Waterproof Magnesia Composites for the Construction of Agro-Industrial Objects

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Abstract. The results of studies evaluating the possibility of increasing the water resistance of pressed magnesia composites for the purpose of their use in the construction of agro-industrial objects are presented. As a modifying filler, a secondary resource was used: the burnt rock from the mines of the Rostov region, which has pozzolanic properties. In the studied compositions, a modifying filler was replaced with 10 to 25% of the magnesian binder. The water resistance of the pressed modified magnesia composites was assessed by changing the values of the softening coefficients and water resistance of the control samples after they were kept in water for 1, 7, 28, 60, and 90 days. It is shown that the modification of the magnesia binder with burnt rock and compaction of molding mixtures by pressing makes it possible to obtain strong and durable composites that retain their physical and mechanical characteristics for a long time in wet conditions. The compositions of modified magnesia composites designed for the manufacture of small-piece pressed products for the walls and floors of low-rise residential buildings, as well as other construction projects of the agro-industrial complex, with indoor air humidity of more than 60%, have been developed. The use of a significant amount of waste from the coal industry as part of the forming mixtures should free up land allocated for dumps and contribute to improving the environmental situation in rural settlements. This allows attribyting the proposed method of manufacturing construction products to the best available technologies.

Keywords*:* Magnesia Binders, Pressed Composites, Water Resistance, Water Resistance Coefficient, Burnt Rock, Secondary Resource, The Best Available Technologies, Agro-Industrial Complex.

1 Introduction

One of the main objectives of the agricultural development program is to stimulate the growth of agricultural production. The expansion of production capacities in this area largely depends on the effective operation of agro-industrial complexes. This requires the construction of new high-production facilities of the agricultural industry. An urgent environmental problem of our time is the disposal of waste and by-products of industrial production. Due to the intensive development of the construction industry, there is a shortage of natural mineral raw materials used for the needs of the production of building materials, including for the construction of agro-industrial facilities that are environmentally friendly and durable. Therefore, the use of secondary raw materials makes it possible to increase the raw material base for the production of building materials and solve the environmental problems of large industrial areas. In this regard, of particular importance is the development of new construction materials based on technological waste, the economic efficiency of which increases significantly with the use of decentralised waste accumulation. For example, slags, ashes of thermal power plants, microsilicon, waste from the production of tires, asphalt, etc. have found wide application. They make it possible to obtain construction materials and products with high structural properties [1-4].

Burnt rocks (the product of self-firing of waste rocks extracted to the surface together with coal) are of increasing interest as secondary raw materials in the construction industry, the volumes of which are significant and rapidly increasing. The chemical composition of the burnt rocks fully meets the conditions for the use of solid waste of the coal industry in the production of building materials. They are used as a material for covering roads, for obtaining rubble stone, crushed stone and sand, which can be used as aggregates for concrete and solutions [5-7].

An important property of the burnt rock is hydraulic (pozzolanic) activity, which is due to the presence of several active components: aluminate (active alumina, dehydrated clay minerals (metakaolin), silica (soluble silica), and ferruginous one (iron oxide (III) in active amorphous form) [8, 9].

In our opinion, a promising direction of utilisation of burnt rocks is their use as a modifier of magnesia binders. The research of many domestic and foreign authors is focused on solving the problem of low water resistance and durability of products based on magnesia binders [10, 11]. Previously, we have developed compositions of magnesia composites with a burnt rock content of 10 to 25%, which have valuable structural properties. Their durability was assessed by the softening coefficients and air resistance with alternating humidification and drying [12-15]. Another method that makes it possible to evaluate the proposed ways to increase the durability of artificial composites based on air binders is their resistance tests under prolonged exposure to wet conditions.

The purpose of this work is to study the effect of a modifying filler with pozzolanic properties on the long-term water resistance of pre-formed magnesia composites, estimated by the change in the physical and mechanical characteristics of control samples after their prolonged exposure to water.

2 Materials and Methods

Caustic magnesite of the PMK-75 brand, the activity of which was 40 MPa in compression and 18 MPa in bending, was used in experimental studies, according to GOST 1216-87 “Caustic Magnesite Powders. Technical Conditions”. A solution of natural bischofite with a density of 1.28 g/cm^3 was used as a magnesia binder, and a finely ground burnt rock of mines of the Rostov region with a clay-ferruginous modulus $M_{g.zh.}$ = 0.49 was used as a modifying filler, which is a product of oxidative self-ignition of rocks extracted together with coal from the mines.

