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Magnesium sulfate attack on hardened blended cement pastes under different circumstances

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Abstract

This paper describes the sulfate resistance of some hardened blended Portland cement pastes. The blending materials used were silica fume (SF), slag, and calcium carbonate ($CaCO_3$, $C\bar{C}$). The blended cement pastes were prepared by using W/S ratio of 0.3. The effects of immersion in 10% $MgSO_4$ solution under different conditions (room temperature, 60 °C, and drying–immersion cycles at 60 °C) on the compressive strength of the various hardened blended cement pastes were studied. Slag and $C\bar{C}$ improve the sulfate resistance of ordinary Portland cement (OPC) paste. Mass change of the different mixes immersed in sulfate solution at 60 °C with drying–immersion cycles was determined. The drying–immersion cyclic process at 60 °C accelerates sulfate attacks. This process can be considered an accelerated method to evaluate sulfate resistance of hardened cement pastes, mortars, and concretes.

Keywords: Durability; Sulfate attack; Cement; Blended cement

1. Introduction

Sulfate attack on mortar specimens made with different types of cement was studied [1–3]. In addition, the effect of initial curing conditions on sulfate resistance of concrete, made with blended ordinary Portland cement (OPC), was investigated [4]. In addition, the effect of $MgSO_4$ in the presence of $MgCl_2$ on mortar samples was evaluated [5,6]. Moreover, the evaluation of sulfate attack on blended cements, incorporating supplementary cementitious materials such as fly ash, slag, and silica fume (SF), has been carried out by many investigators [6–13].

The attack of sodium sulfate on concrete is due to two principal reactions: the reaction of Na_2SO_4 and $Ca(OH)_2$ to form gypsum and the reaction of the formed gypsum with calcium aluminate hydrates to form ettringite. In addition, it is noticed that $MgSO_4$ reacts with all cement compounds, including C-S-H, thus decomposing cement, and subsequently forming gypsum and ettringite [14,15]. In a comprehensive review on the sulfate attack, Mehta [16] pointed out that, in most cases, the loss of adhesion and strength, not expansion and cracking, is the primary manifestation of sulfate attack.

Concrete deterioration due to $MgSO_4$ attack was attributed to the decalcification of C-S-H to form M-S-H, as well as the expansion caused by the formation of expansive salts. Concrete, with the addition of SF, showed a greater degree of deterioration on the surface together with an intense formation of polygonal cracks filled with gypsum [9]. The Ca lost and Mg gained by cement pastes as a result of $MgSO_4$ attack were determined and it was found that the molar ratio of Mg/Ca was much higher than unity [17,18]. Torii and Kawamura [11] studied the resistance of mortars containing fly ash or SF in 2% H_2SO_4, 10% Na_2SO_4, and 10% $MgSO_4$ solutions. Fly ash and SF appeared to significantly increase the resistance, but only above a certain content, which depended on the type of sulfate solution.

Sorrentino et al. [19] demonstrated by expansion and microstructural studies that concrete of moderate strength (40 MPa) was deteriorated in $MgSO_4$ or seawater. Large quantities of secondary ettringite and gypsum and a non-cohesive M-S-H were formed. In higher strength concrete (e.g., 80 MPa), the reaction resulted in some compact layers of gypsum, aragonite, and brucite, which formed a barrier to prevent further attack. Thus, expansion was negligible even after immersion in seawater for 3 years.

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The deterioration of concrete due to sulfate attack is considered a complex problem and it depends on many factors:

(a) factors related to concrete properties:
    0.1. type of Portland cement,
    0.2. W/C ratio,
    0.3. CH content,
    0.4. pore structure of the formed hydrates, and
    0.5. using of mineral admixtures such as fly ash, slag, SF, . . ., etc.
(b) factors related to aggressive medium:
    0.1. type of salt,
    0.2. concentration, and
    0.3. presence of more than one kind of aggressive ions.
(c) factors related to environmental conditions:
    0.1. temperature and
    0.2. drying–wetting cycles.

Therefore, the aim of this investigation is to give a comparative evaluation of sulfate resistance of some hardened blended cement pastes immersed in 10% $MgSO_4$ solution under different conditions, as well as to evaluate the more effective sulfate attack condition.

