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Effects of mix composition and water–cement ratio on the sulfate resistance of blended cements

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Abstract

This paper presents an experimental investigation on the sulfate resistance of blended cements containing various amounts of natural pozzolan and/or Class-F fly ash. The performance of blended cements was monitored by exposing the prepared mortar specimens to a 5% Na_2SO_4 solution for 78 weeks. For comparison, an ordinary Portland cement (produced with the same clinker as blended cements) and a sulfate resistant Portland cement (produced from a different clinker) were also used. In addition to the cement chemistry, water–cement (w/c) ratio of mortars was another parameter selected that will presumably affect the performance of mortars. The experimental results of expansion measurements showed that the effect of w/c ratio was more pronounced for the low sulfate resistant cements with higher C_3A amounts, while the blended cements were less affected by an increase in the w/c ratio.

Keywords: Blended cement; Sulfate attack; Fly ash; Natural pozzolan

1. Introduction

External sulfate attack which was first identified in 1908 by the United States Bureau of Reclamations [1] is one of the durability problems associated with concrete. Since its identification it has been the subject of numerous studies and still not totally understood [2]. The extent to which concrete is affected by sulfates depends on several factors including its permeability, water to cement (w/c) ratio, type of cement, exposure conditions and the environment [3]. Assuming the same environmental conditions, two factors will tend to control the resistance of a given concrete to sulfate attack: the chemistry of the cement and the permeability of the concrete.

- To control the cement chemistry, American Standards [4] suggest a limit on the (C_3A) and ($2C_3A + C_4AF$) contents of sulfate resistant, type V, cements as 5% and 25%, respectively. On the other hand, cements with low C_3A and C_4AF compounds generally tend to have a higher C_3S/C_2S ratio, and an increase in the C_3S content of cement generates a significantly higher amount of calcium hydroxide, as the hydration of C_3S produces nearly 2.2 times more calcium hydroxide (CH) than the hydration of C_2S. CH is known to be responsible for the formation of gypsum, and gypsum is known to be the first step of the formation of ettringite, which can be considered as the principal cause of deterioration [5]. Irassar et al. found mortar bars containing a low C_3A and low C_3S cement showed 10 times less expansion than those with a low C_3A and a high C_3S content [6].
- To control the permeability of concrete, lower w/c ratio and/or pozzolans are recommended [7,8]. Effect of various pozzolans on the resistance of cements to external sulfate attack has also been studied by other researchers [9–11]. Pozzolans reduce not only the permeability but also the C_3A amount if they are a partial replacement of cement. Moreover, use of pozzolans or use of blended cements, in general, reduces the quantity of CH due to the pozzolanic reactions which would otherwise react with sulfates to form gypsum.

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The abovementioned parameters, i.e. the cement composition and w/c ratio are the subject of this study. In order to investigate the effects of these two parameters against external sulfate attack, ordinary, blended and sulfate resisting cements were used to prepare cement mortars with two different w/c ratios, thus different permeabilities. These cement mortars were then immersed in a 5% Na_2SO_4 solution and compressive strength and length change (expansion) of mortar specimens were determined after various periods of immersion. For a better explanation of their performance against sulfate attack, X-ray diffraction (XRD), X-ray energy dispersion analysis and scanning electron microscopy (SEM) of cement pastes subjected to the same solution were also used.

2. Materials and experimental program

2.1. Cements

An ordinary Portland cement (OPC) and five different blended cements were produced with different proportions of clinker, natural pozzolan, fly ash and limestone. The chemical analysis of these raw materials is given in Table 1. The natural pozzolan was obtained from Bilecik and Yenişehir, the low-lime fly ash was obtained from the Seyitömer power-plant, and the limestone with a $CaCO_3$ amount of 95% was obtained from Bursa, Turkey. Labeling for all cements together with their ingredients is provided in Table 2. For comparison a sulfate resistant Portland cement (SRPC) with a different clinker was also obtained. The chemical composition and the major compounds of all Portland cements together with their physical properties are presented in Table 3.

2.2. Mixtures

Mortar mixtures were prepared using the cements mentioned above and the Rilem Cembureau Sand meeting the requirements of ASTM C 778. In all mortar mixtures cement:sand ratio was kept constant as 1:2.75 by weight.

Table 1
Chemical composition of materials

Chemical analysis (%)	Materials used in OPC and blended cement production			
	Clinker	Natural pozzolan (NP)	Fly ash (FA)	Limestone
SiO_2	20.63	66.44	57.10	1.36
Al_2O_3	6.09	12.11	18.67	1.05
Fe_2O_3	3.74	1.78	9.75	0.61
CaO	65.28	5.13	4.71	52.84
SO_3	0.94	1.76	0.67	0.23
MgO	0.44	0.95	4.43	0.28
Na_2O	0.53	0.63	0.38	0.04
K_2O	0.48	2.71	2.05	0.13
Loss on ignition (LOI)	0.36	7.15	2.13	41.93

Table 2
Material proportions of OPC and blended cements

Cement		Material (%)			
Label	Name	Clinker	NP	FA	Limestone
OPC	CEM I 42.5R	96.5	0.0	0.0	3.5
BC	CEM II/B-M(P-V) 42.5N	70.8	10.8	14.9	3.5
BC_{FA}	CEM IV/A-V 32.5R	64.7	0.0	31.8	3.5
BC_{NP}	CEM IV/A-P 32.5R	66.3	30.2	0.0	3.5
BC_{NP-FA}	CEM IV/B(P-V)32.5R	61.2	22.2	13.1	3.5
BC_{FA-NP}	CEM IV/B(P-V)32.5R	60.3	15.3	20.9	3.5

Seven mixtures were first prepared with a w/c ratio of 0.485, and flow and consistency characteristics of these mixtures were determined. Later, another set of seven mixtures were prepared by changing the w/c ratio in order to obtain similar consistency of the blended cements with the previously determined consistency of the OPC and SRPC mortar mixtures. The flow characteristics as determined by ASTM C 1437 and w/c ratios of all 14 mixtures are presented in Table 4. As seen in Table 4, the mixtures can be approximately grouped into two different w/c ratios such as 0.485 and 0.560.

From each mixture, $25 \times 25 \times 285$ mm prismatic mortar bars and 50 mm cubes were cast. The prismatic mortar bars were used for length measurements and the cubes were used to determine the compressive strength. After casting and finishing, the molds were covered with plastic sheets and stored for 24 h in a moist room (relative humidity: above 95% and temperature: 35 ± 3 °C). After the initial curing period, the specimens were demoulded and cured in lime saturated water at 23 °C until the mortar cube specimens gained compressive strength of 19.5 MPa or higher as described by ASTM C 1012. Upon reaching a compressive strength of 19.5 MPa (0-week), all prismatic mortar bars were stored in a 5% sodium sulfate (Na_2SO_4) solution (50 g/L). Length measurements of the prismatic specimens were performed at 1, 2, 3, 4, 8, 13, 15, 17, 26, 52 and 78 weeks after immersing the specimens into the sulfate solution. As the bars were cracked (Fig. 1) length change measurements was not possible for OPC mortar bars with a w/c of 0.560 at the end of 26 weeks, and for OPC mortar bars with a w/c of 0.485 at the end of 52 weeks. In the same way, after reaching compressive strength of 19.5 MPa, cube specimens were stored in a 5% Na_2SO_4 solution at 23 °C. The compressive strength measurements of the cubes were performed after 4, 26 and 52 weeks. In addition to the cement mortars, cement pastes that has equal w/c ratios with mortars were also prepared and subjected to the same sulfate solution. They were cast in plastic cylinders and demoulded the next day. After demoulding, the paste samples were cured in lime-saturated water for an additional 27 days. The paste samples were then exposed to 5% Na_2SO_4 solution at 23 °C. After the sulfate exposure period X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM) was conducted on the paste samples. XRD