The assessment of the resistance of pressed composites based on a modified magnesium binder with burnt rock to prolonged exposure in water was carried out using control samples molded from mixtures, the compositions of which in preliminary experiments showed the best results in compressive strength and water resistance. The pressing pressure during the manufacture of samples was assumed to be equal to 40 MPa. In all the studied compositions, the ratio between magnesium oxide and magnesium chloride was assumed to be 0.072. To conduct comparative tests, control samples made of dough of normal consistency without the addition of burnt rock (composition 1) were also used. The compositions of the studied molding mixtures and the physico-mechanical characteristics of the samples formed from them are shown in Table 1.

Table 1. Compositions of molding mixtures and physico-mechanical characteristics of modified binder.

Composition	Content, [%] by mass		Ultimate compressive strength of samples, [MPa]		Liquefaction ratio	Average density, [kg/m^3]	Water absorption, [%] by mass	Effective porosity, [%]
	magnesia cement	burnt rock	dry	water-saturated				
1	100	–	44.1	22.1	0.54	2000	13.9	27.80
2	100	–	46.1	26.3	0.57	2065	8.9	18.38
3	90	10	48.1	39.1	0.81	2110	8.0	16.88
4	85	15	49.0	41.8	0.85	2138	7.3	15.61
5	80	20	49.3	44.3	0.89	2160	7.1	15.34
6	75	25	46.2	36.9	0.80	2172	8.8	19.11

Before the tests, the samples were hardened for 28 days in air-dry conditions. After that, they were dried in a drying cabinet at a temperature of (100±5) °C to a constant mass and immersed in containers with water, where they were kept for 1, 7, 28, 60, and 90 days at a temperature of (25±3) °C. At specified intervals, 10 samples of each composition were extracted from the water, half of which were immediately tested for strength when compressed in a water-saturated state, and the rest after drying at the above temperature.

The water resistance of the studied compositions was evaluated by changing the softening and water resistance coefficients. The first was calculated as the ratio of the average compressive strength of control samples in a water–saturated and dried to a constant mass state, and the second as a quotient of the division of the strength of the material in the dried state after holding the corresponding time in water, to its strength before the start of the tests. According to the change in the mass of the samples before and after saturation, water absorption by weight was calculated.

3 Results and Discussion

The nature of the change in the compressive strength of control samples in a dry and water-saturated state as the duration of their exposure in water increases is shown in Fig. 1. Analysis of the research results shows that the strength of dried and water-saturated samples molded from all the studied compositions changes non-monotonically. In the first 7 days of testing, the strength of samples of compositions 3-6 (with the addition of burnt rock) increases both in dry and water-saturated states. As the duration of holding the samples in water increases, the strength decreases. It should be noted that after 28 days of testing, even with a slight decrease in strength indicators, they exceed the initial values.

Cast and pressed samples molded from a pure binder without a modifying filler (compositions 1 and 2) after 28 days of their exposure in water, have a loss of strength by 63% and 13%, respectively. This indicates the advantage of pressing as a method of compacting molding mixtures (composition 2). The destruction of samples of composition 1 occurred before 60 days of their storage in water. The pre-tested samples (composition 2) withstood 60 days of testing, and when further held in water, they collapsed. Samples molded by pressing from compositions 3-5 (10%, 15% and 20% of burnt rock, respectively) were significantly more resistant to prolonged exposure in water. It should be noted that in samples of composition 5 (20% of burnt rock) after 90 days of testing, the loss of strength in the dried state is 28%, in the water-saturated state, 52%. A further increase in the content of burnt rock in the magnesia binder gives low strength indicators and after 90 days of exposure in water, it is 18.4 MPa in the dried state and 9.3 MPa in the water-saturated state.

Comparing the data of changes in the strength of the samples (Fig. 1) and their water absorption by weight (Fig. 2) with an increase in the time of holding the samples in water, the following pattern can be traced: the greater the increase in the strength of the material in the first 7 days of testing, the more noticeably its water absorption decreases at the same time. A sharp increase in water absorption after 28 days of storage in water is observed in samples of compositions 1 and 2, which is accompanied by a significant loss of strength in both dried and water-saturated states. It should be noted that the current content of burnt rock (25%, composition 6) after 90 days of storage in water has a negative effect on the structure, as evidenced by an increase in water absorption.

