Studying the processes of early structure formation of a modified cement paste

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Abstract. The article touches the structure formation process studying of cement paste by the results of heat evolution measuring. The features of early structure formation of cement samples obtained with the use of mineral admixture - pre-hydrated cement slurry, chemical admixture S-3 and their complex use are considered. Normal consistencies of cement specimens were compared. The intensification of heat evolution by cement specimens using a mineral additive is detected. The benefit of complex admixture has been revealed.

1. Introduction
Currently, additives are widely used to modify the properties of concrete and mortars. Obtaining modifiers from production wastes is an urgent task. One of these wastes is concrete slurry from washing system at concrete plants.

Aggregates and cement pulp are easily separating from each other by modern recycling system. An important problem is how dispose cement pulp from the settling tanks of recycling system. From the point of obtaining modifying additives for concrete this cement pulp is an interesting substance. Its phase and fractional composition changing in time due to continued processes of hydrations, which suggest additional studies for making recommendations. In view of the size of the crystals of hydrosilicates and other hydration products sized in several hundred nanometers, this type of admixture can be classified as a nanomodifier [1].

It should be noted that complex of admixtures is more effectually than one. In complex admixtures can neutralize the negative effects of each other and significantly change the properties of concrete [2,3]. Together with mineral additive based on cement pulp, it is proposed to use S-3 superplasticizer.

The study of structure formation is a process that requires lengthy research and expensive scientific equipment. However, some structure formation processes on the early stages can be investigated and predicted using indirect methods. One of these methods is the measurement of heat evolution [4,5]. It is based on an analysis of the processes occurring during hydration and hardening of cement samples by measuring the kinetics of heat evolution.
2. Materials and methods

2.1. Cement
To study the processes of early structure formation of the modified cement paste, Portland cement (CEM I 42.5 H) manufactured at the AO “Podolsk-Cement” plant was used. The elemental and mineralogical compositions of clinker are presented in tables 1,2.

Table 1. Elemental composition of clinker AO “Podolsk-Cement”.

| Element loss on ignition | CaO | SiO₂ | Al₂O₃ | Fe₂O₃ | MgO | SO₃ | R₂O |
|--------------------------|-----|------|-------|-------|-----|-----|-----|
| clinker                  | 0,92| 62,75| 20,10 | 4,56  | 8,72| 1,99| 0,57|
|                          |     | 62,75| 20,10 | 4,56  | 8,72| 1,99| 0,57| 1,58|

Table 2. Mineralogical compositions of clinker AO “Podolsk-Cement”.

| C₃S, %      | C₂S, % | C₃A, % | C₄AF, % |
|-------------|--------|--------|---------|
| 60,00       | 12,00  | 3,00   | 21,00   |

2.2. Admixtures
As modifiers a mineral admixture of pre-hydrated pulp of cement and a chemical - superplasticizer S-3 was used.

A pre-hydrated cement pulp or a pre-hydrated admixture (PHA) was obtained by hydrating the cement at a water-cement ratio equals to 0.7. According to previous researches, this admixture includes calcium hydrosilicates and other hydration products that had already reacted or were at later stages of hydration.

Previously was established that hydrated shell on the cement particles begins to form by 6 hours of hydration. It is assumed that such a hydrated state of particles and the presence of hydration products when mixed together with water will accelerate emergence of the primary rigid bonds, change the kinetics of hardening, and increase the density and ultimate strength of cement specimens.

2.3. Specimens producing.
For studies, cement paste specimens of normal density was made. The following mixtures were used:

«Control» mixture was made from Portland cement without admixtures.

«S-3 1%» - mixture differs from the control by adding superplasticizer S-3 in quantity equals 1% by quantity of cement for control mixture (calculated on dry matters). Superplasticizer S-3 was mixed with the required amount of mixing water.

«PHA6 10%» - mixture differs from the control by adding PHA in quantity equals 10% by quantity of cement for control mixture (calculated on dry matters).

«PHA6 10% + C-3 1%» - mixture obtained by the combined introduction of water attenuation of PHA6 and C-3 in the amount of 10% and 1%, respectively.

To prepare mineral admixture the moisture capacity of cement was mixed with water in a ratio of 0.7. Pre-hydration took 6 hours with periodic forced intervention to exclude thickening and setting. After obtaining the pre-hydration with the obtained admixture, it was necessary to mixed with mixing water.

2.4. Normal consistency and heat evolution measurement methodologies
Normal consistency was determined in according with the current standard (GOST 310.3-76). The water quantity spent on obtaining PHA was taken in account when the normal consistency calculating.
The heat evolution study was carried out in a simple calorimeter, consisting of a cardboard vessel, the inner side of which was covered with a layer of foil, a lid with an attached thermocouple and a temperature regulator for recording readings.

All cement mixtures were tested. The cement paste was thoroughly mixed for 5 minutes according to the method of obtaining a normal consistency. After this it was placed into calorimeter and closed. The thermocouple, when lid was closing, was penetrated into cement paste. The countdown began immediately after cement was batched with water. A temperature controller connected to a computer recorded readings with a frequency of 2 minutes. Indications were summarized in a table and processed as follows.

Calculation the measure of heat evolution by the formula:

\[
q = \frac{C}{m_c} \cdot \Delta t,
\]

where

- \( q \) – the measure of heat evolution of the cement paste sample at time \( \tau \), kJ/kg;
- \( C \) – heat capacity of the mixture, determined by the formula 4.2 GOST 24316-80, kJ/kg;
- \( m_c \) – the amount of cement spent on the sample and the admixture introduced into mixture, kg;
- \( \Delta t \) – temperature change at a point in time relative to the initial temperature, °C.

