Research into the Time Factor in the Formation of Phase Composition of the Cement Stone Structure

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Abstract. The challenge of obtaining high-quality concretes rests on the specificity of hydration hardening of a cement binder, during which the introduction of even a small amount of this or that component or a change in the hardening conditions may lead to drastic changes in the structure and properties of cement materials. In order to reveal the nature of the influence of plasticizing additives and their introduction procedure, a set of research efforts targeting microstructure and basic mechanical properties was deployed, including the study of changes of cement stone’s structural and mechanical parameters over a long period of hardening (up to 18 years) and the composition of cement stone’s hydration products. The main variable factors dealt with are: the dosage of SP S-3 and the modifier’s introduction procedure during mixing of cement with water. The paper imparts findings on the kinetics of changes in the content of alite, belite and other hydrosilicates in cement stone, as well as portlandite against the duration of samples’ hardening. It was found that for almost all compositions with S-3, there is a decrease in the intensity of calcite reflections (3.029 Å) compared to the control sample, which speaks of a slight decrease in carbonation processes in the presence of a superplasticizer. When the temperature and humidity conditions of hardening change, especially over a long period, structural changes associated, for example, with the destabilization of hydroaluminate phases, decompression caused by the formation of secondary crystalline hydrates of various densities, and the release of hydrate water can be one of the reasons for changing the strength of cement systems over time. These phenomena were analysed throughout its hardening time lasting up to 18 years.

1. Introduction

Creation of multicomponent cement dispersed systems of a new generation, modified with mineral and complex admixtures is currently a fast-developing line of research; the said admixtures enable a targeted influence on structure formation and hardening of cement mortars and concretes and to obtain materials with specified physical and mechanical properties [1, 2, 3].

The production of powder-activated sand concretes with a high content of the suspension/slurry component causing the formation of self-expanding and self-compacting mixtures [4, 5, 6, 7] serves an
example of sufficiently high physical and technical properties of composite materials obtained after research efforts.

Modern high-quality concretes have a wide range of different types: high-strength and ultra-high-strength concretes, self-compacting, self-leveling, highly corrosion-resistant, reactive-powder, plasticized powder, including fiber-reinforced [8, 9, 10, 11]. These types of concrete meet the high requirements of compression and tension strength.

The creation of a new generation high-quality concretes rests on the use of highly effective superplasticizers in combination with a new formulation of solid components that provide a synergistic effect, especially at the early stage of structure formation [12, 13, 14, 15].

Analyzing the trends in the development of modern construction engineering abroad, we can see that they are increasingly linked to the development of concrete based on new technologies (non-traditional concretes) [16, 17, 18, 19, 20]. Researchers highlight a factor of long-term economic effect from the use of unconventional concrete in structures, which is caused not only by their increased strength, but also by high performance characteristics: frost resistance, corrosion resistance, water proofing qualities, etc. In addition, such concretes have an increased workability of concrete. In the West, a special term "High Performance Concrete" has been introduced for such concretes denoting high-quality concretes.

The challenge of obtaining high-quality concretes rests on the specificity of hydration hardening of a cement binder, during which the introduction of even a small amount of this or that component or a change in the hardening conditions may lead to drastic changes in the structure and properties of cement materials. At the same time, modern concrete technology is not conceivable without modifiers of various chemical compositions and functional purposes.

To understand the nature of the influence of plasticizing admixtures and their introduction procedure, a number of research efforts targeting microstructure and basic mechanical properties was deployed, including the study of changes of cement stone’s structural and mechanical parameters over a long period of hardening (up to 18 years) and the composition of cement stone’s hydration products. The main variable factors taken in to consideration were the dosage of SP S-3 and the modifier’s introduction in to the mixing water.

Research objective: to study the influence of time factors in the formation of the phase composition of the cement stone structure.

Research tasks:
1. to receive X-ray images of experimental samples of cement stone at the age of 18 years.
2. to reveal the effect of the amount of superplasticizer derived from naphthalenesulfonic acid on the phase composition of cement stone.

