

Hydration, Strength Development and Sulphate Attack of Some Cement Composites

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Submitted: Apr 21, 2013; **Accepted:** Jun 4, 2013; **Published:** Jun 10, 2013

Abstract: The aggressive attack by sulphate ions is one of the main reasons for the potentially damaging of Portland cement mortars and concrete. So, an experimental work on multicomponent blended cement pastes from Ordinary Portland cement (OPC), granulated blast furnace slag (GBFS) and pulverized fuel ash (PFA) used against the attack of 4 % Na₂SO₄ solution up to 12 months has been carried out. The results showed that such cement blends have a satisfactory strength development under normal conditions and are more resistant to SO₄²⁻ ions if compared with those of OPC pastes, particularly the cement blend containing sodium silicate (Na₂SiO₃). The calcium silicate hydrate (CSH), calcium hydroxide (CH) and ettringite were detected by XRD patterns and SEM images during normal hydration but increased after immersion in SO₄²⁻ ions.

Key words: Hydration • Setting • Strength • Sulphate attack • XRD • SEM

INTRODUCTION

Recently, the general trend globally is the reutilization of industrial wastes or byproducts in useful applications in order to keep environmental balance and public health. The granulated slag, a byproduct from the production of the pig iron in the blast furnace, is a hydraulically weak due to its glassy nature and hence a highly alkaline medium is required to disintegrate the silicate/aluminate network of this glass structure. So, the Portland cement clinker is usually used to provide the alkalinity [1]. Hence, it is most commonly used by the construction industry as a partial substitution for OPC [2]. The GBFS and PFA, a byproduct from power or fuel stations, are comparatively inferior materials with respect to reactivity when compared with other waste materials [2-6]. On this basis, the main objectives of this work are to study influence of PFA and GBFS on the setting and mechanical properties of OPC cement pastes. The chemical resistivity of such cement blends against 4 % Na₂SO₄ solution up to 12 months was also studied.

MATERIALS AND METHODS

Raw Materials: The used raw materials are Portland cement clinker (P. C. clinker), raw gypsum (CaSO₄ · 2 H₂O),

pulverized fuel ash (PFA) and granulated blast furnace slag (GBFS) which were obtained from local plants, Egypt. Fine grinding has been made to activate these waste materials before its addition to the OPC so as to obtain acceptable blended cements with both satisfactory strength development and setting times. The chemical analysis of the raw materials is shown in Table 1 and the various cement blends as well as the blain surface area of the different mixes is shown in Table 2. The cement blend M₄ was activated by 1 % sodium silicate (Na₂SiO₃ or water glass) during grinding or moulding.

Cement Notation: C: CaO, S: SiO₂, A: Al₂O₃, F: Fe₂O₃, H: H₂O, CH: Ca (OH)₂, NH: NaOH, CS: CaSO₄, NS: Na₂SO₄.

Preparation and Methods: Water of consistency as well as setting times (initial and final) of the OPC (M0) and the other prepared mixes (M1-M4) were directly determined by Vicat apparatus [7, 8] as follows:

$$W.C, \% = A / P \times 100 \quad (1)$$

where, W.C.: water of consistency, %, A: amount of water taken to produce a suitable paste, ml and P: weight of cement, g.

Table 1: Chemical analysis of raw materials, mass %

Oxides	P.C. Clinker	Raw gypsum	PFa	GBFS
LOI	0.52	22.86	3.12	0.43
SiO ₂	21.49	0.59	59.83	35.36
Al ₂ O ₃	5.51	0.12	21.94	11.47
Fe ₂ O ₃	3.15	0.11	5.62	1.34
CaO	64.38	30.08	6.13	48.20
MgO	1.73	0.13	0.15	2.32
Na ₂ O	0.21	0.07	0.17	0.46
K ₂ O	0.11	0.09	0.98	0.32
SO ₃	1.82	45.36	1.33	4.08
Cl ⁻	--	0.58	--	--

