A comparative assessment of gypsum and magnesite composites' air resistance modified by secondary resources

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Abstract. The purpose of this work is a comparative assessment of the resistance to alternating humidification and drying (air resistance) of modified pressed composites based on gypsum binder and magnesia cement. In order to increase the water and air resistance of small-piece gypsum and magnesite products manufactured by pressing, modifying fillers were introduced into the composition of molding mixtures as secondary resources. There are investigated changes in the physical and mechanical properties of pressed modified composites, as well as their durability indicators during cyclic tests for alternating humidification and drying. The studies have shown that the methods of gypsum and magnesia binders' modification make it possible to obtain durable materials with increased water and air resistance by pressing. Gypsum and magnesite construction products become suitable for the construction of walls of low-rise buildings, as well as partitions in rooms with a humid indoor regime manufactured by pressing according to the proposed technologies. The chemical composition and the nature of the crystallization structure of modified gypsum composites cause their better resistance to alternating stresses during cyclic humidification and drying in contrast to magnesite.

Keywords: Gypsum binder, Magnesia binders, Molded composites, Water resistance, Air resistance

1 Introduction

The task of expanding the production of construction products based on gypsum and magnesia binders is very urgent for many regions of the world with developed production of mentioned binders or significant reserves of the corresponding types of raw materials [1, 2]. Gypsum and magnesite building products retain their strength, physical, decorative and other properties in case of use in the internal structures of buildings and structures with a dry indoor regime. However, they are low resistant from water and frost, and show significant creep under load in humid conditions [3-5]. In case of absence of these shortcomings the prospects open up for the use of gypsum and magnesite construction products for the construction of walls of low-rise buildings, as well as partitions in rooms with a value of relative humidity exceeding 60% [6-8].

One of the ways to increase the water resistance of products based on air binders is increasing their average density. This can be achieved by using water-reducing additives in the composition of molding mixtures or (and) using vibrating or pressing methods for compacting them. However, the open porosity still remains significant even for pressed gypsum and magnesite products. This negatively affects the ability of pressed materials to resist the wedging action of water penetrating into the pores and defects of their microstructure during water saturation [9, 10]. The fine fillers as secondary resources were used in these studies in order to reduce the residual porosity of pressed composites. This should help to reduce the cost of products and additionally improve the environmental situation in regions with technogenic waste accumulation. [11-13]. It is important to consider fillers’ ability to have a modifying effect on the physico-chemical processes of hardening of air binders with the formation of insoluble compounds in the structure of the resulting composites [14, 15]. The appearance of such compounds in defects in the structure of the material will ensure a decrease in its residual porosity and an increase in strength and durability [16-18].

In this work, the modification of magnesia cement was carried out by injection of silica and finely ground burnt rock into its composition. Whereas the gypsum binder was modified via complex modifier consisting of carbonate-containing sludge of water treatment of thermal power plants and monoammonium phosphate. There is a described in detail mechanism of action of the additives used and the properties of the resulting pressed composites of increased water resistance in following references [5, 9, 16-18].

However, not all materials that slightly lose their strength during full saturation in laboratory conditions can be considered as sufficiently durable and suitable for use in building enclosing structures and in rooms with a relative humidity of more than 60% [19, 20]. Construction products in real operating conditions can be subjected to partial or complete moisture saturation and subsequent drying many times. Repeated cycles of humidification and drying can lead to significant structural changes and even complete destruction of water-resistant materials according to many researchers [6, 21].

The purpose of this work is a comparative assessment of the resistance to alternating humidification and drying (air resistance) of modified pressed composites based on low-burn gypsum binder β-modification and magnesia cement.

2 Materials and Methods

Experimental studies were carried out using a normal-hardening gypsum binder of medium grinding grade G-5 according to Russian State Standard 125-2018 "Gypsum binders. Technical specifications" and magnesia cement grade PMK-75 according to Russian State Standard 1216-87 "Caustic magnesite powders. Technical conditions".

A complex modifier consisting of sludge from the water treatment of the Rostov-on-Don thermal power plant and monoammonium phosphate ($NH_4H_2PO_4$) was used in order to increase the water and air resistance of pressed gypsum composites.

Modification of the structure and hardening products of magnesite composites was carried out by the introduction of mineral additives with pozzolanic properties – microsilicon and finely ground burnt rock of mines. A solution of natural bischofite was used as a recluse of magnesia cement.

There is a detailed comprehensive description of water treatment sludge, silica and burnt rock, the mechanism of influence of the listed modifying fillers on the strength and water resistance of the developed pressed composites, as well as the method of preparing molding mixtures and manufacturing control samples from them [5, 9].

