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Pressed Composites Based on Gypsum and Magnesia Binders Modified with Secondary Resources

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Abstract. The results of the studies aimed at increasing the water resistance of the pressed building materials based on gypsum and magnesia binders due to their modification with active dispersed fillers from secondary resources are presented. The gypsum binder modification was carried out by the joint introduction of carbonate-containing sludge from it into the chemical treatment of thermal power plants and monoammonium phosphate, and of magnesia cement - silica fume and finely ground burnt mines.

Physical and mechanical characteristics of the materials' control samples were determined according to the standards and generally accepted methods. The increase in water resistance of the pressed modified composites was evaluated by changing the softening coefficient. It is shown that when using gypsum binders, an increase in the water resistance of products based on them can be achieved by changing the structure formation of the pressed material and the formation on the elements' surface of its fine-crystalline structure of the sparingly soluble calcium phosphates' screening protective films.

The increase in water resistance of pressed products made of modified magnesia binders is explained by the appearance of insoluble hydro silicates, hydro aluminates and hydro aluminosilicates of magnesium, in the structure of the hardened artificial stone as well as the formation of a complex combined structure containing coagulation, condensation and crystallization phases. The technical characteristics of the materials obtained are sufficient for their use, in particular, in the building envelope.

The possibility of replacing a significant amount of binders with secondary resources has been identified. This allows not only to increase the water resistance of the pressed products on the basis of the proposed modified binders, but also to reduce their cost, as well as free up the land allocated for dumps.

Introduction

The building materials industry is currently facing particularly urgent issues of innovative development, the answers to which are the development of energy and resource-saving, as well as epy environmentally friendly technologies [1].

The share of epy raw material costs in the cost of various types of building materials is 25-50%, and several million tons of various mineral raw materials are spent on their production. Replacing epy traditional natural raw materials with industrial waste can bring and brings significant economic benefits. An important factor in modern conditions is also the fact that the disposal of large-tonnage waste significantly reduces the area of land alienated for quarries, sharply decreases the pollution of air and water basins [2, 3].

In our opinion, one of the promising directions of expanding the raw material base of the building materials industry through the use of secondary resources is their involvement in the composition of molding compounds for the production of wall and partition products by pressing. Products according to this method are molded from slightly moistened press powder on special machines under pressure, usually from 5 to 40 MPa. Mixing water consumption in this case only slightly exceeds its required amount for the binder hydration [4].

The research results of a scientific school of professor Volzhensky A.V. [5, 6] showed that under such conditions a high-strength fine-crystalline structure of artificial material is formed. In the absence of excess liquid phase in the system, recrystallization of “finely dispersed” neoplasms to larger crystals with a reduced binding ability is excluded. This allows to maximize the potential of binders and to obtain the high-strength pressed composites on their basis. The high strength of such materials should make it possible to replace a significant part of the binder in the composition of the raw material mixture for their production with the fillers from industrial wastes. This should, on the one hand, ensure a reduction in the cost of manufacturing products without losing their functional purpose, and on the other hand, prevent or minimize the negative impact of industrial waste on the environment, contributing to the development of an environmentally sustainable economy [7].

When using gypsum and magnesia binders, the pressing method is usually used for the production of bricks, wall stones and high-strength facing plates. The main disadvantages of such products are their low water resistance, which limits the scope, as well as the increased consumption of binder per 1 m^3 of the finished product.

This paper presents the results of our research, showing the possibility of eliminating these shortcomings by modifying gypsum and magnesia binders and the structure of the pressed composites based on them with the disperse fillers from secondary resources.

When choosing the fillers, we took into account their ability to exert a modifying effect on the physicochemical processes of binders hardening and the structure of the resulting pressed composites. The chemical interaction of modifying additives with the components of binders and between each other should ensure the formation of sparingly soluble compounds, including in the form of screening protective films on crystals of emerging hydrated neoplasms.

Moreover, the use of fillers also makes it possible to expediently influence the organization of the pressed composites’ structure. In mixtures with low water content, the hydration of the binder will occur not only due to free unbound mixing water, but in the future, as it is consumed, and due to water adsorbed by the filler grains. Hydrate neoplasms, located in defects in the structure of the material, will help increasing its strength and water resistance. Modification of the gypsum binder was carried out by the joint introduction of carbonate-containing sludge from it into the chemical treatment of thermal power plants and monoammonium phosphate, and of magnesia cement - silica fume and finely ground burnt mines.

