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Sulfate resistance of plain and blended cement

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Abstract

This paper presents a laboratory study on the sulfate resistance of blended cement combination of reference Portland cement with high volume ground granulated blast-furnace slag (GGBS) and natural pozzolan (NP). The exposure solutions were tap water containing 5% magnesium sulfate solution and 5% sodium sulfate solution. Two types of grinding method (separately grinding and intergrinding, two finenesses (250 m^2/kg and 500 m^2/kg) and three different proportions (10%, 20%, and 30% by weight of mixture)) of each of two different additives (GGBS and NP) in equal amounts were employed. In addition to these blends, plain Portland cements without additives were prepared as references specimens. Standard Rilem sample size (40 mm × 40 mm × 160 mm) was used for the experimental study.

It was observed that the sulfate resistances of blended cements were significantly higher both against sodium sulfate and magnesium sulfate attacks than references cement. Final strength reductions for finer mixes attacked by magnesium sulfate were marginally lower than those attacked by sodium sulfate. On the other hand, no particular relation was found between the sulfate resistance of the mortars and the grinding methods.

Keywords: Ground granulated blast-furnace slag; Basaltic pumice; Sulfate attack; Compressive strength; Strength loss; Sodium and magnesium solutions

1. Introduction

Recently, there has been a growing trend towards the use of supplementary cementitious materials, whether natural, waste, or by-products, in the production of composite cements because of ecological, economical, and diversified product quality reasons. Slag, a by-product of the transformation of iron ore into pig-iron in a blast furnace, is one of these materials the use of which in cement manufacture goes to as far back as 1880 [1,2]. Since then its use has expanded because it has various advantages over other cementitious materials. Firstly, slag has a relatively constant chemical composition compared to fly ash, silica fume and natural pozzolan, etc. [3]. Moreover, it has advantages like low heat of hydration, high sulfate and acid resistance, better workability, higher ultimate strength, etc. These properties are beneficial to specialised applications such as hydroelectric dams, large bridges, power stations, metro systems, motorways, and harbours.

One of the major determinants of cement quality is its specific surface area (Blaine). It is well-known that the compressive strength of plain Portland cement increases with Blaine specific surface area at early ages, and that cements with a narrow-size distribution have higher strength than those with a wide one [3]. Durability of concrete in underground structures depends on the chemical properties of the soil and ground water. Sulfate or acid environment caused by industrial wastes or chemical residues in reclaimed ground is one of the most severe conditions for durability of concrete. Unfortunately, underground or underwater concrete structures can sometimes be exposed to sulfates and acids, because water-soluble sulfate widely exists in soil, groundwater, streams, and seawater. It has been recognised for a long time that sulfate induces damage

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to concrete. Some researchers have reported that the use of low water/cement ratio and the use of admixtures, such as air entraining to protect the chemical attack of a rich mixture, additive, or GBBS, would be the most effective treatment for reducing the sulfate-inducing damage [4–8]. Deterioration of concrete by sulfate attack is commonly observed in structures exposed to soils or ground water containing a high concentration of sulfate ions. To mitigate this attack, concrete codes recommend a concrete mixture with low water/cement ratio and sulfate resistant pozzolanic cement [9,10].

Natural pozzolans, which are a variety of pyroclastic rocks, are natural mineral admixtures for concrete to improve its properties. They are additives, which are rich in silicate minerals and volcanic glass shards, and in powdered form, react with calcium hydroxide, in the presence of water, to form compounds possessing cementitious properties. They show the highest performance as additives [9].

Tuffs have been used in mixture with lime since historical times in Turkey, like in most Mediterranean countries. Today, the cement industry in Turkey is one of the most well-established and developed industries. There is a continuous interest in new supply sources of tuffs. Almost about one-third of the total production in recent years was "trass cement" which is Portland-pozzolan cement [10]. Turkey is rich in natural pozzolan, which are also called "basaltic pumice" in the cement industry. Almost 155 000 km^2 of the country is covered by Tertiary and Quaternary-age volcanic rocks, among which tuffs occupy important volumes. Although there are many geological investigations on these volcanic rocks, their potential as natural pozzolan is not well established [11].

The basaltic pumice cone deposits are of Quaternary age and are located in the Cukurova region (Southern Turkey), and there are reserves estimated to be approximately 1.000 million tonnes. The pumice comprises an average of 85% volcanic glass and 15% phenocrystic feldspars along with minor spheroid hematite minerals, determined by microscopy. XRD tests show the presence of dominant illite and kaolinite as clay minerals along with feldspar. The high porosity of the basaltic pumice is an advantage for easy and economical crushing [12].

