

Technological and operational properties of composite magnesia binders

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ABSTRACT

The article presents the results of studies of magnesia binders of various material compositions. The purpose of the work is to study the technological and operational properties of composite magnesia binders containing metallurgical slag and magnetite ore. Solutions of magnesium chloride and magnesium sulfate, as well as a mixture of them, were used to seal magnesia binders. The technological properties of magnesia binders were evaluated by the consumption of saline solution, consistency, and viscosity changes of the suspensions. To determine the operational quality of composite binders, indicators of density, strength, water absorption and water resistance were used. The dependences of the rheological properties of suspensions on the composition of the dispersed phase and the type of saline solution are revealed. The operational advantages of composite magnesia binders have been established and substantiated: increased density, lower water absorption, increased water resistance and comparable strength compared with caustic magnesite. The directions of using the developed magnesia-slag and magnesia-magnetite binders are proposed. The research results are aimed at developing resource-saving technologies for magnesia binders and concretes.

Keywords: caustic magnesite, metallurgical slag, magnetite ore, composite binders, viscosity of suspensions, stone structure.

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Introduction

Modern trends in the development of construction materials science are aimed at developing resource-saving technologies using man-made waste from various industries [[1], [2], [3]].

Cement production consumes significant volumes of carbonate raw materials and fuel resources, and is also accompanied by harmful emissions into the environment [[4], [5]]. An alternative to energy-intensive Portland cement are composite binders containing active mineral additives (granulated metallurgical slag, waste from thermal power plants, etc.). Composite cements are characterized by a reduced clinker content and improved technical properties. However, cements with a high content of mineral additives often harden slowly early and fail to achieve high design strength values. To address these issues,

technological approaches (increasing the fineness of the binder grinding, introducing water-reducing additives) are used, which complicate the process and require additional costs [[1], [3]].

The development of modern construction technologies is facilitated by the use of effective materials. Magnesia binders, primarily caustic magnesite, are characterized by high activating properties for materials of various origins.

The hydration properties of latent substances are activated by the combined action of caustic magnesite (MgO) and a salt binder ($MgCl_2$ or $MgSO_4$ solutions). Composite binders combined with magnesium chloride exhibit increased hydraulic activity due to the participation of chloride ions in the formation of bridging polymer structures that strengthen the magnesite rock [[6], [7], [8], [9]].

Consequently, the activating capacity of magnesite binders is determined not only by the

caustic magnesite but also by the composition of the salt solution. This advantage of magnesite-chloride activation underlies the production of composite magnesite binders, which are comparable in strength to caustic magnesite. Moreover, composite binders differ from caustic magnesite in their increased resistance to water and aggressive environments [[10], [11], [12]].

The properties of composite magnesite binders depend on the composition of the mineral component. Several studies have confirmed the effectiveness of combining caustic magnesite with fuel combustion ash, metallurgical slag, and other man-made materials [[13], [14], [15], [16]].

A positive effect of iron additives on the physical and mechanical properties and durability of magnesite binders has been revealed [[17], [18], [19]]. It is believed that the reduction in the hygroscopicity of magnesite oxychloride binders containing trivalent iron cations occurs through the neutralization of the negative charge of magnesium hydroxyl chlorides by the positive charge of trivalent ions, as well as by reducing the electrostatic attraction of water dipoles [[20], [21]].

To expand the scope of magnesite concrete applications, research is needed into the properties of composite binders, which determine the nature of the technological process and the intended use of the materials.

The aim of this study is to investigate the technological and operational properties of composite magnesite binders.

Experimental part

The object of the study was composite magnesite binders based on caustic magnesite, aluminosilicate, and iron components.

To produce the composite binders, caustic magnesite grade 75 powder, containing 75–85% MgO and characterized by a specific surface area of 290 m²/kg, was used.

Metallurgical slag containing the following (wt.%) was used as the aluminosilicate component of magnesite composites: SiO₂ 44.1; Al₂O₃ 13.2; Fe₂O₃ 0.9; CaO 31.3; MgO 5.2; SO₃ 2.1; other 3.2. The main phases of the metallurgical slag were åkermanite, anorthite, and gehlenite. Magnetite ore with a magnetite iron content of 89.6% was used as the ferrous component. Non-metallic minerals

accompanying magnetite included pyroxene, garnet, scapolite, actinolite, and epidote.

