Peculiarities of hardening of an astringent system based on orthophosphoric acid and serpentine with an admixture of magnesite

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Abstract. The paper considers peculiarities of hardening of the non-burnt binder system – orthophosphoric acid – natural serpentine with an admixture of magnesite and brucite. The samples were hardened according to the regime: pre-soaking (55 °C, 40 minutes), which ensures the preservation of the viscous-plastic state of the composition during the carbon dioxide evolution, followed by isothermal aging (80 °C, 24 hours). Strength increases with raising the amount of reacted serpentine and decreases with raising the volume of the released gas. The presence of trisubstituted magnesium phosphate, responsible for the strength, was established. In the solidified system, amorphous silica and unreacted serpentine, brucite and magnesite were found. The strength can be controlled by changing the specific surface of serpentine and the ratio between orthophosphoric acid and serpentine. It is possible to obtain a stone with strength of up to 40 MPa on the basis of serpentine and orthophosphoric acid after 1 day of hardening, with a specific surface of serpentine 4000 cm²/g and an amount of orthophosphoric acid of 25 % of the mass of serpentine.

1. Introduction

One of the main components in the production of most building materials and products is the binding system [1]. Its task is to connect all the components of the composite material, in order to ensure their joint work. Currently in the world, the most common binding systems are mineral binding systems, most of which acquire the astringent properties during the heat treatment – burning. Being a process of thermal processing of materials, roasting is necessarily related:

- to burning of fuel or cost of electricity, i.e. costs of strategically important resources;
- to emission of harmful substances from burning of fuel or from fired raw materials into the atmosphere, which worsens the ecological situation in the region of production and thus necessitates purification of waste gases;
- to the use of burning equipment, which has high cost, large dimensions, requires regular replacement of the lining, which requires the attraction of significant labor and material resources;
- to the need to protect personnel and the environment from thermal emissions [1,2].

Unburnt astringents are cleared of such drawbacks, however, their production requires ultrafine grinding and / or activation of the surface of the powder of the binding system. Thus, the traditional technology of non-firing binders is also associated with significant material and financial costs. To
obtain an unburnt binding system based on mineral raw materials, a shutter, able to interact with unburnt mineral raw materials, is needed:

- the speed of thickening of the closed binder system should allow for an item to be manufactured with the accepted method of molding;
- as a result of hardening, a strong bind is formed.

Orthophosphoric acid is capable of interacting with some magnesian rocks, while magnesium hydrophosphates with different degrees of hydrogen substitution are formed. It has also been established that materials consisting of magnesium hydrophosphates can have high strength and water resistance. Three-substituted magnesium hydrophosphates do not undergo changes, when heated to a high temperature, and have a fire resistance of not less than 1200 °C [1,3-7].

However, the interaction of orthophosphoric acid with such magnesian rocks as brucite, magnesite or dolomite occurs very rapidly, as a result of the chemical reaction a large amount of heat is released, which leads to boiling of the mixture [8]. In addition, intensive release of gaseous reaction products or water vapor can occur. These factors make it difficult to form products based on these rocks and reduce the ultimate strength [1].

Acceptable reaction rates with orthophosphoric acid are based on natural magnesian silicates, for example serpentines [9-11]. However, natural serpentines may contain impurities in the form of magnesites, brucites, etc. Further in this work, we will consider the properties of compositions based on natural serpentines and orthophosphoric acid and show the prospects of such systems for obtaining building materials for various purposes. The main goal of the work is to identify the factors determining the ultimate strength of serpentine-phosphate compositions based on natural serpentines.

2. Material and Methods

Orthophosphoric acid was used as the liquid of mixing, with the content of H₃PO₄ 70 %, manufactured in accordance with the requirements of GOST 6552–80 "Orthophosphoric acid. Specifications".

Finely ground natural serpentine 3MgO·2SiO₂·2H₂O (obtained at Kiembaevskoye field (Russian Federation)) was used as the second component of the binder system. This serpentine, being a by–product of chrysotile asbestos extraction, is a gray powder with a residue on sieve No. 02 from 8 to 10 % and a specific surface of about 1800 cm²/g. Serpentine rock has the following composition: SiO₂ – 35.0…39.0 %, A1₂O₃ – 1.4…1.6 %, Fe₂O₃ – 8.2…8.3 %, CaO – 2.0…2.2 %, MgO – 34.0…36.0 %. The composition of the rock includes an admixture of magnesite in the amount of 3.6% (Figure 4) [12, 13].

Determination of the specific surface was carried out by air permeation with the help of the device "PSX-12".

The phase composition was determined by thermal analysis conducted on a Netzsch STA409 Luxx derivatograph. The amount of residual serpentine in the serpentine-phosphate compositions was calculated from the peak area on the DSC curve corresponding to the crystallization of forsterite.

The mobility of the serpentine-phosphate composition test was determined by the Vicat method in accordance with the requirements of the regulatory documentation, but we used a conical pestle and no aggregate [14, 15].

Prior to the beginning of the experiment, we supposed that the properties of serpentine-phosphate compositions after solidification will be mainly influenced by the amount of magnesium hydrophosphates formed. The basis for such supposition was the literature data, the calculation of chemical reactions and the results of previous experiments. When the amount of acid is up to 35 % of the mass of serpentine, the interaction will occur only over the surface of the serpentine particles, because the acid in the system is in short supply. Neoplasms of magnesium hydrophosphates will bind particles of unreacted serpentine, thus forming a conglomerate. When an impurity of magnesite interacts with orthophosphoric acid, it is possible to release carbon dioxide, which will porosize the resulting material, which will reduce its final strength and density.

An incomplete two-factor experiment was planned and implemented according to the Hartley plan.
The first variable factor was the amount of acid as a percentage of the mass of serpentine (range of variation is from 25% to 35%), since the acid/serpentine ratio should have a significant effect on the amount of magnesium phosphates formed, the amount of gas, the mobility of the mixture and its strength [16-19]. Based on the calculations of chemical reactions it is established that the chosen range of variation provides a lack of acid for complete binding of serpentine, this guarantees the absence of free acid in the finished material.

The second factor was the specific surface area of the serpentine powder (2000 to 4000 cm$^2$/g), which makes it possible to vary the homogeneity of the resulting conglomerate and the mobility of the mixture.

The compressive strength and density were determined on specimen cubes with an edge of 2 cm on the 1st day of hardening according to the mode: preliminary aging – 55 °C, 40 minutes; isothermal aging – 80 °C, 24 hours. The temperature of 80 °C provides for an intense hardening of the serpentine-phosphate composition, and the preliminary aging ensures the preservation of the viscous-plastic state of the composition during the release of carbon dioxide [13,17,20].

3. Results and discussion

To analyze the gases and vapors evolved and to prove the release of carbon dioxide (molecular mass of carbon dioxide of 44 amu), the serpentine-phosphate composition was placed into the derivatograph (isothermal regime – 55 °C) combined with a quadrupole mass spectrometer immediately after manufacturing. The results are shown in Figure 1.

Figure 1 shows that during the interaction of serpentine and orthophosphoric acid carbon dioxide is released. The jump-like character of the curve is associated with the breaks of the bubbles on the surface of the analyzed sample. Thus, the obtained serpentine-phosphate stone is a complex conglomerate consisting of a solid substance and pores formed by an evolved gas similar to aerated concrete. Magnesite, potentially, is capable of releasing gas to 1.88% of the mass of the serpentine rock.

Table 1 presents the experimental design matrix and the properties of solidified serpentine-phosphate compositions.
The graphs were constructed on the basis of the mathematical dependencies, obtained in the experiment. The first graph (Figure 2) shows the dependence of the serpentine-phosphate stone density on the variable factors on the first day of hardening.

Table 1. Actual values of experimental factors and response values.

| Amount of acid code | Specific surface of serpentine stone (cm²/g) | Density of serpentine-phosphate stone (g/cm³) | Strength of serpentine-phosphate stone (MPa) |
|---------------------|---------------------------------------------|---------------------------------------------|---------------------------------------------|
| –1 25 –1 2000       | 1.722                                       | 23.0                                        |
| 0 30 –1 2000       | 1.662                                       | 22.5                                        |
| 1 35 –1 2000       | 1.566                                       | 19.5                                        |
| –1 25 0 3000       | 1.737                                       | 27.0                                        |
| 0 30 0 3000       | 1.708                                       | 25.8                                        |
| 1 35 0 3000       | 1.658                                       | 26.2                                        |
| –1 25 1 4000       | 1.939                                       | 41.0                                        |
| 0 30 1 4000       | 1.733                                       | 28.8                                        |
| 1 35 1 4000       | 1.601                                       | 26.5                                        |

The density of aerated concrete is mostly influenced by the amount of the gas released and the viscosity of the mixture. The graph in Figure 1 depicts that if the amount of acid does not change and the specific surface increases, the amount of gas formed does not change, and the viscosity of the mixture increases, which prevents free gas generation and promotes an increase in the density of the samples. However, as the amount of acid increases, the amount of gas increases with the decrease in the viscosity of the mixture, which sharply reduces the density of the material.