2. Methods
Table 1 shows the characteristics of the composition, mixing of cement with water and the introduction of the S-3 into the cement paste. Its dosing procedure in batch 4 was different in that the SP was not dosed at the first stage, and in compositions of series 2 and 3, it was dosed as 50% of its total volume at the first and second stages.

| Series of samples | W/C ratio | SP S-3, % by mass | Cement paste procedure                  |
|-------------------|-----------|------------------|----------------------------------------|
| 1                 | 0.24      | –                | C+0.12H₂O+0.12H₂O                      |
| 2                 | 0.24      | 1.0              | C+(0.12H₂O+0.5SP)+(0.12H₂O+0.5SP)       |
| 3                 | 0.24      | 0.5              | C+(0.12H₂O+0.25SP)+(0.12H₂O+0.25SP)     |
| 4                 | 0.24      | 0.5              | C+0.12H₂O+(0.12H₂O+0.5SP)               |

X-ray phase analysis of the compositions of cement stone hydration products were carried out using DRON-7 diffractometer in the range of Bragg angles of 7-60° with imaging step of 0.05.
3. Research results and their analysis

Figures 1 and 2 show X-ray images of experimental samples of the compared series of cement stone at the age of 18 years.

When analyzing X-ray images of compositions No. 1 and No. 2, it was revealed that for sample No. 2 there is a higher intensity of non-hydrated alite (2.77; 2.74 Å), which may indirectly point to a certain slowdown in hydration. However, the ratio of alite and Ca(OH)$_2$ (2.63 Å) intensities is approximately the same. Samples No. 3 and No. 4 (figure 2) are also characterized by a higher intensity of alite relative to composition No. 1, but for the 3rd and 4th compositions, in respect to alite the intensity of Ca(OH)$_2$ (2.63 Å) increases, which is indicative of some activation of the hydration of silicate phases and the release of hydrated lime due to superplasticizer’s dispersing effect. This is more evident for the 4th composition, which is characterized by a different increase in the intensity of Ca(OH)$_2$ (4.93 and 1.93 Å) reflections.
This also confirms the possibility of activating the hydration of silicate phases. It is obvious that, despite the increase in the contact zone of cement particles with the liquid phase containing SP, the hydration process is most active during the initial interaction of cement particles with clean water. It should be emphasized that the strength of samples of composition No. 4, in which a part of pure water was introduced at the first stage, and then the remaining water with S-3, is higher than the strength of not only control samples, but also samples in which the addition of S-3 was introduced, although in portions, but initially with mixing water. Therefore, the structure formed during the initial contact with clean water retains higher strength properties during the hardening period of up to 18 years.

Figure 2. X-ray images of test samples of series 3 and 4.

The strength increase of compositions No. 4 in comparison with the control samples can also be explained by the dispersing effect of the S-3 admixture owing to an increase in the contact zone area in the dispersed system. The increase in the intensity of Ca(OH)$_2$ reflections – 2.63 and especially 4.93,
of 1.92 Å in the composition No. 4 is indicative of activation of hydration of not only silicate phases, but those of aluminate, as the process of interaction of C₃A and C₆AF with water implies the extraction of CaO structures from aluminates and further interaction of aluminate complexes with Ca(OH)₂ – with the possibility of formation of calcium aluminate hydrates of different basicity, properties and structure.

It is characteristic that almost all compositions with S-3 yield a decrease in the intensity of calcite reflections (3.029 Å) compared to the control sample, which is indicative of a slight decrease in carbonation processes affected by a superplasticizer.

With respect to hydrosilicate phases, it should be underscored that presence of the S-3 admixture (No. 2 and No. 3), causes a slight decrease in the intensity of reflections of the CSH (II) phase (1.82 Å) (except for No. 4). Composition No. 2 and especially No. 3 reveal blurred reflections (1.82 Å) compared to composition No. 1, which indicates that in the presence of S-3, a wide range of fine-crystalline hydrosilicate phases with a similar but distorted structure can be formed. This is indirectly proved by the stepwise asymmetric forms of reflections (peaks) of hydrosilicate phases. The formation of a multiphase fine-crystalline hydrosilicate structure may be one of the reasons for the strength gain of cement systems. Indirectly, a certain slowdown in the hydration of the cement system in the presence of S-3 can be revealed through a significant decrease in the intensity of calcite reflections in compositions with S-3, introduced simultaneously with the mixing water.