2. Experimental

The materials used in this investigation were OPC, SF (Alexandria Company of Ferro-Silicon, Egypt), slag (Helwan Steel, Cairo, Egypt), and fine powder analytical reagent calcium carbonate ($CaCO_3$, $C\bar{C}$). The properties of the used materials are given in Table 1. The composition and designation of the different mixtures are indicated in Table 2. Each dry mixture was thoroughly mixed using a ball mill with a few number of balls for 3 h. The pastes were prepared using a W/S ratio of 0.3. The pastes were moulded into 1-in. cubes. The moulds were vibrated for 1 min to remove any air bubbles and voids. Immediately after moulding, the samples were cured in a moist cabinet for 24 h, demoulded, and cured under water for 28 days.

Table 1
Properties of the used materials

Oxide composition (%)	OPC	Silica fume	Slag
SiO_2	20.00	95	36.47
CaO	62.35	minor	30.72
Al_2O_3	5.14	minor	12.26
Fe_2O_3	3.28	1.80	0.44
MgO	2.12	–	2.31
SO_3	2.45	–	–
BaO	–	–	7.46
MnO	–	–	4.63
LOI	2.80	–	–
Na_2O+K_2O	0.65	1.24	2.26
Blaine area	3479 cm^2/g	20 m^2/g	2470 cm^2/g
LSF	0.94	–	
C_3A	8.10	–	

Table 2
Composition and designation of the different mixtures

	Composition (%)			
Mix number	OPC	SF	Slag	$C\bar{C}$
I	100	–	–	–
II	90	10	–	–
III	85	15	–	–
IV	60	–	40	–
V	80	–	20	–
VI	95	–	–	5
VII	90	–	–	10
VIII	85	10	–	5
IX	75	–	20	5
X	70	10	20	–
XI	65	10	20	5

After 28-day curing under water, excluding control specimens (Series 1), all others were transferred into 10% $MgSO_4$ solution under different conditions at room temperature (Series 2), at 60 °C (Series 3), and at 60 °C with drying–immersion cycles (Series 4). Compressive strength was determined for all samples after 28, 90, 120, and 180 days from the beginning of curing. Mass change was determined for the sample Series 4 (at 60 °C with drying–immersion cycles) after 30, 60, 90, 120, and 150 days of exposure to sulfate solution. Drying–immersion cycles were carried out each 10 days.

3. Results and discussion

3.1. Compressive strength

The values of compressive strength of the different hardened cement pastes immersed in sulfate solutions, under various conditions as well as the control samples (stored in water), relative to those of 28-day samples are represented graphically versus time in Figs. 1–11.

Fig. 1 shows the relative compressive strength of the various hardened OPC pastes (Mix 1) compared to that of 28-day samples. It is obvious that the pastes stored in $MgSO_4$ solution at room temperature (Series 2) did not show any significant difference in compressive strength compared to water-stored samples (Series 1) up to 180 days, whereas samples stored in sulfate solution at 60 °C (Series 3) showed a lower compressive strength in comparison with control samples up to 180 days. The compressive strength of Series 3 decreased up to 90 days, thereafter increased relatively in the period of 90–120 days, and at 180 days no much change in compressive strength was observed. The samples stored in sulfate solution at 60 °C and subjected to drying–immersion cycles (Series 4) showed a higher reduction in compressive strength compared to control samples and others exposed series up to 180 days. The strength

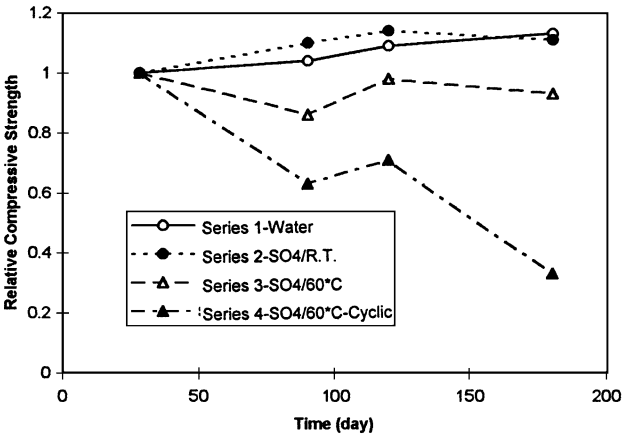

Fig. 1. Relative compressive strength versus time for OPC pastes (Mix I) stored in water and $MgSO_4$ solutions.