Pozzolanic additives are used to improve the mechanical durability, workability and economy of concrete. The additives, basalt and GGBS, used in this study, have been previously investigated for their activities [13]. In that study, it was observed that, both basaltic pumice and GGBS used in this study had more than 61% of major chemical components; SiO_2, Al_2O_3 and Fe_2O_3, conforming with the chemical requirements of the ASTM and Turkish standards. They also fulfilled the mechanical requirements concerning compressive and flexural strengths. The foregoing results show that both NP and GGBS can be used effectively in cement production.

The European Cement Standards and The Turkish standards [14,15], allow the use of many different mineral admixtures in the production of CEM II, III, IV and V. It is necessary to note that Portland composite and composite cements contain at least two different mineral admixtures besides the Portland cement clinker. The total amount of these mineral admixtures is allowed up to 50%. The durability of mortars can be greatly affected by environmental conditions. One of the most destructive effects comes from sulfates (soil, ground water and seawater). In this study, the sulfate attack on the mortars up to ages of 3 years and its effect on the mass loss and compressive strength were evaluated by immersing them into 5% Na_2SO_4 and $MgSO_4$ solutions at room temperature.

2. Material and method

2.1. Materials

Natural pozzolan (basaltic pumice) is one of the main additives used in this study. It contains glass shards, mineral phases and less amount of volcanic rock. Essential minerals in it are feldspar, quartz and biotite. Clay minerals occur as alteration products. The clinker used was obtained from Adana Cement Plant. GGBS was obtained from Iskenderun cement grinding plant. The terminology and composition of the studied cements is given in Table 1. Chemical, mineralogical and physical characteristics of materials used are given in Table 2.

2.2. Method

In this study, the blended cements were prepared using a clinker, 4% gypsum by weight, a natural pozzolan (NP) and GGBS. Different amounts of additives (20%, 40% and 60%) were incorporated into these blends in equal amounts. Cement paste and mortars were prepared using plain Portland cement (PPC), NP and GGBS with two types of grinding process (intergrinding and separate grinding) at two Blaine values ($250 \pm 3\ m^2/kg$ and

Table 1
The terminology and composition of the studied cements

Cement	Composition (% percentages by weight)				Blaine (m^2/kg)
	Clinker	Gypsum	GBFS	NP	
A_1	96	4	–	–	250
A_2	96	4	–	–	500
B_1 (separate grinding)	76	4	10	10	250
B_2 (separate grinding)	56	4	20	20	250
B_3 (separate grinding)	36	4	30	30	250
C_1 (separate grinding)	76	4	10	10	500
C_2 (separate grinding)	56	4	20	20	500
C_3 (separate grinding)	36	4	30	30	500
D_1 (intergrinding)	76	4	10	10	250
D_2 (intergrinding)	56	4	20	20	250
D_3 (intergrinding)	36	4	30	30	250
E_1 (intergrinding)	76	4	10	10	500
E_2 (intergrinding)	56	4	20	20	500
E_3 (intergrinding)	36	4	30	30	500

Table 2
Chemical, mineralogical and physical characteristics of materials used

Specimens	Oxides (%)						
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	LOI (loss on ignition)
Clinker	20.2	5.5	3.8	64.7	1.9	0.8	–
$A_1 = A_2$	19.4	5.5	3.9	63.4	1.8	2.0	–
NP	51.8	22.1	7.3	6.2	8.3	–	0.4
GGBS	41.6	13.7	7.3	28.2	4.9	1.8	0.01

Specimens	Cement modulus				Mineral composition (%)			
	HM	SM	AM	LM	C_3S	C_2S	C_3A	C_4AF
Clinker	2.1	2.1	1.4	98.2	65.7	8.6	8.2	11.7
$A_1 = A_2$	2.1	2.0	1.4	99.7	66.5	5.6	8.1	11.9

Materials	Physical properties of materials			
	Specific gravity (kg/m^3)	Blaine (m^2/kg)	Sieve analysis (%)	
			Residue on 90 μm	Residue on 200 μm
Basaltic pumice	2970	250 and 500	0.2	0.06
GGBS	2890	250 and 500	0.3	0.09
Clinker	3190	250 and 500	0.3	0.09

TS 12142 standard requirements for basaltic pumice (NP) and GGBS		
$SiO_2 + Al_2O_3 + Fe_2O_3$	SO_3	LOI
>61	<3.5	<10

HM: Hydraulic modulus $= \frac{CaO}{SiO_2 + Al_2O_3 + Fe_2O_3}$.

