Structure formation of plasticized cement systems under heat-moisture treatment

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Abstract. Reducing the water-cement ratio is successfully achieved using superplasticizers (SP). However, their use can reduce the early strength of concrete and reinforced concrete. Heat-moisture treatment (HMT) is the leading way to accelerate concrete strength. The use of the latest SP based on polycarboxylate esters (PCE) allows adjusting the HMT mode, in particular, to reduce the presteaming period duration. The structure formation of cement pastes was studied depending on PCE modification and the presteaming period duration. The authors show PCE effectiveness in terms of reducing the water-cement ratio and joint action with HMT. It was found that the most effective use of low PCE dosages when using HMT. Increasing the amount of introduced SP to 1.2-2.0 % doesn't lead to significant changes in initial and final setting times of cement pastes. The results of the study of cement stone compressive strength after HMT and on the 28th day, also the density and capillary porosity revealed a slight deterioration of these physical and mechanical properties (up to 5-10 %) when the presteaming period was abandoned. The results of X-Ray Diffraction analysis indicate no significant differences in the mineralogical composition of cement stone, which hardened at the HMT with the presteaming period of 2 hours and without it. The study of the cement stone microstructure showed that the PCE introduction in cement pastes contributes to the stone structure compaction and reduction of the number of pores. There were no significant changes in the cement stone pore structure, depending on the presteaming period duration. The conducted research shows that it is possible to regulate the HMT modes for the hardening of cement systems with SP.

1. Introduction

The modern construction industry, in particular the concrete industry, is based on obtaining high-quality materials in the shortest possible time [1-3]. Since an essential component of concrete is cement, it is necessary to understand how its structure formation takes place.

It is known that an increase in the water-cement ratio above the optimal one (usually 25-27%) affects negatively the compressive strength of cement systems. This phenomenon is explained by the rise in the volume of pores, primarily capillary ones, which appear due to the presence and subsequent evaporation of mixing water that has not entered into chemical reactions. Superplasticizers are offered to reduce the water requirement [2,4].
The decrease in the water-cement ratio in equal-plastic cement systems accompanies a reduction in the intergranular space occupied by water. Therefore, new cement formations formed in this volume will fill the free zone faster and lead to an increase in strength development. At the same time, superplasticizers have a blocking effect, which is reflected in an increase in the setting time duration of cement systems and, consequently, a decrease in the early strength [3-5].

The use of modifying additives based on PCE can significantly increase the indicators of essential operational properties of concretes, such as compressive strength, freeze-thaw-, water- and corrosion resistance [2,3,6].

Current research shows that the latest PCE is preferably adsorbed at intermediate sites between alite and belite [4,7]. ζ-the potential of the C-S-H and C₃S phases is negative, so it is unlikely that high PCE adsorption occurs at these phases [5,8]. This leads to the conclusion that PCE is initially adsorbed only locally on the aluminate and ferrite phases, and then on the AFm and AFt phases. At a later stage of hydration, they can also be connected to Ca²⁺ on C-S-H surfaces [5]. This fact may indicate that significantly less stress negatively affecting the strength values may occur in plasticized cement systems, which harden under HMT conditions.

Scientists have found that PCE affects the modification of cement crystals growth. Ettringite is formed in long prismatic forms in the presence of PCE. Short prismatic ettringite structures are formed in cement stone without additives or in modified traditional SP [9]. The voids between the particles in cement pastes without superplasticizer and in the presence of traditional SP are filled mainly with long needle-like C-S-H (external product). At the same time, PCE presence leads to the formation of bonds with densely grown C-S-H (internal product) [6,9].

HMT is a leading way to accelerate the strength of concrete. The use of this technology hurts the strength indicators at a later date in comparison with non-additive concretes. Moisture migration in the hardening material contributes to the formation of intercommunicating capillary porosity and the appearance of excessive internal pressures. Liquid and air migrating in concrete between the deep and surface layers connect the pores and voids, increase the effective capillaries radius, destroy the connections that are not yet strong at the contact points of the merging crystalline growths, and create a directional porosity [10,11].

The researchers point that presteaming period reduction leads to a decrease in the durability of cement systems. During the presteaming period, the concrete structure is formed under relatively calm conditions (in the absence of intensive moisture migration, temperature deformations of concrete ingredients, etc.). This structure becomes able to perceive thermal effects when the temperature rises [11,12]. At the same time, there are studies showing that it is possible to reduce the presteaming period of HMT to 1-2 hours without a significant worsening of the physical and mechanical concrete properties [13,14].

