The Influence of the Technological Order for Modifiers Introduction on the Physical and Mechanical Properties of Cement-Mineral Systems

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Abstract. There were studies aimed on the influence of operating practice for solid-phase mechanochemical modification of cement-mineral systems. The effect of the introduction order for modifiers of hydrophobic-plasticizing action on the physical and mechanical properties of cement-mineral compositions (CMC) was studied.

1. Introduction

Such modifiers as superplasticizing admix S-3 and polyphenylsiloxane-PPS were introduced into the mill during mechanoactivation of Portland cement and mineral filling agent in three ways: together and separately, one after the other after a certain period of time. The analysis of the physical and mechanical characteristics of the modified CMC was carried out relative to the CMC with modifiers of simultaneous introduction.

It was found that with the introduction of PPS after S-3, the normal consistency of the cement paste increases by 20-25%, and with the introduction of superplasticizing admix after PPS, on the contrary, it decreases by 20%. A sharp increase in the setting time (2-4 times more) of the cement paste was noted with the introduction of PPS after S-3. At the same time, the technological order of modifiers introduction has practically no effect on the strength of CMC by the age of 28 days.

The softening coefficient of modified CMC was arranged in the following sequence in a descending order: S-3 first, then PPS - 0.97, simultaneous introduction - 0.93, first PPS, then S-3 - 0.53.

The study of frost resistance (-50°C) of cement-mineral compositions by changing the dynamic modulus of elasticity showed that the frost resistance of CMC with the simultaneous introduction of modifiers is a sequence higher than with the sequential introduction of modifiers.

It is established that when using porous structure filling agents of the volcanic slag type in the CMC, the technological order of modifiers introduction does not affect the frost resistance of hardened cement.

Mechanochemical solid-phase modification of cement-mineral systems is carried out in order to obtain composite binders with special properties (increased frost resistance and corrosion resistance, high fluidity of the cement paste, etc.).

Currently, to obtain special types of composite binders obtained by the method of mechanoactivation of Portland cement with mineral filling agents, modifying agents based on naphthalenesulfonic acids (superplasticizing admix or superplasticizers) are used in the form of a dry powder.
The authors conducted research in the direction of modifying cement-mineral systems with a complex modifier of hydrophobic-plasticizing action, including superplasticizer S-3 and non-functional organic-silicon polymer - polyphenylsiloxane (PPS).

Polyphenylsiloxane is a solid substance with the chemical formula (RSiO$_{1.5}$)$_n$, molecular weight 5 thousand cu; it has a predominantly cyclic and linear structure.

The aim of the work was to assess the influence of technological modification orders (order of modifiers introduction) on the physical and mechanical properties of cement-mineral compositions (normal consistency, setting time, strength, frost resistance and softening coefficient).

Modifiers were introduced into the mill during the mechanoactivation of Portland cement and mineral filling agent in three ways.

1st option: modifying agents were introduced simultaneously;
2nd option: superplasticizer S-3 was introduced first; PPS - after 30 minutes;
3rd option: PPS was introduced first, superplasticizer S-3 after 30 minutes.

The amount of superplasticizer S-3 was 1% by weight of cement, polyphenylsiloxane was 0.2%. The total mechanoactivation time was 1 hour.

Samples — cubes with a rib size of 7 cm — were made from modified cement-mineral compositions. After stripping, the samples were steamed at 80°C according to the (2 + 4 + 2) hr mode. After steam curing, the samples were placed under normal hardening conditions.

A slight decrease in the stripping strength (by 10-15%) was established with the separate introduction of modifiers, relative to the stripping strength of CMC with modifiers of simultaneous introduction (Table 1). However, by 28 days of normal hardening, the strength of CMC samples with modifiers introduced in different technological sequences is practically equalized.

**Table 1.** The influence of the technological order for modifiers introduction on the strength properties of CMC (Spassky cement PC 400 D 20, Khalaktyrsky sand, cement: sand ratio 70: 30 by weight).

| No | Modifying agents, % from cement weight | Technological order for modifiers introduction | Specific surface of dry mixture m$^2$/kg | WT | Compression strength after steam curing, MPa | Stripping strength | 28 days of normal hardening |
|----|----------------------------------------|---------------------------------------------|-----------------------------------------|----|------------------------------------------|------------------|--------------------------|
| 1  | S-3 1                                  | PPS                                         | 575                                     | 0.23 | 54.7                                     | 59.4             |
| 2  | 1                                       | Simultaneous                                 | 585                                     | 0.23 | 52.4                                     | 58.8             |
| 3  | 1                                       | First S-3, then PPS                          | 560                                     | 0.22 | 45.3                                     | 58.3             |
| 4  | 1                                       | First PPS, then S-3                         | 580                                     | 0.23 | 48.8                                     | 56.0             |

Studies on the effect of polyphenylsiloxane on the normal consistency and setting time of the cement paste showed that polyphenylsiloxane does not affect the normal consistency of the cement setting, but it changes the setting time with a tendency to increase by 2-3 times compared with the setting time of CMC with the addition of only superplasticizer S-3 (tab. 2). The usual dependence of an increase in the normal consistency of the cement paste and a reduction in the setting time with an increase in the specific surface of the CMC was also recorded.

