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Study of activity of polydisperse mineral modifiers via unstandardized techniques

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Abstract. The paper justifies the possibility of using unstandardized techniques and methods to assess the quality (activity) of components with different composition and method of production. It illustrates physical and chemical properties of mineral modifiers obtained on the basis of crystal and amorphized raw materials with different composition. It also proves their high activity in relation to cellular concrete binding irrespective of the curing method. The obtained properties allow forecasting high efficiency of mineral modifying components within a porous system.

1. Introduction

Currently, the modernized economy is mainly focused on the transition to innovative (modern) technologies [1-7]. At the same time, the introduction of innovative products, including nanotech industry products, is restrained due to lack of established regulatory base that includes documents developed and approved by profile structures (for example, enterprises) and national standards. Besides, there is no database on certification and standardization of materials obtained on the basis of nanomaterials or with the use of nanotechnologies. Hence, it is impossible to assess the critical properties of nanocomponents via simple techniques described in outdated regulations.

Construction is one of the most large-scale industry in terms of consumed raw materials and production output [8-9]. The potential use of nanocomponents in this industry amounts to one million tons. The lack of regulatory framework to assess the quality of construction nanomaterial composites applied in production is one of the reasons constraining their complex utilization. Thus, one of the most important characteristics of mineral modifiers used as pozzolanic admixture in the production of cement-based materials is their activity. However, the current standards imply only the study of activity of a binder with addition of a modifier. As a result it turns out quite difficult to ensure primary (fast) quality assessment of suggested modifiers excluding labor-intensive production of laboratory cement stone samples with additives. The purpose of this work is to justify the possibility of using unstandardized techniques for complex assessment of their activity.

2. Materials and methods

This paper studies raw materials most widely used in construction, namely sand (silicate raw materials) and granite crushing dust (aluminosilicate raw materials). Three sample parties, different in their production method, were studied to analyze the dependence of activity formed while grinding on the level of mechanical activation and grinding of components:



I – dry single-stage grinding in a ball mill up to $S_{sp}=300-350 \text{ m}^2/\text{kg}$ – classical component (filler) of modern composite binders;

II – wet single-stage grinding in a ball mill (slurry) up to $S_{sp}=300-350 \text{ m}^2/\text{kg}$ – used in cellular product technologies under various curing methods;

II – wet stage-by-stage grinding (in case of sand) or wet single-stage grinding (in case of granite) with further production of a nanostructured modifier (NM) up to the following indicators: sieve residue 0063 – less than 1%, solids concentration – at least 70% – the efficiency of this component as one of the constituting elements of various materials is proved earlier by a group of authors [10-11].

The BET active specific surface was assessed via gas adsorption using the Sorbi device (Russia). The device compares the volume of gas adsorbate, which is adsorbed by a test sample and standardized materials with the given dispersion.

The amount of lime absorbed by active silicon dioxide was estimated by the Zaporozhets's method.

The analysis covered the use of the following: 10 g of the studied substance, 1100 ml of lime whitewash with 1.1-1.2 g CaO/l concentration; HCl 0.05 solution; filter paper; phenol-phthalein; volumetric ware and a pipette. At the initial stage of the experiment it is necessary to define the initial concentration of a solution. To achieve this, the glass container is filled with 1100 ml of the solution, which is then mixed within 10-15 minutes via the electric laboratory mixer. Then 100 ml of the solution is collected via the pipette and is then filtered. Then we add several drops of phenol-phthalein to the collected 50 ml of a filtrate and titrate it with hydrochloric acid. The CaO concentration is defined as follows:

$$C_{CaO} = \frac{758 \cdot A \cdot T}{B}, \quad (2.1)$$

where C_{CaO} – CaO concentration, g/l;

A – HCl amount for titration, ml;

T – HCl titer;

B – amount of the solution collected from a cylindrical container, ml.

We add the entire previously prepared sample of the analyzed additive into the remaining 1000 ml of lime whitewash and continue mixing. Through the given periods we take samples 100 ml each, filter, titrate and calculate the CaO concentration in the solution (according to formula 2.1) in a similar manner described above. The experiment is considered complete when two last measurements are identical.