Table 2: Mix composition of the various cement blends, mass %

Mixes	P. C. Clinker	Raw gypsum	PFa	GBFS	Na ₂ SiO ₃	Blaine, cm ² /g
M0	96	4	--	--	--	3650
M1	81	4	15	--	--	3950
M2	66	4	--	30	--	4000
M3	61	4	15	20	--	4080
M4	60	4	15	20	1	4100
Blaine, cm ² /g	3250	2800	5900	6500	--	--

Five sets of cement cubes were cast using the predetermined water of consistency, They were then poured into 2.5 x 2.5 x 2.5 cm³ stainless steel moulds, manually vibrated for two minutes and on a mechanical vibrator of type RMJ Testing Equipment, Via Gromello 57-24127 Bergamo-Italy for 1-2 cycles to ensure the complete elimination of air bubbles and voids where each cycle was only two minute. The surfaces of moulds were smoothed by spatula and cured in a humidity chamber at 100 % R.H and a room temperature (20 ±1°C) for 24 hours, demoulded and soon cured under water. The first set was cured in normal tap water for 1, 3, 7, 28 and 90 days till the time of testing. The second set was cured in water only up to 28 days at which the compressive strength values were considered as zero readings. The remaining specimens were immersed in a previously prepared 4 % Na₂SO₄ solution up to 12 months. All samples were subjected to a compressive strength [9] which was carried out using a digital reading BAUTOFF PRÜF TONI TECHNIK testing machine–Model: TONINDUSTRIE PRÜFTECHNIK GMBH, D-1000 Berlin and Type 2560-249, 1997. Loading was applied perpendicular to the direction of the upper surface of the cubes. The compressive strength was evaluated according to:

$$Cs = L (KN)/Sa (cm^2) KN/m^2 \times 102 (Kg/cm^2)/10.2 (Mpa) \quad (2)$$

where, Cs: Compressive strength (MPa), L: load (KN), Sa: surface area (cm²).

The phase composition of the hydrated samples was investigated by X-ray diffraction method (XRD) and scanning electron microscopy (SEM). The XRD patterns were employed by a Philips X-Ray Diffractometer of Mod. P.W. 1390 with Ni-filtered Cu-K α radiation, while the SEM images were obtained by JEOL-JXA-840 electron analyzer at an accelerating voltage of 30 KV. The fractured surfaces were fixed on Cu-stubs by carbon paste and then coated with a thin layer of gold.

RESULTS AND DISCUSSION

Normal Consistency and Setting Times: Water of consistency and setting time of the various cement blends are represented in Fig. 1. It is clear that water of consistency as well as the setting time increase with the addition of either PFa or GBFS or even together. This is mainly attributed to the relatively higher surface area of PFa which in turn raise the fineness of the total cement mix than that of the pure OPC, i.e. as the surface area of the cement blend increases, the water of consistency is increased too and accordingly the setting times are elongated [2, 10, 11]. Also, GBFS and PFa need more water contents to produce suitable pastes. In contrast, although the setting times of the cement blend M4 mixed with 1 % Na₂SiO₃ increased, the water of consistency was lower than those of the others. This is essentially due to the fact that sodium silicate acts as an activating agent, in addition to the pozzolanic reactivity that was displayed by the PFa [12, 13].

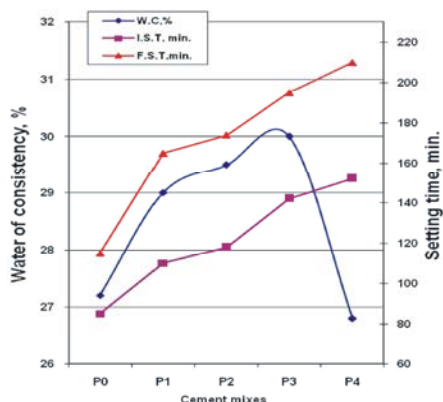


Fig. 1: Water of consistency and setting times (initial and final) of the various blended cement pastes