Materials and Methods

In experimental studies, low-calcined gypsum binder G-5 B II according to GOST 125-2018 and a magnesia binder with a content of 75.8% magnesium oxide were used.

As a finely dispersed filler in gypsum mixtures, the chemical water treatment sludge from TPP-2 in Rostov-on-Don, formed by softening river water with hydrated lime and soda, was used. The calcium and magnesium bicarbonates contained in the water in this case turn into an insoluble precipitate. After sedimentation and filtration, sediment in an amount of up to 15 tons per day is thrown into the dump. The dried sludge is a yellowish powder with a specific surface of 780 m2 / kg, consisting, according to the chemical, derivate-graphic and some other analyzes, 75% of calcium carbonate. The role of the chemical modifying additive was performed by monosubstituted ammonium phosphate (monoammonium phosphate) $NH_4H_2PO_4$. This salt is formed when neutralizing phosphoric acid with ammonia and is widely used in agriculture as a mineral fertilizer. In aqueous solutions, monoammonium phosphate forms an acidic medium with pH = 3.8. This is due to the fact that along with the hydrolysis of this salt in solution, the dissociation of the dihydrogen phosphate ion H_2PO_4 occurs, which prevails over the hydrolysis process.

To assess the effect of the additives used on the properties of the artificial extruded material, the composite binders, in which up to 60% of the gypsum binder was replaced with sludge from the chemical treatment of thermal power plants, were prepared.

The mixture of dry components during mixing was closed with an aqueous solution of monoammonium phosphate. The consumption of anhydrous chemical additives was changed from 0 to 3% of the mass of the binder and sludge, and the water-solid ratio was from 0.17 to 0.20.

As pozzolanic additives in magnesia cement, silica fume and finely ground burned mines of the Rostov Region were used. Silica fume is a by-product of the production of silicon and ferro-silicon alloys, which is a highly dispersed silica dust (specific surface of 2000 m^2 / kg) containing at least 85% amorphous SiO_2. Burnt rock is a product of oxidative self-firing of mine rocks, extracted together with coal on the surface of heap mines.

A wide range of various chemical compounds and elements (germanium, rare earth elements, alumina, iron ore and others) with high availability, low price and practically unlimited volumes of rock makes the use of burned rocks in the construction industry promising. The burnt rock used is a highly active burnt rock with a clay-ferruginous module of 0.49.

To assess the effect of silica fume and burned rock on the strength and water resistance of magnesia cement, the composite binders were prepared with an additive content of up to 25% by weight. A natural bischofite solution with a density of 1.28 g / cm^3 was used as a hardener.

The preparation of the investigated raw mixes was carried out on a laboratory slider mixer. The duration of mixing the moistened molding sand was established experimentally and varied from 2 to 20 minutes [8].

The physical and mechanical characteristics of the materials were determined by the standards and generally accepted methods on specimen cylinders with a height and diameter of 50.5 mm, made by pressing under pressure from 20 to 60 MPa in special molds.

The control samples hardened in air-dry conditions. The curing time of the samples molded from the modified gypsum binder was 3 days, and that of magnesia cement was 28 days. Before the test, the gypsum samples were dried in a drying oven to constant weight at a temperature of (55 ± 2) ° C, and of magnesia cement - (105 ± 2) ° C.

After that, half of the samples of each series were immersed in water for 48 hours. The dried and water-saturated samples were tested for compressive strength. According to the results obtained, the softening coefficient of the material was determined as the ratio of its compressive strength in a water-saturated and dry state.

The chemical, mineralogical, and phase compositions of the raw materials for the pressed composites' production, as well as their hardening products, were studied using the methods of physical and chemical analysis.

Discussion and Results

It is known that the low water resistance of hardened calcium sulfate dihydrate is due to its significant solubility (about 2 g per 1 liter of water), which leads to a decrease in the bonds between its crystals upon wetting [9], as well as a wedging effect on the structure of the material of water films adsorbed on the internal surfaces of microcracks and pores [10].

The results of our studies show that the complex modification of gypsum binder with carbonate-containing sludge from chemical water treatment of thermal power plants and monoammonium phosphate has a positive effect on the structure, strength and water resistance of the hardened pressed material. This is primarily due to the chemical interaction of monoammonium phosphate with calcium binder and calcium carbonate filler, leading to the formation of screening phase films hydrated neoplasms and filler grains particles of sparingly soluble dicalcium phosphate dihydrate $CaHPO_4{\cdot}2H_2O$ (brushite) on the surface [11].