The experimental correlations obtained are consistent with the data of physico-chemical methods for studying the structure of hardened masnesite stone at different stages of hardening. It was found that the mineralogical and phase composition of the hardening products of magnesia composites modified by burnt rock is represented by intractable magnesium hydrosilicates of the serpentine type and magnesium hydroaluminates of the palygorskite type, as well as complex compounds of magnesium chloride with oxides and hydroxides of metals such as kenetite and circlerite [16-18].

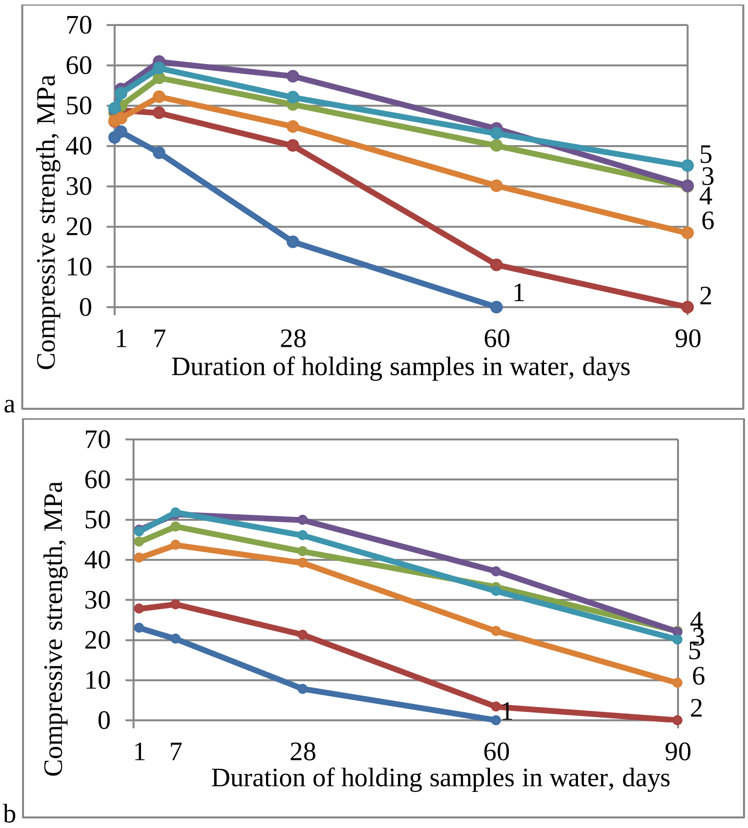

Fig. 1. The effect of the duration of exposure of control samples in water on their strength in the dried (a) and water–saturated (b) state: 1-6 - composition numbers.

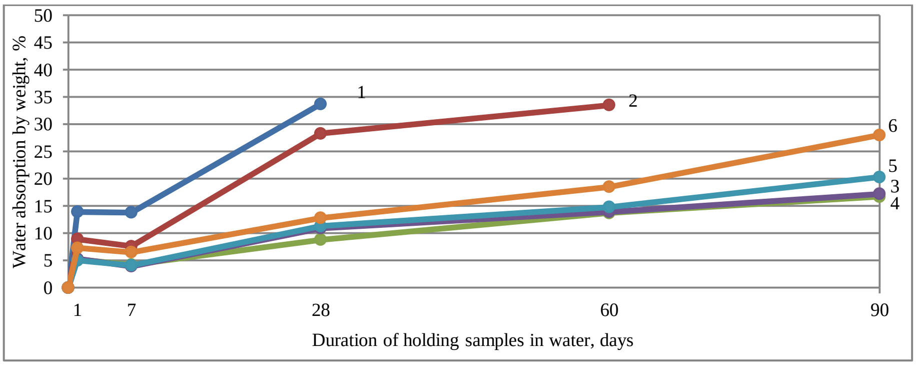

Fig. 2. The effect of the holding time of samples in water on their water absorption: 1-6 – composition numbers.

