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Magnesia binder preparation from local natural and technogenic raw materials

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Abstract

The preparation of magnesia binders based on natural and technogenic mineral was the result of the research. The obtained magnesia binders possess the increased flexural and compressive strength which values are close to ones of natural materials. High flexural and compression strengths are associated with the features of the hardened caustic dolomite containing magnesium oxyhydrochlorides which crystallize as a fiber. The fibrous crystals not only increase the cement strength, but also act as a reinforcing material. The resulting magnesia binder does not require a moist environment at hardening. It is characterized by decorativeness and ecological compatibility, has a neutral hardening product composition.

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1. Introduction

Under modern conditions the development of the building industry as well as the safety and quality of building products are the key economic and political state challenges. The building complex has a huge impact on the economy and on the situation in the social sphere, in particular¹.

In building industry energy saving is one of the most important components of saving the energy because building industry ranks third among other industry branches in terms of the use of fuel and energy resources. Saving the energy and other resources is a serious challenge facing the state building industry.

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The present level and extent of the consumption of mineral raw materials cause the primary importance of the complete use of raw materials and the involvement of recycled resources in the production. Integrated use of raw materials and wastes is associated with the problem of creating the non-waste and environmentally friendly industrial technologies. The design and development of non-waste technologies is of great importance for companies of resource-intensive industries such as chemical industry, metallurgy, industry of building materials, etc.².

In Kazakhstan the preference is given to the Portland cement production, but in terms of the economy it is also effective to produce the magnesia binder that comes to Kazakhstan market mainly from Russia and China. Many properties of magnesia binder exceeds ones of Portland cement: it does not require a moist environment at hardening, has a neutral composition of the hardening products, the technological advantages of magnesia binder production allow reducing its cost in 2-3 times in comparison with Portland cement.

The efficiency of magnesia binder is defined by low power consumption of production; ability to intensive hardening; high strength and wear resistance, adhesion to any type of aggregates, particularly to organic ones; resistant to oils, alkalis and salts³.

In this regard, there is a need to find other binders that do not require an expensive technological processing. One of such available and promising materials is a binder based on magnesium oxide.

The purpose of the work was to obtain the magnesia binder based on local natural and technogenic magnesium-containing raw materials.

2. Experimental part

Research of many scientists in the magnesia binder preparation from a variety of raw materials reduces to the selection of the optimal temperature range of raw material roasting, within which decomposition of only required component will occur, i.e. magnesium carbonate decomposition to magnesium oxide and CO₂.

Dolomite of Kara-Tau deposits and tailings of polymetallic ores ("tails") were selected as raw material. Chemical dolomite composition (wt. %): 21.39 MgO; 31.07 CaO; 0.36 Fe₂O₃; 40.98 loss on ignition. The tailings used represent the finely divided product that does not require any additional grinding before use. Percentage composition of the main minerals in the waste are the following (wt. %): dolomite – 50-60; limestone – 10-15; barite – 10-20; clay substances – 5-8; ore minerals – 2-3. The chemical composition of the tails is characterized by stability and is given in wt. %: 5.17 SiO₂; 1.09 Al₂O₃; 3.18 Fe₂O₃; 28.14 CaO; 14.03 MgO; 13.1 BaSO₄; 1.44 FeS₂; 0.03-0.05 PbSO₄; 0.09-1.2 PbCO₃; 0.14-0.2 PbS; 35.25-37 loss on ignition. Low activity of radionuclides (53-55 Bq/kg), absence of toxic emissions and low volatility of heavy metals indicate the radiation and environmental waste safety⁴.

Magnesium oxide content in dolomite rock must be at least 15% to produce the binder. The tailings of polymetallic ores prepared for the study contained 14.03% of magnesium oxide. To increase the magnesium oxide content the dolomite was added to the waste in amount of 30%.

The differential thermal analysis was performed to determine the optimum calcination temperature of dolomite and tails.

3. Results and discussion

There are two endothermic effects of calcined dolomite in the thermogram. They characterize the magnesium carbonate decomposition to MgO and CO₂ at a temperature of 765-770 °C and the decomposition of CaCO₃ to CaO and CO₂ at a temperature of 900-905 °C. X-Ray diffraction of dolomite calcined at 770 °C was also performed. The XRD pattern of calcined dolomite showed that at the temperature of 770 °C the decomposition of the double salt - dolomite CaCO₃·MgCO₃ occur, and calcium carbonate in dolomite remained intact. It is because the CaCO₃ starts to decompose at higher temperatures. However, it should be noted that there are reflexes of calcium oxide ($d / n = 2.339; 1.69; 1.545 \text{ \AA}$) in the XRD pattern of dolomite calcined at 770 °C. XRD data of caustic dolomite obtained in an optimum mode (770-800 °C) indicated that there are peaks corresponding to magnesium oxide and calcium carbonate of composition of (0.94) CaO·(0.06) MgO^{5, 6}.

In dolomite-barium enrichment waste of polymetallic ores the dolomite dissociation is completed at 750 °C. Isothermal holding time was 30 minutes. Phase composition and quantity of new structure in calcined wastes depend

preliminary on calcination conditions. Kinetic curves of the phase composition changes at thermal tails treatment were determined directly at given temperatures by high-temperature X-ray diffraction⁷.

