Structurization of cement systems with nanodispersed silica stabilized with acetate ions

N P Lukutsova, S N Golovin
Department of Production of Building Structures, Bryansk State Engineering and Technology University, 3 Stanke Dimitrov Str., Bryansk 241037, Russia

E-mail: natluk58@mail.ru

Abstract. The influence of a modifying additive in the form of silica sol stabilized with acetate ions on the structure and properties of cement stone has been studied. The mechanism of structure formation in the system of "cement-nanodispersed silica (NDS) stabilized with acetate ions" is proposed. It includes two aspects. In the initial period of hydration the crystallization of calcium hydroacetoaluminates occurs, the rate of their formation being higher than the rate of ettringite formation. Their crystals have some micro-reinforcing effect on cement stone, increasing its density and strength. The nanodisperse silica in combination with the calcium hydroacetoaluminates is directly involved in the structurization of cement stone, colmataging the pores. Si4+ atoms, building-in in the structure of portlandite phases, increase the impermeability of cement stone. The generation of calcium hydroacetoaluminates leads to the formation of the primary carcass, providing the strength development of cement stone in the early stages of hardening. It is established that adding the modifier results in pore redistribution in size: a decline in the amount of macropores and an increase in the quantity of the gel pores and submicropores (5-0.1 µm) at a constant micropore volume (0.1-20 µm).

1. Introduction

One of the directions of properties control of composite building materials of hydration hardening is the application of modifiers based on environmentally friendly [1,2] micro- [3,4] and nanocomponents [5-8] of natural [9-14] and man-made origin [15-17].

The review analysis of literature sources and the studies performed reveals that the cheapest and most effective produce methods of nanomodifiers based on silicon dioxide are sol-gel methods, providing homogeneous particles in size, but not being thermodynamically equilibrium, thus limiting the period of their viability.

Therefore, nanodispersed silicon dioxide in the form of sol stabilized by acetate ions can be referred to more promising for application in composite building materials.

The objective of the work is to study the effect of modifying additives, in the form of silica sol stabilized by acetate ions, on the structure and properties of cement stone.

2. Discussion of results

Nanoparticles with a large specific surface (up to 1000 m²/g) are characterized by chemical activity. They can act as centres accelerating the hydration reaction, as well as, fillers reducing porosity [18].
Silica sol is a non-crystalline condensation nanodispersed structure of metastable solutions. It is characterized by sedimentation and aggregate instability with temperature changes from -10°C to +40°C, leading to the formation of hydrogels, and then xerogels [19].

The synthesis of silica sol as a nanodispersed additive was carried out by chemical polycondensation according to sol gel method.

It is established that gelatinization of silica sol comes at a minimum speed with pH 2.0÷3.0, corresponding to the isoelectric state of silica. The maximum speed of the process falls on the pH of 5.0-7.0. The sol stability is explained not only by the pH area, but also by the nature of the acid. It is known that in the weakly acidic area (pH 3.0÷5.0) the acceleration of gelatinization corresponds to the acid strength, and since CH₃COOH is a weak acid, the gel formation is significantly slowed down, thus ensuring sol stability [20]. The synthesis of silica sol is described by the following equation:

$$\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O} + \text{CH}_3\text{COOH} = 2\text{CH}_3\text{COONa} + \text{H}_2\text{SiO}_3$$  \hspace{1cm} (1)

The additive is a transparent liquid with a density of $\rho=1018$ kg/m³. The concentration of active SiO₂ is 0.23%, the amount of particles of 90-120 nm is 92%.

The studies of the additive with a scanning electron microscope have revealed the particle size and structure of nanodispersed silica. Separate particles of 30-85 nm were recorded due to the analysis of the microstructure of nanodispersed silica.

In the process of sol formation the nucleus growth at one or another stage can be suspended by the creation of the so-called adsorption layer of acetate ions as stabilizer’s ions. The positively charged nucleus attracts the counter-ions CH₃COO left in the solution. At that, some counter-ions are in the adsorption layer, the others are in the diffuse layer [21]. The analysis of dispersion change of the nano-additive suggests that its activity remains for 14 days, as evidenced by 90-94% of non-polymerized forms of nanosilica ranging in size from 20 to 100 nm.

The byproduct of silica sol production is sodium acetate, which is part of the mother liquor. The interaction of calcium hydroxide with sodium acetate results in calcium acetate. Calcium acetates and other calcium salts belong to the group of additives entering into an addition reaction with binders and forming hydrates being sparingly soluble mixed salts. The interaction of calcium hydroxide with sodium acetate follows by the reaction:

$$\text{Ca(OH)}_2 + 2\text{CH}_3\text{COONa} = \text{Ca(CH}_3\text{COO)}_2 + 2\text{NaOH}$$  \hspace{1cm} (2)

The interaction of tricalcium aluminate with calcium acetate leads to the formation of an insoluble hydrated salt:

$$3\text{CaO} \cdot \text{Al}_2\text{O}_3 + \text{Ca(Ch}_3\text{COO)}_2 + 10\text{H}_2\text{O} = 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Ca(CH}_3\text{COO)}_2 \cdot 10\text{H}_2\text{O}$$  \hspace{1cm} (3)

The interaction of alite with calcium hydroxide and subsequent hydration results in a polymer mixed hydrated salt. Its formation can be simplified by the oxygen transition from donor-acceptor bonding to calcium ion bonding, being its stable state.

