Effect of Nano-Aluminum Component on the Cement Properties

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Abstract. The possibility of using a nano-aluminum component in the cement composition has been considered. To ensure uniform distribution of the nano-aluminum component throughout the cement matrix, its suspension was stabilized using a sulfonaphthalene formaldehyde-based plasticizer and acoustic cavitation. It has been established that the nano-Al₂O₃ suspension is best stabilized when adding a plasticizer in an amount of 3-5 g/l and after an acoustic exposure at the optimal dispersion parameters: dispersion temperature–25±2 °C (the process is thermostated); dispersion time–20 minutes; and oscillation frequency–44 kHz. The study has shown that the compositions modified with a nano-aluminum component have improved strength and structural properties. On the first day of hardening, the compressive strength of the modified specimens increased by 20-24 % and at the grade age–by 31-35 % compared to the reference one. Introducing the stabilized nano-Al₂O₃ particles reduces the porosity for the first day of hardening by 12-13 % and at the grade age–by 27-29 %. It is recommended to add a nano-aluminum component as a stabilized suspension in an amount of 0.5-1.0 g/l to the cement composition.

1. Introduction

Currently, much attention is paid to the development of nanotechnology in various fields of science and engineering. Promising nanodispersed materials include nanocomposites based on aluminum compounds [1-7].

Most often, nanosized particles of aluminum oxides and hydroxides are used in the manufacture of ceramic products, refractory materials, and polymers [8, 9]. E.g., to combine the low-temperature processability of the organic polymer matrix (at a temperature of <250 °C) with the desired dielectric properties of the filler, the authors of [8] have developed a polymer/aluminum nanocomposite having the characteristics of both polymer-ceramic and polymer-metal systems. A self-passivated aluminum particle with a core-shell structure (metallic aluminum-alumina) was anchored to the polymer using an epoxy-functionalized silane binder, which contributed to an increase in the dielectric constant and processability of the resulting nanocomposite.

The authors of [9] have shown that introducing nano-alumina improves the properties of the refractory ceramic composite MgO-C. It has been noted that the specimens containing nano-Al₂O₃ have better properties compared to those containing micro-Al₂O₃.

For the manufacture of medical materials with high biocompatibility, a chemically homogeneous composite powder based on graphene and nano-alumina is used [10].
For the cement industry, nanosized aluminum compounds are also of interest [11-14]. E.g., in [11], it is shown that the inclusion of nano-SiO$_2$ and nano-Al$_2$O$_3$ in cement at low relative humidity (60%) and air pressure (50 kPa, 60 kPa, 70 kPa) contributes to the microstructure compaction, the increase in the cement hydration degree, and the improvement of flexural and compressive strength, in contrast to specimens free of nanocomponents. The authors of [12] studied the effect of Nano-SiO$_2$, Nano-TiO$_2$, and Nano-Al$_2$O$_3$ additives on the fluid loss in cement slurry in an oil well. The research was performed at 70, 80, and 90 °C and a gas pressure of 7 MPa. It has been found that adding Nano-SiO$_2$, Nano-TiO$_2$, and Nano-Al$_2$O$_3$ particles independently of each other reduced the fluid loss in the cement. The decrease in water filtration can be explained by the ability of nanoparticles to fill the pores in the cement slurry matrix. It has also been established that nanoparticles accelerate the generation of hydration products by creating dense blocking C-S-H gels between cement grains, due to which a closed structure is formed, preventing the fluid from leaving the suspension. In [13], the resistance of cement pastes containing Al$_2$O$_3$ nanoparticles to physicochemical effects and high temperatures has been studied. It has been found that the addition of nano-diamonds increases the compressive strength and fire resistance. In [14], microscopic images are given, reflecting the denser microstructure of a cement stone formed when adding nano-Al$_2$O$_3$ is to the composition of cement pastes.