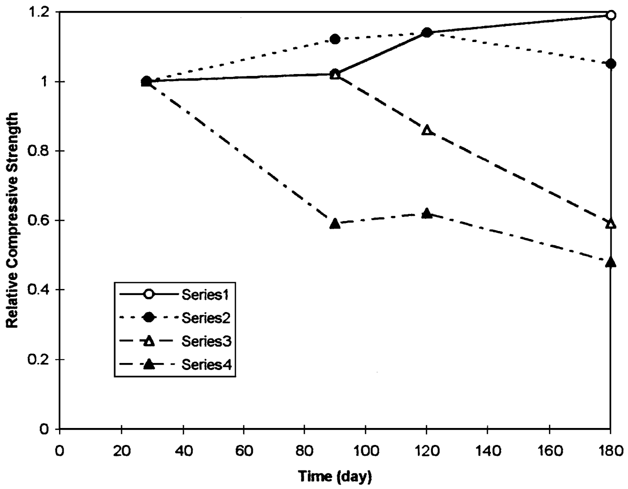

Fig. 3. Relative compressive strength versus time for 85% OPC–15% SF pastes (Mix III) stored in water and $MgSO_4$ solutions.

slightly increased during the period 90–120 days, then decreased again at 180 days.

Figs. 2 and 3 show the relative compressive strength of the various series of hardened SF–Portland cement blends (Mixes II and III) compared to 28-day values. There was a little variation in compressive strength of the samples stored in sulfate solution at room temperature (Series 2) compared to the control for Mixes II and III. Sulfate attack was more obvious in case of Mix III (which contains more SF) stored in sulfate solution at 60 °C (Series 3) compared to Mix II. Both mixes showed a high reduction in strength in case of Series 4.

Hardened cement pastes containing slag, Mixes IV (40%) and V (20%), showed nearly the same behavior of relative strength change with curing age for Series 1, 2, and 3. Mix IV samples had a relatively high sulfate resistance compared to Mix V and other mixes as noticed from the results of Series 4 (see Figs. 4 and 5).

The hardened cement pastes containing $C\bar{C}$, Mixes VI and VII, showed nearly similar trends in the variation of relative compressive strength with curing age for the different series (see Figs. 6 and 7). In addition, they showed analogous behavior to Mix I but with relatively high sulfate resistance. The different hardened cement pastes containing a combination of $C\bar{C}$ with SF and/slag, or Mixes VIII–XI, showed analogous behavior in the variation of relative strength versus curing age with those of the previous mixes. The sulfate resistance of these mixes seemed to be slightly higher than the hardened plain Portland cement pastes (Mix I), but lower than Mixes IV and VI (Figs. 8–11).

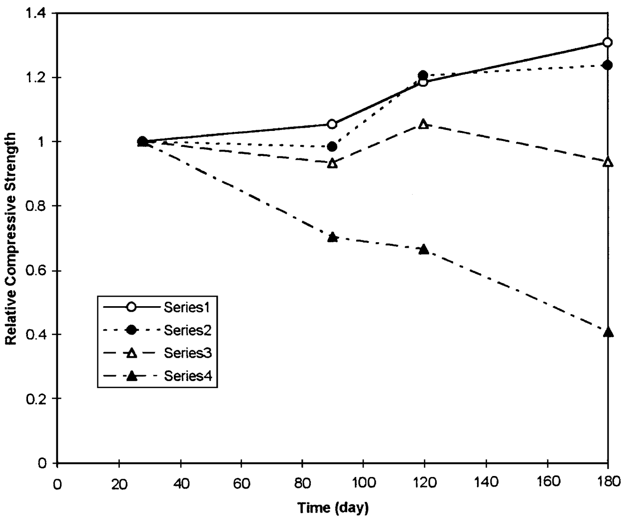

Fig. 2. Relative compressive strength versus time for 90% OPC–10% SF pastes (Mix II) stored in water and $MgSO_4$ solutions.

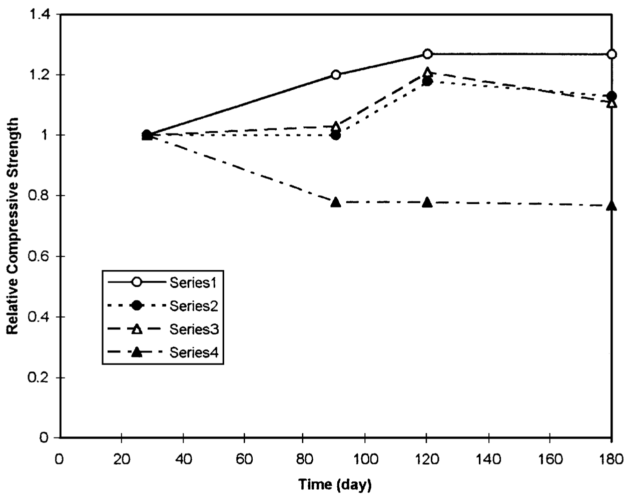

Fig. 4. Relative compressive strength versus time for 60% OPC–40% slag pastes (Mix IV) stored in water and $MgSO_4$ solutions.

