Portland cement hydration and early setting of cement stone intended for efficient paving materials

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Abstract. Due to the growth of load on automotive roads, modern transportation engineering is in need of efficient paving materials. Runways and most advanced highways require Portland cement concretes. This makes important the studies directed to improvement of binders for such concretes. In the present work some peculiarities of the process of Portland cement hydration and early setting of cement stone with barium hydrosilicate sol were examined. It was found that the admixture of said sol leads to a shift in the induction period to later times without significant change in its duration. The admixture of a modifier with nanoscale barium hydrosilicates increases the degree of hydration of the cement clinker minerals and changes the phase composition of the hydration products; in particular, the content of portlandite and tricalcium silicate decreases, while the amount of ettringite increases. Changes in the hydration processes of Portland cement and early setting of cement stone that are caused by the nanoscale barium hydrosilicates, allow to forecast positive technological effects both at the stage of manufacturing and at the stage of operation. In particular, the formwork age can be reduced, turnover of molds can be increased, formation of secondary ettringite and corrosion of the first type can be eliminated.

1. Introduction

Currently, both constant growth of road traffic and increasing in load on highways are observed. Due to this, modern transportation engineering is in need of efficient paving materials. Till present, the most of such materials are based on asphalts as binders. However, traditional asphalt concreted cannot be characterized by extreme operational properties. Because of this, runways and most advanced highways require Portland cement concretes. At the same time, high cost of production of Portland cement, as well as environmental impacts (CO₂ emission are 0.83 tons per 1 ton of Portland cement produced [1]) make important the studies directed to improvement of binders for Portland cement concretes. A number of researchers have shown the efficiency of various nanoscale modifiers of cement systems [2-8]. The barium hydrosilicate sols (nBHS) that are the reaction product between silica sol synthesized in the presence of iron hydroxide and water-soluble barium salt [9-10], are the example of such modifiers. The efficiency of modification is due to increase of the strength of cement stone [11]. In addition, the delay in the setting time of the cement paste modified with nBHS is noted in [12].

However, the reasons causing the positive phenomena and explanations of the effect of nBHS on the hydration of portland cement still not investigated. Both shift in the setting time (that is an indicator of the influence of nBHS on early structure formation) and change in the mechanical properties of the cement stone, indicate a change in the hydration kinetics, as well as the phase
composition of the Portland cement hydration products. The change in the phase composition of the cement stone has a natural effect on the durability of products. Hence, it is advisable to establish the peculiarities of the influence of various nBHS on the hydration processes of Portland cement and phase composition of nanomodified cement stone.

2. Materials and methods
The ordinary Portland cement by RU GOST 31108-2003 was used during experiments.

Two compositions of nanoscale modifiers were used; the first was of gross formula BaO\( \cdot \)17.99SiO\(_2\)\( \cdot \)nH\(_2\)O, the second was BaO\( \cdot \)26.47SiO\(_2\)\( \cdot \)nH\(_2\)O. Detailed description of the preparation process was previously given in [13].

A study of the effect of nBHS on Portland cement hydration was carried out by analyzing the heat release kinetics on an 8-channel TAMAir calorimeter in adiabatic mode during 72 hours. The proper amounts of Portland cement were mixed with water or with nBHS colloidal solution. The water/cement ratio was 0.5. Mixing was 1 minute long.

Investigation of the phase composition of hydration products and the degree of hydration was carried out by wide angle X-Ray scattering (WAXS) method. The sampling is carried out at 12, 17 and 72 hours from the moment of mixing. To remove the water and stop the hydration process the acetone was used [14]. Samples were abraded in an agate mortar together with 2 ml of acetone and then placed in a desiccator for drying to constant weight. The diffraction patterns were recorded with help of ARL X‘tra device in the range of angles 2\( \Theta \)=10-43\(^\circ\), in a step-by-step mode (step was 0.02\(^\circ\)) and exposure time of 1 second.

3. Results and discussion
The amount and rate of heat flux during very early stage of hydration (5-8 minutes) depend on wettability of cement by the liquid that is used for tempering (either water or nBHS colloidal solution). Low wettability leads to low homogeneity and slow hydration.

For Portland cement with water, the maximum heat release is observed at 9 minutes. The use of nBHS colloidal solution leads to a shift in the heat release to earlier time (5 and 8 minutes). The shift of the hydration maximum for 1 minute is insignificant; however, a decrease in the maximum of heat release is also observed (figure 1). In general, the heat flux is close in value to the control composition; therefore, nBHS does not significantly affect the wetting of the binder. After the wetting period, an induction period follows. The intensity of this period in case of nBHS changes significantly, while its duration is mostly preserved (figure 2).

![Figure 1](image-url)  
Figure 1. Heat flux at early stage of hydration: 1 – with nBHS #1; 2 – with nBHS #2; 3 – with water.
The slowing down of Portland cement hydration in the presence of nBHS is probably due to the blocking of the surface of clinker minerals during the initial hydration. However, the duration of the induction period is preserved; therefore, the strength of shells with hydration products on the surface of Portland cement grains that are formed during the initial hydration period is comparable to the strength of the shells in the control composition with water.

