

Methods of obtaining modifying supplement based on calcium hydrosilicates for lime dry mixes

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Abstract. The article considers the possibility of using a supplement, based on calcium hydrosilicates (CHS), synthesized in the presence of diatomite, as a modifying additive for finishing lime dry mixes. The results of the physicochemical analysis of the supplement are given. The impact of the method of obtaining CHS supplements on the compressive strength of lime samples was researched. The X-ray phase analysis of supplements, based on calcium hydrosilicates, is presented. The technological and operational characteristics of lime finishing mixes with the use of calcium hydrosilicates, synthesized in the presence of diatomite in the their recipe, are given.

1. Introduction

Currently, for the finishing and restoration of buildings and structures lime compositions based on dry mixes are used. Vapor permeability and bioresistance of coatings based on lime dry mixes are high. However, lime mixes are characterized by low values of strength and durability, limiting their use. To increase the lifespan of lime dry mixes, various modifying supplements are injected into their recipe. In domestic dry mixes, foreign modifying supplements are most often used, which affect the cost of dry mixes and make domestic production of lime mixes dependent on foreign deliveries [1-9].

The use of local resources as raw materials for obtaining modifying supplements for finishing dry mixes will allow either to refuse the use of modifying supplements imported from abroad or to reduce their consumption. Previous studies have confirmed the possibility of regulating the structure and properties of lime compositions by adding to their recipe supplements based on calcium hydrosilicates (CHS), which increase the operational resistance [10-14].

The method of obtaining calcium hydrosilicates in the ratio C/S=1.5.

Since the high-basic calcium hydrosilicates are unstable and the low-basic calcium hydrosilicates are more strength, further research will be directed towards the development of a method for the production of CHS-based supplements containing in greater quantities low-base calcium hydrosilicates.



2. Methods

The liquid glass modulus was calculated in accordance with National standard of Russia 13078 [15]: for soluble glass, based on the values of density and concentration of Na_2O using the following equation:

$$n = \frac{A \cdot (\rho - 1)}{10 \cdot \rho} - C \quad (1)$$

$$x \cdot \frac{10 \cdot \rho}{m \left(1 - N \cdot \sqrt{x \cdot \frac{10 \cdot \rho}{m}} \right)}$$

where A , N and C – constants, which for soluble glass respectively equal 24,88; 0,071 and 2,071; ρ – density of soluble glass, g/cm^3 ; x – mass fraction of sodium oxide, % (by analysis); m – molecular mass of alkali metal oxide ($\text{Na}_2\text{O} = 62$).

The activity of the mineral supplements was determined from their solubility in a 20% KOH solution as follows: the original mineral supplement was shredded until completely passed through a sieve No. 008 and dried to constant mass in a drying oven for 2 hours at a temperature of $(105 \pm 5)^\circ\text{C}$. The dried supplement was placed in a glass beaker and a 20% KOH solution was poured to it. The resulting solution was placed for 3 hours in a boiling water bath, after which the settled solution was filtered through a low resistance ashless filter. The sediment in the beaker was rinsed with hot distilled water until the sediment was completely transferred to the filter. The rinsed sediment together with the filter on the funnel was dried to constant mass.

The amount of substance of the mineral supplement soluble in KOH was determined by the equation:

$$M = \frac{P - P_1}{P} \cdot 100\% \quad (2)$$

where M – amount of substance of the supplement soluble in KOH, %; P – reference mass, g; P_1 – mass after dissolution in KOH and drying at $(105 \pm 5)^\circ\text{C}$, g.

The dependence between the solubility in a 20% solution of KOH and the activity of the supplement (in mg CaO per 1 g of supplement) is shown in figure 1.

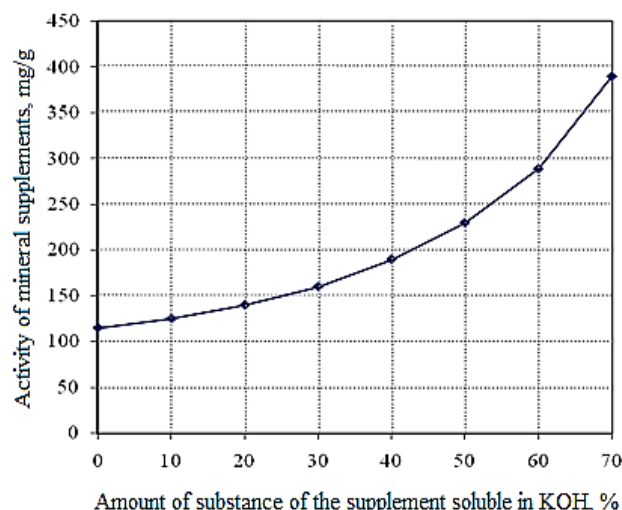


Figure 1. The graph of the dependence of the activity of mineral supplements on solubility in a 20% KOH solution.

