

## Structure Formation of Cement Stone in the Presence of Additive on Amorphous Silica-Alumina

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**Abstract:** The data on the effect of additives made on the basis of amorphous aluminum silicates on the cement stone structure formation are given. Chemical and mineralogical composition of additives is shown. The analysis of the mineral composition of cement stone in the presence of synthetic additives is given. Formulation of adhesive dry mortar using an additive on amorphous aluminosilicates and main characteristics of tile adhesive manufactured on its basis are given.

**Key words:** Amorphous aluminum silicates, structure formation, dry mortar, tile adhesive, composition

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### INTRODUCTION

Tile adhesives manufactured on the basis of Dry Mixes (DM) are used for finishing the exterior and interior walls of buildings and structures. To improve technological and operational properties of tile adhesive special additives accelerating curing and increasing resistance to slipping are introduced into the recipe of Dry Mortar (DM) (Botka, 2014; Lothenbach, 2011; Sharma and Rani, 2016). It is promising to use cement additives containing amorphous aluminosilicates in the recipe of DM. Currently, such additives are used as inorganic adsorbents. The presence of amorphous aluminosilicate structure in the additives creates prerequisites for chemical reaction of aluminosilicate and hydrolysis lime with formation of complementary products, contributing by cement composite hardening (Nagrockiene *et al.*, 2014; Jian *et al.*, 2013).

**The results of the research:** The additive on amorphous aluminosilicate was got by aluminosilicate precipitation from liquid sodium glass by introducing 15%-technical aluminum sulphate  $Al_2(SO_4)_3$ , followed by watering the resulting precipitate with distilled water, drying it to constant weight and grinding. The resulting additive is a white powder with a specific surface area measured by the BET method equal  $S_{sur} = 688.6 \text{ m}^2 \text{ kg}^{-1}$ . Chemical analysis of the additive on amorphous silica-alumina has shown high level of such chemical elements in its composition as O, Si, Na, S and Al containing respectively 48.71%, 19.59, 16.42, 9.67 and 4.7% in its composition. According to XRA mineralogical composition of additives is presented by thenardite-rhombic modification of sodium

sulphate  $Na_2SO_4$ , gibbsite  $Al(OH)_3$ , sodium aluminum silicate of Na hydrate  $[AlSi_2O_6] \times H_2O$ . The concentration of the additive synthetic amorphous phase is 77.5%.

It is found that the introduction of additives on amorphous silica-alumina into cement paste changes its normal density and setting time (Table 1). It is found that the introduction of additives on amorphous silica-alumina into cement paste in an amount of 10-30% increases its normal density up to 34-43% (28-normal density of cement paste without additives) and accelerates setting time, depending on the additives content. For example, in cement paste without an additive the beginning and the end of setting up is, respectively, 2 h 30 min and 5 h while in the binder with additives it is, respectively 40 min and 1 h 30 min. With increase in the percentage of additives in the cement paste the setting time reduces.

For the liquid phase of the cement paste it is characteristic to have higher initial pH value 12.08 while for the cement paste with additive on the basis of amorphous aluminosilicate in an amount of 10 and 20%, a pH value is 11.88 and 11.50, respectively.

Evaluation of the kinetics of heat dissipation while cement binder hardening has revealed that the temperature during the cement paste hydration is maximum in samples with additives on amorphous aluminosilicates. Introduction into cement paste formulation an additive on amorphous aluminosilicates results in earlier structure formation of cement stone (Fig. 1).

On the third day of air-dry hardening, we can observe an increase of compressive strength in the sample (depending on the additive content) on 23.0-34.1% in comparison with a control sample aged 90 days-on

Table 1: Changing the timing of normal consistency of cement paste and setting time depending on the content of additives

| An amount additives (%) | Normal density of cement paste (%) | Setting time                |                       |
|-------------------------|------------------------------------|-----------------------------|-----------------------|
|                         |                                    | The beginning of setting up | The end of setting up |
| -                       | 28                                 | 2 h 30 min                  | 5 h                   |
| 10                      | 34                                 | 50 min                      | 1 h 40 min            |
| 20                      | 41                                 | 40 min                      | 1 h 30 min            |
| 30                      | 43                                 | 20 min                      | 1 h 15 min            |