Dicalcium silicate interacts with calcium acetate by the reaction:

$$2\text{CaO} \cdot \text{SiO}_2 + \text{Ca(Ch}_3\text{COO)}_2 + 10\text{H}_2\text{O} = 2\text{CaO} \cdot \text{SiO}_2 \cdot \text{Ca(CH}_3\text{COO)}_2 \cdot 10\text{H}_2\text{O}$$  \hspace{1cm} (4)

The interaction of tricalcium aluminate with calcium acetate, acting as the initiator of crystallization, results in the formation of calcium hydroacetoaluminates.

Four-calcium aluminoferrite reacts with calcium acetate. The reaction below describes the process:

$$4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3 + \text{Ca(Ch}_3\text{COO)}_2 + 10\text{H}_2\text{O} =$$

$$=4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3 \cdot \text{Ca(CH}_3\text{COO)}_2 \cdot 10\text{H}_2\text{O}$$  \hspace{1cm} (5)
In the initial period of hydration, the crystallization rate of calcium hydroacetoaluminates and hydroacetosilicate is above the rate of ettringite formation. Needle-shaped crystals of these formations have a micro-reinforcing effect on cement stone, increasing its strength.

3. Experimental part

The following raw materials were taken to prepare concrete mix: standard plain normally hardening Portland cement CEM I 42.5N according to GOST 31108 "Belarusian cement plant" (Kostyukovichi, Belarus); pit sand with 1.2 fineness modulus (Polpino deposit, Bryansk district), and water. The diluent S-3 (TU 5745-001-97474489-2007) based on sulfonated naphthaleneformaldehyde was used as a super plasticizer.

The silica sol stabilized with acetate-ions was added into the composition of cement paste.

The study of microstructure and particle size of silicon dioxide was performed with a scanning electron microscope TESCAN MIRA 3 LMU. X-ray phase analysis was carried out with diffract meter ARL X’TRA (Thermo Scientific company). The porosity was studied with mercury porosimeter AutoPore IV 9500.

The properties of the cement stone were investigated on test cubes of 20×20×20 mm. The samples become hard under natural conditions at t=20±2°C and a humidity of 95-100%.

The studies of the hydration degree and pore structure of the modified cement stone (Table 1) showed that the introduction of nanodispersed silica modifier into the cement stone leads to a decrease in the total porosity of the cement stone from 22% to 18% and to a change in the ratio between the gel (1 nm<d<5 nm), capillary (5 nm<d<20 microns) and technological (20 µm <d<1000 µm) pores. The modifier introduction results in pore redistribution in size: a decrease in the macropores proportion and an increase in the amount of the gel pores and submicropores (5-0.1 µm) at a constant micropore volume (0.1-20 µm).

| Composition          | Content of pores in size,% | Hydration degree, % |
|----------------------|-----------------------------|---------------------|
|                      | 1-5 nm | 5 nm-0.1 µm | 0.1-20 µm | 20-1000 µm |
| Control composition  | 9.4    | 16.2        | 1.6       | 6.2        | 64.3 |
| Cement stone +NDS 0.23% | 14.1 | 18.6        | 1.3       | 2.4        | 69.2 |
| Cement stone + NDS 0.46% | 15.5 | 18.7        | 1.3       | 2.7        | 70.1 |

The qualitative and quantitative phase analysis by the Rietveld method has established a decrease in the intensity of portlandite reflection in the modified samples by 14% (0.491; 0.263; 0.275; 0.270 nm), an increase in the intensity of ettringite reflection by 8% (0.981; 0.386; 0.257; 0.562 nm) and an increase in the reflection of calcium hydrosilicates of CSH type as compared with the control sample (0.126; 0.1184; 0.102; 0.307 nm). Unlike the modified sample, in the control one the reflection of monohydrusulfoaluminate (0.893 nm) was recorded, indicating a partial ettringite recrystallization.

Silica sol in combination with the calcium hydroacetoaluminates is directly involved in the structure formation of cement stone, colmataging the pores (Figure 1,2) and increasing the density and impermeability of concrete. It also leads to the formation of the primary carcass, providing the strength development of cement stone in the early stages of hardening.

It is established that the best indicators of compressive and bending strength after 28 days of hardening are typical of the samples with nanodispersed silica additives at the age of 3 and 7 days of storage. The analysis of changes in the physical and mechanical properties of cement stone with
nanodispersed silica stabilized with acetate ions with hardening for 2 years indicates an additional increase in strength by 22%.

The strength results obtained are consistent with the study findings of the structure parameters of cement stone samples.

4. Conclusions
The influence of modifying additive in the form of silica sol stabilized with acetate ions on the structure and properties of cement stone was investigated.

The mechanism of structure formation in the system of "cement-nanodispersed silica stabilized with acetate ions" is proposed. It includes two aspects. In the initial period of hydration the crystallization of calcium hydroacetoaluminates occurs, the rate of their formation being higher than the rate of ettringite formation. Nanodisperse silica in combination with the calcium hydroacetoaluminates is directly involved in the structure formation of cement stone, colmataging the pores. Si⁴⁺ atoms, building-in in the structure of portlandite phases, increase the impermeability of cement stone. The generation of calcium hydroacetoaluminates leads to the formation of the primary carcass, providing the strength development of cement stone in the early stages of hardening.

It is established that the application of the modifier results in some pore redistribution in size: a decline in the amount of macropores and an increase in the amount of the gel pores and submicropores (5-0.1 µm) at a constant micropore volume (0.1-20 µm).

The qualitative and quantitative phase analysis by the Rietveld method has revealed a decrease in the intensity of portlandite reflection in the modified samples by 14%, an increase in the intensity of ettringite reflection by 8% and an increase in the reflection of calcium hydrosilicates of CSH type as compared with the control sample.

It is established that the best indicators of compressive and bending strength after 28 days of hardening are typical of the samples with nanodispersed silica additives at the age of 3 and 7 days of storage.

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