The pH change kinetics of the solution was measured during the hardening of the samples with the help of pH-meter "Akvilon" pH - 410 №9514. Into the lime solution the pestle of instrument dived every 5 minutes. The pH of the test solution was recorded on the instrument. The experiment was

considered as completed when the pestle of instrument did not penetrate into the solution under test, because the solution hardened.

The ultimate compression strength of samples was determined in accordance with National standard of Russia 5802-86 "Mortars. Test methods". As equipment for testing the compression strength of samples, a test machine of the type "IR 5057-50" was used. Depending on the type of used power sensor of "IR 5057-50", the force measuring range was from 50 to 50000 N with an accuracy of 1 N (0.1 kgs). Built-in cross-bar speed controllers allow to set the speed of application of the load from 1 to 100 mm / min (in terms of displacement). The compression strength (MPa) of the samples was determined by the formula:

$$R_{\text{com}} = \frac{P}{F} \quad (3)$$

where P – destructive force, N; F – cross-sectional area of the sample before the test, m^2 .

The phase composition of the material samples was determined by X-ray phase analysis. The ionization radiographs of the test samples were taken at the X-ray station ARL 9900 X-ray Work Station (Thermo Scientific) model ARLX`TRA from Thermo Electron SA (Switzerland).

X-ray diffraction spectrums were obtained using $\lambda\text{-Co}_{K\alpha 1,2}$ radiation. The diffraction angle interval is $2\theta = 12^\circ - 80^\circ$, the scanning step is 0.02° . The decoding of the radiographs was carried out by comparing the interplanar distances and the intensity of the corresponding lines on the obtained radiographs with the data for the standard materials [16].

3. Test results

It is established that low-basic CHSs are formed at a C/S ratio equal to $C/S = 0.5\text{-}1.33$ [17]. In this connection, in order to obtain a C/S ratio of 0.5-1.33 during formation of CHS, substances containing amorphous silica, in particular diatomite, were injected.

Two methods of obtaining CHS were researched:

1 method – precipitation in the presence of a 15% solution of calcium chloride in an amount of 50% of the mass of soluble glass;

2 method – precipitation in the presence of a 10% solution of calcium chloride in an amount of 50% of the mass of soluble glass with the addition of a diatomite suspension, in this the ratio of liquid:solid phase (L:S) equals $(L:S) = 1:2$.

The prepared composition was stirred and filtered, and the resulting sediment was dried at a temperature of $(100 \pm 5)^\circ\text{C}$.

Depending on the method of preparation of the calcium hydrosilicate supplement, the pH value and the strength of lime samples based on the resulting dry mixes are changed (Table 1).

Table 1. Impact of the method of obtaining CHS supplements on the compressive strength of lime samples

Method of obtaining	Silica modulus of soluble glass	Density of soluble glass, kg/m^3	pH	Compressive strength, MPa
2	2.9	1335	10.2	7.5
1			8.3	4.7
2	2.5	1410	10.8	6.9
1			9.1	4
2	2	1576	11.6	6.1
1			9.8	3.6
2	1.5	1663	12.4	5.4
1			10.4	3.1

Analyzing the data of Table 1 it was established that the pH of the solution obtained by the 2nd method, using soluble glass with a density $\rho = 1335 \text{ kg/m}^3$ and a silica modulus $n = 2.9$, is $\text{pH} = 11.8$, and the pH of the solution, obtained by the second method using soluble glass with a density $\rho = 1663 \text{ kg/m}^3$ and a silica modulus $n = 1.53$, is $\text{pH} = 13.6$.

Thus, an increase in the soluble glass modulus leads to an increase in the compressive strength of lime samples. Thus, when using soluble glass with a modulus $n = 2.9$ for the synthesis of CHS, the strength of a lime sample is $R_c = 7.5 \text{ MPa}$, and when using soluble glass with a modulus of $n = 2.5$ and $n = 2$, the strength is $R_c = 6.9 \text{ MPa}$ and $R_c = 6.1 \text{ MPa}$, respectively.

In carrying out further research on the obtaining of CHS supplement, soluble glass was used with the optimum value of the silica modulus of $n = 2.9$ and with the addition of a diatomite suspension.

The chemical composition of the hydrosilicate supplement obtained in the presence of diatomite was analyzed. During evaluation the elemental composition of the CHS supplement obtained with the use of diatomite, the predominance of silicon is found, which is of 35.25% (figure 2).