The studies by many scholars have shown the relevance of using nanosized alumina in the composition of various materials, including cements. However, the introduction of nanosized particles into a cement matrix has some difficulties associated with their uneven distribution throughout the material. The authors of [15-18] performed research on stabilizing nanocarbon tubes in an aqueous dispersion medium using combined chemical and physical effects. To stabilize nanoparticles, plasticizing additives (chemical effect) have been used, which have found wide application in the manufacture of building materials [19-22]. The physical effect was an acoustic cavitation of a polymer-aqueous suspension of nanotubes. The specimens containing stabilized nanotubes have shown improved strength and structural properties [15-18].

Based on the above, herein, it is planned to study:
- stabilizing a suspension of nano-Al$_2$O$_3$ using chemical and physical effects to ensure uniform distribution of nanoparticles throughout the cement composite,
- a cement stone containing stabilized nano-Al$_2$O$_3$ particles.

2. Materials and techniques

As the study object, modified Portland cement and a stabilized suspension based on nano-Al$_2$O$_3$ were used.

As the source materials, additive-free Portland cement (PC), a sulfonaphthalene formaldehyde-based plasticizer (R-SO$_3$-Na), and nano-Al$_2$O$_3$ with an average grain size of 60 nm were used.

To introduce nanodispersed alumina into the Portland cement composition, suspensions were prepared using the acoustic cavitation technique. To ensure maximum dispersion of nanodispersed particles, the optimal dispersion parameters were chosen: dispersion temperature – 25±2 °C (the process is thermostated); dispersion time – 20 minutes; and oscillation frequency – 44 kHz.

A plasticizer was used as a stabilizer for aqueous suspensions of nano-Al$_2$O$_3$. The stabilizing effect of the plasticizer on the nano-Al$_2$O$_3$ suspension has been studied. The plasticizer with a concentration of 2 g/L in an amount of 0.1-1.0, 1.0-2.5, and 3-5 g/L was added to the aqueous suspension of nano-Al$_2$O$_3$ at a pitch of 0.2, 0.5, and 1 g/L, respectively. The protective factor indicating the protective effect of the stabilizer on the suspension was determined by the formula [16]:

$$S = \frac{C_s V_s}{V},$$

where $S$ is the protective factor, g/L; $C_s$ is the stabilizer concentration, g/L; $V_s$ is the stabilizer solution volume, ml; $V$ is the suspension volume, ml. The calculation and observation results are given in Table 1.
followed, which give it a positive charge. This allows 

\[ \text{pH} \text{can be explained as follows.} \]

\[ \text{3. Results and discussion} \]

To determine the nanosized aluminum component effect on the properties of cement compositions, the construction properties of cements have been studied, compressive strength tests performed, and the degree of hydration and porosity of specimens defined. The construction properties of the specimens are given in Table 2.

**Table 1. Aggregate Stability of Water-Polymer Nano-Al<sub>2</sub>O<sub>3</sub> Suspensions.**

| Plasticizer concentration, g/L | 0.1 | 0.2 | 0.4 | 0.6 | 0.8 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 4.0 | 5.0 |
|-------------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Suspension protective factor, *10<sup>-3</sup> g/L | 0.01 | 0.04 | 0.16 | 0.361 | 0.64 | 1 | 2.25 | 4 | 6.25 | 9 | 16 | 25 |
| Aggregate nano-Al<sub>2</sub>O<sub>3</sub> suspension stability, h | 7 | 7 | 8 | 9 | 10 | 12 | 16 | 24 | 36 | 48 | >48 | >48 |

The tabular data allow estimating the stabilizing effect of the plasticizing additive. It has been determined that to achieve stability of the nano-Al<sub>2</sub>O<sub>3</sub> suspension, the plasticizer should be added in an amount of 3-5 g/L.

The construction and physicomechanical characteristics of cements were determined according to the national standard GOST 30744-2001. The porosity of the specimens was determined by the volume-weight pycnometry.