Studies on the influence of the technological order for the modifiers introduction on the normal consistency and the setting time of cement-mineral compositions showed (Table 2) that with the introduction of polyphenylsiloxane after superplasticizer S-3 (second option), the normal consistency of the cement paste increased by 20-25%, and when a superplasticizer was introduced after
polyphenylsiloxane (third option), the normal consistency on the contrary decreased by 20% relative to the normal consistency of CMC with modifying agents introduced simultaneously.

A sharp increase in the setting time of the cement paste was observed with the introduction of polyphenylsiloxane after the superplasticizer S-3 (second option): the start of setting increased by 2 times and the end by 4 times compared with the setting time of CMC with modifiers introduced simultaneously (first option).

In the third variant (S-3 was introduced after PPS), such jumps in the setting time were not observed. The start of setting did not change, and the end of setting did not increase significantly (by 20-30%).

It has been established that the technological order of modifiers introduction has a significant effect on the softening coefficient of hardened cement. The softening coefficient of samples made from cement-mineral compositions modified in the first variant (simultaneous introduction) was 0.93, in the second (first S-3, then PPS) - 0.97, in the third (first PPS, then S-3) - 0.53.

Table 2. The influence of the technological order for the modifiers introduction on the normal consistency and the setting time of the CMC (cement: sand = 70: 30% by weight).

| No. | Modifying agents, % from cement weight | Technological order of the modifiers introduction | Specific surface of CMC, m²/kg | Normal consistency, % | Setting time |
|-----|--------------------------------------|---------------------------------|-------------------------------|------------------------|-------------|
| 1   | 1 -                                  | -                               | 340                          | 19.5                   | 1 h 30 min 2 h 25 min |
| 2   | 1 -                                  | -                               | 590                          | 29.5                   | 50 min 3 h 00 min    |
| 3   | 1 0.2                                | simultaneous                    | 375                          | 21.0                   | 4 h 05 min 6 h 00 min|
| 4   | 1 0.2                                | simultaneous                    | 525                          | 24.0                   | 1 h 10 min 2 h 05 min|
| 5   | 1 0.2                                | First PPS, then S-3             | 600                          | 18.4                   | 1 h 00 min 2 h 48 min|
| 6   | 1 0.2                                | First PPS, then S-3             | 640                          | 30.0                   | 2 h 50 min 9 h 30 min|

The study of frost resistance of samples made on the basis of cement-mineral compositions was carried out at -50 °C on samples-beams with a size of 4x4x16 (cm). Evaluation of frost resistance was carried out by changing the dynamic modulus of elasticity over time (table. 3).

Two types of cement-mineral compositions were studied: with a mineral sand filling agent (Khalaktyrskoye deposit) and volcanic slag filling agent (Kozelskoye deposit). The amount of mineral filling agent was 30% of the total mass of CMC.

2. Conclusion

It was found that the sequential introduction of modifiers adversely affects the frost resistance of hardened cement with sand filling agent. Samples modified according to the second and third options were destroyed after 14-18 cycles of freezing and thawing. In hardened cement samples, when modifiers were introduced simultaneously after 34 cycles, on the contrary, an increase in the dynamic modulus of elasticity was observed (Table 3).

In samples filled with volcanic slag, the technological order of modifiers introduction did not affect the frost resistance of hardened cement, which is probably due to the damping effect of the filling agent with respect to structural stresses caused by ice freezing.
Table 3. The influence of the technological order for the modifiers introduction on the frost resistance of cement-mineral compositions.

| Variants of modifiers introduction | Change in dynamic modulus of elasticity (MPa) depending on freeze-thaw cycles |
|-----------------------------------|--------------------------------------------------------------------------------|
|                                   | freeze-thaw cycles | 0   | 2   | 4   | 10  | 13  | 18  | 25  | 27  | 34  |
| Filling agent – Khalaktyrsky sand | 1st                | 1.95| 2.44| 2.42| 2.49|     |     |     |     |     |
|                                   | 2nd                | 2.05| 2.68| 2.78| 2.80| 2.80| 2.70| 2.77| 2.82| 2.95|
|                                   | 3rd                | 2.04| 2.40| 2.30| 2.50|     |     |     |     |     |
| Filling agent – Kozelsky slag     | 1st                | 2.06| 2.22| 2.78| 2.89| 2.82| 2.84| 2.52| 2.81| 2.75|
|                                   | 2nd                | 2.84| 2.26| 2.63| 2.73| 2.92| 2.81| 2.71| 2.79| 2.76|
|                                   | 3rd                | 1.97| 2.55| 2.67| 2.61| 2.73| 2.70| 2.70| 2.70| 2.57|

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