**Figure 2.** Hydration during induction period: 1 – with nBHS #1; 2 – with nBHS #2; 3 – with water.

Early structure formation of cement stone that depends on the concentration and mechanical characteristics of the products of Portland cement hydration, is usually characterized by technological properties – setting time (which indicates the duration of the structure formation with the required strength). Since the induction period is delayed, the setting of the nanomodified cement also occurs later. In addition, there is an increase of duration between the end of the induction period and the start of setting period, as well as between the start and end of setting. This indicates a slowdown of the structure formation of cement stone with the required strength, and consequently, indicates formation of a smaller amount of hydration products. Also, often at a slow rate of crystal formation, a large-crystalline structure of the material is formed, which is less susceptible to recrystallization. Such materials retain their mechanical properties for a long time without changes.

To evaluate the degree of hydration of Portland cement it is possible to analyze the change of the content of clinker minerals during the hydration process.

To determine the effect of nBHS on the hydration of tricalcium aluminate (C₃A) and alite (C₃S), it is useful to analyze differential and integral heat dissipation curves (figures 3 and 4). Hydration of the primary minerals of cement clinker is accompanied by the high heat release. Analysis of the differential heat dissipation curves (figure 3) shows that the use of the nanomodifier leads to an increase in the degree of hydration of the clinker minerals (C₃A and C₃S). These data are also confirmed by integral heat dissipation curves of the cement paste (figure 4) that indicate an increase in the degree of hydration of the C₃A and C₃S.
Figure 3. Differential thermal curves: 1 – with nBHS #1; 2 – with nBHS #2; 3 – with water.

Figure 4. Integral thermal curves: 1 – with nBHS #1; 2 – with nBHS #2; 3 – with water.

As it follows from figures 3 and 4, the use of nBHS does not affect the C₃A hydration time and has a different effect on the hydration of C₃S (accelerating or slowing hydration depending on the composition of the nanomodifier). At the same time, on the whole, the amount of Portland cement that has been hydrated increases, mostly for nBHS with the composition BaO•17.99SiO₂•nH₂O.

The degree of hydration of C₃S can be determined by the analysis of Ca(OH)₂ amount (the increase) and content of C₃S (the decrease). For C₃A – it can be determined by the analysis of C₂AN₈ and C₄AH₆ content during initial stages and C₃AN₆ content during the subsequent ones, provided that these products are not chemically transformed. X-ray phase analysis data (figures 5 and 6, where: E – ettringite, P – portlandite, A – alite, B – belite, Al –aluminate phase) shows that the content of ettringite, portlandite, belite and aluminate phase does not change significantly in the phase composition of cement stone modified with nBHS #1 in the initial period (12 and 17 hours).
The content of alite after 12 hours of hydration in the composition that is modified by nBHS #1 is higher than in the control composition. That is consistent with the established phenomenon of shift of the induction period at a later time (figure 2). However, after 17 hours, the alite content is significantly reduced (by 20.8-31.0%), while no new peaks on the WAXS data are observed. Hydration of the alite is accompanied by the formation of calcium hydrosilicates, and the lack of their peaks may indicate the formation of amorphous or slightly crystallized products.

Significant differences in the phase composition are observed after 72 hours of hydration: an increase in the content of ettringite and portlandite occurs. It should be noted that the formation of ettringite, according to [15-18], is accompanied by the formation of a solid solution in an alkaline medium and by the binding of calcium hydroxide. In this case, during the topochemical reaction of crystallization of ettringite, calcium hydroxide is formed. However, the amount of bound portlandite is much higher. This indicates that portlandite is bound to newly formed chemicals. Taking into account absence of new WAXS peaks, it is likely that these chemicals are amorphous or slightly crystalline.

Figure 5. WAXS data for control sample (no nBHS).
The alite content after 72 hours of hardening in the nanomodified composition is higher by 31.6%. However, it should be noted that with the admixture of nBHS the hydration of alite occurs mainly up to 17 hours; for control composition it occurs after 17 hours. Hence, nBHS accelerates the hydration of the alite, despite the shift of the induction period to later times. This can be explained by the composition of nBHS. It is known that silicic acid slows the hydration of cement [19], while the iron (III) hydroxide sol is intensified it. In addition, a significant decrease in the content of portlandite is possible when it is bound by silicic acid to calcium hydrosilicates [20, 21]. The calcium hydrosilicates crystallize at later period, so they are not identified in the WAXS data.

4. Conclusions
It is shown during experimental research that the use of nBHS nanoscale modifier does not significantly affects the wettability of Portland cement particles. The surface of these particles is still blocked, and that leads to a shift of the induction period to later times, while the duration of induction period is mostly the same. The admixture of nBHS increases the degree of hydration of C₃A and C₃S
and also changes the hydration mechanism – intensification of C₃S hydration is observed. The change in the hydration mechanism affects the chemical composition of the cement stone at the age of 72 hours. With the admixture of nBHS, an increase in the content of the primary ettringite and a decrease in the content of portlandite are observed.

Changes in the hydration processes of Portland cement and early setting of cement stone that are caused by the nanoscale barium hydrosilicates, allow to forecast positive technological effects both at the stage of manufacturing and at the stage of operation. In particular, the formwork age can be reduced, turnover of molds can be increased, formation of secondary ettringite and corrosion of the first type can be eliminated.

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