This compound is isomorphic with two-water gypsum, has 10 times less solubility compared to it, and changes the crystallization structure of the pressed material. The structural identity of $CaSO_4{\cdot}2H_2O$ and $CaHPO_4{\cdot}2H_2O$ crystals is based on the fact that the only geometric difference between these compounds is the additional hydrogen atom in $CaHPO_4{\cdot}2H_2O$. Such isomorphic and isostructural compounds are capable of forming the solid solutions with each other with isomorphic substitution in each other's crystal lattices, which is most characteristic of the periodic system neighboring elements, such as phosphorus and sulfur.

The films from insoluble brushite on the elements of the material's crystallization structure have an additional cementing effect on it, contribute to an increase in its strength and water resistance. It should also be noted that the formation of these films on the surface of the gypsum binder grains in the initial period of hardening significantly slows down hydration, which is a positive technological factor in the formation of products from mixtures with low water-gypsum ratios.

The formation of a new phase of the dicalcium phosphate dihydrate material is proved by the x-ray phase methods and the derivate-graphic analyzes, as well as infrared spectroscopy.

The pressed material based on a modified gypsum binder with increased water resistance (softening coefficient more than 0.6) can be obtained when it contains from 20 to 60% chemical sludge together with 2% monoammonium phosphate. Moreover, obtaining a material with equal water resistance can be achieved both by regulating the content of sludge in its composition, and by changing the pressure of pressing. So, a material with the same degree of water resistance in our case was obtained with a content of 20% sludge and a compaction pressure of 30 MPa and with a sludge content of 40% and a pressure of 40 MPa.

The highest physical and mechanical properties (compressive strength 45-65 MPa, softening coefficient 0.65-0.70) are possessed by the samples made from the mixtures containing 60-80% gypsum binder, 20-40% sludge and 2% monoammonium phosphate.

The reason for the insufficient water resistance of magnesia cement is the composition of its hardening products. Thus, magnesium hydroxide in the presence of magnesium chloride is relatively readily soluble in water. Magnesium oxychlorides, which form the basis of hardened cement stone, are unstable under the action of water and are hydrolyzed [12].

In the present work, it was found that the modification of magnesia cement with silica fume and fine-ground burned rock provides an increase in the strength and water resistance of the pressed material. This is due, on the one hand, to the appearance of insoluble compounds among the products of its hardening, and, on the other hand, to a change in the process of structure formation in a hardening knitting stone.

It should also be noted that a decrease in the amount of curing agent (a solution of magnesium chloride - bischofite) reduces the content of unbound chloride ions in the hardened magnesia stone. This causes a decrease in the solubility of the resulting magnesium hydroxide and oxychlorides, and also prevents the appearance of efflorescence on the surface of the product.

The main product of hardening of magnesia cement without additives is magnesium hydroxide $Mg(OH)_2$, which passes into the solid phase in the process of hardening from a saturated solution [13].

Physical and chemical methods of the study showed that the content of magnesium hydroxide in the modified micro silica cement stone decreases, and sparingly soluble magnesium hydro silicates such as serpentine $3MgO\cdot2SiO_2\cdot2H_2O$ and sepiolite $8MgO\cdot12SiO_2\cdot nH_2O$ appear.

The composites with burned rock, in addition to hydro silicates, also contain hydro aluminates and hydro aluminosilicates of magnesium, such as palygorskite $MgO\cdot Al_2O_3\cdot4SiO_2\cdot5H_2O$.

The thermodynamic aspects of the formation of these compounds under ordinary hardening conditions have been proved [13, 14]. In addition, it was revealed that the hardening proceeds through the gel phase in combination with the formation of microcrystalline hydro silicates, hydro aluminosilicates and magnesium oxychlorides, and colloidal particles of silica fume and burned rock are additional centers of crystallization of these neoplasms.

The samples made from the mixtures containing 10-15% silica fume possess the highest physical and mechanical properties: compressive strength 60-65 MPa, softening coefficient 0.78-0.84 [15]. When using 20-25% disperse burned rock as a pozzolanic additive, the compressive strength of the modified magnesia cement was 45-50 MPa, and the softening coefficient was 0.85-0.90 [16].

