

Use of amorphous aluminosilicates as modifying additive in formulations of lime mortars

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Abstract. The article considers the possibility of using an additive based on amorphous aluminosilicates in the formulation of calcareous dry construction mixtures. Methods for the preparation of an additive, based on amorphous aluminosilicates, are considered. The results of the physicochemical analysis of the additive are given - the particle size, their distribution, and the oxide content in the additive composition. The mineralogical composition of the additive was studied using full-profile RFA with the help of the program DDMv.1.95d. The distribution and concentration of acid-base centers (active sites) on the surface of additive particles was revealed using the indicator method for the adsorption of indicators with different pKa values.

1. Introduction

The use of various modifying or special additives in the formulations of dry building mixtures (DBM) is necessary to obtain the specified technological and technical characteristics of the DBM, mainly - to increase the strength and water retention capacity in the mortar after the application of the material.

Most of the modifying additives used in DBM formulations are made by foreign companies, such as: "EMP1", "Sopro", "Scanmix", "SKW Polymers", Samung Fine Chemicals, EVONIK, Wacker Chemie AG, etc. [1-9].

To expand the market of raw materials and reduce the supply of imported additives, the possibility of using additives based on amorphous aluminosilicates in the formulation of dry construction mixtures was investigated.

Recently, there has been an increasing interest in obtaining new aluminosilicate adsorbents. Obtained adsorbents have high thermal stability and at high temperatures are able to remove metal cations from aqueous solutions, which make promising their use for cleaning water and gas environments at nuclear power plants, as well as enterprises of the fuel and energy complex [10-14].

The aluminosilicate adsorbent is characterized by the presence of a free porous space, which is a three-dimensional labyrinth of interconnected extensions and constrictions of various sizes and shapes in the form of nano- and micropores, giving the adsorbent a high specific surface area and the ability to absorb various substances from liquids and gases.

The presence of amorphous aluminosilicates in the adsorbent structure makes promising their use in construction when developing calcareous, cement, and gypsum DBM.

However, the issues of their application in the construction industry are not covered and require careful consideration. The mechanism of interaction of synthetic adsorbents with astringent is not revealed, the patterns of structure formation of the composite have not been established. This indicates

the feasibility of investigating the possibility of using additives based on amorphous aluminosilicates in calcareous, gypsum and cement composites.

An analysis of existing patents for the preparation of amorphous aluminosilicates was carried out.

The patent [15] describes the preparation of a synthetic aluminosilicate zeolite based on alumina and silicon oxides, comprising the preparation of a reaction mixture containing a source of aluminum, silicon, an alkali metal, water and an organic structure-forming additive, crystallizing the reaction mixture, separating the precipitate formed, drying and calcining.

Patent [16] describes an amorphous silica-alumina composition having a surface-to-volume ratio of Si / Al (SB ratio) in the range of from 0.7 to 1.3 and containing less than 10% of the crystalline aluminum phase. This amorphous aluminosilicate is prepared by mixing a solution of silicate (sodium silicate) and a solution of an acidic aluminum salt (aluminum sulphate) while maintaining the pH of the stirred solution below 3, then a basic precipitating reagent is gradually added to the stirred solution to form a precipitated co-gel that can be extracted, washed and spray-dried. This co-gel can be used to produce an aluminosilicate catalyst or catalyst support.

2. Methods

The mineralogical composition was evaluated by differential thermal analysis using the "Thermoscan-2" unit. Thermal analysis (TA) of the samples was carried out in the temperature range 20-1000 ° C in an air atmosphere at a heating rate of 10°C/min [17].

The phase composition of the samples was evaluated from the X-ray workstation ARL 9900 WorkStation. Radiographs were obtained from the cobalt anode radiation. X-ray diagnostics of mineral phases was carried out on the basis of the diffraction database of PDF-2 baths using the program CrystallographicaSearchMatchv 2:0 (OxfordCryosystems). Quantitative determination of the concentrations of crystalline mineral formations was performed by fully profiled RFA using the DDMv.1.95d program [18].

Determination of acid-base characteristics of additives based on amorphous aluminosilicates. The methodology is based on the adsorption of single-base indicators on the surface of solids from the aquatic environment. The adsorption of the indicator under the analysis conditions occurs both at the Bronsted centers and at the Lewis centers, on which the molecules of water are adsorbed by the coordination mechanism in accordance with its value pK_a^x .