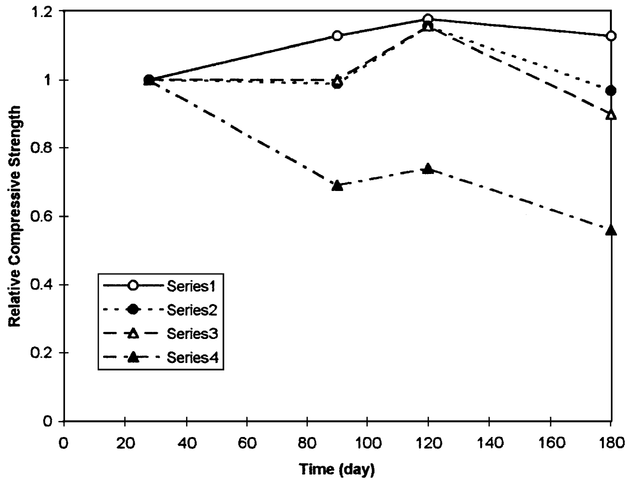

Fig. 5. Relative compressive strength versus time for 80% OPC–20% slag pastes (Mix V) stored in water and $MgSO_4$ solutions.

Fig. 12 shows the relative compressive strength of Mixes I, II, IV, and VI for Sample Series 3 and 4 (more aggressive media) for comparison. Obviously, Mixes IV (40% slag) and VI (5% $C\bar{C}$) had the highest sulfate resistance than all other mixes, whereas the partial replacement of Portland cement by SF did not significantly improve the sulfate resistance of the hardened cement pastes.

3.2. Mass change

Mass change was determined for all the hardened pastes stored in sulfate solution at 60 °C and subjected to drying–immersion cycles (Series 4). The results of mass change with exposure time for the various mixes are shown in Figs. 13 and 14.

There was a continuously mass increase for all the hardened pastes with exposure age with different extents except Mixes III (with 15% SF) and VIII (10% SF + 5% $C\bar{C}$) showed mass loss at earlier ages, up to 120 days, then at later age a mass increase was observed. Generally, the least mass increase was found in mixes containing SF. It is obvious that the use of mass loss to predict the sulfate resistance is not an accurate method.

A nearly similar trend was observed in the change of relative compressive strength for different series of all mixes with curing age. All the hardened pastes (Series 2) showed a continuous increase in compressive strength up to 120 days. Thereafter, the strength decreased at the later age (180 days). The first increase in strength may be attributed to two types of reactions: (I) the continuous hydration of unhydrated cement components to form more hydration products in addition to the reaction of SF or slag (in case of blended cements) with the liberated lime to form more C-S-H

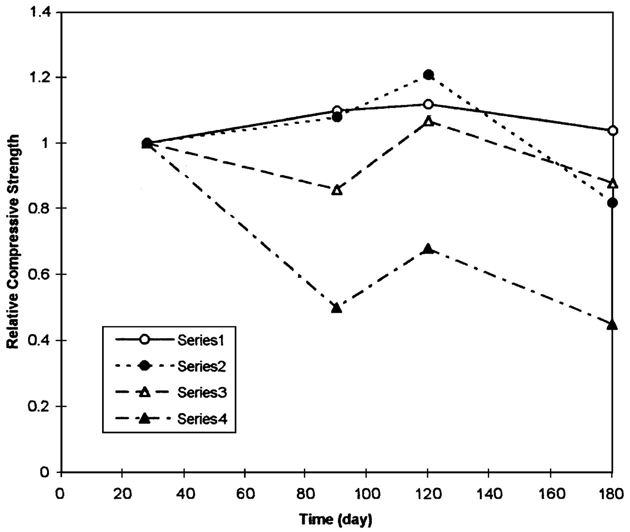

Fig. 7. Relative compressive strength versus time for 90% OPC–10% $C\bar{C}$ pastes (Mix VII) stored in water and $MgSO_4$ solutions.