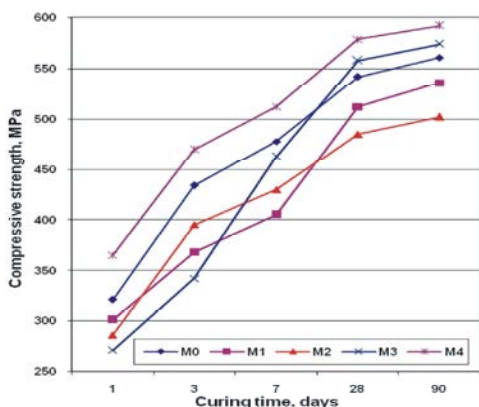


Fig. 2: Compressive strength of the various blended cement pastes up to 90 days

Compressive Strength: The compressive strength of the various blended cement pastes increase with curing time up to 90 days of hydration (Fig. 2). The addition of either Pfa or GBFS to the OPC tends to decrease the compressive strength nearly at all curing time periods. However, when they are added to the OPC paste, the early strength was slightly reduced, which in turn becomes higher than that of the pure OPC pastes at the later ages of hydration (28 and 90 days). This is primarily due to the fact that the GBFS has latent hydraulic properties. Therefore, they hydrate very slowly during the early ages up to 7 days. Hence, the early compressive strength is adversely affected, but the GBFS hydrated faster during the later ages up to 90 days particularly in the presence of Pfa which activates the GBFS and increases its rate of hydration recording higher compressive strength. Furthermore, both Pfa and GBFS act as a pozzolanic material or a consumer of a part of the released $\text{Ca}(\text{OH})_2$ resulting from the hydration of C_3S and $\beta\text{-C}_2\text{S}$ phases of the OPC cement and can react with it to form CSH and/or

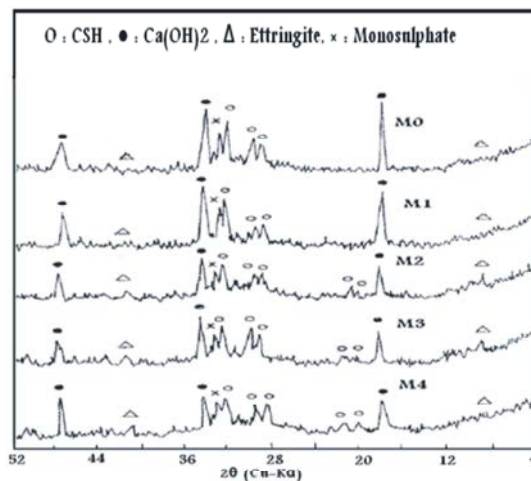


Fig. 3: XRD patterns of the various blended cement pastes cured in water up to 28 days

CAH [10-12]. This tends to improve and enhance the compressive strength of the cement blends containing them [10-12]. The addition of 1 % sodium silicate to the cement blend (M₄) during grinding improves the compressive strength to a large extent so that it becomes better and higher than that of the OPC alone at all curing periods. This is essentially due to that the sodium silicate that acts as an activator which consequently helps to develop higher compressive strength under normal curing conditions, especially during the later ages of hydration [10, 13, 14].

Fig. 3 indicates the XRD patterns of the various blended cement pastes cured in water up to 28 days. All samples show CSH and Free lime, $\text{Ca}(\text{OH})_2$ resulting from the hydration of C_3S and $\beta\text{-C}_2\text{S}$ of the OPC. The ettringite phase is also detected which is resulted from the hydration of both C_3A and GBFS with the raw gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) in the presence of water. A part of the formed ettringite was converted to the monosulphate form after 28 days of hydration. The intensity of the peaks that characterize $\text{Ca}(\text{OH})_2$ was slightly decreased in the other cement blends due to the partial consumption of $\text{Ca}(\text{OH})_2$ by both GBFS and Pfa for the formation of CSH and/or CAH hydrates [13, 14].