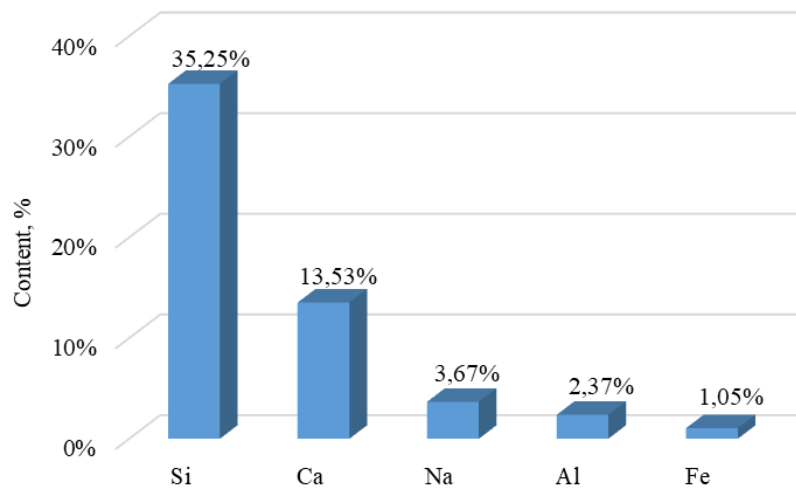


Figure 2. Elemental composition of the calcium hydrosilicate supplement obtained in the presence of diatomite

During evaluation the oxide composition of the CHS supplement obtained in the presence of diatomite, the predominance of silicon oxides is found, which are of 70.81% (figure 3).

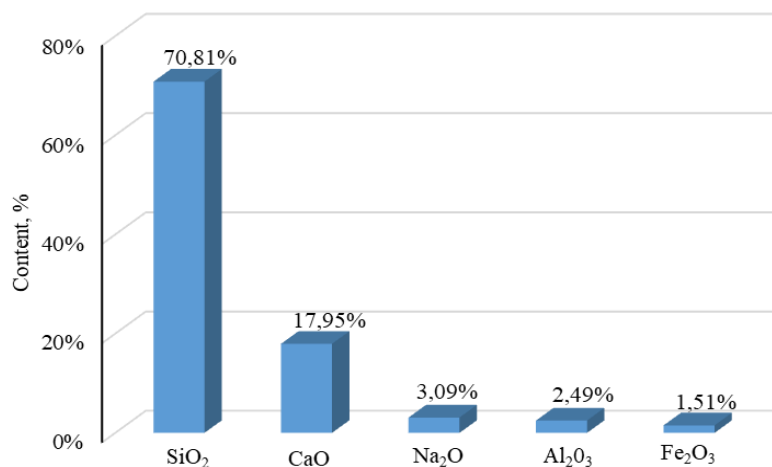


Figure 3. The oxide composition of the calcium hydrosilicate supplement obtained in the presence of diatomite

X-ray phase analysis (XPA) was performed to analyze the phase composition of CHS. X-ray workstation ARL 9900 WorkStation was used for getting radiographs of samples.

Figures 4, 5 show the radiographs of samples of supplements based on calcium hydrosilicates.

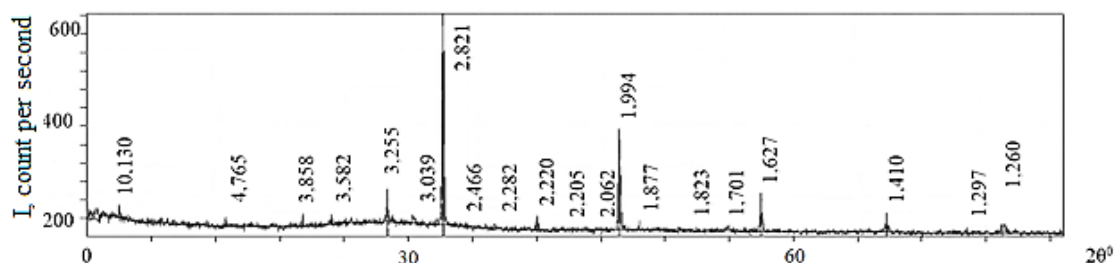


Figure 4. Radiograph of the supplement of calcium hydrosilicates obtained without the use of diatomite.

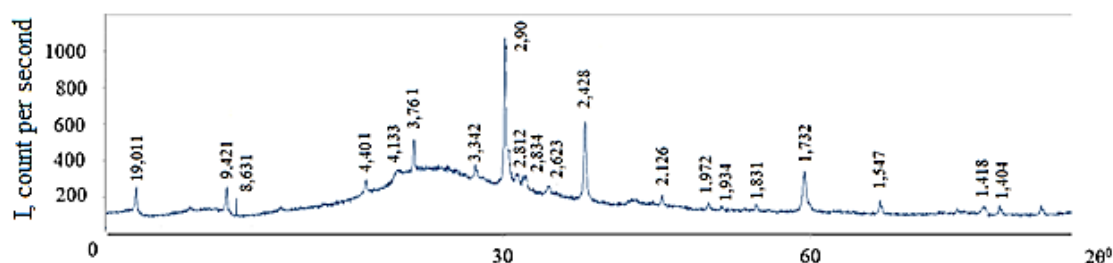


Figure 5. Radiograph of the supplement of calcium hydrosilicates obtained with the use of diatomite.