Composite binders were obtained by combined milling of the components to a specific surface area of 300–320 m²/kg. The dispersion of the binders was assessed using a PSKh-10M device (manufacturer: Own Technologies (Sobstvennyye Tekhnologii) from Russia).

Magnesia binders are mixed with salt solutions. The combination of caustic magnesite and magnesium chloride solution ensures intensive hardening and high strength. When caustic magnesite is mixed with magnesium sulfate solution, the hardened stone is more stable in an aqueous environment [9]. For mixing the studied composite magnesia binders, a magnesium chloride solution with a density of 1250 kg/m³, a magnesium sulfate solution with a density of 1220 kg/m³, and a mixture of these solutions with a magnesium chloride content of 70% were used. The density of the salt solutions was determined with a hydrometer at a liquid temperature of 20–22 °C.

An important technological parameter determining the performance characteristics of composite materials is the rheological properties of molding suspensions. Molding binders are non-Newtonian fluids. During the preparation and compaction of molding mixtures, internal friction occurs between the layers of the suspensions, which is characterized by viscosity. Suspensions exhibit thixotropy if their viscosity decreases over time and under mechanical stress. Suspensions are rheopexic if their viscosity increases over time [22].

Suspensions were prepared using the binders studied, and their state was assessed using a standard instrument — a Suttard viscometer — based on the diameter of the suspension's flow. The amount of salt solution was adjusted to produce a suspension with a flow diameter of 250–270 mm.

This state of magnesite suspensions is necessary for viscosity measurements using an M3600 automatic rotational viscometer, which operates on the "cylinder-in-cylinder" principle (manufacturer: Grace Instrument, USA). The viscometer's cylindrical measuring vessel was filled with the suspension, and then the cylindrical rotor sleeve was immersed in the suspension. The study algorithm involved rotating the rotor at 10 revolutions per minute (rpm) for 60 seconds, followed by 200 rpm for the next 3600 seconds. Selecting the rotational viscometer mode allowed us to observe changes in the viscosity of the

suspensions during the period of active technological impact on the molding mixtures.

The performance characteristics of magnesite binders were measured using physical and mechanical properties such as density, strength, water absorption, and water resistance of the hardened stone.

To evaluate the properties of the hardened binders, 20 x 20 x 20 mm samples were molded from suspensions tested in a rotational viscometer. The samples were allowed to harden in air.

Strength testing of the samples was performed using a 100MG4A compact hydraulic test press (manufactured by Special Design Bureau Stroyprapor, Russia).

Water absorption of the hardened stone was determined based on the change in sample weight after 24 hours of exposure to water.

The water resistance of the binders was assessed using the softening coefficient, which was calculated as the ratio of the strength of the material exposed to water for two days to the strength of the material hardening in air. Physical and mechanical tests of the binders were conducted on six samples from each series. The range of test results was 4.5–6.7%.

Discussion of results

Preliminary studies demonstrated the preference for composite binders containing 50% mineral component (Table 1).

The liquid component content influences the consistency of molding sands, the curing behavior,

and strength properties. The combination of caustic magnesite with mineral components reduces the need for a salt solution to form a slurry of a given consistency. The use of magnesium sulfate solution increases the liquid-to-solid ratio for the studied slurries.

The graphical dependencies (Figure 1) reflect the nature of the change in suspension viscosity when the rotor is running at 200 rpm. In the first 500 seconds, a decrease in viscosity is observed in all suspensions due to the increased mixing speed in the viscometer. Subsequent changes in viscosity characterize the structure formation processes in the suspensions. Initial viscosity values depend on the composition of the binders. The use of magnesium sulfate solution is accompanied by a decrease in initial viscosity (Figure 1).

The viscosity of the MX suspension increases starting from 1000 s and reaches 420 Cp (centipoise) by the end of the tests. The MS suspension, containing a magnesium sulfate solution, increases its viscosity to 580 Cp in the period from 500 to 2400 s; subsequently, the suspension remains unchanged. The MC suspension, containing a mixed salt solution, increases its viscosity in the period from 700 to 2500 s. After reaching a viscosity of 580 cP, the suspension remains unchanged until the end of the tests.