The methodology for assessing the resistance of pressed composites to alternating wetting and drying was developed on a basis of other authors' works who conducted similar tests earlier [6, 21]. For this purpose, the samples were kept in water at a temperature of (20±2) °C for 3 hours, and then dried for 15 hours at the same temperature. After that, they were dried for 6 hours in a drying cabinet at a temperature of (55 ±2) °C. These water saturation and drying operations were taken in one test cycle. The duration of holding the samples in water was determined from the time when water saturation reaches about 85% of the maximum possible value. After every 10 cycles of humidification-drying, 10 samples were taken for physical and mechanical tests. The gypsum samples were dried in a drying cabinet before the test to a constant mass at a temperature of (55±2) °C, and from magnesia cement - (105±2) °C. After that, a half of the samples of each series were immersed in water for 48 hours. Dried and water-saturated samples were tested for compressive strength. The ratios of softening (Ks) and air resistance (Kr) were determined by the parameters of the compressive strength of the samples. The first one is the ratio of the compressive strength of control samples in both water-saturated and dry states. The second one is a quotient of the division of the strength of samples dried to a constant mass that passed N-number of test cycles to the strength of control samples (with a "zero" test cycle). The occurrence and development of irreversible deformations during alternating humidification-drying were studied on 40×40×160 mm prism samples. Monitoring of measurement reliability and accounting for temperature errors was provided by the steel sample with same geometric characteristics as the prototypes. The samples were measured every 10 cycles of alternating humidification and drying.

3 Results

The air resistance of pressed composites based on modified gypsum binder and magnesia cement was evaluated for the developed compositions that showed the greatest strength and water resistance in previous studies [5, 9]. There are studied compositions of pressed composites and the physical and mechanical characteristics of the control molded samples before starting tests for alternating moistening and drying in Table 1.

Table 1. Compositions of molding compounds; physical and mechanical characteristics of modified binders

Composition	Content, % by weigt					Compressive strength of samples, MPa		Softening coefficient	Average density, kg / m^3	Waterabsorption, % by weight	Open porosity, %
	Magnesia binder	Silica fume	Burnt rock	Low-temperature calcined gypsum binder	Slime of chemical water purification of thermoelectric power station	Dry	Water-saturated				
1	100	–	–	–	–	41,1	22,1	0,54	1900	13,9	26,41
2	85	15	–	–	–	62,8	44,6	0,71	2108	5,7	11,30
3	80	–	20	–	–	49,3	44,3	0,89	2160	7,1	15,34
4	–	–	–	100	–	32,0	5,3	0,17	1800	11,0	19,80
5	–	–	–	80	20	61,7	44,0	0,71	1950	5,8	11,30
6	–	–	–	60	40	46,8	29,5	0,63	1860	8,5	15,80

There is also a change in the compressive strength of dried and water-saturated control samples tested at the end of the set number of cycles of alternating humidification-drying in Fig. 1.

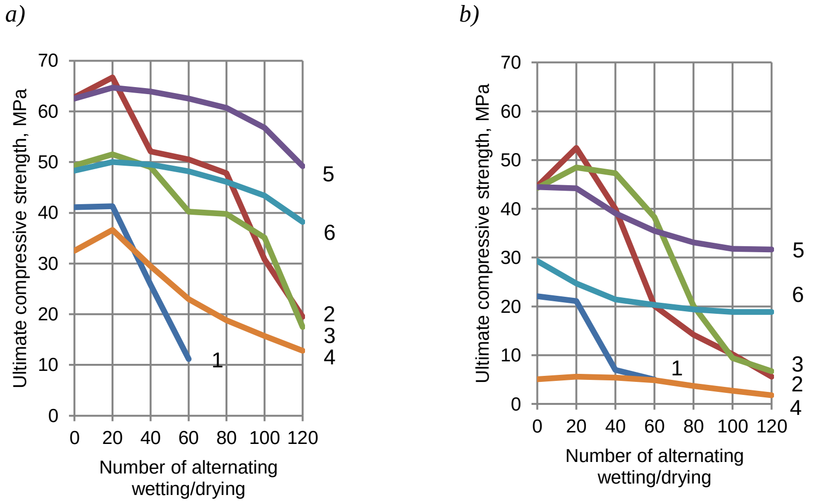

Fig. 1. Dependence of compressive strength of samples in the dried (*a*) and water-saturated (*b*) condition on the number of alternating wetting/drying cycles: 1-6 – composition numbers

From the graphs shown in Fig. 1, it can be seen that the compressive strength of pressed composites increases slightly during the first 20 test cycles of all the studied compositions in the dried state. Then the compressive strength is decreased significantly with growing number of humidification and drying cycles. Therefore, all of pressed samples without modifying additives (composition 1 – magnesia cement, composition 4 – gypsum binder) lose strength as expected in the results of our preliminary experiments [5, 17, 18]. At the same time, samples from additive-free magnesia cement were removed from the tests after 60 cycles of alternating moistening and drying due to a significant decrease in strength and the presence of visible signs of destruction. Pressed samples from magnesia cement with pozzolan additives (compositions 2 and 3) and from modified gypsum binder (compositions 5 and 6) demonstrated significant resistance to cyclic influences.