The XPA method revealed that the mineralogical composition of the CHS supplement obtained with the use of diatomite is represented by calcium hydrosilicates of the tobermorite group, calcium hydrosilicates C-S-H (II), quartz, kaolinite and hydrogalites (figure 5).

The injection of diatomite in the synthesis of calcium hydrosilicates leads to a general increase in the intensity of the maxima corresponding to calcium hydrosilicates, especially the 2.90 Å line belonging to various calcium hydrosilicates. It has been established that the mineralogical composition of the CHS supplement obtained in the presence of diatomite contains more peaks related to low-basic calcium hydrosilicates.

The activity (A) of the supplement based on CHS was determined from the solubility (M) of calcium hydrosilicates in a 20% KOH solution [18]. The results of the research showed that the supplement based on CHS has a high activity of $A = 370$ mg/g and $M = 70\%$, that higher than activity of supplement based on calcium hydrosilicates prepared without diatomite - $A = 320$ mg/g, $M = 65\%$.

To determine the compressive strength of lime samples with the CHS supplement content of 30% by the mass of binder the powder lime of class II with an activity of 86% was used. Tests were carried out in accordance with the requirements of National standard of Russia 5802-86 "Mortars. Test methods" [19]. The results are shown in figure 6.

The analysis of figure 6 showed that at the age of 28 days of air-dry hardening, the compressive strength for the control composition is $R_c = 2.1$ MPa (figure 6, curve 4), while the compressive strength of lime samples using the CHS supplement obtained in the presence of diatomite is $R_c = 7.59$ MPa (figure 6, curve 1), and the compressive strength of lime samples with the addition of CHS without diatomite is $R_c = 4.7$ MPa (figure 6, curve 2).

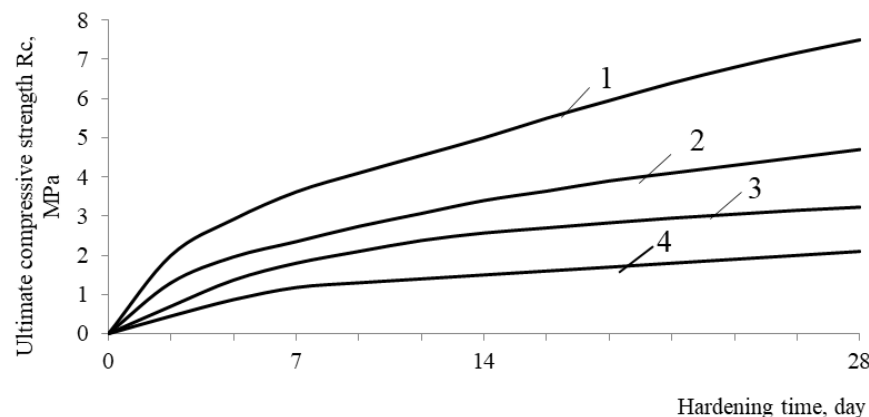


Figure 6. Impact of the method of obtaining CHS on the compressive strength of lime samples: 1 - with the supplement obtained by the 1st method; 2 - with the supplement obtained by the 2nd method; 3 - with diatomite (without CHS supplements); 4 - control composition.

Table 2 shows the technological and operational properties for the finishing composition and coatings on the basis of a dry mix prepared with the use of a CHS supplement prepared using diatomite, and a prototype composition.

Table 2. Technological and operational properties of finishing mixes.

Property name	Value of property of the developed composition	Value of property of the prototype [20]
Compressive strength, MPa	5,5	2,5
Adhesive strength, MPa	0,89	0,7
Mark on frost resistance F	35	35
Water holding capacity, %	97,9	97
Water absorption by mass, %	10,15	12
Softening coefficient	0,73	-
Shrinkage deformation, %	0,024	-
Water vapor permeability coefficient μ , mg/(m·h·Pa)	0,049	0,01
Viability, h	1,5	2-3
Presence of cracks due to shrinkage	no	no

Analyzing the data of Table 2 it was found that coatings based on the developed dry mix have higher operational properties such as compressive strength, adhesive strength, frost resistance and others in comparison with the prototype.

4. Summary

It was found that an increase in the resistance of lime coatings is possible by using in the dry mixes recipes a supplement based on calcium hydrosilicates obtained in the presence of diatomite. The presence of silicon oxide in the CHS supplement, obtained with the use of diatomite, contributes to an increase in the quantity of low-basic calcium hydrosilicates and, accordingly, the compressive strength of lime coatings. Supplement based on CHS, obtained in the presence of diatomite, speeds up the

curing of coatings, increases strength and water resistance due to the formation of low-basic calcium hydrosilicates.

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