Mechanism of Hydration: The major phases of the OPC can hydrate [2, 10, 11] as follows:



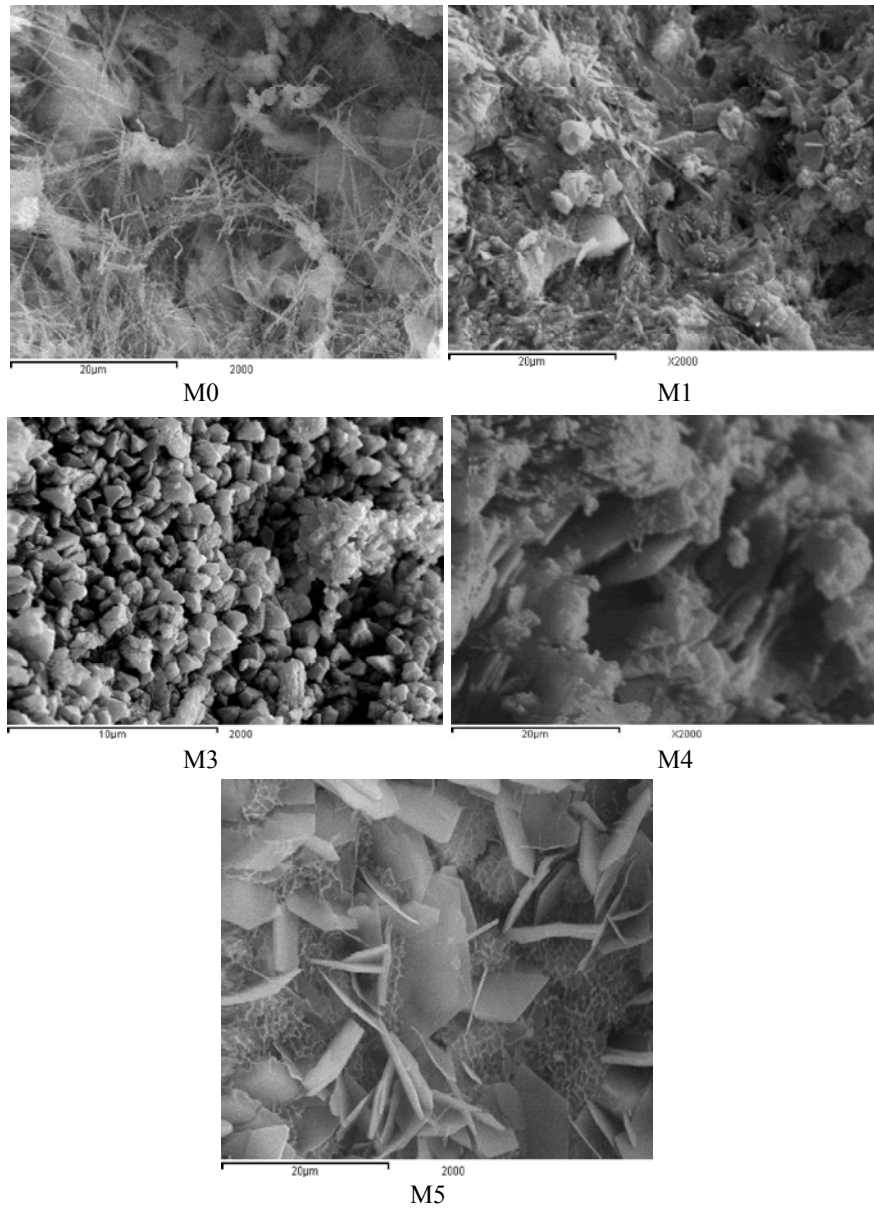
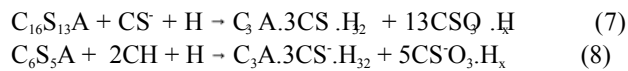


Fig. 4: The SEM images of the hardened OPC and the other blended cement pastes cured in water up to 28 days

