Technological efficiency of mineral modifiers for cement materials with photocatalytic activity

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Abstract. It is known that the efficient kinds of photocatalytic additives for cement materials are "core–shell" compositions synthesized by precipitation of photocatalyst particles on mineral substrates (dispersed carriers). The study aim was to install patterns of influence of 5 mineral modifiers on the technological characteristics of cement systems with finding of the most promising raw materials for dispersed carriers of photocatalytic agents. The increased technological efficiency of silica fume, metakaolin and expanding sulfoaluminate modifier in cement paste, due to the peculiarities of their granulometric composition with high dispersity and defectiveness of particles, was revealed by the research results. It predetermines the prospects of using these mineral additives in the composition of photocatalytically active self-cleaning cement materials.

1 Introduction

The creation of high-performance cement systems characterized by multicomponent composition and improved operational characteristics is current direction of construction materials science [1–6]. The management of structure parameters and physico-mechanical properties for such materials can be achieved through the use of organic and mineral modifiers of different mechanisms of action, which are used individually or combined into complexes according to the principles of synergism and additivity [7–12]. Special group of modifiers includes photocatalytic additives, which make it possible to obtain photocatalytically active cement materials capable of exhibiting a number of positive properties when irradiated with light, such as self-cleaning ability, decompose atmospheric air pollutants, etc. [13–15].

It is aware that the efficient kinds of photocatalytic additives for cement materials are "core–shell" compositions synthesized by precipitation of photocatalyst particles on mineral substrates (dispersed carriers) [16–19].

Analysis of the research results made it possible to identify promising raw materials for carriers of photocatalytic agents:

• Pozzolanic modifiers of natural and man-made origin (diatomite, mordenite, silica fume, metakaolin, zeolite, etc.) having elevated concentration of amorphous silica or

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alumina. These mineral modifiers have high pozzolanic activity and chemical affinity with cement stone crystalline hydrates [8–11, 17, 19, 20].

• Expanding additives of sulfoaluminate composition that allows you to control the cement stone deformations through stimulate the formation of increased phases in size (ettringite, etc.) [12, 21].

• Carbonate rocks consisting mainly of calcite (chalk, limestone, marble, dolomite) [22–24]. These modifiers can act as crystallization centers for new phases in the hydration process of cement systems.

Foreign and domestic experience in obtaining "core-shell" photocatalytic systems for cement materials shows that the type of photocatalytic agent carrier has a primary influence on the final parameters of the synthesized composite modifier [16–19]. In this regard, it is necessary to have data on the composition, structure parameters and physico-chemical characteristics of the mineral raw materials used in order to qualitatively assess the effectiveness of the substrate.

The study aim was to install patterns of influence of 5 mineral modifiers on the technological characteristics of cement systems with finding of the most promising raw materials for dispersed carriers of photocatalytic agents in compositions with "core–shell" structure.

2 Materials and methods

2.1 Materials

Portland cement CEM I 42.5R (PC) (Mordovcement PJSC) was binder in the cement materials.

Five mineral additives (MA) of silicon, aluminosilicate, sulfoaluminate and carbonate composition were used as modifiers:

- MS-85 condensed non-compacted silica fume (SF) (Kuznetsk Ferroalloys JSC).
- MKZhL-2 metakaolin (MTKN) (Plast-Rifey LLC).
- Fly ash (FA) (Aleksin Ceramic Plant LLC).
- Expanding sulfoaluminate modifier (ESAM) (Parad-Rus LLC).
- Microcalcite (MCCT) (Polipark LLC).

2.2 Methods

The effects of type and dispersity of mineral additive particles on the main technological characteristics of modified cement paste, such as water demand and water-holding capacity, were studied wthin the framework of this study.

The dispersity of mineral modifier particles was controlled by specific surface area and granulometric composition parameters determined by the Carman–Kozeny and laser diffraction methods on the PSKh-12 and Shimadzu Sald-3101 devices, respectively.