Based on the above, there are prospects for regulating the HMT modes of cement systems, in particular, concretes modified with modern superplasticizers based on PCE.

The main objective of the present investigation is to study the effect of the presteaming period duration and PCE presence on the hydration processes of cement stone.

2. Materials and methods
Portland cement CEM I 42.5 N produced by Gornozavodskcement was used as a binder. Its physical and mechanical parameters and mineralogical composition of cement clinker are shown in table. 1.

| Mineral composition (wt. %) | Surface area (cm²/g) | Normal consistency (%) | Compressive strength after HMT according to GOST 10178-85 | Setting time |
|---------------------------|----------------------|------------------------|----------------------------------------------------------|-------------|
| C₃S | C₃S | C₃A | C₄AF | 3370 | 27.0 | 36.0 | 125 | 190 |

Table 1. Some quality indicators of the cement used.
The reduction of the water-cement ratio was achieved by using Sika ViscoCrete 24HE PCE. The dosage was taken in accordance with the technical passport of the additive (0.4-2.0% by cement mass).

The assessment of the setting time of plasticized cement pastes was carried out by GOST 310.3-76, and the samples were at different temperature conditions (20 °C, 40 °C, 60 °C).

The samples were formed with dimensions of 20x20x20 mm to assess the physical and mechanical properties of the cement stone. The compressive strength after TVO and on day 28, the density and open capillary porosity of the stone were measured.

X-Ray Diffraction (XRD) analysis (diffractometer D8 ADVANCE) was chosen for determination of the mineralogical composition and identification of growth products in the process of the cement stone hardening. We used CuKα monochromatized radiation (\(\lambda(\text{Cu-K}) = 1.54184 \text{ Å}\)) of 30-40 kV and 20-30 mA, with a 0.05° step size and step time of 2 s.

The density of the cement stone structure was estimated by using the BIOLAR polarization-interference microscope.

3. Results and Discussion

3.1. Study of cement pastes setting time.

Cement pastes of normal consistency were made (following GOST 310.3-76) to analyze the setting time of cement pastes in the presence of PCE at different temperatures.

The water-cement ratio of cement pastes decreased due to the water-reducing effect of Sika Viscrete 24 HE by 13.3 – 33.3 % (see table 2).

| №  | Sika Viscocrete 24HE dosage, % by cement mass | Water-cement ratio |
|----|------------------------------------------|-------------------|
| 1  | -                                       | 0.27              |
| 2  | 0.4 %                                   | 0.234             |
| 3  | 1.2 %                                   | 0.20              |
| 4  | 2.0 %                                   | 0.18              |

A graphic representation of the cement pastes setting time depending on the dosage of the superplasticizer is shown in Fig. 1.

![Figure 1. Setting time of the cement pastes hardening at variable temperature values depending on the dosage of PCE](image-url)
The studies have shown that at 20 ºC the setting time of the cement pastes increases with the introduction of Sika Viscocrete 24 HE in an amount of up to 1.2 %. Further increase in the amount of SP introduced does not lead to a significant increase or decrease in the start and end times of the cement setting. According to Yamada et al. [15] the specific surface area of the cement paste constantly increases during the first 120 minutes after adding water. The recent changes occur faster at high temperatures. Consequently, an increase in temperature is more critical for the influence on the kinetics of the cement stone hardening than PCE action [6]. On the other hand, the plasticizer amount in cement stone may be sufficient for adsorption on the surface of the resulting hydration products, and increasing its content from 1.2 % to 2.0 % is not ineffective.

The setting time of the cement pastes modified PCE depending on the steaming temperature is shown in Fig. 2.

![Figure 2. Setting time of the cement pastes hardening at different PCE dosage values depending on the steaming temperature](image)

The experiment results shown in Fig. 2 also indicate a more significant influence of the hardening temperature than the PCE content in the cement system.

When manufacturing structures with high concrete consumption, the heat capacity will decrease. Therefore, the following conditions are accepted for further research: the steaming temperature is 60 ºC, SP dosage is 0.4 % by cement mass.

### 3.2. Study of modified cement stone physical and mechanical properties after HMT.

The experiment plan with the obtained physical and mechanical properties is represented in Table 3.