The quantitative determination of adsorption centers ($q_{pK_a^x}$, mg-eq / g or mg-eq / m²) of a given acid strength was carried out by a photometric method. The solutions were photographed in cuvettes relative to the solvent on a KFK-3KM photoelectric colorimeter at a wavelength corresponding to the maximum absorption of each indicator (λ_{max}). The change in optical density as a result of the indicator adsorption process (ΔD) on the sample surface was calculated by the formula:

$$\Delta D = \left| (D_0 - D_1) \right| \pm \left| (D_0 - D_2) \right| \quad (1)$$

The content of active centers of a given acid strength, equivalent to the amount of adsorbed indicator, was calculated by the formula:

$$q_{pK_a^x} = \frac{C_{ind} \cdot V_{ind}}{D_0} \cdot \left(\left| \frac{D_0 - D_1}{a_1} \right| \pm \left| \frac{D_0 - D_2}{a_2} \right| \right) \quad (2)$$

where C_{ind} - concentration of indicator solution, mg-mol/ml; V_{ind} - volume of indicator solution taken for analysis, ml; D_0 - optical density of the indicator before sorption; D_1 - the optical density of the indicator after sorption; D_2 - optical density of the "idle" solution.

The sign "-" corresponds to a unidirectional change D_1 and D_2 relatively D_0 , t.e. D_1 and $D_2 < D_0$ or D_1 and $D_2 > D_0$. The sign "+" corresponds to a multidirectional change D_1 and D_2 relatively D_0 , i.e. $D_1 > D_0$, $D_2 < D_0$ or $D_1 < D_0$, $D_2 > D_0$.

This technique allows quantitative determination of the total acidity for Lewis and Bronsted with the differentiation of reaction centers by type and strength, depending on the pK_a^x of the indicator used.

For photometry was prepared 3 series of samples.

Series 1 - working solution. In the centrifuge tubes with a capacity of 10 ml, the required volumes of indicators with a certain pK_a^x value were poured, diluted to the mark with water, mixed and after 30 minutes weighed the sample ($a \approx 0,04$ r) of clay. After the establishment of adsorption equilibrium was measured at a wavelength (λ_{max}) corresponding to each indicator, the value of optical density D_1 . Before measuring, the tubes with the material were centrifuged for 3-5 minutes. In this experiment, the interaction of the material with the solvent and the adsorption process are taken into account.

Series 2 - "blank an experience". The sample ($a_2 \approx a_1$) were placed in dry centrifuge tubes in capacity and filled with 6 ml of water. After 1 hour, the solution was decanted into another tube with pre-centrifugation as described above. The necessary volumes of indicators were added to the solution, the water was added to the mark, the suspension was stirred, aged for 30 minutes, and the optical density value (D_2) was taken into account, taking into account $\pm \Delta D_2$ by changing the pH of the medium and dissolving the sample. In this experiment, the sorption of the indicator was excluded.

Series 3 (indicators solute's). In the tubes with a capacity of 10 ml, the required volumes of indicators were filled, diluted to the mark with water, mixed and after 30 minutes the optical density (D_0) was measured.

Based on the data obtained, a distribution curve of acid-base centers was constructed on the diatomite surface in coordinates $q_{pKa} = f(pKa^x)$.

The following indicators were used in the tests: diamond green ($pKa = + 1.5$), fuchsin ($pKa = + 2.1$), methyl orange ($pKa = + 3.46$), bramfen blue ($pKa = + 4.1$), bromine cresol purple ($pKa = + 6.4$), bromothymol blue ($pKa = + 7.3$), thymol blue ($pKa = + 8.8$), Nile blue ($pKa = + 10.5$) and ethylene glycol ($pKa = + 14.2$).

3. Test results

In the course of the studies, an additive based on amorphous aluminosilicates was prepared by adding microdispersed aluminum powders to sodium liquid glass at a temperature of 60°C for 90 minutes. A liquid sodium glass with a silicate module of 2.9 was used in the work.

The synthesized additive is a light powder of light gray color with a bulk density of 0.55 ± 0.05 g/cm³. During the synthesis of the additive, a large amount of gaseous molecular hydrogen is formed, which creates in the additive pores of various sizes and shapes. The yield of the finished product is 90%.

With the TescanVEGA3 scanning electron microscope, it was found that the granulometric composition of the additive to be synthesized is 2.48% of 0.01-2.0 μm particles, the particle size of 80.000-100.000 μm is 8.20% (Figure 1).