Unlike caustic magnesite suspensions, the viscosity of magnesite-slag suspensions begins to increase later and exhibits increased sensitivity to the composition of the brine. The viscosity of the FX suspension increases in the range of 1200–2500 cP, reaching 580 cP, and subsequently remains stable.

Table 1 – Composition of magnesite binder suspensions

Composition code	Composition of the binder, %			Composition of the mixing fluid, %		Liquid to binder ratio
	caustic magnesite	metallurgical slag	magnetite ore	magnesium chloride	magnesium sulfate	
MX	100	–	–	100	–	0.65
MS	100	–	–	–	100	0.73
MC	100	–	–	70	30	0.75
FX	50	50	–	100	–	0.51
FS	50	50	–	–	100	0.53
FC	50	50	–	70	30	0.54
KX	50	–	50	100	–	0.43
KS	50	–	50	–	100	0.48
KC	50	–	50	70	30	0.50

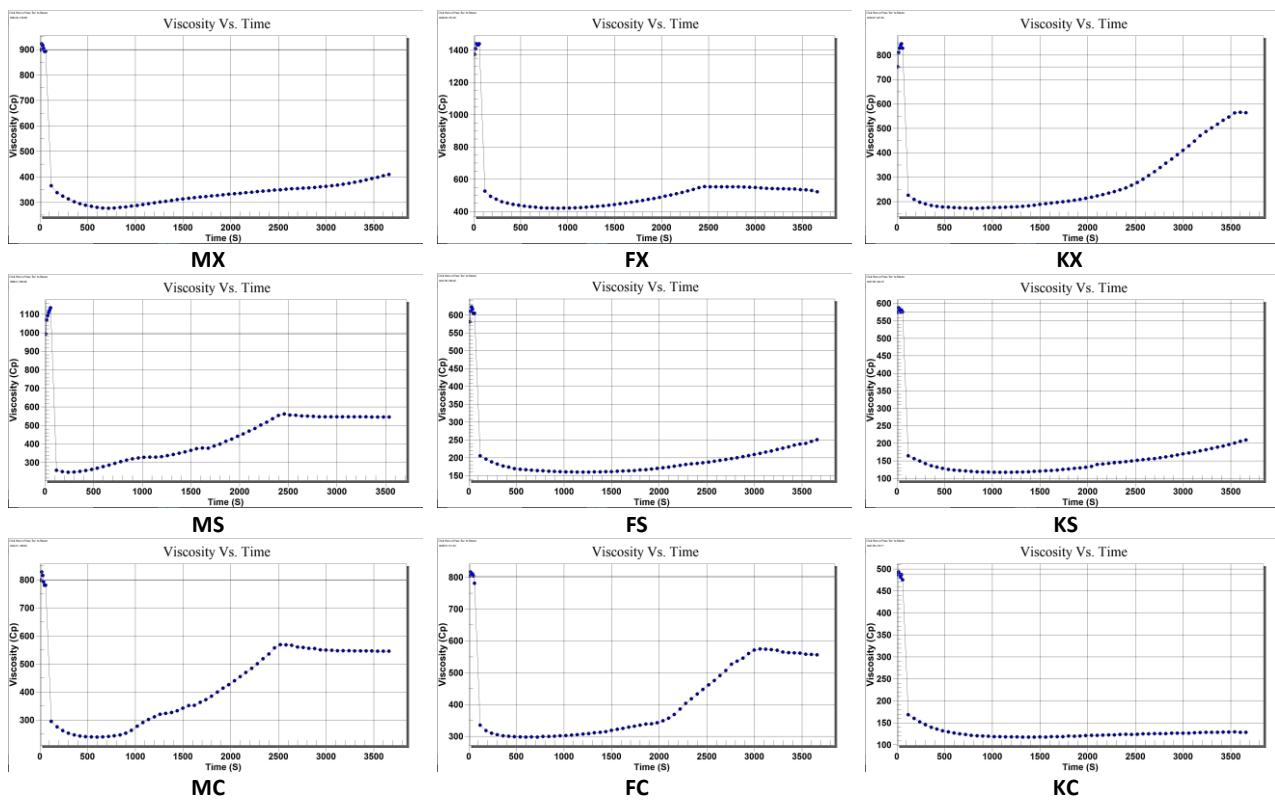


Figure 1 – The influence of the composition of binder suspensions on the change in viscosity in a rotational viscometer (binders' designations as in Table 1)

The viscosity of the FS suspension increases starting from 1600 cP and by the end of the tests it is 250 cP.