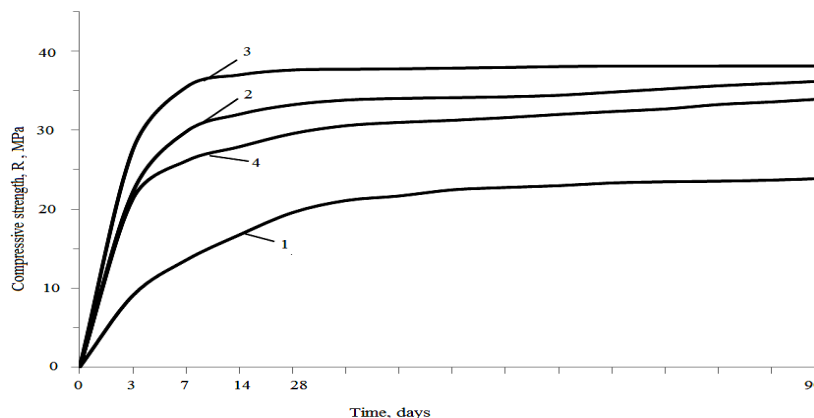


Fig. 1: Kinetics of curing cement samples in air-dry conditions: control (no additives); a sample containing 10% additive by weight of cement; a sample containing 20% additive by weight of cement; 4 the sample containing 30% additive by weight of cement

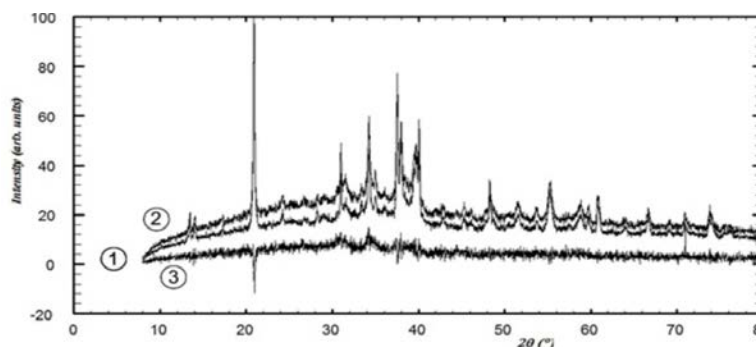


Fig. 2: Radiographs of cement stone: control sample; cement with additive; differential curb

40.2-52.7% (Loganina *et al.*, 2014; Zhegera *et al.*, 2014). To study physical and chemical processes of the cement stone hardening X-ray analysis was carried out. Radiographs of control cement stone with an additive on amorphous silica-alumina are shown in Fig. 2.

The differences in radiographs (Fig. 3) lie in a high intensity of background curve of the sample with an additive that is probably due to the presence of amorphous form in the additive. Small profiles on differential curve from diffraction angles  $2\theta = 30-40^\circ$  are due to different background intensity in the “basis” of the diffraction peaks.

For getting more information about the mineral composition of the analyzed samples full quantitative

XRA was performed. Calculations were done using DDM program v. 1.95e, it adapted to carry out calculations with polyatomic structures. Preliminary radiometric diagnostics of crystalline phases (qualitative XRA) was conducted using the PDF-2 database of diffraction data. Structural models for full-profile calculations are taken from the structural base of inorganic substances (ICSD). The calculation results are shown in Table 2.

It is established that the additive on amorphous aluminosilicate is a potential “carrier” of phase formation components, dissociates in an alkaline medium and mixing water and contributes to hydrate phase formation of X-ray amorphous C-S-H-formations.