However, if the loss of the initial strength by 25% is accepted, the resistance to alternating wetting and drying of the pressed modified gypsum binder turned out to be about 1.5 times higher. Thus, the compressive strength of dried samples made of 2 and 3 compositions decreased by 25%, respectively, after 80 and 85 cycles of alternating humidification and drying, and the specified decrease in the strength of gypsum samples (5 and 6 compositions) did not occur even after 120 test cycles.

A normative decrease in strength (by 25%) of control samples occurs after fewer test cycles. It is a characteristic of all the studied compositions in the water-saturated state. At the same time, the strength of water-saturated control samples of modified magnesia cement even increases slightly after the first test cycles, and then its drop has a sharper character compared to gypsum samples. We have described a similar change in the strength of composites in the dry state above. When using 15% of microsilicon as a modifying additive (composition 2), a 25% decrease in strength of magnesite samples is observed after 45 test cycles, and if 20% of finely ground burnt rock (composition 3) is used, there is a strength decrease after 60 cycles. At the same time, the strength in the water-saturated state of the hardened modified gypsum binder begins to gradually decrease after the first test cycles. When the gypsum mixture contains 20% of thermal power plant water treatment sludge (composition 5), the initial softening coefficient is 0.71, and the strength of water-saturated samples decreases by 25% after 75 test cycles. In the case of replacement with 40% sludge, the material becomes less water-resistant (the initial softening ratio is 0.63) and a decrease in its strength in the water-saturated state occurs after 35 cycles of humidification and drying, however, during subsequent test cycles, the decrease in this indicator slows down. The above-described increase in the strength of control samples during the first period of cyclic tests can be explained by a complex of physical and chemical states in the structure of pressed materials during alternating humidification and drying. These states are accompanied by an increase in the specific surface area of neoplasms, which leads to a compaction of the structure of the hardened binding stone and a decrease in its open porosity. This is due to the partial transition of the amorphous phase of magnesium hydrosilicates into the crystalline phase in the form of hardly soluble sepiolite and serpentine in case of the hardened modified magnesite stone. As for the gypsum there is an additional hydration of calcium sulfate semihydrate, as well as recrystallization of small dihydrate crystals into larger ones. So, it is the nature of a change in water absorption by weight of the pressed composites of samples with an increase in the number of test cycles (Fig. 2).

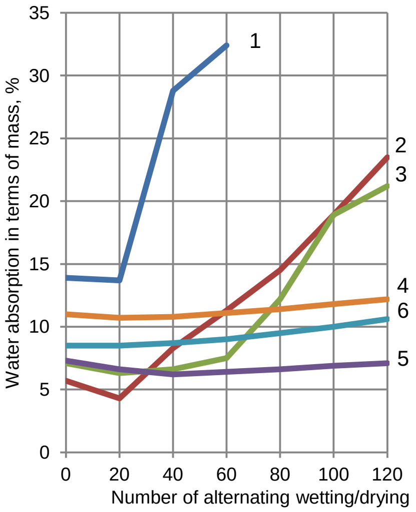

Fig. 2. Dependence of water absorption on the number of alternate wetting/drying cycles in terms of the mass of samples: 1-6 – composition numbers

4 Discussion

Comparing the test results presented in Fig. 1 and Fig. 2, there is a following pattern: the stronger the material before the start of the tests and the higher its water resistance, the more significantly its strength increases after the first cycles of humidification and drying, which is accompanied by a decrease in water absorption by weight.

The described changes in the structure of pressed materials, as well as the type and nature of neoplasms, can explain the strength loss of 25% in the studied compositions of magnesite composites occurs much earlier in contrast to gypsum. The fine-crystalline structure with an additional carbonate-phosphate framework of the solidified calcium sulfate dihydrate demonstrates a more noticeable decrease in moisture strength compared to the structure of pressed magnesia cement. However, it shows the ability to heal defects and microcracks of a fatigue nature more fully as a result of the removal of free and adsorption-bound water when dried to a constant mass. This is clearly well confirmed by the results of measurements of linear deformations of the prism samples presented in Fig. 3.

It was found that the pressed modified gypsum composites (compositions 5 and 6) are characterized by minor irreversible linear deformations with several times smaller quantity in contrast to magnesite composites (compositions 2 and 3). The irreversible linear deformations were comparable to deformations of samples from modified magnesia cement (compositions 2 and 3) in gypsum prism samples without a complex modifier (composition 4), but still significantly lower compared to composition 1 (additive-free magnesia cement). This point additionally indicates the ability of the structure of fine-crystalline calcium sulfate dihydrate to heal microdefects resulting from cyclic effects and restore the strength of crystallization contacts during drying.