**Table 3.** The experiment plan and the results of the cement stone compressive strength, density, and capillary porosity

| №   | HMT mode | Sika Viscocrete 24HE dosage, % by cement mass | Water-cement ratio | Compressive strength, MPa | Density, g/cm³ | Capillary porosity, % |
|-----|----------|---------------------------------------------|-------------------|--------------------------|----------------|-----------------------|
|     |          |                                             |                   | After HMT | On the 1st day | On the 3rd day | On the 7th day | On the 28th day |                       |                  |
| 1   | 0-6-2    | -                                           | 0.27              | 41.8       | 43.5           | 45.2           | 45.8           | 47.5           | 2.09                    | 15.46            |
| 2   | 0-6-2    | 0.4                                         | 0.234             | 53.4       | 55.9           | 58.1           | 60.1           | 60.8           | 2.25                    | 9.74             |
| 3   | 2-6-2    | -                                           | 0.27              | 46.5       | 46.8           | 47.3           | 49.2           | 49.3           | 2.11                    | 13.66            |
| 4   | 2-6-2    | 0.4                                         | 0.234             | 58.5       | 59.5           | 60.4           | 62.7           | 61.7           | 2.25                    | 10.36            |
| 5   | Without HMT | -                                           | 0.27              | -          | 13.6           | 23.1           | 32.6           | 50.2           | 2.12                    | 16.50            |
| 6   | Without HMT | 0.4                                         | 0.234             | -          | 6.1            | 18.5           | 38.6           | 64.4           | 2.27                    | 11.49            |
The samples-cubes with an edge of 2 cm were made of the same normal density (by GOST 310.3-76) and hardened when exposed to HMT. The steaming temperature was 60 °C with a duration of 6 hours, and the cooling time was 2 hours. The samples of cement stone № 1-2 were subjected to TVO without presteaming (HMT mode (0-6-2) h). The samples № 3-4 had a presteaming period of 2 hours (mode (2-6-2) h). The PCE content was 0.4 %. The test samples hardening under normal conditions (№ 5-6) were also molded.

The kinetics of strength gain up to 7 days of cement stone hardening under different HMT modes is shown in Fig. 3.

Figure 3. The kinetics of compressive strength gain up of cement stone that hardens under various HMT modes in PCE presence/absence.

The compressive strength of the cement stone was evaluated immediately after the HMT, on days 1, 3, 7, and 28. Besides, the density and open capillary porosity of the obtaining material were measured.

The strength after HMT of cement stone modified with Sika Viscocrete 24HE PCE increases by 25.8-27.8 % in comparison with the strength of the samples without additives. There is a slight decrease in the strength after HMT without presteaming period (for 8 hours of hardening in the 0-6-2 h mode, the strength lags by 9.6-11.2 % in comparison with the strength of the cement stone, which hardened for 10 hours in the 2-6-2 h mode).

However, the strength values of cement stone that hardens under the HMT modes (0-6-2) h and (2-6-2) h on the 28th day are almost equal, the discrepancy is within 1.5-1.9%, which indicates the suitability of abandoning the presteaming period and the possibility of HMT time reduction.

The compressive strength of the cement stone that hardens under HMT according to the scheme (0-6-2) h is 28 days lower than the strength of the stone that hardens under normal conditions by 5.7-5.9 %.

The density of cement stone modified with PCE is higher than the density of samples without additives up to 7.8 %, which indicates that the structure is compacted in the first case.

The capillary porosity of the stone with 0.4% of Sika Viscocrete 24HE from the cement mass is lower than these indicators of non-additive compositions by 24.1-37.0%.
3.3. X-Ray Diffraction (XRD) analysis of plasticized cement stone

The study of the cement stone for the identification of growth products was carried out with the use of XRD analysis. The XRD patterns of the cement stone samples № 1 and № 2 after HMT are shown in Fig. 4 and Fig. 5, respectively.

There is a reduced content of portlandite \( d = [4.91; 3.11; 2.63; 1.93 \text{ Å}] \) for composition with PCE (sample № 2) in comparison with non-additive cement stone. Similarly, the ettringite content is lower in sample № 2, as evidenced by diffraction maximums with interplane distances \( d = [9.73; 5.61; 4.70, \ldots] \).
2.20 Å], which is associated with a cement hydration slowdown due to selective PCE adsorption on C₃A and C₄AF minerals, as well as ettringite and monosulfate growths.

The XRD patterns of the cement stone samples after HMT for samples № 3 and № 4 are represented in Fig. 6 and Fig. 7 respectively.