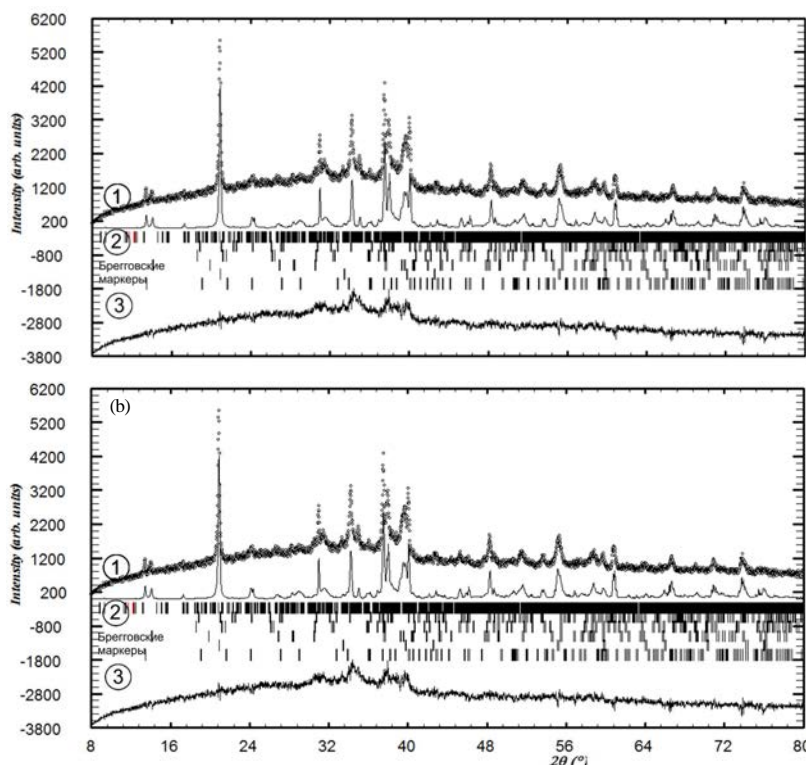


Fig. 3: Full profile chart diagrams for calculating quantitative mineral composition: a; control sample, b; a sample with an additive. Experimental diffraction curve; calculated curve; differential curve of the experimental and calculated diffraction profiles

Table 2: Results of full-profile quantitative XRA (mineral composition (wt. %))

| Variables                        | ICSD   | Control sample | Sample with additive |
|----------------------------------|--------|----------------|----------------------|
| C <sub>3</sub> S                 | 4331   | 26.95±1.15     | 24.54±1.03           |
| β-C <sub>2</sub> S               | 81096  | 6.40±1.02      | 6.67±1.24            |
| α <sub>H</sub> -C <sub>2</sub> S | 82997  | 4.51±1.07      | 6.82±1.97            |
| C <sub>4</sub> AF                | 9197   | 15.28±1.47     | 15.47±1.50           |
| CH                               | 202226 | 11.19±1.14     | 9.89±1.15            |
| Gypsum                           | 2057   | 4.40±0.60      | 4.77±0.61            |
| Vaterite                         | 15879  | 24.45±4.82     | 24.05±3.56           |
| Calcite                          | 18166  | 3.13±0.39      | 4.01±0.45            |

Figure 4 shows differential curves of both samples posted by axes of intensity. A comparison of the relevant sections of the reflection intensities with the data base PDF-2 showed their compliance with sodium silicate (possible poorly crystallized product of sodium aluminosilicate dissociation) and hydrate formations of C-S-H (II) (Taylor).

To confirm the influence of the additive on additional formation in the sample with an additive C-S-H (II), in comparison with the control sample differential profile I was subtracted from differential profile II (designation in Fig. 2). The results of this procedure are presented in Fig. 5.

Underlining of positive profiles of the mentioned phase of intensity as the result of subtraction: differential curve of the sample with addition-(minus) differential

curve of the control sample, allows to state with high degree of confidence about a more intensive phase formation C-S-H (II) in a sample with aluminosilicate additive.

Considering that concentration of portlandite and carbonate derivatives-vaterite and calcite is really identical in both samples we can state that the increase of C-S-H (II) intensity in the sample with the additive is the effect of the latter.

In cement stone with an additive on the basis of amorphous aluminosilicates we can observe a decrease of free water quantity and increase of chemically bound water in comparison with the control sample. In the samples on the basis of control composition the content of free and chemically bound water is 7.3 and 14.5%

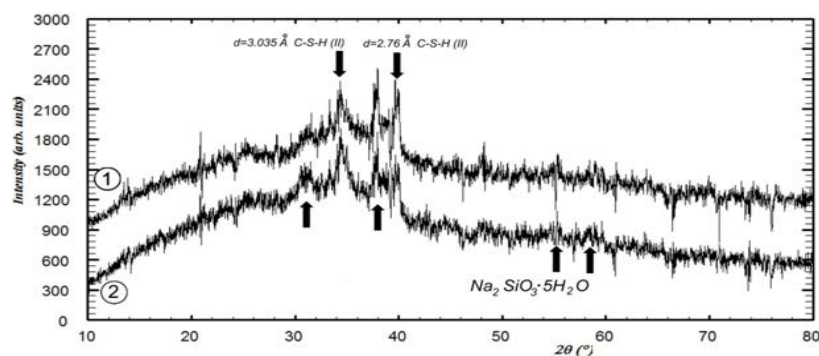


Fig. 4: Differential curves 1; Control sample; 2; Sample with an additive

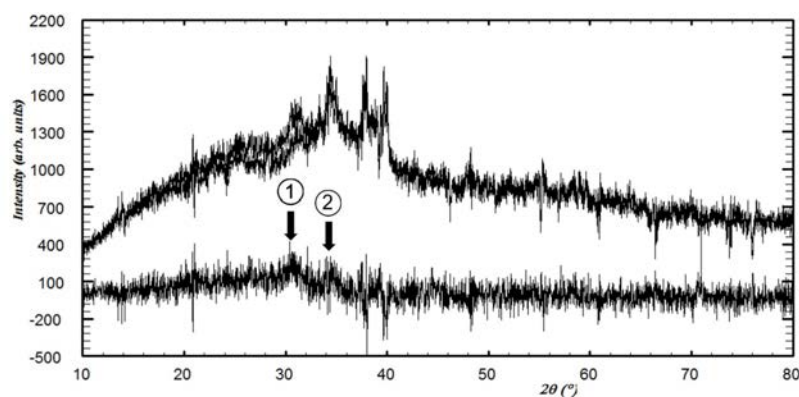


Fig. 5: Differential curve (below) as a result of subtracting differential profiles of the control sample from the sample with additive: 1-sodium silicate diffraction profile; 2-diffraction profile corresponding to the reflection with  $d = 3.035 \text{ \AA}$  C-S-H