It should be noted that pressing, as a compaction method, allows more than halving the content of the magnesium chloride liquid phase in composite binders, which reduces the solubility of the formed oxychlorides and magnesium hydroxide and prevents efflorescence on the surface of the products based on modified magnesia cement.

The studies conducted using the methods of physical and chemical analysis showed that the proposed methods for modifying gypsum and magnesia binders have a positive effect on the formation of the structure of pressed composite materials based on them.

When sludge and monoammonium phosphate are introduced into the composition of the gypsum molding mixture, the total porosity decreases in the structure of the compacted material and the number of closed pores increases, which positively affects its water resistance.

At the same time, the largest average radius of capillary pores (λ_1) and the average pore size ($\overline{\lambda}$) decrease with a simultaneous increase in their uniformity index (α). The structure of the pressed material from the hardened modified gypsum binder can also be characterized as medium and large pore ($1 \le \overline{\lambda} \le 7$), and by pore uniformity - as a structure of medium uniformity ($0{,}15 \le \alpha \le 7$).

This indicates a close relationship between the water resistance of gypsum materials and the parameters of their pore space.

Due to the introduction of silica fume and burnt rocks into the magnesia cement composition, it is also possible to significantly improve the porosity parameters of the hardened pressed material. Compared to the initial hardened magnesia cement, the modified pore homogeneity index is two times larger and the average pore size is three times smaller.

This is due to the fact that the hydro silicates, hydro aluminates and magnesium hydro aluminosilicates formed in the modified cement stone, as well as their complexes with magnesium chloride, have a slightly larger volume than the starting materials. Neoplasms fill part of the capillary and other open pores of the hardened material, which is consistent with a decrease in its water absorption.

The studies have shown that the water resistance of the extruded products based on air binders, estimated by the value of the softening coefficient, depends on the type and the number of added additives, the water-solid ratio and the pressure value, and for magnesian cement, also on the concentration of bischofite.

However, it should be noted that for any combination of the listed prescription and technological factors, the softening coefficient of the studied materials is closely related to their open porosity [17]. As a result of statistical processing of the results of all performed experiments and the use of regression analysis methods, we obtained a linear dependence of the softening coefficient (k_s) of the hardened modified composites on the amount of water absorption by volume, %, characterizing their open porosity (ϕ), %:

$$k_s = 1 - a\phi, \tag{1}$$

where $a = 0.015$ for magnesia cement;
$a = 0.024$ for a gypsum binder.

Thus, it was found that the softening coefficient of pressed materials based on air binders increases in direct proportion to the decrease in open porosity. However, at the same value, the softening coefficient of the hardened modified magnesia cement is higher than the softening coefficient of the pressed modified gypsum binder.

So, with an open porosity of, for example, 15%, the softening coefficient of a pressed material based on magnesia cement is 0.78, and on the basis of a gypsum binder, only 0.64. This can be explained by the fact that the solubility of calcium sulfate dihydrate in water is much higher than the solubility of magnesium hydroxide and, especially, hydro silicates, hydro aluminates and magnesium hydro aluminosilicates, which are the main products of the pressed modified magnesia cement hardening.

Summary

As a result of the research, the compositions of molding mixtures based on modified gypsum and magnesia binders, that are recommended for the production of pressed building products for building envelopes, have been developed. The pressed composites based on modified magnesia cement, in addition, can be used for flooring buildings for various purposes with dry and wet conditions.

It was revealed that an increase in the water resistance of pressed composites based on low-calcined gypsum binders is achieved due to their complex modification with the addition of finely dispersed calcium carbonate and a monosubstituted salt of phosphoric acid. Modifiers have a positive effect on the process of organizing the structure of the material and contribute to the formation of shielding protective films of insoluble calcium phosphate on the surface of the elements of its crystallization structure.

The increase in water resistance of magnesia cement modified with silica fume and finely ground burned rocks is explained by the appearance in the structure of hardened cement stone of insoluble hydro silicates, hydro aluminates and hydro aluminosilicates of magnesium, as well as the formation of a complex combined structure containing a coagulation, condensation and crystallization phase.

The possibility of replacing a significant amount of binders in the composition of molding mixtures to obtain pressed composites for secondary resources is shown. This allows not only to increase the water resistance of wall products based on the proposed modified binders, but also to reduce their cost, as well as free up land allocated for dumps.

The dependence of the softening coefficient of pressed materials based on gypsum and magnesia binders is obtained on the value of their open porosity, which allows predicting their water resistance without complicated tests.