Magnesia-slag suspension FC, containing a mixed salt solution, increases its viscosity in the range of 1100–3000 s to 580 cP, and then remains unchanged. Magnesia-magnetite suspensions, compared to similar magnesia and magnesia-slag suspensions, are characterized by a lower initial viscosity. The viscosity of the KX suspension increases in the range of 1500–3600 s and reaches 580 cP. The viscosity of the KS suspension increases in the period from 1500 to 3600 s and reaches 210 cP. Magnesia-magnetite suspension containing a mixed salt solution increases its viscosity from 110 to 130 cP in the range of 1600–3600 s. Iron, being an acceptor metal, is capable of liquefying binder suspensions [21].

The revealed patterns of influence of the material composition of magnesite binders on the rheological properties of suspensions will allow to regulate the technological parameters of processing molding mixtures in the manufacture of products.

The density of hardened binders reflects the structural properties of the stone and depends on the material composition (Figure 2). The binders tested, hardened with magnesium sulfate solution, are characterized by a stone density 16–19% lower

than similar oxychloride-cured binders. The reduced density of oxysulfate-cured binders is due to the lower density of the magnesium sulfate solution, the increased amount of liquid used to obtain the suspensions, and the amount and morphology of hydrates.

The density of hardened magnesite composite binders exceeds that of caustic magnesite due to the chemical and mineral composition of metallurgical slag and magnetite ore and the formation of hydrates with their participation. The density of hardened magnesite-slag binders is 3–14% higher than that of caustic magnesite. The density of magnesite-magnetite binders is 26–32% higher than that of hardened caustic magnesite.

The water absorption of binder stone characterizes the porosity of the structure and affects the strength and durability of the material (Figure 3). Open porosity of the stone, accessible to water penetration, is formed due to unbound liquid and also depends on the structure of hydrate formations.

There is no direct correlation between stone water absorption and the liquid-to-solid ratio. The type of salt solution and the presence of aluminosilicate and ferrous components have a significant impact on stone water absorption (Figure 3).

The loose structure of binders produced using magnesium sulfate solutions exhibits increased water absorption. For example, the water absorption of MS, FS, and KS stones exceeds that of MX, FX, and KX stones by 1.8, 2.8, and 3.1 times, respectively. However, the differences in water absorption between MS, FS, and KS are insignificant. KX, a magnesia-magnetite binder of oxychloride hardening, exhibits the lowest water absorption. The amount of water absorbed by KX is 2.3 times less than that of MX and 1.5 times less than that of FX.

The strength of hardened stone at 28 days demonstrates the superiority of oxychloride-cured binders (Figure 4). The strength of MX, FX, and KX binders exceeds that of MS, FS, and KS binders by 2.0, 2.3, and 1.9 times, respectively. Binders tempered with a mixed salt solution are comparable in strength to oxychloride-cured binders.

The strength of magnesia-slag and magnesia-magnetite binders is 87-102% and 85-95% of the strength of caustic magnesite, respectively.

This proves that the strength of composite binders is formed not only by magnesium hydroxychlorides and hydroxysulphates, but also by hydrates based on metallurgical slag and magnetite ore [[11], [15], [16]].

The widespread use of magnesite binders is hampered by their low resistance to water. It is

known that the combination of caustic magnesite with mineral components increases the binder's water resistance [[10], [12], [19]]. The results of the study confirm the operational advantages of composite magnesite binders (Figure 5). The softening coefficient of oxychloride-cured composite binders is 1.5-1.6 times higher than that of caustic magnesite mixed with magnesium chloride solution.