**Table 2. Construction Properties of Cements.**

| Item No. | Specimen | Concentration of finely dispersed slag (g/L) | Normal density (%) | Setting Time (h-min) start | end |
|----------|----------|-----------------------------------------------|--------------------|--------------------------|-----|
| 1        | PC       | -                                             | 25.5               | 2-50                     | 3-40|
| 2        | PC + plasticizer* | - | 23.0 | 2-40 | 3-30 |
| 3        | PC + nano-aluminum suspension* | 0.5 | 21.5 | 3-05 | 4-40 |
| 4        | PC + nano-aluminum suspension* | 1.0 | 21.5 | 3-10 | 4-45 |
| 5        | PC + nano-aluminum suspension* | 1.5 | 21.0 | 3-15 | 4-50 |
| 6        | PC + nano-aluminum suspension* | 2.0 | 20.5 | 3-20 | 5-00 |

*The plasticizer concentration is 5 g/L.

The data in Table 2 show that when adding a plasticizer to specimens with nano-Al<sub>2</sub>O<sub>3</sub>, a decrease in the water requirement of the cement paste and a slowdown in setting are observed. The water requirement decreased by 6.5-11 % and the slowdown in the start and end of setting was 16-25 and 33-43 %, respectively, compared to the specimen containing the plasticizer. The slowdown in setting can be explained as follows. In the humid air and an aqueous dispersion medium, the nano-Al<sub>2</sub>O<sub>3</sub> particles are hydrated and hydroxylated. On the surface of nano-Al<sub>2</sub>O<sub>3</sub> particles, hydroxyl ions are formed, which give it a positive charge. This allows writing the nano-Al<sub>2</sub>O<sub>3</sub> micelle formula as follows:

\[
\{ \text{m[Al}_2\text{O}_3\cdot y\text{H}_2\text{O}]\cdot \text{nAl(OH)}_2^{\text{z}^-}\cdot (\text{n-x}) \text{OH}^- \}^{\text{z}^-}\cdot \text{xOH}^-. \quad (2)
\]

or

\[
\{ \text{m[Al(OH)}_3\text{]}\cdot \text{nAl(OH)}_2^{\text{z}^-}\cdot (\text{n-x}) \text{OH}^- \}^{\text{z}^-}\cdot \text{xOH}^-. \quad (3)
\]

When adding a plasticizer, the below chemical reaction occurs:

\[
\text{Al(OH)}_2^{\text{z}^-} + \text{OH}^- + \text{R-SO}_3\text{Na} \rightarrow \text{Al(OH)}_2\text{-OSO}_2\text{-R+NaOH}. \quad (4)
\]
As a result, nano-\( \text{Al}_2\text{O}_3 \) particles stabilized by the plasticizer acquire a negative charge:

\[
\{ m[\text{Al(OH)}_2\text{-OSO}_2\cdot R]\cdot n\text{R-SO}_3\cdot (n-x) \text{Al(OH)}_2^+ \}\cdot x \text{Al(OH)}_2^+
\]  

(5)

Hydrated cement grains also have a negative surface charge due to the hydrolysis on the cement grain surface [18].

Thus, the negatively charged stabilized nano-\( \text{Al}_2\text{O}_3 \) particle and hydrated cement grain repel one another, causing a slowdown in the specimen setting and an increased fluidity of the cement paste.

With further hydration, the shell of hydrated neoplasms on the cement particle surface acquires a positive charge due to the accumulation of \( \text{Ca}^{2+} \) ions in it. Stabilized nano-\( \text{Al}_2\text{O}_3 \) particles are attracted with their anionic part to hydrated cement ones, thereby reinforcing the cement matrix. With further hydration, the reinforcing frame becomes surrounded with crystalline hydrates causing the formation of a durable and dense cement stone, which is confirmed by the specimen tests shown in Fig. 1.