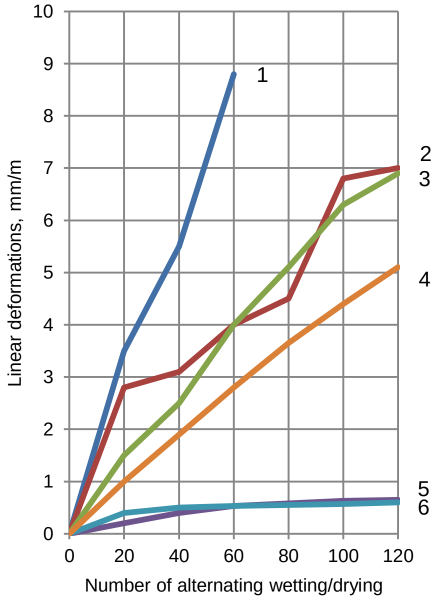

Fig. 3. Linear deformations of samples in the course of wetting and drying: 1-6 – composition numbers

Figure 4 shows the change in the calculated softening ratio and air resistance of control samples with growing number of cycles of alternating humidification-drying.

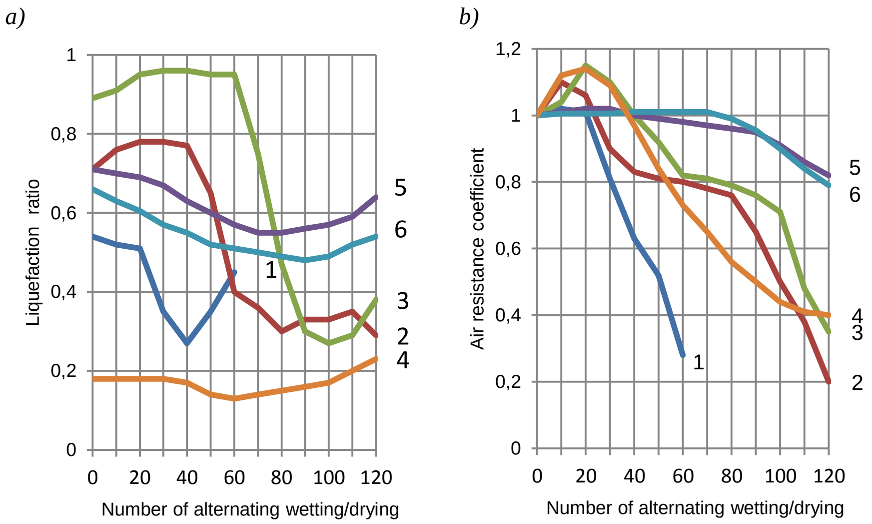

Fig. 4. Dependence of liquefaction (*a*) and airproof performance (*b*) ratios on the number of alternating wetting/drying cycles: 1-6 – composition numbers

Modified gypsum composites have a gradual decrease in the softening ratio after the first test cycles, and this indicator begins to increase (Fig. 4 (a)) after reaching the minimum value, after about 80-90 test cycles. The softening ratio of hardened magnesia cement modified with both silica and burnt rock increases at the beginning of the tests, which can be explained by a more significant accumulation of fatigue stresses in the material. Its sharp drop occurs after 50-70 cycles of humidification-drying.

The coefficient of air resistance increases slightly during the first 10-20 test cycles in pressed magnesite composites, as well as pressed additive-free gypsum binder. Then its sharp decrease occurs. However, modifying the magnesite stone allows the material to maintain a Ks above 1.0 for about 40 cycles. The ratio of air resistance of modified gypsum composites remains almost unchanged for 80 test cycles and only further alternation of humidification and drying leads to a noticeable decrease in this indicator.

5 Conclusion

The conducted studies have shown the use of modifying fillers, which are secondary resources. They made it possible to produce durable gypsum and magnesite products with increased water and air resistance by pressing. At the same time, the higher water resistance of the material, estimated by the softening coefficient, does not necessarily guarantee its better resistance to alternating humidification-drying. The chemical composition and the nature of the crystallization structure of the hardened artificial gypsum stone cause its better resistance to alternating stresses under cyclic influences. As a result, fatigue destruction of modified gypsum composites occurs slower compared to magnesite. Pressed gypsum and magnesite construction products manufactured become suitable for the construction of walls of low-rise buildings according to the proposed technologies, as well as partitions in rooms with a humid indoor regime. There is a potentially helpful use of silica, burnt rock and sludge from the water treatment of a thermal power plant as modifying additives of a significant amount of secondary resources. It should reduce the cost of products and additionally improve the environmental situation in regions where man-made waste accumulates.

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