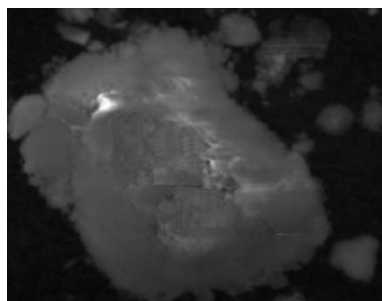


Figure 1. Electron microscope image of the additive.

When evaluating the properties of the additive, an analysis of the particle size distribution was carried out using Fritsch particle sizer Analysette 22. The data obtained show that 2.48% are 0.010-2.0 μm particles, the particle size of 200.000-300.000 μm is 0.07% (Table 1).

Table 1. Granulometric composition of the additive.

Fraction, μm	The percentage content, %
0,01–2,0	2,48
2,0–5,0	7,50
5,0–10,0	10,81
10,0–20,0	13,35
20,0–45,0	18,60
45,0–80,0	17,92
80,0–100,0	8,20
100,0–200,0	21,08
200,0–300,0	0,07

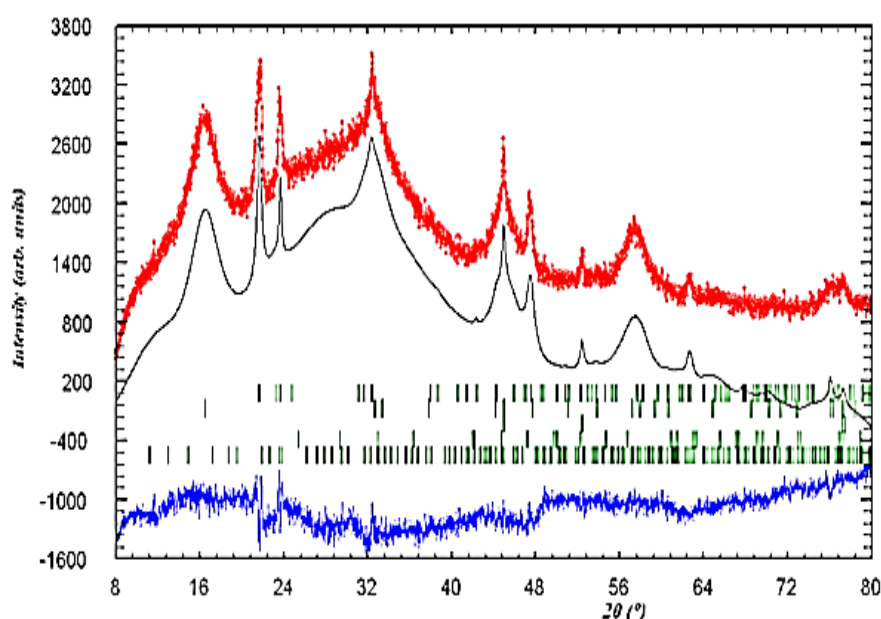
Table 2. The content of oxides in the composition of the additive.

The name of oxide	The percentage content, %
Al ₂ O ₃	51,03
SiO ₂	36,36
Na ₂ O	11,89
Fe ₂ O ₃	0,110
CaO	0,107
MgO	0,105
SO ₃	0,0290
TiO ₂	0,0124
K ₂ O	0,0112
Other	0,3454
Σ	99,6546

The oxide chemical composition of the additive based on amorphous aluminosilicates is presented in Table 2. It has been established that aluminum oxides predominate at 51.03%.

A high content of Al₂O₃, SiO₂, Na₂O oxides is found corresponding to 51.03%, 36.36%, 11.89%, respectively.

To assess the mineralogical composition of the synthesized additive, X-ray phase analysis was performed. The quantitative determination of the concentrations of crystalline mineral formations was carried out by full-profile RFA using the program DDMv.1.95d (Figure 2).

**Figure 2.** Full profile calculation of the X-ray diffraction pattern of aluminosilicate samples.

X-ray phase analysis (XRD) showed that the mineral composition of the sample is mainly represented by nanostructured silica and sodium aluminate. In addition, on the roentgenogram there are reflections of metallic aluminum (Figure 2). The content of the amorphous phase is 83%.

The most of the processes occurring during the interaction of the synthesized additive with the binder are of a local nature and are largely determined by the energy parameters of the specific active centers [19-21].