Table 3: Technological and operational properties of tile adhesive on the basis of the developed adhesive DM

| Parameters  | Unit                                  | Value for the composition |                    |                    |
|---|---------------------------------------|---------------------------|--------------------|--------------------|
|   |                                       | Designed                  | Prototype 1        | Prototype 2        |
| Averagedensity of DM  | $\text{kg m}^{-3}$                    | 1800                      | 1870               | 1500               |
| Mixing time   | min                                   | 3                         | 4                  | 4                  |
| Correction time   | min                                   | 20                        | 30                 | 20                 |
| The viability at storing in open containers                               | min                                   | 100                       | 180                | 120                |
| Placement   | -                                     | good                      | good               | good               |
| Recommended thickness of a layer  | mm                                    | 3-5                       | до 10              | до 45              |
| Consumption of the composition for acoating layer 5 mm thickness          | $\text{kg m}^{-2}$                    | 5,8                       | 6,0                | 4.8                |
| Water retention   | Percentage                            | 97.8-99.3                 | 95-97              | 96.2-98.8          |
| Tile slipping, max  | mm                                    | 0,3                       | 0.5                | 0.5                |
| The strength of adhesion with the baseAfter storage in air-dry conditions | MPa                                   | >1.4                      | 1.1                | 0.8                |
| After keeping in water  | MPa                                   | >1.1                      | 0.9                | 1.0                |
| After 50 freeze-thaw cycles of the watersaturated sample                  | MPa                                   | 0.97                      | 0.7                | 0.9                |
| Adhesion strength at shear  | MPa                                   | 0.92                      | 0.6                | 0.7                |
| Frost resistance of tile adhesive   | mark                                  | F50                       | F50                | F50                |
| Frost resistance of contact zone  | mark                                  | F <sub>cz</sub> 50        | F <sub>cz</sub> 50 | F <sub>cz</sub> 50 |
| Water absorption at capillary leak  | $\text{kg m}^{-2}\cdot\text{h}^{0.5}$ | 1.43                      | 2.00               | 1.78               |
| Shrinkage deformation   | Percentage                            | 0.028-0.034               | 0.030-0.040        | 0.029-0.038        |
| Maintenance temperature   | °C                                    | -50 ot +70°C              | -50 to +50°C       | -50 to +70°C       |
| Warranty period of storage in undamaged packaging                         | month                                 | 12                        | 12                 | 12                 |

respectively and in the sample with additive equal 20% by cement weight it is 6.1 and 17.0%, respectively. It was revealed a reduction of free lime in cement stone with additive on amorphous aluminosilicates. Free lime content in the control sample was 13% while in the sample

containing 20% additive by cement weight 6.5%. The results indicate on interaction of amorphous aluminosilicate with hydrolysis lime. The total and capillary porosity of control samples is 1.1 and 1.6 times higher than in the sample withan additive (additive amounts 20%

by cement weight) and gel and contractual porosity is 1.2 times lower. Thus, the additive on amorphous silica-alumina has a structure-forming effect.

We have developed a formulation of tile adhesive on cement basis using amorphous aluminosilicate as an additive, comprising: Portland cement, sand fractions 0.63, -0.315; 0.315, -0.16 in a ratio of 80: 20%, amorphous aluminosilicates, plasticizing additive Kratasol PFM and redispersible powder Neolith P 4400.

Table 3 shows main performance characteristics and properties of tile adhesive on the basis of developed formulation using additives on amorphous aluminosilicates. Tile adhesive Eunice 2000 on the basis of cement, produced by a group of companies "UNIS" was chosen as a prototype 1, tile adhesive CM 11, manufactured by Ceresit was taken as a prototype 2.

### CONCLUSION

Analysis of the data shows that the developed composition of adhesive DM with an additive on amorphous aluminosilicate and tile adhesives based on

it has a number of advantages compared with similar products: a high resistance to slipping, high adhesion strength to the surface with different operating conditions and a low value of shrinkage deformation.

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