\[
\begin{align*}
\text{Dependence of Physicomechanical and Structural Properties on the Specimen Hydration Time} & \text{(1-6 specimens according to Table 2):} \\
& \text{a) 1 day of hardening; b) 3 days of hardening; c) 7 days of hardening; d) 28 days of hardening.}
\end{align*}
\]

The results of physicomechanical tests showed that adding a stabilized suspension based on nano-\( \text{Al}_2\text{O}_3 \) to the cement composition contributed to an increase in compressive strength at all times of hardening. However, it has been found that adding a nano-aluminum component in the amount of 1.5-2.0 g/L (specimens Nos. 5 & 6) is inappropriate since in this case, the properties under study are inferior to those of specimens containing 0.5-1.0 g/l of this component (specimens Nos. 3 & 4). The compressive strength of specimens Nos. 3 & 4 increased by 20-24, 25-29, 24-29, and 31-35 % for 1, 3, 7, and 28 days of hardening, respectively, compared to the reference specimen. When studying the structure of a cement stone containing a complex additive, an increase in the hydration degree and a decrease in porosity of the specimens were also noted at all times of hardening. Porosity of specimens Nos. 3 & 4 reduced by 12-13, 16-18, 20-22, and 27-29 % for 1, 3, 7, and 28 days of hardening, respectively.

\[
\begin{align*}
\text{Figure 1.} & \text{ Dependence of Physicomechanical and Structural Properties on the Specimen Hydration Time (1-6 specimens according to Table 2):} \\
& \text{a) 1 day of hardening; b) 3 days of hardening; c) 7 days of hardening; d) 28 days of hardening.}
\end{align*}
\]
The research results have shown that due to prolonged hydration, self-reinforcement processes occur in the system, accompanied by the formation of crystalline hydrates participating in building a dense and durable cement stone structure, which allows using the stabilized nano-Al₂O₃ suspensions in the manufacture of cement compositions and products.

4. Conclusions
The study has shown that the compositions modified with a nano-aluminum component have improved strength and structural properties.

To ensure the stabilization of the nano-aluminum component and its uniform distribution throughout the cement system, nano-Al₂O₃ particles were exposed to physical and chemical effects in an aqueous dispersion medium. The physical effect comprised processing the nano-Al₂O₃ suspension by acoustic cavitation at optimal dispersion parameters: dispersion temperature – 25±2 °C (the process is thermostated); dispersion time – 20 minutes; and oscillation frequency – 44 kHz. The chemical effect was ensured by introducing the plasticizing additives into the aqueous nano-Al₂O₃ suspension. It has been determined that to ensure maximum stabilization of nano-Al₂O₃ particles in the suspension, the sulfonaphthalene formaldehyde-based plasticizer should be added in an amount of 3.5 g/L.

When studying the construction properties of the cement paste, it has been found that the water requirement decreases by 6.5-11 % and the slowdown in the start and end of setting is 16-25 and 33-43 %, respectively, compared to the reference specimen. The slowdown in setting is explained by the mutual repulsion of the stabilized nano-Al₂O₃ particles and hydrated cement ones at the initial moment of hydration.

It has been determined that to ensure improved physicomechanical and structural properties of the cement stone, it is recommended to add a nano-aluminum component in the amount of 0.5-1 g/L. On the first day of hardening, the compressive strength of the modified specimens increased by 20-24 % and at the grade age – by 31-35 % compared to the reference specimen. Adding the stabilized nano-Al₂O₃ particles ensured a decrease in porosity for the first day of hardening by 12-13 % and at the grade age – by 27-29 %.

The studies confirm the uniform distribution of nano-Al₂O₃ particles stabilized by the plasticizer and acoustic cavitation throughout the cement matrix. As a result of prolonged hydration, in a cement system with a nano-aluminum component, self-reinforcement processes occur, accompanied by the formation of crystalline hydrates participating in building a dense and durable cement stone structure. Thus, the studies testify to the possibility of using stabilized nano-Al₂O₃ suspensions in the manufacture of cement compositions and products.

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