The constituents of GBFS can react with the raw gypsum in the presence of water to produce ettringite and CSH or can react with a part of the free lime $\text{Ca}(\text{OH})_2$ resulting from the hydration of the OPC portion to form ettringite and CSH [2, 10, 11] as follows:



On the other side, the main components of PFa are A and S which can react with a larger part of the resulting

$\text{Ca}(\text{OH})_2$ from normal hydration to form cubic crystals of hydrogarnet ($\text{C}_3\text{A} \cdot \text{S}_2 \cdot \text{H}_n$) [2, 10, 12] as follows:



SEM Images at the Normal Hydration: Fig. 4 illustrates the SEM images of the interfacial layers of OPC (M0) and the other blended cement pastes (M1-M4) hydrated in water up to 28 days. It is clear that the major hydration products are CSH in all samples. Also, the ettringite phase and portlandite or free lime, $\text{Ca}(\text{OH})_2$ are clearly shown in

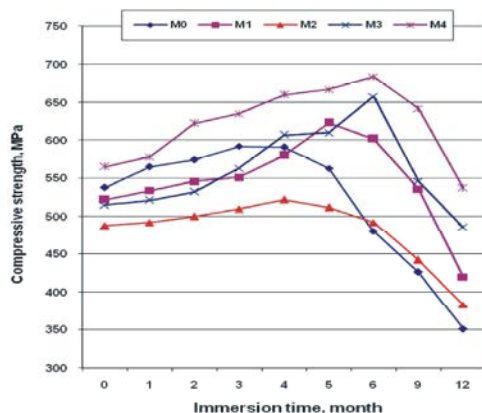


Fig. 5: Compressive strength of the various blended cement pastes immersed in 4 % Na_2SO_4 up to 12 months

the matrix (M0) as needle-like crystals and white granules which decreased or disappeared gradually with the blended cement pastes particularly in case of mix M4. This is mainly due to the transformation of ettringite into monosulphate and the pozzolanic action of GBFS and Pfa [2, 10, 11], respectively.

Sulphate Attack: It is clear from Fig. 5 that the compressive strength of OPC cubes slightly increases up to 3 months of immersion in 4 % CaSO_4 solution. This is mainly attributed to that during the early stages of immersion, the total porosity of the hardened cement cubes are often the minimum. Therefore, the rate of diffusion of SO_4^{2-} ions was partially diminished and cannot penetrate into the hardened cement cubes. As a result, a slight increase of compressive strength was obtained due to hydration. No clear effect on cured samples was observed [15]. Three months later, the compressive strength decreases gradually and sharply up to 12 months. This is essentially due to the fact that the major phases of the OPC cement are very sensitive to SO_4^{2-} ions particularly C_3A which is easily disintegrated by the aggressive attack of these ions on the long run. Moreover, some deleterious reactions had been taken place between SO_4^{2-} ions and the constituents of the OPC forming ettringite ($\text{C}_3\text{A} \cdot 3 \text{CaSO}_4 \cdot \text{H}_{32}$) and/or gypsum ($\text{CaSO}_4 \cdot \text{H}_2$). These products are characterized by their higher specific volume due to their higher crystal growth causing a high rate of expansion, swelling and internal minor cracks [10, 13]. Hence, the formation of these products is the main reason for the decrease in mechanical strength. Six months later, fine cracks started to appear at the edges of the hardened OPC cubes and also, light swelling at the corners which increased with the time of

immersion up to 12 months. On the other hand, the compressive strength of the cubes of M1 and M2 increased up to 4 and 5 months while this appears at 6 months for M3 and M4, respectively. However, no cracks or signs of deterioration were detected. This is mainly due to several factors as: the deficiency of the sensitive OPC phases to SO_4^{2-} ions, the presence of GBFS which is not easily affected by SO_4^{2-} ions due to higher glassy structure, lower amount of free lime or $\text{Ca}(\text{OH})_2$ due to its consumption, the interaction of GBFS and OPC by Pfa and Sodium silicate (Na_2SiO_3), the good dispersion of GBFS and Pfa as well as the good compaction of samples during molding [10, 13, 14]. So, the rate of penetration of SO_4^{2-} ions into the hardened blended cement cubes are the lowest. Accordingly, the compressive strength tends to increase [10, 11, 15].