It is known [21] that during the adsorption of plasticizers, especially high-molecular ones, they affect the morphology of hydrate phases. Adsorption not only changes the shape of crystals, but slows down their growth. The structure of hydrosilicate phases becomes fine-crystalline consisting of various similar hydrates. On the one hand, this has a positive effect on the hydrosilicate system, since the interweaving of various phases generally strengthens the structure; on the other hand, the crystallization of hydrosilicates – the main carriers of the strength of cement stone – slows down.

Organic admixtures have a slightly different effect on the hydration of the cement’s aluminate components. Its distinctive features are the stabilization of metastable calcium hydroaluminates and slowing down of the release of interlayer water in the structure of AFm phases. The structure of hydroaluminates due to the high rate of their formation and the presence of admixtures almost from the moment of mixing becomes not only fine-crystalline, but also significantly distorted. At the same time, with the presence of some organic admixtes containing active functional groups, the number and intensity of reflections of C₃AH₈ and C₆AN₃₋₅ hydrates sharply increase as it can be seen from X-ray images of hydrated C₃A and C₆AF, in contrast to the control compositions, where X-ray images contain many clear reflections characteristic of the stable phase of C₆AN₆. The mechanism of this stabilization is not completely clear, however in its essence it has to do with electrochemical phenomena (ion-dipole, dipole-dipole, etc.), which mainly lead to changes in the structure of bound interlayer water and impair its release and, consequently, the processes of AFm phases recrystallization into the most stable C₆AN₆.

During hydration of aluminate phases in the presence of organic surfactants containing active functional groups, adsorption mainly occurs on the products of hydration of aluminate phases, since the dispersion of hydrates is significantly higher than the dispersion of the initial minerals. Being in the diffusion flow, the AFm-phase hydrate nuclei formed almost from the moment of mixing fall under the influence of SP’s anion-active functional groups affecting the coordination medium of AL₃⁺ interlayer ions destroyed by aluminate complexes. This transforms the charge state of the interlayer space, impairs the release of interlayer water, and, as a result, leads to stabilization of hydrates. During their crystallization taking place in the kinetic region, not only the type and activity of functional groups, but also the concentration of additives has a great influence on this stage.

Under certain conditions, during the adsorption of organic surfactants on the hydrates’ active centers (which appear already at the stage of formation of three-dimensional nuclei from supersaturated solutions), not only adsorption (chemisorption) of additives’ molecules is possible, but also the formation of new chemical compounds, for example, when naphthalene-formaldehyde SP interacts with aluminate phases [22]. Such complexes, as well as the additives themselves, can not
only have a stabilizing effect on the hydrates, but also prevent the dissolution of the initial phase, blocking the active centers.

Regarding the analysis of X-ray images of cement stone compositions without additives and with S-3 additives, we have to emphasize that hydrated aluminate phases are characterised by the presence of clear reflections of the CAH\textsubscript{10} phase in samples No. 1 and No. 4, in which the primary contact of the cement system was with clean water (No. 1 – the control composition; No. 4 – with the addition of S-3 0.5% of the cement mass with a two-stage water mixing procedure, in which the additive is introduced into the second stage).

In samples No. 2 and No. 3, there are no such reflections in the area of small angles (2\(\Omega\) = 15-20\(^\circ\)). In the area of mean angles (2\(\Omega\) = 25-30\(^\circ\)), samples No. 2 and No. 3 demonstrate CAH\textsubscript{10} reflections but they are multi-staged pointing to the distortion of the crystal structure. It is possible that in the presence of the S-3 additive introduced at the first stage of preparation, the crystal structure of CAH\textsubscript{10}, which is formed in the cement system at an early stage and retained at later stages, has a distorted structure due to the electrostatic influence of SP functional groups. The presence of cluster crystals of CAH\textsubscript{10} phase in the form of hexagonal prisms may be one of the reasons for the strength gain of samples No. 4 both in the early and late periods.

