtainment of magnesium oxide and chloride, as well as an economic evaluation of the profitability of the production of magnesium-containing products on their basis, including magnesia binders and composite magnesia binders.

EXPERIMENTAL

To obtain magnesium oxide MgO and bischofite MgCl\textsubscript{2} \cdot 6H\textsubscript{2}O (solution of MgCl\textsubscript{2}), we used calcium chloride brines, magnesium chloride brines, and mixed-type brines. Table 1 lists the compositions of the applied brines: the drain brine of the diamond opencast mine (pipe Udachnaya pipe, Sakha Republic), the underground brine of Znamenskoe exposure...
Magnesium compounds were precipitated by lime milk (CaO act of 10%) or soda–alkali solutions at room temperature and stirring for 1–2 h. After settling, the thickened pulp was filtered and washed with recycle solutions in the counterflow [5].

The magnesium and calcium contents in liquid and solid phases were determined by complexometric methods [6, 7], the content of carbon dioxide was determined by the volumetric method [8], and the contents of alkali elements (Li, Na, K) were determined by flame photometry using an AAS-1 device [9].

The phase composition of magnesium-containing products and binders was evaluated using X-ray phase analysis (a DRON-3 diffractometer, Cu Kα radiation, copper anticathode), DTA (a Paulik-Paulik-Erdey Q1500D derivatograph), and crystal optical analysis (a POLAM L-211 microscope JSM 20T, JEOL, resolution 1–1000 μm). The specific surface of the MgO samples was determined by the BET method, and the true density was determined by pycnometry. The physical—mechanical properties of the magnesia binder, namely, normal thickness (NT, %), times of stiffening (h-min), specific surface (m²/kg, cm²/g), bulk density (kg/m³), ultimate compressive and flexural strength (MPa), and water resistance (Rcomp medium/Rcomp air), were determined according to GOST (State Standard) by methods accepted for the characterization of the properties of binders [10].

RESULTS AND DISCUSSION

Magnesium hydroxide was precipitated from calcium chloride and magnesium chloride brines (see Table 1, brines 1, 2) by two methods, namely, by the precipitation of Mg(OH)₂ by lime milk (CaO act 10%, underburning of limestone CaCO₃ of 6–8% [5]) in the presence of polyacrylamide (PAA), and by the precipitation of the collective precipitate (Mg(OH)₂ + CaCO₃) with the use of a soda solution of Na₂CO₃ and alkali (NaOH or Ca(OH)₂) [11–13]. Simultaneously, the solution of magnesium chloride was obtained from the pulp containing Mg(OH)₂ via its carbonization in the presence of CaCl₂ obtained from the same brine [13].

The chemistry of obtaining magnesium oxide and magnesium chloride is described by the following totality of reaction equations:

**Method I:**

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

\[
\text{Mg(OH)}_2 \rightarrow \text{MgO} + \text{H}_2\text{O}, \quad (2)
\]

\[
\text{Mg(OH)}_2 + \text{CaCl}_2 + \text{CO}_2 = \text{MgCl}_2 + \text{CaCO}_3 + \text{H}_2\text{O}. \quad (3)
\]

**Method II:**

\[
\text{MgCl}_2 + \text{CaCl}_2 + \text{Na}_2\text{CO}_3 + 2\text{OH}^- \rightarrow \text{Mg(OH)}_2 + \text{CaCO}_3 + 2\text{NaCl}, \quad (4)
\]

\[
2\text{Mg(OH)}_2 + \text{CaCO}_3 + \text{CaCl}_2 + \text{CO}_2 \rightarrow 2\text{CaCO}_3 + \text{MgCl}_2 + \text{H}_2\text{O}, \quad (5)
\]

\[
4\text{MgCl}_2 + 3\text{Na}_2\text{CO}_3 + 5\text{H}_2\text{O} \rightarrow 3\text{MgCO}_3 \cdot \text{Mg(OH)}_2 \cdot 3\text{H}_2\text{O} + 2\text{NaCl} + 2\text{HCl}, \quad (6)
\]

\[
3\text{MgCO}_3 \cdot \text{Mg(OH)}_2 \cdot 3\text{H}_2\text{O} \rightarrow 4\text{MgO} + 3\text{CO}_2 + 4\text{H}_2\text{O}. \quad (7)
\]

To transfer magnesium hydroxide into magnesium chloride, we used a solution of calcium chloride obtained after the precipitation of Mg(OH)₂ (reaction (1)) or via the dissolution of CaCl₂ ⋅ 6H₂O forming during the lift of the brine of the calcium chloride type supersaturated by CaCl₂ on the surface after its cooling [13]. During the realization of method II, reaction (4) is performed under the subsequent introduction of Ca(OH)₂ (stage 1) and Na₂CO₃ (stage 2), while the collective precipitate of Mg(OH)₂ and CaCO₃ is used for the treatment of the pulp by the CaCl₂ solution. As follows from Eqs. (3) and (5), the chemically precipitated calcium carbonate is formed simultaneously with the MgCl₂ solution [13].

**Method III**

As applied to brines of the magnesium chloride type (see Table 1, brine 3), magnesium was precipitated by a soda—alkali solution with the obtainment of carbonic-acid magnesium [13, 14]. Instead of sodium hydroxide, in the mixture with soda, we used lime milk during the introduction of Ca(OH)₂ at the first stage:

In summary, the obtained magnesia binders from natural highly mineralized (Irkutsk oblast), and the synthetic brine of magnesium chloride imitating the diluted (by a factor of 2.7–2.75) solution of bischofite of the Bolgograd deposit.

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**Table 1. Compositions of natural multicomponent brines**

<table>
<thead>
<tr>
<th>Brine no.</th>
<th>Deposit name</th>
<th>Composition, g/l</th>
<th>Weight ratio MgCl₂ : CaCl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Udachnaya pipe</td>
<td>LiCl NaCl KCl MgCl₂ CaCl₂ Br Σ salts</td>
<td>4.1</td>
</tr>
<tr>
<td>2</td>
<td>Znamenskoe</td>
<td>2.5 6.1 8.2 115.0 330.0 9.3 370</td>
<td>2.8</td>
</tr>
<tr>
<td>3</td>
<td>Emulator of the solution of the Volgograd deposit</td>
<td>– 4.9 5.2 170.0 1.85 – 182</td>
<td>0.01</td>
</tr>
</tbody>
</table>