After 4-6 months of immersion in SO_4^{2-} ions, the compressive strength gradually decreased up to 12 months. As the time of immersion was proceeded, the amount of ettringite and gypsum increased causing a continual expansion. Moreover, the calcium sulphide (CaS) existed in GBFS was often hydrated to $\text{Ca}(\text{OH})_2$ and $\text{Ca}(\text{HS})_2$ which decreased the pH value of the cement solution. This tends to increase the chance of the hardened cement pastes to be easily attacked by the SO_4^{2-} ions resulting in a further decrease in the compressive strength due to the creation of more open pore structure [13, 16, 17]. However, after 12 months of SO_4^{2-} ions curing, the OPC pastes attained the lowest compressive strength and the highest degree of deterioration, while M4 recorded the highest value of compressive strength and the lowest level of disintegration. Consequently, the various types of blended cement pastes are more resistant to 4 % SO_4^{2-} ions if compared with those of the OPC pastes, specially the cement mix M4. This is mainly due to the activation effect of both Pfa and Na_2SiO_3 to the GBFS and OPC [13, 18, 19]. Therefore, the expansion and cracking are the main reasons of the aggressive attack by SO_4^{2-} ions leading ultimately to the loss of adhesion properties and accordingly the strength development is consequently reduced.

Mechanism of Sulphate Attack: At the beginning of the reaction, the normal hydration can take place with a slight activation by the SO_4^{2-} ions. This could be continued up to 3 months of immersion and then has been started the negative attack of these ions on the compressive strength. This is mainly due to the reaction of ions with a part of the released CH from hydration or with C_3A phase of the cement to produce gypsum and ettringite phases [10-12] as follows:

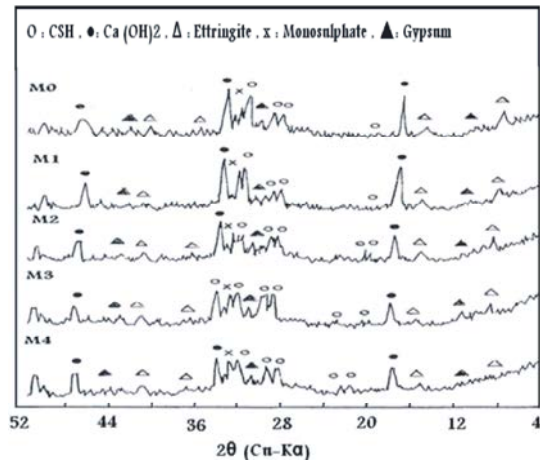


Fig. 6: XRD patterns of the various blended cement pastes immersed in 4 % Na₂SO₄ solution up to 9 months

