Influence of thermoactivation on properties of mineral additives in dry mixtures

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Abstract. Information on the effect of thermal activation of silicate and aluminosilicate rocks used as a filler in dry building mixtures on their reactivity of interaction with lime binder is presented. The change in the distribution of acidic Bronsted and Lewis centers on the filler surface as a result of thermal activation is shown. It was found that the number of Bronsted and Lewis acid centers on the surface of fired clays exceeds the number of the same centers on the surface of unbaked clays. The number of adsorption centers at pKa from 0 to 7 and pKa> 13 on the surface of fired diatomite is $2.435 \times 10^{-5}$ mol/g, and on the surface of unbaked diatomite $1.678 \times 10^{-5}$ mol/g. The heat treatment of diatomite at low temperatures ($200^\circ$C and $300^\circ$C) does not significantly affect the values of the compressive strength of the mortar. An increase in the firing temperature to $700^\circ$C leads to an increase in strength characteristics up to R = $4.38$ MPa. However, the greatest effect is achieved when diatomite is fired at a temperature of t = $900^\circ$C. The value of the ultimate strength in compression was R = $5.1$ MPa.

1. Introduction

When finishing buildings and structures, dry building mixtures 1-3 are widely used [1-3]. The reactivity of the surface of dispersed materials that are widely used in the formulation of dry mixtures is determined, among other factors, by a combination of acid and basic Lewis and Bronsted centers [4-6]. It is known that silicate and aluminosilicate rocks (diatomite, clay) in a finely dispersed state in the presence of moisture interact with lime-cement binders, but the strength of such solutions is low. Therefore, it is necessary to enhance the interaction of such fillers with lime-cement binders, for which it is necessary to increase the surface activity of fillers [7-10]. However, the effect of changes in the surface chemistry of diatomite and clay and an increase in its reactivity in the process of modification has been insufficiently studied. In this regard, it is important to study the spectrum of the distribution of adsorption centers and the nature of its change depending on certain conditions.

2. Materials and methods

The work investigated the change in acid-base properties during thermal activation of dry mixture fillers. The indicator method (RCA) was used to study the distribution of adsorption centers. The clay of the Kameshkir quarry and the diatomite of the Akhmatov deposit (Penza region) were used. The chemical composition of clays is presented in table. 1. The content of SiO$_2$ in diatomite is 83.4%, Al$_2$O$_3$ - 6.23%.
Table 1. The chemical composition of the clay of the Kameshkir quarry.

| Chemical compound | Content of chemical compounds (%) |
|-------------------|-----------------------------------|
| SiO₂              | 75.41                             |
| Al₂O₃             | 11.04                             |
| Fe₂O₃             | 6.61                              |
| others            | 6.94                              |

Additionally, to assess the nature of the energy inhomogeneity of the filler, the amount of lime adsorbed on the filler surface from a saturated solution of Ca (OH)₂ was investigated. For this purpose, a saturated lime solution was prepared, then 200 ml of lime water was taken and 10 g of the powder under study was added. After holding for a day, 100 ml of the liquid phase was taken, 2-3 drops of phenolphthalein were added and titrated with 0.1N HCl until the solution became discolored. Indirectly, the amount of adsorbed lime was estimated by the change in water hardness, determined by the formula

\[ H_W = \frac{V_{HCl}V_{HC}1000}{V_{H2O}} \]  

where \( V_{H2O} \) is the volume of HCl used for titration, ml; 
\( V_{HCl} \) - acid titer; 
\( V_{HC} \) - volume of water extract, ml.

The evaluation of the compressive strength was carried out on a hydraulic press. The tests were carried out at a temperature of 20°C and a relative humidity of 60%. The ultimate compressive strength was estimated for at least four specimens. The compressive strength \( R \) for each sample was calculated by the formula

\[ R = \frac{P}{S} \]

where \( P \) - loading at the time of a rupture, N; 
\( S \) - the initial cross-sectional area of a sample, mm².

3. Results and discussions

The results of the X-ray analysis of the clay, the data on the cationic absorption capacity allow us to assert that, in terms of the mineralogical composition, the clay of the Kameshkir deposit belongs to the montmorillonite type of clay. Thermal activation consisted in firing at a temperature of 400-700°C. In figure 1 shows the distribution curves of adsorption centers on the surface of clays in the natural state and after treatment at temperatures \( t = 400-600°C \), plotted in coordinates

\[ q_{oKa} = F(pK_a) \]

where \( q_{oKa} \) is the content of active centers, equivalent to the amount of adsorbed indicator of a certain acidic strength \( pK_a \).

Analysis of the data indicates that the number of Bronsted and Lewis acid sites on the surface of fired clays exceeds the number of the same centers on the surface of unbaked clays. Table 2 shows the results of the change in the number of clay adsorption centers depending on the firing temperature.
Figure 1. Distribution of acid-base centers on the clay surface: 1 - without firing; 2 - at a temperature of 450°C; 3 - at a temperature of 600°C; 4 - at a temperature of 400°C.