A characteristic feature of samples No. 3 and No. 4 with a low content of S-3 in the angle range of 15-30\(^\circ\) is that, in contrast to samples No. 1 and No. 2, their X-ray images display reflections typical of ettringite (3.85 and 4.69 Å) and C\(_3\)AH\(_6\) (3.37 Å) (especially well formed in sample No. 4!). Although reflections of 3.37 Å can also be seen on the X-ray image of sample 1, their intensity is significantly lower than those of composition 4. Probably the introduction of a small amount of clean water (composition No. 4) facilitates the formation of a stable C\(_3\)AH\(_6\) phase and the subsequent introduction of the remaining water with the S-3 does not affect the state of the C\(_3\)AH\(_6\) phase. This is a very positive factor in terms of the formation of stable hydroaluminate structures in the cement system.

The forms of reflections characteristic of ettringite, 2.209 Å in all samples with S-3 have a multi-stage character, and their intensity is slightly higher (especially in sample No. 2) than in composition No. 1. This is indicative of the possibility to stabilize ettringite in the presence of S-3 additives in the period of up to 18 years, and, apart from that, the nature and shape of the peaks also speak of possible defects and distortions of the ettringite structure. The presence and intensity of reflections characteristic of hydrated monosulfocalcium aluminate in samples No. 3 and No. 4 are slightly lower than in samples No. 1 and No. 2, and this is indicative of the stable presence of this phase over a long time, along with ettringite.

The widespread use of high-molecular organic SP additives in construction practice is such that when calculating their dosages and especially with significant low water content in cement systems, it is necessary to take a more careful approach to the analysis of the processes of hydration of cement minerals and cement stones in general, especially in restricted conditions, as well as to the introduction procedure of an additive that can significantly affect the state of the microstructure and composition of hydrate phases during a sufficiently long period of hardening.

Despite the fact that the number of hydroaluminate phases in the cement system is insignificant and they affect the strength of the cement stone to a lesser degree than hydrosilicates, their stabilization and inhibition of recrystallization processes (due to changes in the densities of hydroaluminate phases, the release of free water, etc.) can affect fluctuations in the strength of the cement system as a whole, and even more so if it is hydrated in the presence of SP in restricted conditions with a lack of water.

Therefore, in the cement system with organic additives containing active functional groups, parallel processes occur, on the one hand, activation of hydration due to dispersion of binder particles, on the other hand, changes in the morphology of calcium hydroaluminates and stabilization of hydroaluminate phases. Moreover, the latter can have a negative impact on long-time strength. It is known [21, 23] that cement concretes are characterized by a "sawtooth" change in strength, namely, both its increase and decrease.

Research findings have shown that organic additives with active functional groups cause the processes of recrystallization of hydrates in the cement system even during a long period of hardening.
For silicate components, the most characteristic feature is a certain inhibition of hydration at the early stages of hardening (at equal W/C ratio) and the formation of different in morphology, but similar in structure, calcium hydrosilicates, which in general, and especially with significant water reduction in the presence of SP, works toward the strength gain of cement stone.

Hydroaluminate structures in the presence of organic additives are characterised by the stabilization of AFm- and Aft-phase hydrates and the slowing down of their recrystallization into the most stable phases, for instance into C₃AH₆, etc.

When the temperature and humidity conditions of hardening change, especially over a long time, structural changes associated, for example, with the destabilization of hydroaluminate phases, decompression caused by the formation of secondary crystalline hydrates of various densities and the release of hydrate water can be one of the reasons for changing the strength of cement systems over time. These very processes were analysed in our researches during the hardening period of up to 18 years.

4. Conclusions
1. A set of physical and chemical research efforts supplemented with X-ray structural analysis of cement stone samples fabricated with the use of superplasticizer additives during long-time hardening was completed.
2. The influence of the time factor (18 years) on the formation of cement stone’s composition and structure was revealed.
3. The dependences of changes in the content of 3CaO•SiO₂, 2CaO•SiO₃, 3CaO•Al₂O₃, 4CaO•Al₂O₃•Fe₂O₃, Ca(OH)₂ in the cement stone during a long hardening were identified.
4. It was discovered that compositions with the superplasticizer derived from naphthalene sulfonic acid have a lesser intensity of calcite reflections, which speaks of a slight decrease in carbonation processes influenced by it.

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