SM: Silicate modulus $= \frac{SiO_2}{Al_2O_3 + Fe_2O_3}$.

AM: Aluminate modulus $= \frac{Al_2O_3}{Fe_2O_3}$.

LM: Lime modulus $= \frac{100 \cdot CaO}{2.8SiO_2 + 1.1Al_2O_3 + 0.7Fe_2O_3}$.

$500 \pm 3\ m^2/kg$). The compressive strengths at 3, 7, 28, 90 and 180 days and sulfate resistance of blended cements were investigated. The latter was examined in the laboratory by storing specimens in solutions of sodium and magnesium sulfate. The effect of exposure was determined by compressive strength and mass loss of the specimens. Rilem standard experiments were carried out on 630 sets of PPC and blended mortars (210 for compressive strength in pure water, 168 for compressive strength in sodium sulfate solution, 168 for compressive strength in magnesium sulfate solution, 42 for mass loss in sodium sulfate solution and 42 for mass loss in magnesium sulfate solution). The solutions were replaced once a month with fresh ones and pH value was kept in the range 6–6.5 during the 36 months immersion period. The concentrations of the sodium and magnesium sulfate solutions were both 5%. The sulfate exposures of mortars were carried out in curing tanks of lime-saturated water for 28 days. Compressive strength was determined for 6, 12, 24 and 36 months and loss of mass was measured for the same periods. A reduction in compressive strength was calculated as follows:

$$\text{Reduction ratio in compressive strength} = \frac{S_{\text{solution}}}{S_W}$$

where S_W (in MPa) is the average compressive strength of three specimens cured in pure water and S_{solution} (in MPa) is the average compressive strength of three specimens cured in test solution. The same equation was used to determine the mass reduction ratio, S_W being replaced by the mass of the three specimens (in g) cured in lime-saturated water for 28 days at the beginning of the experiment and S_{solution} being replaced by the mass of the three specimens (in g) cured in sodium solutions for the specified time period.

2.3. Development of compressive strength

Two hundred and ten prismatic compressive strength test specimens (40 mm × 40 mm × 160 mm) were prepared and tested according to TS 24 [16]. In the experiment, moist curing was applied to the specimens. The specimens were dried 24 h prior to testing for every mix at the required age, and the average strength of three specimens was used.

2.4. Sulfate attack

Compressive strength is the main feature that allows an appreciation of cement quality. That is why the effect of exposure of mortars to sulfates was determined by the compressive strength and the mass loss of the specimens. The sulfate attack on the mortars up to ages of 36 months and its effect on the mass loss and compressive strength were evaluated. Fourteen different specimens were prepared for determining the effect on the mass loss. To find out the mass loss after 28 days, 42 specimens were immersed in sodium sulfate solution and 42 specimens were immersed in magnesium sulfate solution. The mass losses of the specimens were measured after the immersion periods stated in the test procedure.

3. Results and discussion

3.1. Development of compressive strength

The compressive strength development of the tested cement is given in Figs. 1 and 2. From Fig. 2, it can be said that, the compressive strengths of the mortars made with blended cements with separately ground finer specimens were higher than those of the PPC at all tested ages after 28 days. The strength development characteristics of the blended cement mortars were affected not only by the finenesses of the cements, but in some cases, also by the grinding method. Specimen C_2 had the highest compressive strength at 180 days. However, this value was lower for the other blended cement mortars than the reference mortars.

The relative strength (the ratio of the blended cement to the strength of PPC) of the blended cements in relation to curing age is given in Figs. 3 and 4. It can be observed from Fig. 3 that relative strength values of the coarser specimens were lower at early ages, up to the age of 180 days. On the other hand, the relative strengths of the finer blended cement specimens were higher at early ages. Compared to those for the coarser specimens (C_1, C_2, C_3 and E_1) this value is even higher than those for the reference specimens.

