MATEC Web of Conferences **86**, 04043 (2016) DOI: 10.1051/matecconf/20168604043
*IPICSE-2016*

# Nano-modified concretes initial structuring

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**Abstract**. The article considers the aspects related to initial formation of the structures in concretes containing nano-additives that significantly influence the type of newgrowths and their concentration during the cement hydration. The article depicts the role of the aggregate in formation of the contact zone structure between the cement stone and the aggregate, which mainly consists of ettringite and portlandite. Mathematical models of the cement stone hydrational hardening kinetics and its performance properties have been obtained.

## 1 Introduction

For cement composites, the initial hardening and the structure formation period (SFP), i. e. transition from the plastic and viscous state to the hard state, may be determined by any method: ultrasound, mixture temperature variation kinetics, electric resistance, contraction, and others. The studies have demonstrated that the values of the variables being measured change abruptly after completion of the initial structure formation period [1, 2, 3].

In "cement with nano-modifier - water" systems, the hydration and heat release kinetics at the same hardening conditions are determined by the water-cementitious ratio. A different situation is, when there is an aggregate. The beginning of the intensive heat release is determined not by the mixture water content, but by W, which occurs in the concrete mixture exposed to the aggregate [4, 5, 6]. Table 1 shows the compositions of concretes with nano-modifiers characterized by different structure formation periods (SFP), and, consequently, different water-cementitious ratio (W) and cement with nano-modifier volumetric concentration in the concrete mixture ($C = 0.001(Ts/\rho_{ts} - W)$).

According to Table 1, when the volumetric concentration is constant (C=0.2) in composites 4-6, the intensive heat release coincides with the end of the structure formation period corresponding to W. The concrete mixtures characterized by constant W=0.2 (composites 1-4), but with different C, had the same structure formation period.

The further heat release process after the transition of the concrete mixture to the concrete state occurs in the compositions that contain nano-modifier and the aggregate in a more intensive manner in comparison with the pure cement stone. This is evident of the fact that the water mechanically bound by the aggregate at an early stage of hardening begins to actively participate in the cement-water paste hydration process [10, 12]. The main structuring component of the concrete mixture is the cement paste with the nano-modifying aggregate, which determines the hydration and cements hardening kinetics [11].

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**Table 1**. Concrete mixtures compositions

| No. | Materials consumption in kg per 1 $m^3$ | | | | | V/Vy | SFP, h | C | W |
|---|---|---|---|---|---|---|---|---|---|
| | cement | nano-modifier | water | sand | gravel | | | | |
| 1 | 1376 | 344 | 447 | - | - | 0.26 | 7 | 1 | 0.26 |
| 2 | 544 | 136 | 250 | 537 | 880 | 0.367 | 7 | 0.4 | 0.26 |
| 3 | 413 | 103 | 219 | 625 | 1025 | 0.425 | 7 | 0.3 | 0.26 |
| 4 | 274 | 69 | 186 | 716 | 1170 | 0.542 | 7 | 0.2 | 0.26 |
| 5 | 290 | 72 | 180 | 716 | 1170 | 0.5 | 6 | 0.2 | 0.23 |
| 6 | 222 | 55 | 208 | 716 | 1170 | 0.75 | 9 | 0.2 | 0.4 |

Table 2 illustrates the detailed studies of the cohesives hydration kinetics in the presence of nano-modifiers using the example of TES22 (Moscow) production waste, the fly ash.

**Table 2.** Composition and properties of the cement composite consisting of portland cement and nano-modifier obtained from the activated fly ash with specific surface area equal to 700 m2/kg.

| No. | Specific surface area, $m^2$/kg | Content of nano-modifier, % | Density, g/$cm^3$ | SFP, h-min. | Strength, MPa |
|---|---|---|---|---|---|
| 1 | 265 | - | 2.10 | 8-45 | 49 |
| 2 | 265 | - | 2.42 | 9-15 | 57 |
| 3 | 330 | 15 | 2.26 | 4-15 | 62 |
| 4 | 395 | 30 | 2.12 | 2-00 | 47 |
| 5 | 461 | 45 | 2.00 | 2-30 | 22 |
| 6 | 526 | 60 | 1.9 | 3-00 | 11 |

Note: 1 - portland cement, 2-6 - mixtures of portland cement with 0.8 % C-3 and nano-modifier

The analysis according to table 2 has demonstrated that when the nano-modifier is added to the mixture at an early period, the exothermy abruptly growth, and decreases by the end of the period in comparison with the reference composition, which corresponds to the end of the SFP. When increasing the quantity of the additive and reducing the content of cement in the concrete mixture, the exothermy decreases, but does not reach the beginning and the end of the reference composite setting [13].