**Figure 6.** XRD pattern of cement stone sample without additives after HMT in the mode (2-6-2) h (sample № 3)

**Figure 7.** XRD pattern of cement stone sample with PCE of 0.4 % by cement mass after HMT in the mode (2-6-2) h (sample № 4)

The analysis of diffraction maximumes shows a similar tendency of decrease in the number of ettringite and portlandite minerals in the cement stone in the presence of PCE.

The quantitative analysis of the mineral content in the cement stone samples is shown in table 4.
Table 4. Mineralogical composition of cement stone

| №  | HMT mode | Sika Viscocrete 24HE dosage, % by cement mass | Mineral content, % | C₃S | C₂S | C₄AF | Ca(OH)₂ | Aft | C₃A |
|----|----------|---------------------------------------------|-------------------|-----|-----|------|---------|-----|-----|
|    |          |                                             | After HMT         |     |     |      |         |     |     |
| 1  | 0-6-2    | -                                           | 43.3              | 22.4| 11.8| 17.4 | 0.6     | 4.5 |
| 2  | 0-6-2    | 0.4 %                                       | 47.7              | 20.3| 12.2| 16.1 | 0.5     | 3.2 |
| 3  | 2-6-2    | -                                           | 43.7              | 22.5| 12.1| 17.3 | 0.6     | 3.8 |
| 4  | 2-6-2    | 0.4 %                                       | 47.4              | 20.6| 12.4| 16.3 | 0.5     | 2.8 |
|    |          |                                             | On the 28th day   |     |     |      |         |     |     |
| 1  | 0-6-2    | -                                           | 43.1              | 21.9| 11.6| 23.2 | 0.2     | -   |
| 2  | 0-6-2    | 0.4 %                                       | 44.5              | 20.3| 12.1| 23.0 | 0.1     | -   |
| 3  | 2-6-2    | -                                           | 43.2              | 21.5| 11.5| 23.7 | 0.1     | -   |
| 4  | 2-6-2    | 0.4 %                                       | 44.0              | 21.1| 11.9| 22.9 | 0.1     | -   |

The analysis of the cement stone mineralogical composition indicates minor structural changes when the presteaming period of the cement systems modified by PCE is abandoned. The study of the cement stone mineralogical composition at the age of 28 days showed a tendency for equalizing the mineral content.

3.4. Analysis of cement stone microstructure.

The polarization-interference microscopy was used for studying the microstructure of the cement stone. The micrographs are shown in Fig. 8-9.

**Figure 8.** The microstructure of the cement stone: a) a control sample without additives (HMT mode 0-6-2) h; b) a sample with PCE (HMT mode 0-6-2) h at 800-fold magnification

**Figure 9.** The microstructure of the cement stone: a) a control sample without additives (HMT mode 2-6-2) h; b) a sample with PCE (HMT mode 2-6-2) h at 800-fold magnification
From the micrographs presented, it is clear that the introduction of PCE in the cement paste mixtures contributes to the stone structure compaction and the reduction of capillary pores quantity. No significant changes in the cement stone pore structure were recorded, depending on the duration of the presteaming period.

4. Conclusions

- The increase in the setting time of modified cement pastes by modern PCE shows that it is possible to regulate the HMT modes, in particular the presteaming period duration. It was found that the most effective use of PCE low dosages is when using HMT.
- There is an increase in the strength after HMT and on 28 days by 25-28 %, an increase in density by 6.6-7.7 %, and a decrease in capillary porosity by 24-37 % of plasticized cement stone in comparison with non-additive compositions.
- Plasticized cement stone samples show a compressive strength during 8 hours of hardening (HMT mode according to the scheme (0-6-2) h) only by 9.5 % lower in comparison with the strength of samples for 10 hours of hardening (HMT mode according to the scheme (2-6-2) h).
- There is a decrease in the content of ettringite and portlandite minerals in the cement stone with the PCE addition, which is associated with its selective adsorption, in particular on the minerals C$_3$A, C$_4$AF, and ettringite.
- There were no significant differences in the mineralogical composition of the cement stone hardening during HMT with the presteaming period of 2 hours and without it.
- The experiments prove the low efficiency of the presteaming period during the HMT for the formation of early cement systems strength. It is possible to regulate the HMT mode in terms of accelerating the construction rate without significantly reducing the physical and mechanical properties.

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