The possibility of the formation of the latter allows us to talk about the binding of chloride ions into complex complexes. This leads to a decrease in their concentration in the drying stone and, as a consequence, there is a decrease in the solubility of the hardening products, on the one hand, as well as an increase in insoluble compounds on the other. It was found that the hardening process of pressed magnesia composites is stretched over time. The rate of formation of oxychlorides and magnesium hydroxide is higher than the rate of formation of complex silicate and aluminosilicate phases.

Fig. 3a and 3b show the dependences of the change in the coefficients of softening and water resistance, respectively. The change in the values of the softening and water resistance coefficients for compositions 3-6 is consistent with the dynamics of the strength set of samples in the dried and water-saturated states.

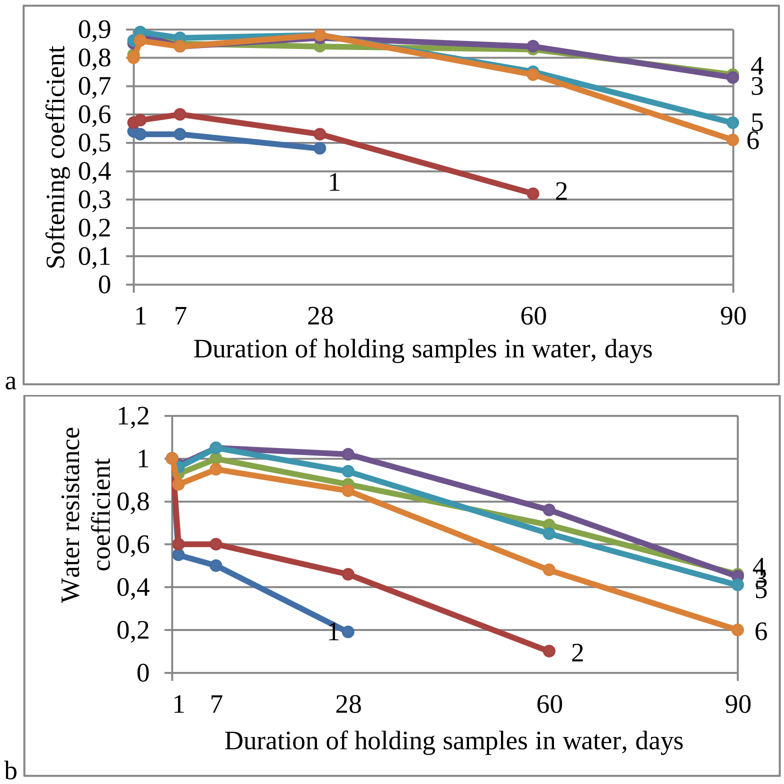

Fig. 3. Change in softening coefficients (a) and water resistance (b) with an increase in the duration of holding control samples in water: 1-6 – composition numbers.

After 28 days of hardening, non-hydrated magnesium oxide and highly dispersed silicon and aluminum oxides remain. When samples are kept in water, hydration of the above-mentioned components occurs and further formation of sparingly soluble compounds, which contribute to a decrease in porosity and a corresponding decrease in water absorption [19, 20]. At the initial stages of testing, the condensed and crystallisation structures prevail in the hardened modified magnesia stone. With further hydration, the predominance of the coagulation structure is observed. The combination of crystalline and amorphous phases causes the formation of a dense structure, which increases the strength and water resistance of the modified magnesia binder.

4 Conclusion

The conducted studies have shown that the replacement of a part of the magnesian binder with a modifying filler from finely ground burnt rock of mines with pozzolanic properties has a beneficial effect on the long-term water resistance of pressed magnesite composites. This is due to the formation of intractable magnesium hydroxylates of the serpentine type and magnesium hydroaluminates of the palygorskyte type in the structure of the hardened binder stone, as well as complex compounds of magnesium chloride with oxides and hydroxides of metals (iron, aluminum) such as kenetite and circlerite.

It was found that that magnesia composites containing 10-20% of modifying filler have the highest resistance during long-term storage in water. After 60 days of testing, the softening coefficient of these compositions of composite binders was in the range from 0.83 to 0.75, and the coefficient of water resistance was 0.76-0.65.

The developed compositions of composite magnesia binders are recommended for the production of pressed construction products operated in rooms with a humidity of more than 60%. The use of a significant amount of waste from the coal industry (up to 20%) in the composition of molding mixtures should free up land allocated for landfills and contribute to improving the environmental situation in rural areas. This allows attributing the proposed method of manufacturing construction products to the best available technologies.

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