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The sulfate resistance of various cementitious binders according to different performance indicators at Nordic countries conditions

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HIGHLIGHTS

- Sulfate resistance (SR) of cementious binders according 5 performance indicators was evaluated.
- Testing temperatures (20 °C and 7 °C) are not crucial evaluating SR of plain cements.
- Mentioned temperatures are only essential evaluating SR of fly ash (FA) modified cements.
- Slower development of hardening structure of FA modified cements affects SR only at 7 °C.
- Test on SR of FA modified cements corresponding to CEM IV/B-SR "failed" at 7 °C.

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ABSTRACT

The sulfate resistance of moderate C_3A Portland and Portland limestone cements (respectively PC and PLC) and their mixes with fly ash (FA) was monitored according to five performance indicators: changes in length, in mass, in strength, in ultrasonic pulse velocity and in appearance. Mortar samples (40 × 40 × 160 mm) were immersed in sodium sulfate solution (16 g/l of SO_4^{2-}) for up to 12 months at ambient +20 °C conditions and more common for Nordic countries +7 °C conditions. The water/binder ratio in mortars was 0.6, pre-curing period before immersion of mortar samples in sodium sulfate solution was 28 days in water at +20 °C.

Research results demonstrated that rating of sulfate resistance using different indicators is not simple and depends on the binder type and exposure temperature. The deterioration of mortar samples in sulfate environment can occur without noticeable expansion. Firstly surface degradation begins and then deterioration throughout the sample volume (loss in strength, decrease of UPV) occurs. The signs of deterioration occur quicker at +7 °C. Research results have showed that a significant positive effect of partial replacement of cement by FA for both PC and PLC was observed only at 20 °C. At +7 °C this effect is much weaker for normal hardening PC and there is almost no effect for rapid hardening PLC.

1. Introduction

Sulfate resistance of cementitious materials, assuming that the environmental conditions and geometry of structure are the same, is determined by two main factors: the chemistry of the cement binder and permeability of concrete or mortar [1]. Contrary, the sulfate resistance of the same cementitious materials in different environment (e.g. different temperature) may vary considerably [2–8]. Sulfate performance of cementitious structures in field conditions can differ significantly from the performance expected according to the laboratory tests [8–10]. The advantages and disadvantages of currently used sulfate resistance testing procedures are fully analyzed in CEN documents [11] and the main features of the available test methods at the European level are given. According to them, to select the test solution temperature, the prevailing local conditions (e.g. for Nordic countries it should be 10 °C or lower) should be taken into consideration. For the testing, prism shaped (40 × 40 × 160) mm hardened cement mortar samples are made, and minimum pre-curing period of 4 weeks at 20 °C is suggested for them. Of all performance indicators applicable to evaluate sulfate resistance (expansion, changes in mass, in appearance and in strength) the pass/fail criteria should be based on the change in strength.

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In European level [12] only few types of CEM cements are considered to be sulfate resistant (SR), namely CEM I with limited C_3A content, blast furnace cement CEM III/B and C and pozzolanic cement CEM IV ($C_3A \leqslant 9\%$) with natural pozzolanas and siliceous FA. The effect of siliceous FA is the same as of other pozzolanas, i.e. gradual depletion of CH during pozzolanic reaction (chemical effect) and reduction of permeability during the formation of C—S—H gel (physical effect) [1,5,7,13]. According to authors [9,10], the improved sulfate resistance of FA concrete in field conditions primarily results from the changes of their physical properties (lower permeability) rather than their chemical properties. It was determined [1,2,7] that the effectiveness of FA against the sulfate attack is better than natural pozzolanas. Ambient temperature is also very important for the effect of FA (as well as of other pozzolanas) to appear, because pozzolanic reaction and microstructure development are slower at low temperatures. Thus, the composition of hydration products (C—S—H) and porosity of hardened cementious material also change [14,15]. According to Liu et al. [3] the sulfate resistance of cement-fly ash mixtures, compared to ordinary cement mixtures, can become even worse at higher temperature, e.g. 30 °C, when the sulfate concentration is higher.