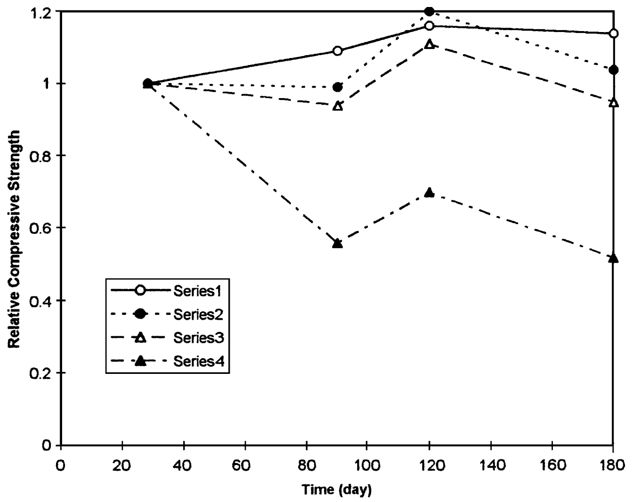

Fig. 6. Relative compressive strength versus time for 95% OPC–5% $C\bar{C}$ pastes (Mix VI) stored in water and $MgSO_4$ solutions.

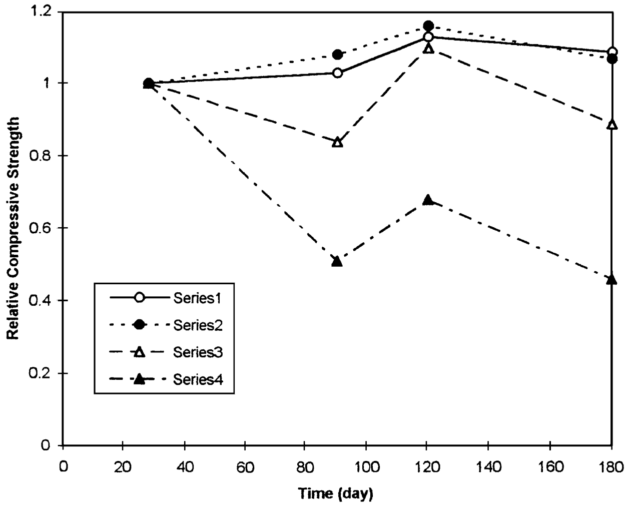

Fig. 8. Relative compressive strength versus time for 85% OPC–10% SF–5% $C\bar{C}$ pastes (Mix VIII) stored in water and $MgSO_4$ solutions.

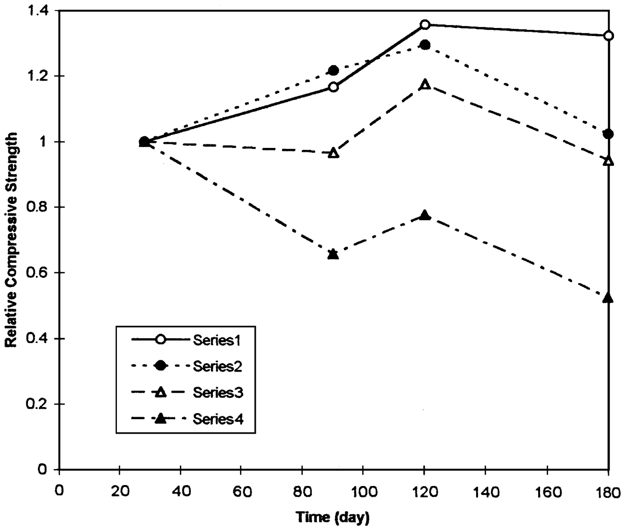

Fig. 9. Relative compressive strength versus time for 75% OPC–20% slag–5% C$\bar{C}$ pastes (Mix IX) stored in water and $MgSO_4$ solutions.

leading to increasing compressive strength and (II) reaction of sulfate ions with hydrated cement components to form gypsum and ettringite. Therefore, at earlier ages, these two reactions lead to a denser structure as a result of precipitation of the products within voids and micropores. Whereas, at later ages, the second type of reactions (sulfate attack) become more dominant leading to formation of microcracks and this decreases strength.