References

[1] I.V. Trishchenko, A.V. Kaklyugin, On assessing the effectiveness of investments in innovative areas of development of the building materials industry, The universities' news. Investments. Construction. The property. 8 (2) (2018) 73-83. DOI: 10.21285 / 2227- 2917-2018-2-73-83.1.

[2] Yu.A. Alekhine, A.N. Lyusov, Economic efficiency of using secondary resources in the production of building materials, Stroyizdat, Moscow, 1988, pp. 344 p.

[3] A.V. Kaklyugin, I.V. Trishchenko, A.V. Kozlov, L.I. Kastornykh, Using apparatus with vortex layer of ferromagnetic particles for production of unburnt synthanite, MATEC Web of Conferences XXVII R-S-P Seminar 2018, Theoretical Foundation of Civil Engineering, 196 (2018) 04053. Information on http:// matec-conferences.org/articles/matecconf/pdf/2018/55/matecconf_rsp2018_04053.pdf.

[4] G.A. Ayrapetov et.al., Building materials: textbook, edited by G.A. Ayrapetova, G.V. Nesvetaeva, Phoenix, Rostov n / a, 2004, 608.

[5] A.V. Volzhensky, K.N. Rozhkova, The structure and strength of hemihydrate formed during hydration of semi-aquatic gypsum, Building Materials, 5 (1972) 26-28.

[6] A.V. Volzhensky, The dependence of the strength of the binder on their concentration in the hardening mixture with water, Construction Materials, 6 (1974) 26-26.

[7] A.V. Kaklyugin, I.V. Trishchenko, The best available technologies in the production of building materials and products, Construction and Architecture - 2017. Faculty of Civil Engineering: Materials of a scientific and practical conference. Rostov-on-Don: DSTU, (2017) 185-191.

[8] Patent 2078745, Russian Federation, IPC C 04 B 28/14 / C 04 B 111: 20. Raw mix for the manufacture of gypsum products and the method of its preparation, A.V. Kaklyugin, A.N. Yundin; Applicants and patent holders Kaklyugin A.V., Yundin A.N., No. 94027027/03; declared 07/18/1994; publ. 05/10/1997. Bull. No. 6. 6 p.

[9] P.P. Budnikov, Gypsum, its research and application, Stroyizdat, Moscow, 1951, 418 p.

[10] P.A. Rebinder, Physico-chemical basis for the permeability of building materials, Gosstroyizdat, Moscow, 1953, 184 p.

[11] A.N. Yundin, A.V. Kaklyugin, R.G. Akopjanov, The increase in strength and water resistance of pressed building gypsum, Effective technologies and materials for wall and walling: Materials of the international scientific and practical conference. (December 12-15, 1994). Rostov-on-Don: Rostov State Academy of Civil Engineering, (1994) pp. 87-92.

[12] A.Ya. Vaivad, Magnesia binders, Zinatne, Riga, 1991, 331 p.

[13] N.S. Step, Building materials based on magnesium silicates, The Brest University Herald. Series 5, 3 (24) (2005) pp. 75–78.

[14] N.S. Step, Magnesium silicates - a promising raw material for the production of modern building materials, Sat. Mater. Int. scientific-practical conf. in chemistry and chemical education "Mendeleev Readings 2016" (February 26, 2016). Brest: BrCEU named after A.S. Pushkin, (2016) pp. 74–77.

[15] Pat. 2035427, Russian Federation, IPC C 04 B9 / 00. Knitting / A.N. Yundin, V.T. Maltsev, N.S. Stage; Applicants and patent holders Yundin A.N., Maltsev V.T., Stupen S.S. No. 92011154/33; declared 12/9/1992; publ. 05/20/1995, Bull. No. 5. 6 p.

[16] Pat. 2038335, Russian Federation, IPC C 04 B9 / 00. Binders / V.T. Maltsev, A.N. Yundin, N.S. Stage; Applicants and patent holders Maltsev V.T., Yundin A.N., Stupen N.S. No. 5058172/33; declared 08/07/1992; publ. 06/27/1995, Bull. No. 6. 4 p.

[17] A.V. Kaklyugin, N.S. Step, L.I. Kastorny, V.V. Kovalenko, Dependence of water resistance of pressed materials based on air binders on the value of open porosity, University News. Investments. Construction. The property, 10 (1) (2020) 68–75. DOI: 10.21285 / 2227-2917-2020-1-68-75