Portland-limestone cement CEM II (PLC), which is very popular for its technical, economic and ecological benefits, is also considered to be SR cement in certain warm climate countries [12]. A comprehensive review of results for sulfate attack of cementitious materials containing limestone fillers was made by Irassar [16]. Water/cement ratio, limestone and C_3A contents in the cement were found to be three main variables that influence the sulfate resistance of the concrete. It is concluded that sulfate attack is first of all controlled by the resistance to the penetration of sulfate ions and that low limestone filler (LF) content (<10%) caused no significant changes in sulfate resistance of the cement, whereas high LF content (>15%) may worsen sulfate performance. It was found [17] that cement mortar with 20% of limestone filler is more permeable than PC mortar. According Schimdt et al. [18], adding 5% of limestone in Portland cement systems decreases the initial capillary porosity and sulfate-induced deterioration reduces, especially at 20 °C, whereas adding 25% of limestone decreases the sulfate resistance. Lee et al. [19] also concluded that replacement of PC with 10–30% of LF has a negative effect on sulfate resistance. In [2,20,21] it was concluded that thaumasite formation intensifies due to the presence of LF at low positive temperatures. Some papers state that thaumasite is also formed at ambient (20 °C) temperatures [17,19,22,23]. The effect of pozzolanas for PLC is the same as for ordinary PC, but the presence of ultrafine carbonate particles in PLC alters both the physical and chemical effects of pozzolanas. Tsivilis et al. [2,7] found that at low positive temperatures natural, slowly reacting pozzolanas, which is known to be a very good pozzolanic material used in construction, decrease sulfate resistance of PLC, while FA, ground granulated blast furnace slag and metakaolin greatly improve the sulfate resistance. This positive effect is most probably attributed to lower permeability and pore refinement, as well as to improved resistance due to retardation of the thaumasite formation. Lower porosity of cement paste with addition of limestone filler and silica fume is also noticed in [24]. According to [25] the addition of silica fume to PLC significantly improves sulfate resistance, while FA and slag do not have any influence on sulfate resistance. In [6] it is concluded that PC and PLC with high C_3A content can be resistant to sulfate attack at both ambient and low temperatures, if they are combined with a sufficient amount of supplementary cementitious materials (SCM).

The present paper reports the testing of sulfate resistance (at ambient 20 °C and low 7 °C temperatures) of moderate C_3A Portland cement CEM I and Portland limestone cement CEM II/A-LL produced from the same clinker and their mixtures with FA by assessing various performance indicators (linear expansion, changes in mass, in strength, in ultrasonic pulse velocity and in appearance). Sulfate resistant blast furnace cement CEM III/B was used as the reference cement. The aim of this study is to explore the effectiveness of adding siliceous FA in order to improve sulfate resistance of widely used cements at Nordic countries conditions.

2. Materials and methods

2.1. Materials

The following raw materials were used as binders: cements CEM I 42.5 N (PC), CEM II/A-LL 42.5 R (PLC), CEM III/B 32.5 N (BFC) according to standard EN 197-1 produced from the same clinker and siliceous fly ash (FA) according to standard EN 450-1. The mineralogical composition of clinker (Bogue calculation): C_3S – 68.1%; C_2S – 13.8%; C_3A – 8.6%; C_4AF – 7.1%. The content of limestone in PLC ~ 15%, the content of slag in BFC ~ 70%. The chemical composition and fineness of used materials are shown in Table 1. For the production of mortar samples, sand of 0/4 fraction according to standard EN 12620 was used.

2.2. Preparation of forming mixtures and mortar samples

The raw materials used for preparation of forming mixtures were weighed by electronic balance SI-8001A with capacity of 8.0 kg, precision of 0.1 g and verification value of 1.0 g. Compositions of forming mixtures: 1 part of binder (any cement or its mix with FA, see Table 2) and 3 parts of sand. Water/binder ratio – 0.60.

The preparation of forming mixture, moulding and conditioning of the mortar samples was carried out according to standard EN 196-1. The forming mixtures were prepared by mechanical mixing using planetary mixer Maren with a bowl capacity of 30.0 L and low/high speeds of blade – 65/125 rpm respectively. The forming mixture was compacted in a moulds using jolting apparatus B 2808 RT (60 jolts in 60 ± 3 s). The prismatic steel moulds were used to form mortar samples with (40 × 40 × 160) mm dimensions for the tests. The composition of binder and codes of corresponding mortar samples are shown in Table 2.

The mortar samples were demoulded after 24 h of hardening (at temperature of 20 °C and relative humidity of 100%) and were kept immersed in a water for 27 days at 20 °C. Afterwards the mortar samples of each composition were divided into four sets (each of 15 prisms) and stored in the following conditions: sets 1 and 2 in water at 20 °C and at 7 °C respectively (control samples), sets 3 and 4 in sodium Sulfate solution (16 g/l of SO_4^{2-}) at 20 °C and at 7 °C respectively. Tanks with Sulfate solution were refilled every month.

2.3. Methods of testing

The rating by the following five performance indicators – change in length, change in mass, in compressive and flexural strengths, in ultrasonic wave velocity (UWV) and in appearance – was made periodically (every 3 months). These characteristics of mortar samples were determined at temperature of 20 ± 2 °C and relative humidity 60 ± 10%.

The length comparator E077 with digital indicator ID-C112B (resolution 0.001 mm, measuring range 12.7 mm, accuracy 0.003 mm, measuring force 0.9 N) was used to measure the change in length of mortar samples. The final test result was taken as the average value calculated out of at least 3 successful measurements. The change in length (Δ_l) of mortar sample was calculated from the following equation: