Modification of the structure of gypsum-cement-pozzolan binder

Ekaterina Potapova^{1,*}, *Aung Kyaw Nyein*¹, *Elena Tsvetkova*¹, and *Hans-Betram Fischer*²

¹Mendeleev University of Chemical Technology, Russian Federation

²Bauhaus Universität Weimar, Germany

Abstract. Modification of the structure of gypsum-cement-pozzolan binder allows you to expand the range of gypsum binders for creating dry building mixes and structural elements of low-rise buildings. It was found that in the presence of functional additives, the character of crystallization of hydrate neoplasms changes, which leads to a change in the properties of the hardened binder. The study of the effect of individual and complex additives on the properties of gypsum-cement-pozzolan binder allowed us to develop water-resistant gypsum binders.

1 Introduction

Products and structures made of binding materials are used everywhere today. At the same time, the new time requires the development of new structural and composite materials in conjunction with new technologies. Complex environmental and economic conditions in Russia also determine a new approach to the creation, production and use of building materials for various functional purposes [1-5]. At the same time, special attention should be paid to resource conservation, maximum use of local raw materials and waste from various industries, increasing the competitiveness of construction products, and using efficient high-tech technologies and materials. One of the ways to solve these difficult problems is the widespread use of gypsum materials in the construction.

Gypsum binders and materials based on them have a number of valuable qualities: good heat and sound insulation properties, fire safety, relatively low density, decorative properties. Their production is non-toxic and has a low fuel and energy consumption (about 4-5 times less than cement production) [6-9]. Gypsum binders are included in the composition of dry mixes for different purposes.

But till with the positive properties of gypsum products, low water resistance is inherent. There are several ways to increase the water resistance of a gypsum binder, one of the most effective is to create a gypsum-cement-pozzolan binder. Gypsum-cement-pozzolan binders (GCPB) are characterized by high water resistance, which contributes to a significant expansion of the application areas of products based on them.

Gypsum-cement-pozzolan binder is a composition of gypsum binder, Portland cement and active mineral additives. Depending on the type and composition of each component, as well as the method of preparation, the physicochemical and mechanical properties of the

* Corresponding author: 55pen@mail.ru

binder change. In addition, the use of various functional modifying additives in the composition of dry building mixes leads to a change in the morphology of hydrate neoplasms, which, in turn, also causes a change in the properties of hardened systems [10-16].

2 The materials and research methods

Gypsumcement-pozzolanic binders were prepared by mixing gypsum binder G-5 B (II) ("Knauf Gips", Krasnogorsk), Portland cement CEM I 42.5 N (Ltd "HeidelbergCementRus" in the village Novogurovsky) and active mineral additive metakaolin (Ltd "MetaRus"). The content of components in the composition of GCPB (gypsum binders – 53.3%; Portland cement – 33.3%; metakaolin – 13.4%) was determined by a special technique (TU 21-31-62-89) by the method of absorption by the addition of lime from lime solution

The binder was modified with the addition of Melflux 5581 superplasticizer, Vinnapas LL5999/2 redispersing polymer powder, and Mecellose 7117 cellulose esters. Tartaric acid was used as a setting retarder.

To save the binder and improve its properties, river and dolomite sands, limestone dropout, and microcalcite were added to GCPB.

The structure of GCPB was studied by x-ray phase analysis and electron microscopy. The strength of the solidified binder was determined by standard methods. Water resistance was evaluated by the coefficient of water resistance (K_w).

3 Study of the structure of gypsumcement-hardened binder

The composition and structure of a gypsumcement-pozzolanic binder that hardened for 28 days were studied. According to x-ray phase analysis, gypsum-cement-pozzolan stone contains the following hydrate phases: $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ($d = 7,608; 4,281; 3,822; 3,064; 2,878; 2,679; 2,082; 1,898; 1,877; 1,810; 1,664$ and $1,620 \text{ \AA}$); ettringite ($d = 9,699; 5,608; 4,957; 3,869; 3,472; 3,244; 2,556; 2,212$ and $2,149 \text{ \AA}$); calcium hydroaluminate of the composition C_4AH_{19} ($d = 3,869; 2,886; 2,878; 2,556; 2,491; 1,664$ and $1,620 \text{ \AA}$); calcium hydrosilicates C-S-H (I) ($d = 3,064; 2,775; 1,810$ and $1,664 \text{ \AA}$) and as SiO_2 impurities (probably from metakaolin) ($d = 3,339; 2,491; 2,356; 2,082; 1,810; 1,664$ and $1,436 \text{ \AA}$).

The addition of modifying additives to the GCPB does not change the phase composition of neoplasms, but only changes the ratio between the phases [17-19].

Electron microscopic studies have confirmed the results of the X-ray phase analysis method. The products of GCPB hydration are calcium sulfate dihydrate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, hydroaluminates, and calcium hydrosilicates. Moreover, the size and type of neoplasms formed differ depending on the composition of the binder.

The microstructure of GCPB cement stone without the introduction of additional additives is dense, calcium sulfate dihydrate crystals have a size of 7-10 microns, calcium hydrosilicates are not visible, there are single ettringite crystals less than 1 micron in size (Fig.1).

The addition of tartaric acid to GCPB slows down the processes of hydration and hardening, which leads to a deterioration in crystallization. Calcium sulfate dihydrate is found with a size of 3-5 microns and less than 1 micron, there are no ettringite crystals (Fig. 2).

Fig. 1. Microstructure GCPB without additives.

Fig. 2. Microstructure of GCPV with the addition of tartaric acid.

The introduction of a complex of additives into the binder reduces the size of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystals to 5 microns. Clearly crystallized crystals of calcium hydrosilicates and ettringite crystals appear (Fig. 3).

Fig. 3. Microstructure of GCPV with a complex of additives.

The structure of the composite gypsum binder obtained by mechanical activation is rather fine-crystalline (Fig. 4). All crystals have not clear, but as if blurred edges.

Fig. 4. Microstructure of composite gypsum binder obtained by mechanical activation.

Adding the placeholders and fillers also leads to changes in the structure of gypsum-cement-pozzolan stone.

For the composition of GCPB with river sand, cement stone is characterized by elongated prisms with indistinct edges, ettringite crystals are not visible (Fig. 5).

Fig. 5. Microstructure of GCPB with river sand.

For GCPB with dolomite sand, gypsum crystals have an irregular shape, their size is less than 5 microns (Fig. 6).

Fig. 6. Microstructure of GCPB with dolomite sand.

No ettringite crystals or calcium hydrosilicate crystals are observed.

If limestone screenings are used as filler (Fig. 7), then the crystallization of the solidified binder is clear for GCPB, the crystal size is about 5 microns. There are separate crystals of calcium hydrosilicate crystals and ettringite.

Fig. 7. Microstructure of GCPB with limestone screening.

For comparison, the structure of GCPB with microcalcite was studied (Fig. 8). The structure of crystals of neoplasms is less clear, in comparison with compositions with limestone screening.

Fig. 8. Microstructure of GCPB with microcalcite.

This indicates that the nature of the material (filler) has a great influence on the structure of the hardened binder, which, in turn, should leads to a change in properties.

4 Strength and water resistance of the hardened binder

The study of the strength parameters of the solidified binder confirmed the assumption that the nature of crystallization of hydrate neoplasms affects their properties.

The introduction of additives, in particular the superplasticizer Melflux 5581, leads to an increase in the strength of both bending and compression by almost 2 times (table 1). Redispersing polymer powder Vinnapas compacts the structure, which is expressed in increasing the water resistance of the hardened binder. The addition of cellulose esters increases the amount of water required during mixing, which leads to an increase in porosity and leads to a decrease in strength and water resistance. However, the introduction of a complex of additives, as is often required by various formulations of dry building

mixes, eliminates the negative aspects. And in this case, there is an increase in both strength (up to 12.6 MPa when bending and 20.3 MPa when compressing) and water resistance (up to 0.84).

Table 1. Durability and water resistance of a GCPB stone with additives

Composition		Durability 28 day, MPa		Water resistance, K _w
№	Additive	a bend	at compression	
1	-	8.4	11.2	0.81
2	SP Melflux	13.8	28.6	0.90
3	RPP Vinnapas	12.6	22.1	0.85
4	Cellulose ether Mecellose	7.5	10.8	0.76
5	Complex of Additive	12.6	20.3	0.84
6	Wine acid	10.2	20.9	0.82
7	River sand	10.9	23.8	0.86
8	Dolomite sand	10.5	21.7	0.84
9	Limestone screening	10.8	20.0	0.81
10	Microcalcite	10.0	17.4	0.79

For compositions with tartaric acid, there is a slight of slowing down in the processes of hydration and hardening, which leads to a slight decrease in strength indicators.

With the introduction of filler additives, the bending strength practically does not change. However, the type of aggregate affects the density and strength of the resulting structure. The strongest structure is formed in the presence of quartz sand – compressive strength of 23.8 MPa and water resistance coefficient of 0.86.

5 Conclusions

Modification of the gypsum-cement-pozzolan binder with functional additives leads to a change in the nature of crystallization of hydrate neoplasms of the hardened binder. Moreover, each type of modifying additive has its own special mechanism of action, which is reflected in the morphology of the formed hydrate phases. Changing the nature of crystallization of neoplasms, in turn, leads to a change in the properties of the hardened binder. The study of the effect of individual and complex additives on the properties of gypsum-cement-pozzolan binder allowed us to develop water-resistant gypsum binders with increased strength indicators.

References

1. A. V. Ferronskaya, *Development of the theory and technologies in the field of silicate and plaster materials* (M., MGSU, 2000)

2. M.Ilg, J. Plank, RILEM Bookseries **24**, 143 (2020)

3. V. F. Koroviakov, Dry mixes **1**, 16 (2013)

4. J. Plank, Alitinform **1 (50)**, 30 (2018)

5. N.R. Rakhimova, R. Z. Rakhimov, Journal of Materials Research and Technology **8(1)**, 1522 (2019)

6. C. Riechert, H.-B. Fischer, *20.International Baustofftagung* **1**, 913 (2018)

7. A. Pundir, M. R. Garg, Journal of Building Engineering **4** 223 (2015)

8. M. S. Morsy, Y. F. Al-Salloum, T. H. Almusallam, KSCE Journal of Civil Engineering **3(21)**, 863 (2017)

9. R. Mukhametrakhimov, A. Galautdinov, L. Lukmanova, MATEC Web of Conferences **106**, 03012 (2017)

10. Kani E. Najafi, Alitinform **2(34)** 76 (2014)
11. E. N. Potapova, I. V. Isaeva, Construcion Materials **7** 20 (2012)
12. E. Potapova, M. Zyryanov, E. Dmitrieva, *20.International Baustofftagung* **2** 519 (2018)
13. M. Sanytsky, T. Kropyvnytska, O. Horpynko, M. Shturmay, *3. Weimar Gypsum Conference*, 31 (2017)
14. E. Potapova, E. Dmitrieva, Material Today: Proceedings **19(5)** 2193 (2019)
15. S. Wansom, P. Chintasongkro, W. Srijampan, Cement and Concrete Composition **103(5)** 134 (2019)
16. E. Potapova, A. Manushina, *19.International Baustofftagung* **2** 675 (2015)
17. X. Kong, Z. Lu Zichen, Alitinform **1(46)**, 46 (2017)
18. E. N. Potapova, Alitinform **1(58)**, 50 (2020)
19. S. P. Sivkov, O. N. Matuchina, A. E. Zaychev, S. A. Golunov, Dry plasters and mortars **1** 5 (2008)