Binders obtained using magnesium sulfate solutions are generally characterized by increased water resistance due to the stability of magnesium hydroxy sulfates [[9], [17], [18]]. The low softening coefficient values of the studied hydroxy sulfate-hardening binders are due to the loose structure of the stone obtained from suspensions with a low content of the dispersed phase. The reason for the low strength of MS, FS, and KS in water is the erosion of contacts between hydrates, which is facilitated by the high-water absorption of the stone.

Increased water resistance of composite binders is ensured by the helicrystalline structure of the stone, which, along with magnesium hydrochlorides and hydroxysulfates, is formed by weakly crystallized hydroaluminosilicates, hydrosilicates, magnesium hydroferrites, hydrogarnets and iron hydroxides [[12], [16]].

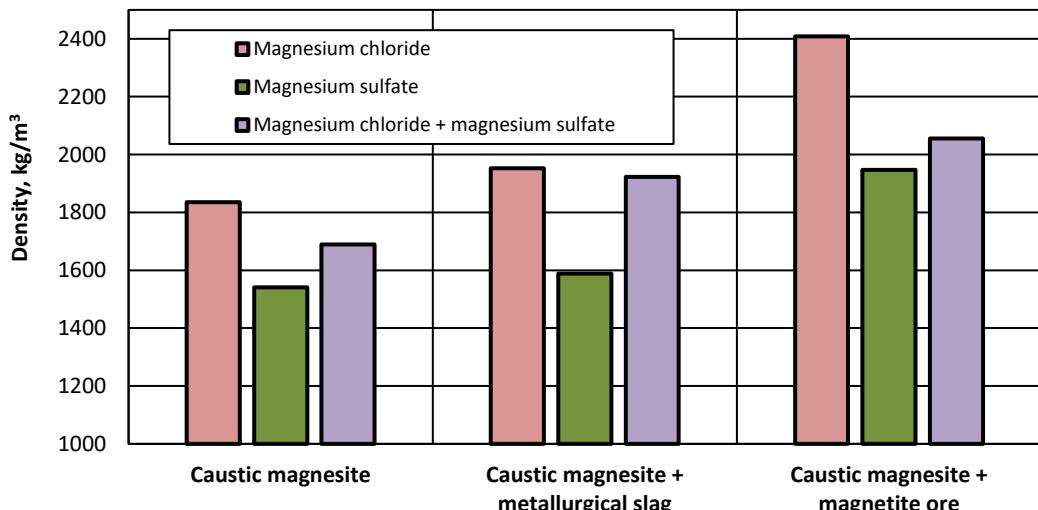


Figure 2 – The influence of the composition of magnesite binders mixed with various salts on the density of hardened stone

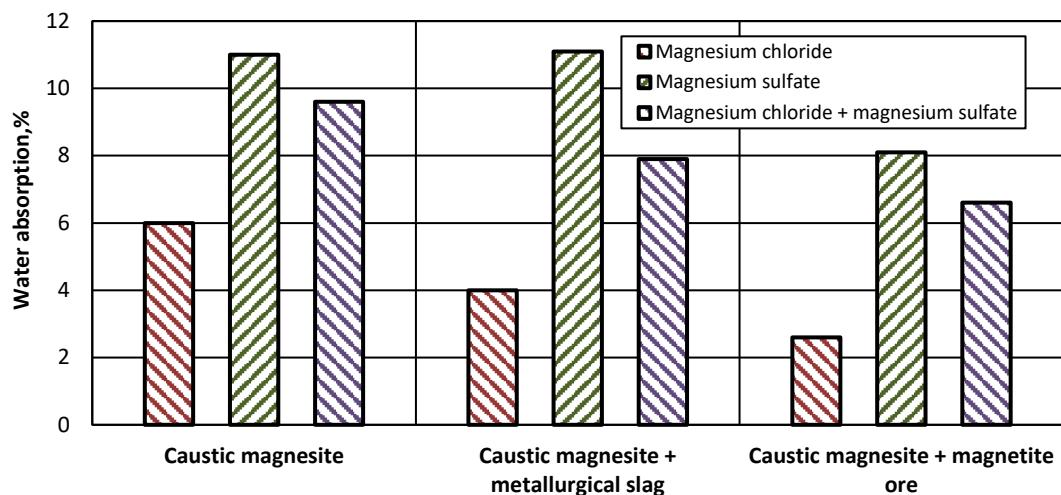


Figure 3 – The influence of the composition of magnesite binders mixed with various salts on the water absorption of hardened stone