The water separation of cement paste made up of mixed binder (90 % PC+10 % MA) and water (W/(PC+MA)=1) was parameter of the water-holding capacity of cement systems in according to the Russian State Standard GOST 310.6.

The water/binder ratio (W/(90% PC+10% MA)) of normal density cement paste was parameter of the cement system water demand in accordance with the Russian State Standard GOST 310.3.

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3 Results and discussion

Integral curves of the particle size volumetric distribution for samples of the studied mineral modifiers are shown in Figure 1.

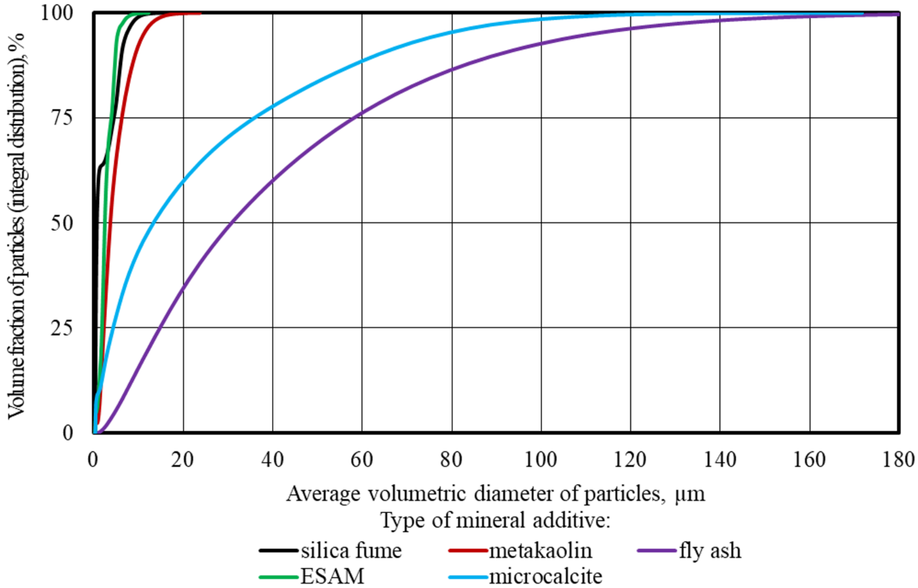

Fig. 1. Integral curves of the particle size volumetric distribution for samples of the studied mineral modifiers.

The specific surface area of silica fume, metakaolin, fly ash, ESAM and microcalcite was 20.0, 1.65, 0.30, 1.00 and 0.25 m^2/g, and the average volumetric diameter of particles (d 50 %) was 0.7, 3.7, 30.7, 2.5 and 13.3 µm, respectively (Table 1), which was determined using the Kozeny-Carman and laser diffraction methods.

Table 1. Values of specific surface area and average volumetric diameter of particles of the studied mineral modifiers.

Type of mineral modifier	**Specific surface area, m^2/g**	**Average volumetric diameter of particles (d 50 %), µm**
Silica fume (SF)	20.00	0.7
Metakaolin (MTKN)	1.65	3.7
Fly ash (FA)	0.30	30.7
Expanding sulfoaluminate modifier (ESAM)	1.00	2.5
Microcalcite (MCCT)	0.25	13.3

Correlation dependencies between the specific surface area of mineral additives used (S_{ss}) and the parameters characterizing the water demand (W_1) (Fig. 2) and water-holding capacity (W_2) (Fig. 3) of cement systems were established according to the research results.

In general, increase in the specific surface area of mineral additives in the studied range of 0.25–20.00 m^2/g contributes to growth in water demand for cement systems (from 26.50 to 31.25 %) (Fig. 2), while the thickening ability of modifiers decreases in the series (SF, MTKN) → FA → ESAM → MCCT, which was revealed based on analysis of experimental data.