Figure 3 shows the dependence of the strength of the solidified serpentine-phosphate composition on the specific surface of the serpentine powder and the amount of acid.

The dependencies show that the character of the isolines in Figures 3 is similar to this in Figure 1, thus, the strength of the porous serpentine-phosphate stone in this range of factors varies directly with the density of the material, the deviation from the directly proportional relationship between density and strength is related to the change in the amount of serpentine that has reacted.

To clarify the processes occurring during the interaction of serpentine and orthophosphoric acid, a thermal analysis of serpentine-phosphate stone samples was carried out.
Figures 4 and 5 show differential-thermal-analysis pattern of the initial serpentine and serpentine-phosphate stone samples.

On the differential-thermal-analysis pattern (Figure 4), the following effects can be distinguished:

Endothermic effects at 131.9 and 666.0 °C are gradual dehydration of lizardite.

The endothermic effects at 256.4 °C and 728.9 °C correspond to the stepwise dehydration of serpentine.

Endothermic effect at 421.6 °C dehydrates the brucite admixture, according to stoichiometric equations its amount is 5.4 %.

Endothermic effect at 516.5 – dehydration of ferrous magnesite.

The endothermic effect at 594.3 °C is the decarbonization of the magnesite impurity, its amount is 3.6 %.

After the decomposition of serpentine at 832.1 °C, an exothermic effects observed which corresponds to the crystallization of forsterite 3MgO·2SiO₂.

On the differential-thermal-analysis pattern (Figure 5), the following effects can be distinguished:

The endothermic effect at 664.1 °C is the dehydration of lizardite, the first step can not be identified due to the dehydration of tripartite magnesium phosphate.

Dehydration of trisubstituted magnesium phosphate corresponds to the endothermic effect at 191.7 °C with the formation of amorphous Mg₃(PO₄)₂, which crystallizes at the temperature of 709.2 °C.

The endothermic effect at 423.5 °C corresponds to the dehydration of brucite.
Crystallization SiO₂, formed during the interaction of serpentine and orthophosphoric acid occurs at the temperature of 505.9 °C.

The endothermic effect at 594.5 °C corresponds to the decarbonization of magnesite.

The endothermic effect at 740.6 °C corresponds to the dehydration of serpentine, the amount of serpentine significantly decreased compared to the initial serpentine, so the first peak (131.9 °C) is not traced, and also due to the dehydration of tripartite magnesium phosphate.

After the decomposition of serpentine at 835.5 °C, an exothermic effect is observed, which corresponds to the crystallization of forsterite 3MgO·2SiO₂.

As can be seen from the presented differential-thermal-analysis pattern, as a result of the interaction of serpentine with acid, a stone is formed composed of trisubstituted magnesium phosphate, amorphous silica and unreacted serpentine, brucite and magnesite. Serpentine-phosphate stone retains: magnesite in the amount of 1.68 % and brucite – 0.6 % of the initial mass of serpentine in the serpentine-phosphate system (acid 25 %, serpentine 75 %).

Figure 6 shows the dependence of the amount of unreacted serpentine in the serpentine-phosphate stone.

Figure 6 shows that the amount of unreacted serpentine in the serpentine-phosphate stone decreases with increasing amount of acid and/or specific surface of serpentine.

4. Conclusion

In the course of the work, it was revealed that, based on natural serpentine and orthophosphoric acid, it is basically possible to obtain a stone with the strength of up to 40 MPa, with a specific surface of serpentine 4000 cm²/g and the amount of orthophosphoric acid 25 % of the mass of serpentine. The
density and strength of the solidified composition depend on the amount of the reacted components and the degree of porosity of the stone. As this material is eventually water-proof and heat-resistant, it is necessary to investigate this aspect of serpentine-phosphate compositions.

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