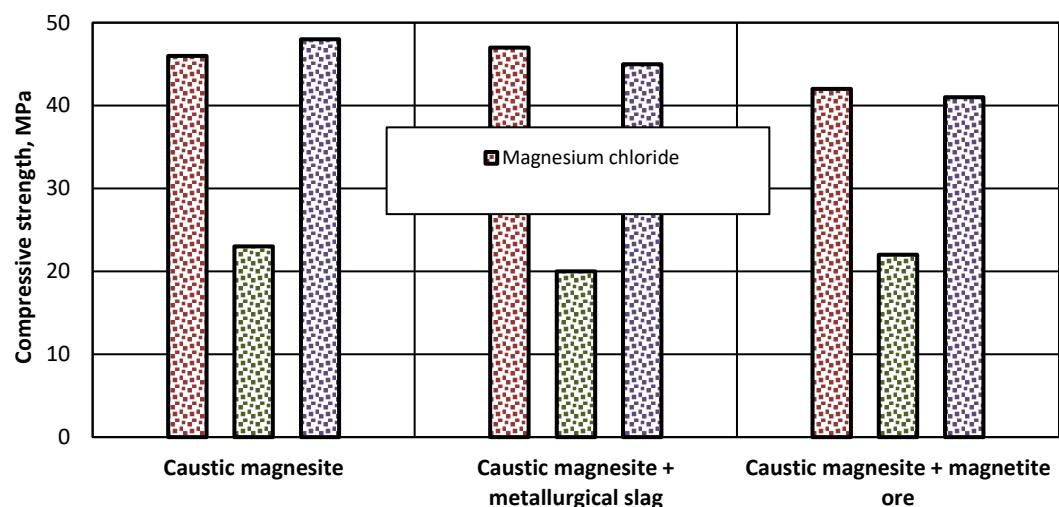


Figure 4 – The influence of the composition of magnesite binders mixed with various salts on the strength of hardened stone

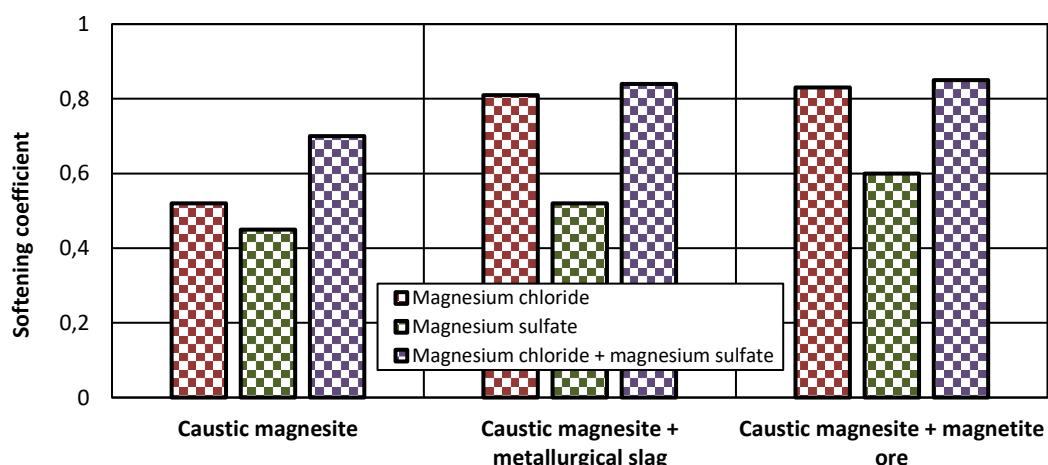


Figure 5 – The influence of the composition of magnesite binders mixed with various salts on the water resistance of hardened stone

Hardened binder is the component of concrete structure that determines the strength and performance properties of construction projects. Magnesia binders offer a wide range of compositional possibilities due to the combination of caustic magnesite with mineral components and salt solutions of varying compositions.

The ability to influence the physical and mechanical properties of composite magnesite binders through targeted selection of mineral components and the composition of the salt solution makes it possible to obtain building materials with a wide range of changes in structural characteristics.