Most of the hardened pastes exposed to sulfate solution at 60 °C (Series 3) showed a decrease in strength at 90 days, while at 120 days the strength was relatively increased. At 180 days, the strength was decreased again. The first decrease in compressive strength can be attributed to the acceleration of sulfate attack by increasing the temperature to 60 °C. This leads to the formation of much products from the reaction of magnesium sulfate with cement hydrates.

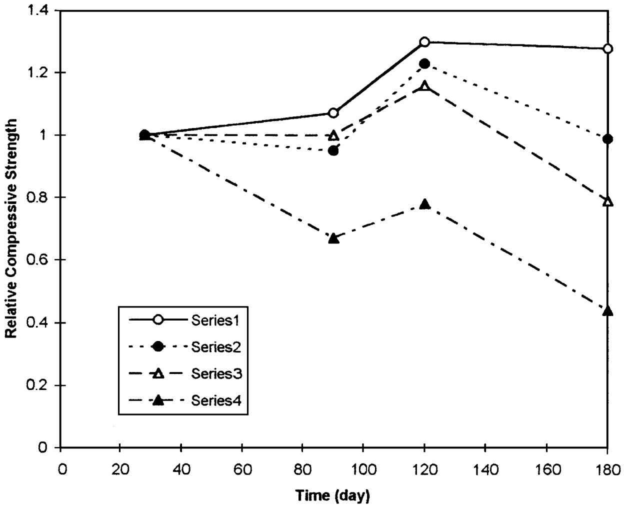

Fig. 10. Relative compressive strength versus time for 70% OPC–20% slag–10% SF pastes (Mix X) stored in water and $MgSO_4$ solutions.

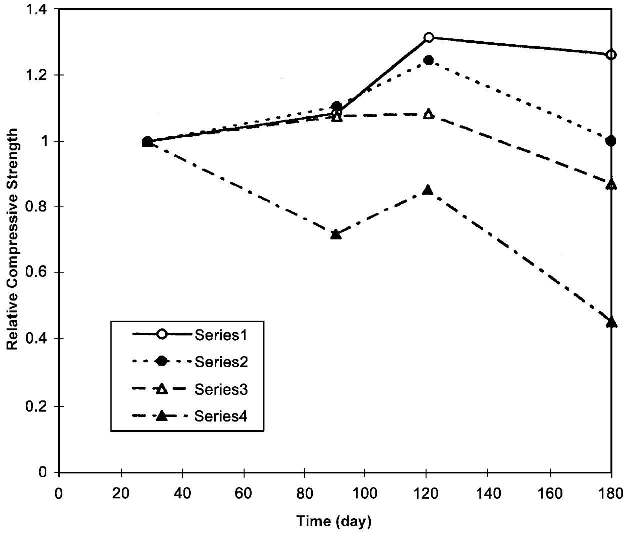

Fig. 11. Relative compressive strength versus time for 65% OPC–20% slag–10% SF–5% C$\bar{C}$ pastes (Mix XI) stored in water and $MgSO_4$ solutions.

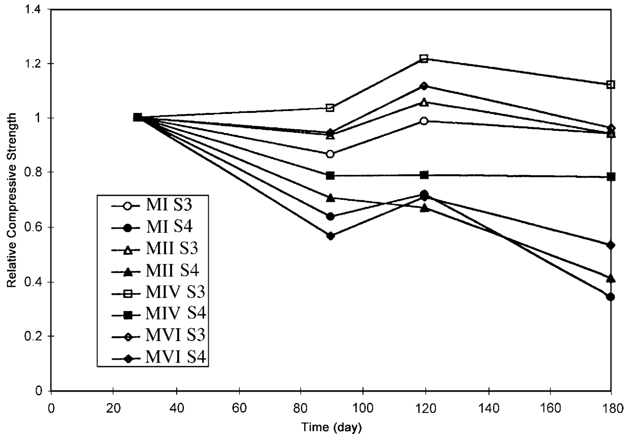

Fig. 12. Relative compressive strength versus time for Mixes I, II, IV, and VI.