The amount of absorbed lime of 1 g quartz component from the solution is calculated by subtracting the end measurement of CaO concentration in the solution from its initial concentration, and then the received difference is divided by 10.

The exchange capacity in relation to calcium ions allows defining the number of active Bronsted acidic sites. The following is required for the experiment: 20 g of the analyzed substance; 20 ml of saturated $\text{Ca}(\text{OH})_2$ solution; methyl orange; 0.1 solution of hydrochloric acid; filter paper; distilled water; volumetric ware.

The substance sample is placed in a conic flask with $\text{Ca}(\text{OH})_2$ solution. The container is sealed to exclude air penetration and is then placed in a mixer for 2-4 hours.

Then the suspension is washed with distilled water three times and filtered. Methyl orange is added to 100 ml of a filtrate and titrated with 0.1 solution of hydrochloric acid until the indicator changes its color from yellow to pink.

The number of active Bronsted acidic sites K (mg eq/g) is calculated by the following formula:

$$K = \frac{(V_1 - V_2) \cdot 0.1 \cdot 100}{m} \quad (2.2)$$

where V_1 – acid volume sent for titration with 20 ml of initial $\text{Ca}(\text{OH})_2$ solution (blank test), ml;

V_2 – acid volume sent for solution titration after interacting with a mineral, ml;

m – mineral sample weight, g.

The formation of chemically active bonds on a solids surface of modifying components was assessed via Chemisorb 2750 chemisorption analyzer (Micrometrics, USA) connected to QMS-300 gas quadrupole mass spectrometer (Stanford Research Systems) in the Tomsk Regional Center of Collective Use of Scientific Equipment. The technique includes preliminary drying of samples (annealing at 200 °C within 15 hours) with further removal of any adsorbed substances from the surface of the studied samples with subsequent water sedimentation. Water adsorption was carried out in the isothermic mode at 100 °C thus supplying 3 consecutive 1 mql water pulses to a sample. Then, all samples pass thermoprogrammable water desorption in gas (helium) (heating up to 500 °C at 10 °C/min.).

3. Results and discussion

According to the obtained data (Figure 1), 2 areas of water release may be defined for all samples: 100-250 °C referring to adsorbed water and 250–500 °C referring to chemically bound (structural) water.

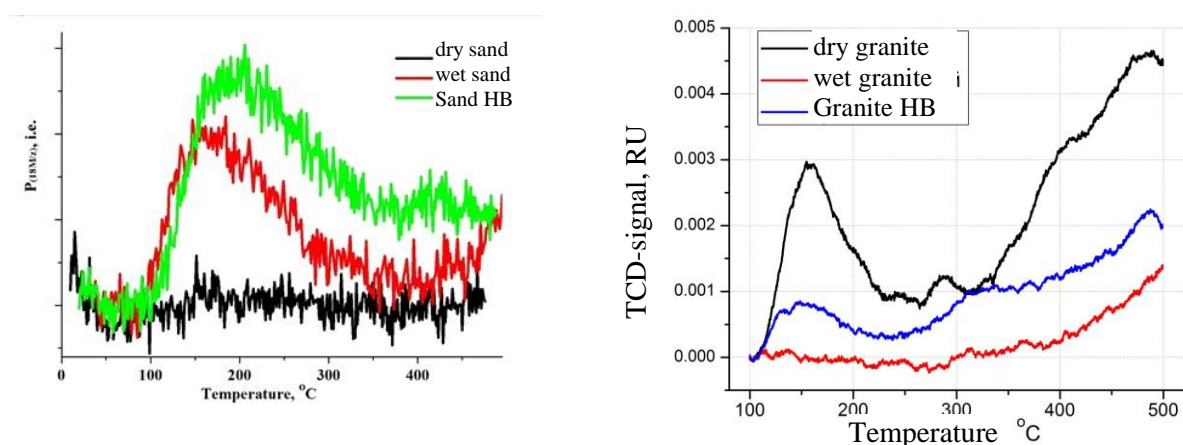


Figure 1. Mass spectrometry of a thermoprogrammable desorption from sample surfaces

The samples obtained by wet grinding to low specific surface are characterized by the smallest amount of desorbing water. It should be noted that these samples are characterized by high-temperature peak of water desorption only, i.e. a sample only contains chemically bound structural water, which was not removed from a sample since it was pre-processed at 200 °C.