The high density of magnesia-magnetite rock makes it suitable for use in radiation-protection concrete.

Magnesia-slag binders of oxychloride hardening, comparable in strength and other technical characteristics to caustic magnesite, contain up to 50% man-made components and contribute to the development of resource-saving concrete technologies with a low carbon footprint.

The diversity of composite magnesite binders is the basis for targeted modification of the processes of structure formation and regulation of the properties of concrete for general construction and special purposes.

Conclusions

The possibility of regulating the technological and operational properties of magnesia binders of oxychloride and oxysulfate hardening by using metallurgical slag and magnetite ore in their composition has been proven.

Composite magnesia-slag and magnesia-magnetite suspensions differ from magnesia suspension of equal consistency by a decrease in the content of salt solution by 1.2-1.5 times.

Composite magnesite suspensions are characterized by long-lasting thixotropy. This will expand the processing capabilities of molding mixtures containing magnesite composites.

Hardened composite binders form a stone of increased density, which reaches 1950-2400 kg/m³, and it can be used to produce particularly heavy concrete.

Composite binders are characterized by slow structure formation, while they are not inferior in design strength to caustic magnesite.

The reduced water absorption of composite binders is predetermined by the denser structure of the stone. Magnesia-slag and magnesia-magnetite binders exhibit increased water resistance due to the helicrystalline structure of the stone. Weakly crystallized hydrates formed with the participation of metallurgical slag and magnetite concentrate are compacted by undissolved particles of the original phases, clogging the voids of the composite binders, promoting compaction and increasing the stability of the crystalline framework of magnesium hydroxychlorides and hydroxysulfates.

The use of a mixed solution of magnesium chloride and magnesium sulfate does not impair the technological properties of magnesite suspensions and allows for the regulation of the formation and properties of the stone structure.

The developed composite binders ensure resource conservation by reducing the proportion of caustic magnesite by up to 50% and decreasing the consumption of salt solution, expanding the possibilities of using magnesite concrete for various construction areas.

Composite magnesite binders are an alternative to Portland cement. The excellent physical and mechanical properties of magnesite binders, coupled with their pronounced adhesive properties, allow for the production of effective concretes based on various aggregates. A promising application for magnesite binders is multilayer concrete with variable structure for enclosing structures of buildings with various operating conditions.

Conflicts of interest. On behalf of all co-authors, the corresponding author states, that no conflict of interest exists.

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Композициялық магнезиялық тұтқыр заттардың технологиялық және пайдалану қасиеттері

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ТҮЙІНДЕМЕ

Түйін сөздер: каустикалық магнезит, металлургиялық қож, магнетит кені, композициялық түткір, суспензияның түткірлігі, тастың күрүлымы.

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Технологические и эксплуатационные свойства композиционных магнезиальных вяжущих

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АННОТАЦИЯ

В статье приведены результаты исследований магнезиальных вяжущих различного вещественного состава. Цель работы – исследование технологических и эксплуатационных свойств композиционных магнезиальных вяжущих, содержащих металлургический шлак и магнетитовую руду. Для затворения магнезиальных вяжущих использовали растворы хлорида магния и сульфата магния, а также их смесь. Технологические свойства магнезиальных вяжущих оценивали по расходу солевого раствора, консистенции и изменению вязкости суспензий. Для определения эксплуатационного качества композиционных вяжущих использовали показатели плотности, прочности, водопоглощения и водостойкости. Выявлены зависимости реологических свойств суспензий от состава дисперсной фазы и вида солевого раствора. Установлены и обоснованы эксплуатационные преимущества композиционных магнезиальных вяжущих: повышенная плотность, меньшее водопоглощение, повышенная водостойкость и сопоставимая прочность по сравнению с каустическим магнезитом. Предложены направления использования разработанных магнезиально-шлаковых и магнезиально-магнетитовых вяжущих. Результаты исследований направлены на развитие ресурсосберегающих технологий магнезиальных вяжущих и бетонов.

Ключевые слова: каустический магнезит, металлургический шлак, магнетитовая руда, композиционные вяжущие, вязкость суспензий, структура камня.

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