Table 2. Influence of clay firing temperature on the energy state (mmol/g) of its surface.

| Clay firing temperature, °C | Zone of acid-base centers (pKa) |  
|---------------------------|---------------------------------|  
|                           | 0-7                             | 7-13 | >13  |  
| 600                       | 56.32                           | 4.29 | 55.36|  
| without firing            | 83.50                           | 22.73| 104.57|  
| 400                       | 87.70                           | 36.85| 413.65|  
| 450                       | 55.36                           | 55.36| 129.17|  
| 600                       | 135.24                          | 38.36| 104.57|  

The distribution of adsorption centers on the diatomite surface is shown in figure 2.
Table 3. Influence of the firing temperature on the total number of active centers.

| Clay firing temperature, °C | Total number of active centers, mmol/g |
|-----------------------------|---------------------------------------|
| without firing              | 210.8                                 |
| 400                         | 413.65                                |
| 450                         | 216.96                                |
| 600                         | 278.17                                |

Figure 2. Distribution of acid-base centers on the surface of diatomite 1 - unbaked diatomite; 2 - diatomite, heat treated at t = 700°C.

Table 4 shows data on water hardness.

Table 4. Water hardness above the surface of diatomite.

| Diatomite processing temperature, °C | Water hardness, meq/dm³ |
|--------------------------------------|-------------------------|
| 20                                   | 19.2                    |
| 200                                  | 19                      |
| 300                                  | 18.8                    |
| 700                                  | 18.5                    |

Analysis of the data (table 4) shows that firing diatomite leads to an increase in the number of active sites on the surface. This is evidenced by data on a decrease in water hardness caused by an increase in the amount of Ca(OH)₂ adsorbed on the filler. Thus, the water hardness above the surface of unbaked diatomite was 19.2 meq/dm³, thermal activation of diatomite at a temperature of 700°C reduced the water hardness to 18.5 meq/dm³. The hardness of the original lime water was 37 meq/dm³.
The higher reactivity of clay and diatomite after firing contributes to an increase in the strength of the lime-sand mortar. The hardening of lime-sand samples, in addition to carbonization and crystallization of calcium hydroxide with the introduction of fired clay, is also accompanied by the formation of hydrosilicates, hydroaluminates and hydroaluminosilicates of calcium. The latter compounds contribute to an additional increase in the strength of the finishing compounds. Table 5 shows the strength values of lime-sand mortars with the introduction of clay as a mineral additive in an amount of 10% by weight of lime.

**Table 5.** Strength of lime-sand mortars, Mpa.

| No additive | With the addition of clay without firing | Clay firing temperature, °C |
|-------------|-----------------------------------------|----------------------------|
|             |                                         | 400 | 450 | 500 | 550 | 600 |
| 0.84        | 1.22                                    | 1.75 | 1.70 | 1.69 | 1.63 | 1.58 |

**Table 6.** Compressive strength of the mortars as a function of the temperature of diatomite heat treatment.

| Processing temperature, °C | Compressive strength at the age of 28 days, MPa |
|----------------------------|-----------------------------------------------|
| 20                         | 0.9                                           |
| 200                        | 0.94                                          |
| 300                        | 0.98                                          |
| 700                        | 4.38                                          |
| 900                        | 5.1                                           |

Note. Lime: diatomite ratio = 1: 3

An analysis of the data (table 6) indicates that the heat treatment of diatomite at low temperatures (200°C and 300°C) does not significantly affect the values of the compressive strength of the mortar. An increase in the firing temperature to 700°C leads to an increase in strength characteristics up to R = 4.38 MPa. However, the greatest effect is achieved when diatomite is fired at a temperature of t = 900°C. The value of the ultimate strength in compression was R = 5.1 MPa. At firing temperatures of 700°C and 900°C, diatomite acquires a bright orange hue, which allows you to diversify the color range of the finishing layer without the introduction of pigments. However, from the point of view of energy consumption, it is more expedient to heat the filler of the dry mixture at t = 700°C.

Thermal activation of diatomite made it possible to significantly accelerate the process of structure formation in the initial period of hardening. At the age of 7 days, the compressive strength of the mortar based on diatomite fired at t = 700°C was 1.8 MPa. This is significantly exceeds the compressive strength of specimens based on unfired diatomite not only at this stage of hardening (R = 0.22 MPa), but also at the age of 90 days (R = 1.55 MPa).
4. Summary
Thus, the use of thermal activation for the modification of fillers improves the quality of dry building mixtures. It was found that clay firing leads to the formation of a large number of Lewis centers. A higher reactivity of clay and diatomite after firing has been established, which contributes to an increase in the strength of the lime-sand mortar. It is shown that the thermal activation of diatomite made it possible to significantly accelerate the process of structure formation in the initial period of hardening.

5. References
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