Adding the nano-modifier to the cohesive composition leads to the reduction of time for the setting start and end in comparison with the cement-water paste with no additives; however, in some extent the increased SFP is observed with regard to the impalpable additive; this may be explained by the fact that the C-3 superplasticizing agent in some extent slows down the setting processes and beginning of the concrete mixture initial structuring.

According to Table 1 and plots (Fig. 1, 2, 3), when the quantity of the nano-modifier increases up to 30 %, the time of setting is reduced; and with further increase of the additive quantity, the structure formation period (SFP) increases. Reduction of the setting time, improvement of the cement stone plastic strength may be explained by the fact that the adding of the nano-modifiers contributes to improvement of the system viscosity and more rapid occurrence of the crystallization centers, which leads to the reduction of the energy demands for the nucleation, and contributes to the formation of the cement stone structure with less stresses and acceleration of the cement systems hardening [14].

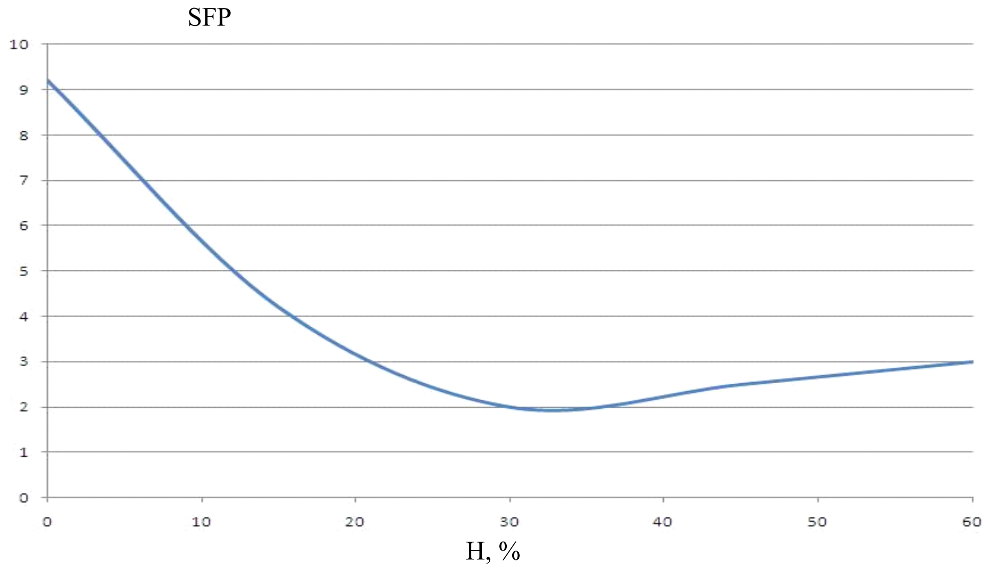


**Fig. 1.** Cement composite SFP vs. nano-modifier content (H).

The cement-water past structure formation period is consistent with the data related to the gaining of the plastic strength by the cement-water paste with the nano-modifier. When adding the superplasticizing agent, the reference composition structure formation period increases by 0.5 h, which is related to formation of the cement and aggregate grains on the surface owing to the absorption of the thickened enclosure polar groups with significant negative ξ-potential, thus increasing the dispergation effect and particles repulsion [8, 9].

The nano-modifier, from the mixing moment, provides the peptizing and structuring effect, thus accelerating the cement stone hydration and hardening process. Such effect provided by the disperse particles may be explained by that the mineral aggregate particles, when between the separate grains of the cement, move them apart and ensure better access of water to them. The hydration products formed are distributed within the large volume, since they are diverted from their reaction zone to the aggregate particles surface.

The following mathematical models have been obtained:

- Structure formation period vs. the content of nano-modifier based on the activated fly ash from TES 22 (Moscow).

$T = 9.21 - 0.371H + 0.00456\,H^2$ with the correlation coefficient equal to 0.98;