Modifier samples are characterized by several water forms: the adsorbed water and at least two forms of chemically bound water (peaks with maxima of 340 and 480 °C).

The easily bound and physically sorbed water is connected with water sorption at functional surface groups, while the strongly bound water is formed at the condensation of these functional groups. The figures below show that the intensity of both peaks is higher for modifier samples, which indicates higher concentration of functional groups on their surface. At the same time it is obvious that the functional groups on sample surfaces lead to reaction capacity not only in relation to water, but also to other chemical compounds.

The obtained data are confirmed by the integrated assessment regarding the activity of mechanoactivated components with different structure and production methods (Table 1).

Table 1. Integrated activity of mechanoactivated silica-containing components

Raw material	Grinding method	Active specific surface, m ² /kg	Number of active Broensted acidic sites, mg·gE	Number of absorbed CaO following the Zaporozhets's method, mg/g
Granite	Dry grinding	3 900	17.2	74
Sand		3 800	21.8	73
Granite	Wet single-stage grinding	8 200	32.4	90
Sand	Wet stage-by-stage grinding	9 100	30.6	81

The specific surface of modifiers exceeds the threshold values reached through dry grinding almost twice. This is explained by the fact that modifiers are obtained through dispersion in water and dispersive medium, which increases the threshold dispersion of initial materials. Besides, a smaller specific surface of granite is explained by the following: polymineral composition of granite contains micaceous minerals, the hardness of which varies within 2-3 according to Mohs scale. First, this leads to grinding of biotite acting as a lubricant between particles of a more solid quartz and field spars reducing the grinding efficiency.

The measurement of optical density of a suspension of dispersed raw materials via the photocolorimeter confirms the double increase of active sites on particle surfaces of solid granite and quartz suspension in comparison with materials crushed by dry grinding.

The study of activity and the results thus obtained make it possible to draw a conclusion on increased activity of modifiers based on aluminosilicate raw materials. Thus, the granite modifier is characterized by hyperactivity in comparison with that of sand (activity in relation to calcium hydroxide is 10% higher). Besides, there is an increase in the composition of an amorphous phase in granite modifier, which is caused by bigger amorphicity of aluminosilicates (field spars, hornblende) and explains higher amount of active sites. This fact may be explained by polymineral nature of a source rock and different hardness of rock-forming minerals. As a result, we get better grindability of raw materials leading to the increase in bonds of a solid phase surface evenly distributed within the volume of a dispersive medium.

4. Conclusions

Thus, the possibility of integrated assessment of activity of mineral modifiers with different structure by unstandardized methods using physical and chemical methods of analysis is confirmed.

It is shown that for source sand samples the water adsorption is not present, which is caused by hydrophobic nature of sand particles, i.e. absence of functional groups on a surface that interact on physical and chemical levels. The water desorption is typical for slurry samples and the modifier, which indicates the hydrophilic properties of a surface, i.e. functional groups appear on a surface that interact on a chemical level, participate in chemical interaction and form hydrogen bonds with water molecules. The presence of functional groups on sample surfaces leads to reaction capacity not only in relation to water, but also to other chemical compounds. This demonstrates the efficiency of mechanical activation of raw materials in water medium thus reducing the grinding period with the increase in the activity ratio of a substance.

The activity of modifying additives caused by genetic features and specifics of production technology is confirmed by high amorphicity (vitreous phase); substantial polydispersity and for aluminosilicate systems – by their polymineral nature. At the same time the substantial polydispersity of obtained suspensions ensures high-density packaging within the system 'binder – modifier' and within composites due to microfilling of formed pores and voids.

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