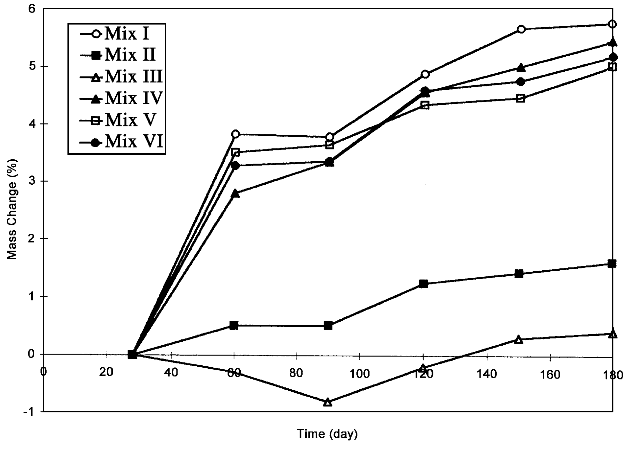

Fig. 13. Percentage mass change versus time for Mixes I, II, III, IV, V, and VI.

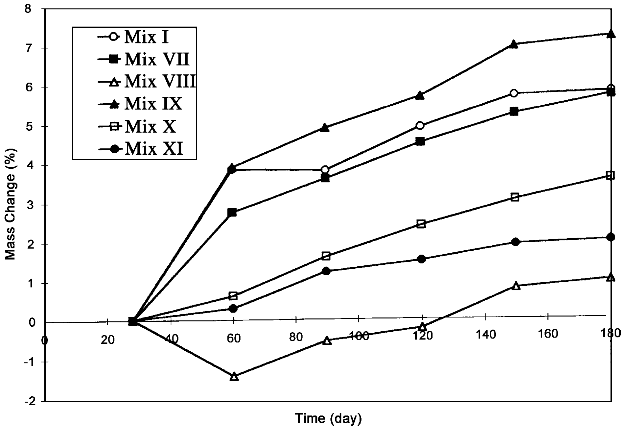

Fig. 14. Percentage mass change versus time for Mixes I, VII, VIII, IX, X, and XI.

The formed products are M-S-H as a result of decalcification of C-S-H, gypsum, and ettringite. All of these lead to a decrease of compressive strength and the last two products can cause crack formation; whereas the increase observed in strength at 120 days may be attributed to the pore and crack filling by the reaction products.

All the samples stored in sulfate solution at 60 °C and subjected to drying–immersion cycles (Series 4) showed lower compressive strength than those of the control and other sulfate-exposed series. This can mainly be attributed to the high severity sulfate attack condition of this series, because the damage of hardened cement paste structure resulted from two main phenomena: (a) the deterioration as a result of the reaction of $MgSO_4$ with cement hydrates and (b) the repetitive crystallization cycles of $MgSO_4 \cdot nH_2O$ by drying–immersion of the hardened pastes that can produce internal stresses in pores leading to the formation of cracks. This explanation of the mechanism of sulfate attack is in accordance with that reported in other publications [14–16]. The reactions of $MgSO_4$ with cement hydrates can be illustrated as follows:

$$MgSO_4aq + Ca(OH)_2 = CaSO_4 \cdot 2H_2O + Mg(OH)_2$$

$$MgSO_4aq + C - S - H = CaSO_4 \cdot 2H_2O + M - S - H$$

The formed gypsum from the above two reactions reacts with calcium aluminate hydrate (C_4AH_{13}) and calcium monosulfoaluminate hydrate (C_4ASH_{12}) to form ettringite as follows:

$$C_4AH_{13} + 3CaSO_4 \cdot 2H_2O + 14H_2O$$

$$= C_3A \cdot 3CaSO_4 \cdot 32H_2O + Ca(OH)_2$$

$$C_3A \cdot CaSO_4 \cdot 12H_2O + 2CaSO_4 \cdot 2H_2O + 16H_2O$$

$$= C_3A \cdot 3CaSO_4 \cdot 32H_2O$$

The sequence of chemical reactions of magnesium sulfate with cement hydrates in the different hardened cement pastes may slightly vary from mix to another depending on the CH content. The pastes that contained SF seemed to have lower sulfate resistance than the others blended with slag or $C\bar{C}$ and this may be attributed to the depletion of CH content. Therefore, the decalcification of C-S-H to form noncohesive M-S-H is accelerated and this result is in agreement with that reported by Bonen [9].

4. Conclusion

The main conclusions could be derived from this investigation are summarized as follows:

1. Partial replacement of Portland cement by SF (10–15%) did not show a significant improvement in sulfate resistance of hardened cement pastes.
2. The hardened cement pastes contained 40% slag or 5% $C\bar{C}$ showed a noticeable high sulfate resistance compared to the plain OPC pastes.
3. Exposure to sulfate solution at 60 °C with drying–immersion cycles can be considered an accelerated method for sulfate attack.

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