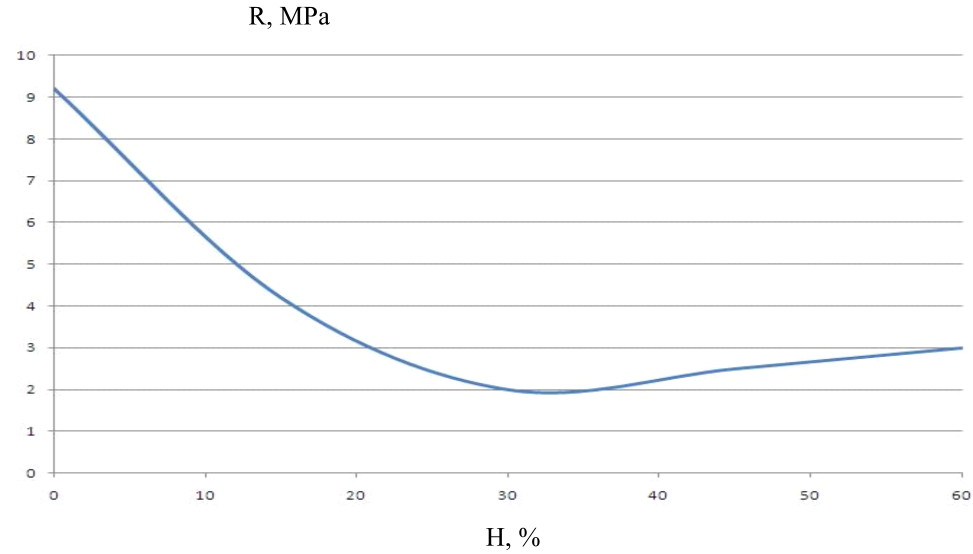


**Fig. 2.** Cement composite strength (*R*) vs. nano-modifier content (*H*).

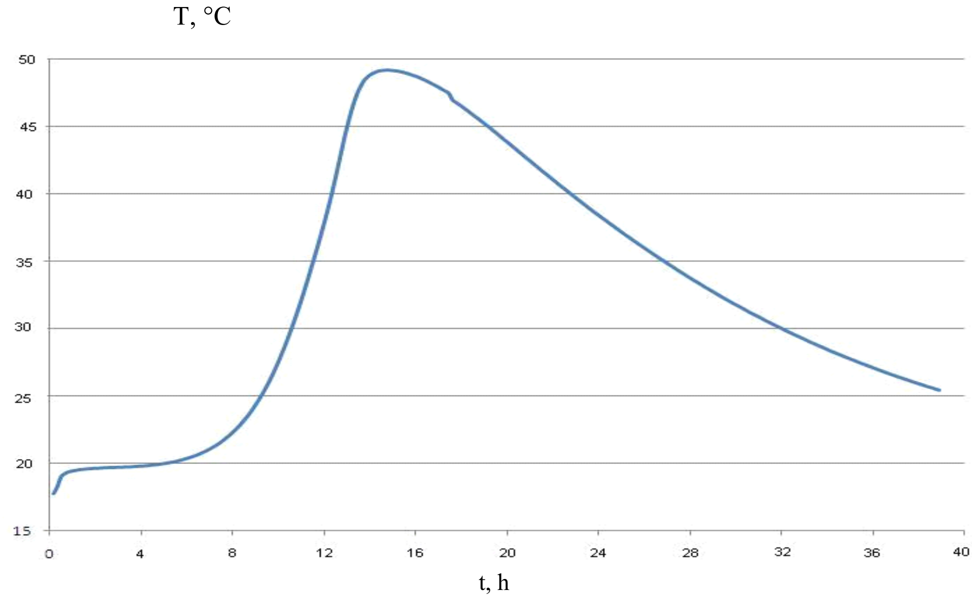


**Fig. 3.** Temperature (*T*) of the cement composite withnano-modifier (*H*) vs. time from the moment of mixing.

- Cement composite hardness vs. the nano-modifier content:

$R = 60.2857 - 0.1181\ H - 0.0127\ H^{2;}$ with the correlation coefficient equal to 0.97

- Mathematical model of the optimal composition No. 3 of the cement composite with nano-modifier hydration kinetics in Table 2:

$T = 19.218 - 7.819\ \tau + 2.703\ \tau^2 - 0.241\ \tau^3 + 0.008\ \tau^4$; with the correlation coefficient equal to 0.975.

By analyzing the hard cement composite with nano-modifier hydration kinetics, as determined by the temperature measurements provided in Fig. 3, it is possible to track the same regularities as in the ultrasound method; however, some exothermy peculiarities are noticeable in different compositions. As such, when adding 15 % of the additive to the mixture, the temperature drops by 30-50 °C in comparison with the reference mixture temperature; and when increasing the quantity of the additive (up to 60 %), gradual reduction of the exothermy is observed. When using the C-3 superplasticizing agent, the rate of temperature growth decreases, but the heating temperature increases.

A positive quality of the filled cements are their low exothermy, which makes them efficient for use in the massive structures.

## Conclusion

Based on the accomplished studies, an active role of the nano-modifiers in the cement stone and contact zone initial structure formation has been established; this is due to the physical and chemical processes that are mainly related to the re-distribution of water and its bonding forms in the concrete mixtures, which are crucial in formation of porosity in the concrete.

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