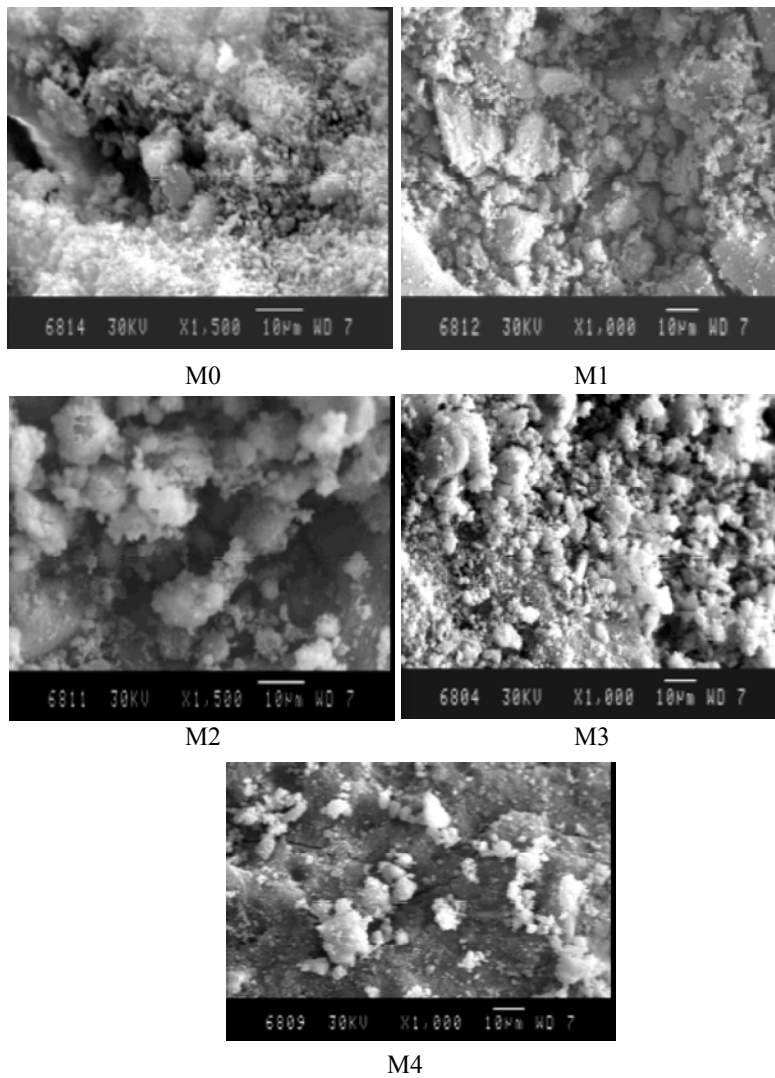
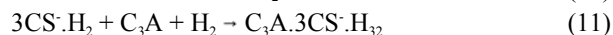


Fig. 7: The SEM images of the hardened OPC and the other blended cement pastes cured in 4 % Na₂SO₄ solution up to 12 months



The formation of gypsum and ettringite phases is the main reasons for the decrease in mechanical strength [14]. Fig 6 shows the XRD patterns of the various blended cement pastes immersed in 4 % SO_4^{2-} ions for 9 months. Comparing the hardened cement cubes cured in SO_4^{2-} ions with the same samples cured in water, the amount and intensity of the peaks that characterized ettringite was increased and also new peaks of gypsum were formed due to the deterioration reactions between the constituents of cements and SO_4^{2-} ions. This led to the partial disintegration of CSH because neither ettringite nor gypsum has binding characteristics when compared with CSH phases. Therefore, these products are often responsible for the deterioration of samples and the reduction of its compressive strength.

SEM Images After Immersion in SO_4^{2-} Ions: The SEM images of the interfacial layers of M0 and M1-M4 immersed in SO_4^{2-} ions up to 12 months are shown in Fig. 7. It is clearly shown that the amount of the formed ettringite and gypsum phases resulting from the reaction of cement constituents with SO_4^{2-} ions decreased gradually by time of immersion and type of cement blend. This is the main reason for the higher resistance of blended cements to SO_4^{2-} ions.

CONCLUSION

The addition of either PFa or GBFS, or even both together to the OPC cement increased the water of consistency and setting times (initial and final). Grinding of 1 wt. % Na_2SiO_3 with the cement blend (M4) decreased the water of consistency, whilst the setting time was elongated. The various blended cement pastes recorded a satisfactory strength development under normal curing conditions according to the following sequence: M4 > M3 > M0 > M1 > M2. The different cement blends showed a superior resistance to the attack of SO_4^{2-} ions, particularly those containing Na_2SiO_3 . Thus, the degree of deterioration after 12 months of immersion is a decreasing order was: M4 > M3 > M1 > M2 > M0. The XRD patterns indicated that the major phases that were formed during normal hydration are CSH, CH and ettringite whilst after immersion in SO_4^{2-} ions are ettringite and gypsum. This was evidently confirmed by the SEM images.

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