The performed high-temperature X-ray analysis of tailings of polymetallic ores suggests that the dolomite dissociation has a lower temperature of 550 °C. This process is completed at 750 °C.

Firstly, magnesium carbonate of dolomite dissociates:



then calcium carbonate is dissociated with increase of temperature:



The reduced temperature of the first reaction is explained by a smaller ionic radius Mg^{2+} (0,74 Å) compared with Ca^{2+} (1,04 Å). Magnesium ion deforms the oxygen ion more strongly. Therefore, CO_3^{2-} -anions surrounded by magnesium ions which are highly polarized and have smaller sizes break first. Complete dissociation of dolomite limestone is caused only by an increase in temperature to 800 °C. Calcite dissociation starts at 600 °C and ends at 800 °C. At the temperature of 900 °C the phase composition of calcined dolomite is represented by CaO and MgO.

There are the diffraction peaks of magnesium oxide ($d/n = 2.102$; 1.485 Å), calcite ($d/n = 3.03$; 2.49 Å), calcium oxide ($d/n = 2.76$; 2.39; 1.695 Å) in XRD patterns of the products of calcination at a temperature of 800 °C. It is undesirable for further processes of magnesia binder hardening to use the calcined product containing calcium oxide, but the formation of CaO-containing product is quite possible at calcination in industrial furnaces.

Specific surface area of the wastes calcined at 750 °C is 3600 cm²/g. Caustic dolomite was milled in a ball mill as long as 008 sieve residue was not more than 10%, thoroughly mixed with finely divided, calcined wastes and joined with the solution of technical bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) of density of 1.25 g/cm³ at a ratio of bischofite –magnesia binder of 0.3.

To study the basic physical- mechanical characteristics of magnesia binder prepared from the artificial raw mixture – caustic dolomite and calcined tails – the samples with dimensions of 4×4×16 cm were made. Samples for the study were made of normal density test in accordance with the requirements of GOST 1216-87 “Magnesite caustic powder. Specifications”. The results of physical-mechanical tests are shown in table. 1.

Table 1. Physical-mechanical characteristics of the obtained magnesia binder

| Setting time | | Flexural strength, MPa (28 days) | Compressive strength, MPa (28 days) | 008 sieve residue, % | Normal consistency, % | $K_{\text{softening}}$ |
|--------------|------------|-------------------------------------|--|----------------------|--------------------------|------------------------|
| start | end | | | | | |
| 46 min. | 5 h 56min. | 9.6 | 68 | 10 | 38.5 | 0.58 |

The high sample compression strength is due to the phase composition of crystalline hardening products. As shown by X-ray analysis they represent thri-oxyhydrochloride ($d/n = 8.3$; 3.88; 2.71 Å) and penta-oxyhydrochloride of magnesium ($d/n = 7.7$; 4.17; 1.97 Å), which crystallize as fibers⁸. Fibrous crystals do not only increase the strength of the cement, but also act as a reinforcing material.

Fig. 1 shows the microstructure of the hardened magnesia binder obtained by a scanning electron microscope JSM-6490 LV (JEOL, Japan).

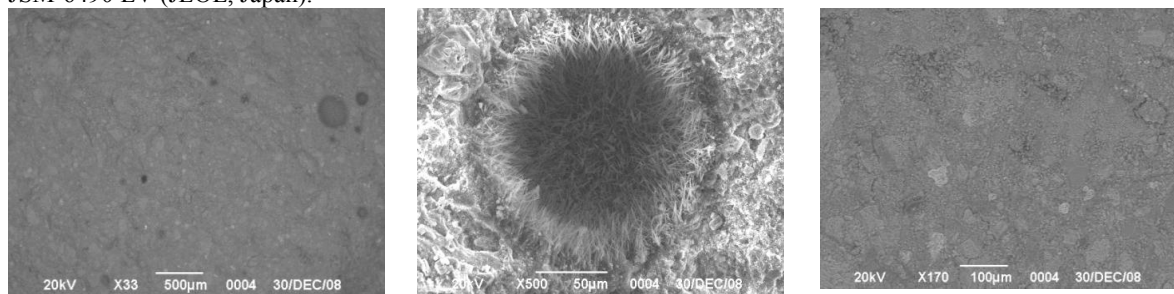


Fig. 1. Microphotographs of cleavage surface of hardened magnesia stone

The bulk of new stone structure is well-formed columnar and flat prismatic crystals of penta- and tri-oxyhydrochlorides of magnesium.

In the cavities and voids with dimensions less than 100 microns the needle-shaped crystals are formed on the inner surface of the voids. They form a continuous layer of fine needles of the size of 0.01-0.06 microns. The secondary prismatic crystals grow on the layer of the needles. They reach 0.10-0.13 μm in size. Such type of crystallization is typical for most micropores, which free volume is filled by the oxychloride crystals or the formed crystals cover the inside surface of voids with a continuous layer⁹.

The result of the research revealed that it is possible to produce the magnesium binders using local natural and technogenic mineral.

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