The initial temperature was the temperature of the ambient air at the time of mixing of the sample. The obtained values were reduced to a graph of the change in measure of heat evolution over time.

3. Results and discussions

3.1. Normal consistency study

According to the results of determining the normal consistency (Table 3), it was established that the modification of the mixture with pre-hydrated cement slurry leads to increase water requirement of the mixture, which is typical for this type of additives.

| Specimen               | Normal consistency, % | Relative to «Control» |
|------------------------|------------------------|-----------------------|
| «Control»              | 29.75                  | 100%                  |
| «S-3 1%»               | 27.50                  | 92%                   |
| «PHA6 10%»             | 33.63                  | 113%                  |
| «PHA6 10% + S-3 1%»    | 30.88                  | 104%                  |

Water requirement with adding of «PHA6 10%» increased by 13% compared to the control mixture. The most probable explanation for this phenomenon can be considered as increasing the total number of mineral particles, the addition of fine particles with high adsorption ability, and a change in the phase composition. Together, these changes lead to trouble in mutual movement of particles, that is, to a decrease movemobility.

The use of S-3 superplasticizer reduces water demand by 8% relative to the «Control». As a result of the simultaneous use of mineral and chemical admixtures («PHA6 10% + C-3 1%»), the increase in water requirement was compensate by the plasticizing effect of S-3. In this case, the increase was only 4%. Thus, the simultaneous use of S-3 with PHA6 provides to avoid the negative impact of increased water requirement.

3.2. Heat evolution study

The results of measuring the heat evolution of cement pastes are presented in Figure 1. The heat evolution graph is inherently a reflection of the course of hydration processes. In the presented graph, all 4 stages of hydration can be traced for each of the mixture.
The first stage of hydration ends regardless of composition after about half an hour from the moment of mixing. It corresponds to the first peak in the heat release graph. At this stage of hydration, chemical reactions take place, the rate of which depends only on the rate of interaction of cement minerals and water, which determines the intense heat evolution [6–8]. Further, according to the hydration mechanism, hydration shell is formed around these particles from the hydration products. This shell preventing reaction cement particles with water and as a result exothermic reactions and, consequently, the heat generation slow down and practically stop.

The implicit first peak with a lower heat evolution values for «Control» mixture and «PHA6 10%» are explained by the method of preparing a normal consistency specimens, which it is necessary to thoroughly mix for 5 minutes. And since the interaction reaction did not slow down, as in specimens using S-3, heat was largely evolved during mixing and was not recorded by the device.

The second stage of hydration named the induction period has even more difference for mixtures with and without using S-3. According to the mechanism of the superplasticizer action [9, 10], it is adsorbed on the surface of the cement and creates a protective shell and prevents further interaction of the cement with water. As a result of this effect, the induction period is prolonged and ends at about 8-9 hours of hydration, regardless of the presence of PHA in the specimen. In specimen prepared without S-3, the induction period ends after 2.5 and 2 hours for the «Control» and «PHA6 10%» mixtures, respectively. The reduction in the induction period for «PHA6 10%» is probably caused by reactivity of cement particles already being in the next stage of hydration. The effect of shortening the induction period by the addition of pre-hydrated particles was noted at Taylor’s work [11]. Due to this superposition of the second and third stages of hydration at same time, the difference in the heat release of these mixtures by the time becomes more and more obvious.

Furthermore, as a result of the substance volume increase under the hydration shell to a critical state, shell is destroyed and the crystal nuclei are released [11,12], which leads to the resumption the interaction reactions of partially or completely freed cement grains with water. Reactions proceed very actively, which is reflected in the form of powerful heat evolution. The graph shows that a greater amount of heat is generated in the specimens using PHA. The increase in the peak value for the «PHA6 10%» over «Control» was about 4 kJ/kg, and for «PHA6 10% + S-3 1%» over «S-3 1%» was about 3 kJ/kg.

The released crystal nuclei gradually with time sediment onto cement particles [11, 12]. These hydrosilicates crystallize, grow and coat the particles, and again forming a shell that impedes interaction. This fourth stage begins after the second peak. It should be noted that for each compared pair, this stage occurred at approximately the same time. For mixtures without S-3 it was after 12 hours from the moment of mixing, and for formulations with S-3 - after 19 hours.

According to the well-known relations between heat release, degree of hydration, and porosity of cement samples [4,5,13,14], the revealed intensification of heat evolution allows to speak about acceleration of strength gain in the early stages, which was confirmed by tests [15]. Also a phenomenon of a decrease in early strength, without negatively affecting the final strength after using S-3 superplasticizer is known [16]. However, if we consider a complex of the proposed additives (mineral PHA and chemical S-3), then a rational selection of their amount will compensate for the negative properties of both of them. Namely, the increase in water demand from PHA is compensated by the plasticizing effect of S-3, and the decrease in early strength from S-3 is compensated by intensification of hydration and, consequently, by an increase in the initial strength from PHA.

4. Conclusion

Thus, some processes of early structure formation based on the heat evolution of cement paste were considered.

The deceleration of hydration processes from admixture of S-3 has been experimentally confirmed.

It was found that the use of the mineral admixture PHA leads to the intensification of heat release. At peak, this increase was 3-4 kJ / kg.
The combined use of PHA and S-3 will compensate for disadvantages of both admixtures. Namely, an increase in water requirement from using PHA and a decrease in early strength from S-3.

Figure 1. Measure of heat evolution in time

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