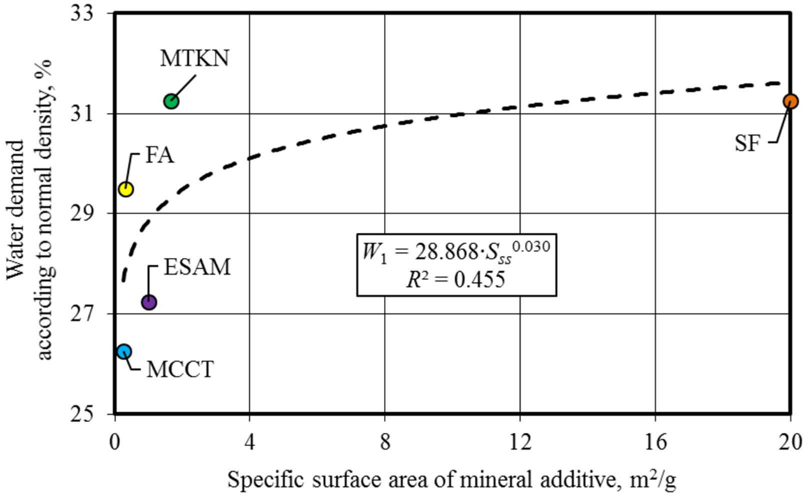

Fig. 2. Specific surface area effects of the mineral modifiers on the water demand of normal density cement paste.

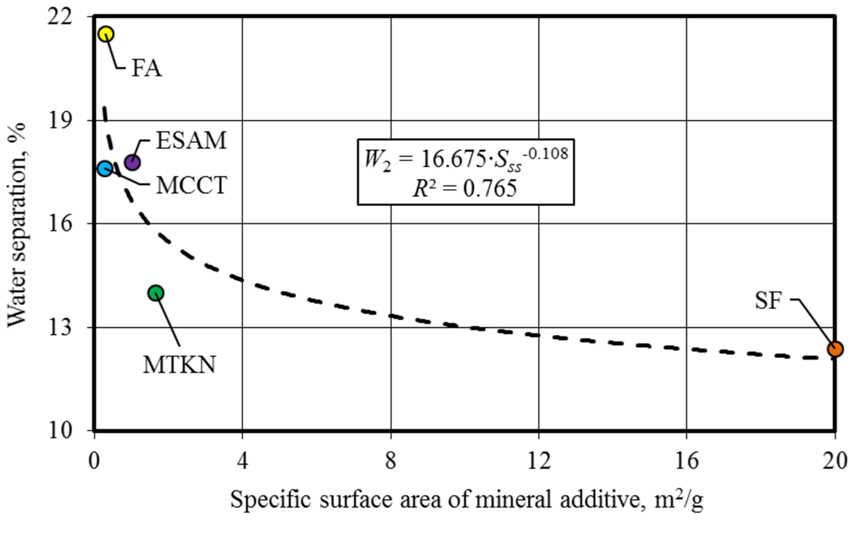

Fig. 3. Specific surface area effects of the mineral modifiers on the water separation of cement paste.

The water separation of cement paste, on the contrary, decrease when the dispersity of mineral additive particles grows (Fig. 3). The correlation between this technological parameter and the specific surface area of modifiers used is characterized by sufficiently high coefficient of determination (R^2=0.765). At the same time, the cement binders modified with silica fume and metakaolin have highest water-holding capacity with the coefficient of water separation by volume is 12.4 and 14.0%, respectively.

4 Conclusions

The following study results were obtained:

- The specific surface area and granulometric composition parameters of 5 types of mineral additives (silica fume, metakaolin, fly ash, sulfoaluminate expanding modifier, microcalcite) were determined.
- The influence of these modifiers on the water demand and water-holding capacity of cement paste was revealed.
- The most promising types of mineral additives for photocatalytic self-cleaning cement materials, such as silica fume (SF), metakaolin (MTKN) and expanding sulfoaluminate modifier (ESAM), were established.

The increased technological efficiency of SF, MTKN and ESAM additives in cement systems is due to the peculiarities of their granulometric composition, in particular, the high dispersity of particles characterized by a developed surface with the presence of numerous defects. The listed factors determine the prospects for using these modifiers as a substrate in "core-shell" photocatalytic systems.

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