In this connection, the study of the spectrum of the distribution of adsorption centers with respect to the acid-base type acquires particular importance. The modern theories of acids and bases are based on the ideas of Bronsted and Lewis.

To reveal the distribution and concentration of acid-base centers (active sites) on the surface of the additive particles, an indicator method for adsorption of indicators with different values pK_a .

The quantitative determination of adsorption centers (q_{pK_a} , mg-eq/g or mg-eq/m²) of a given acid strength was carried out by a photometric method. This technique allows quantitative determination of the total acidity for Lewis and Bronsted with the differentiation of reaction centers by type and strength, depending on the pK_a of the indicator used.

The adsorption of the indicator under the analysis conditions occurs both at the Bronsted centers and at the Lewis centers in accordance with its pK_a value. Quantitative determination as a result gives the total content on the surface of the test sample of the Lewis and Bronsted centers of the corresponding force.

Studies were carried out in the field of Brönsted acidic (pK_a from 0 to 7) and basic (pK_a from 7 to 13) centers, and Lewis acid ($pK_a > 13$) centers. The values of $pK_a = +7$ correspond to centers of a neutral nature. An increase in the pK_a values characterizes the increase in the donor properties of metal atoms, the decrease in the acceptor properties.

Based on the data obtained, a distribution curve of the acid-base centers on the surface of the additive based on amorphous aluminosilicates in the coordinates was constructed $q_{pK_a} = f(pK_a^x)$. (Fig. 3).

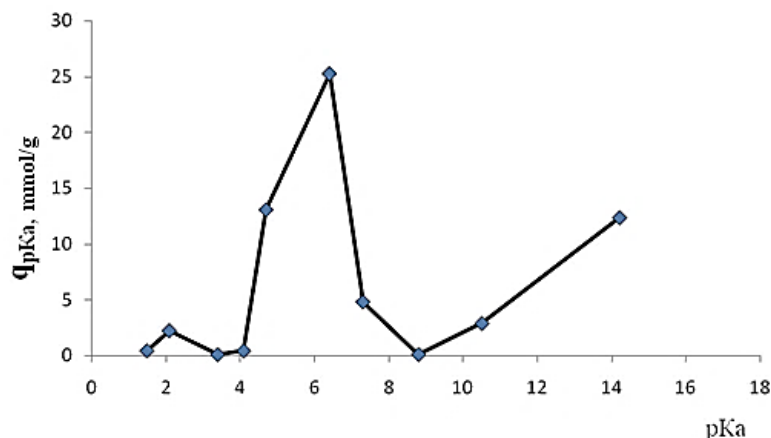


Figure 3. Distribution curve of acid-base centers.

It has been established that the acid-base center of the surface of the additive sample is characterized by the predominance of the $pK_a = +4.7$, $pK_a = +6.4$ centers. The total number of acid centers is $\sum q_{pK_a} = 53.72$ mmol/g and the main centers are $\sum q_{pK_a} = 7.70$ mmol/g.

An increase in the acidity of the surface center along the Bronsted ($pK_a < 7$) promotes an increase in the acceptor capacity of the element atom.

Such a structure of the acid centers of aluminosilicates is explained by the isomorphous replacement of tetravalent Si in the SiO₂ lattice by the atoms of trivalent Al. At the same time, Al tends to interact with the water molecule, giving the Bronsted center. The acid center of Bronsted is a hydroxyl group formed near the Al atom, which is bound to two silicon-oxygen tetrahedra. The Lewis

acid center arises in aluminosilicate when two hydroxyl groups (in the form of a water molecule) are removed to form three coordinated Al atoms and presumably Si atoms with an excess positive charge.

4. Summary

The granulometric composition of the additive is established, in which particles of round and needle shape with sizes from 0.11 to 10.49 microns are present. Bulk density of the additive on the basis of amorphous aluminosilicates makes bulk $\rho_{\text{bulk}} = 550 \text{ kg/m}^3$. It was revealed that in the oxide composition of the aluminosilicate additive, aluminum oxides account for 51.03%.

The XRD method established that the mineral composition of the sample is mainly represented by nanostructured silica and sodium aluminate. The amorphous phase is 83%.

The nature of the energy properties of the surface of the additive is studied. It has been established that the acid-base centers of the surface of the sample of the additive are characterized by the predominance of the Bronsted centers. The content of active centers in the $\text{pK}_a < 7$ region is 53.72 mmol/g, in the $\text{pK}_a > 13$ region it is 7.70 mmol/g.

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