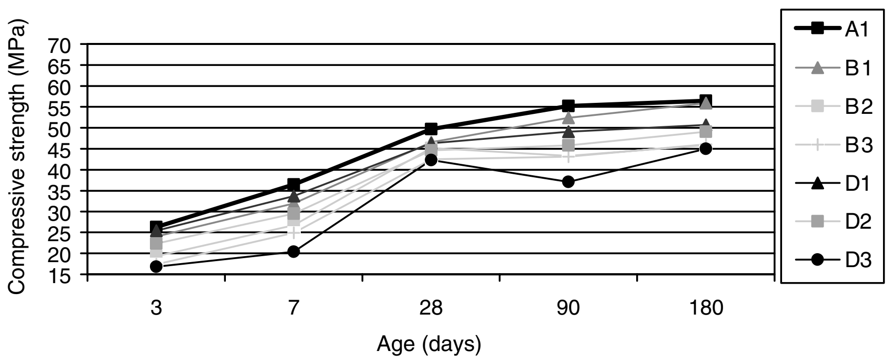

Fig. 1. Compressive strength development of tested cement (fineness: 250 m^2/kg).

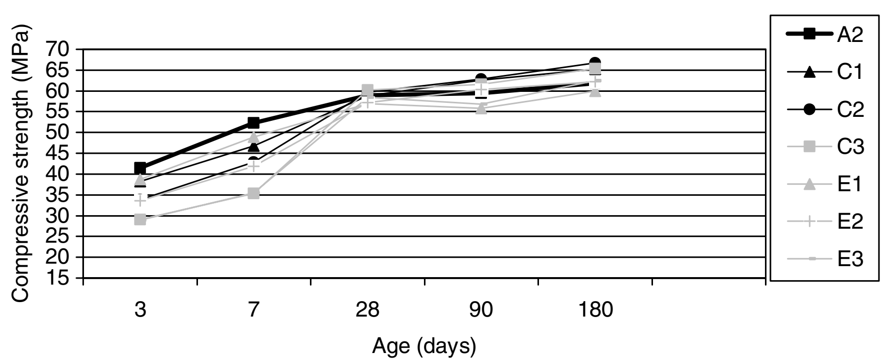

Fig. 2. Compressive strength development of tested cement (fineness: 500 m^2/kg).

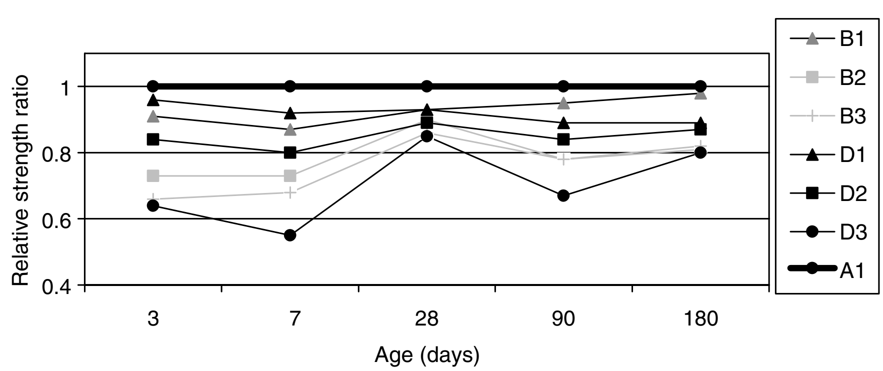

Fig. 3. Relative strength of blended cements in relation to curing age (fineness: 250 m^2/kg).

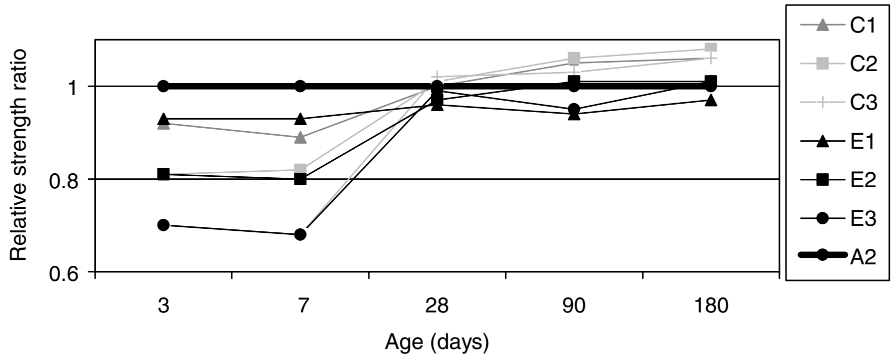

Fig. 4. Relative strength of blended cements in relation to curing age (fineness: 500 m^2/kg).

The development of the relative strength of the blended cements in relation to the curing ages is observed to be different. The relative strength ratio values for the coarser specimens were lover than those for the finer ones.

All blended cement mortars fulfill the compressive strength requirements of TS 24. Hence, it can be said that blended cement can achieve adequate early compressive strength, while maintaining a high long-term strength.

3.2. Effect on sulfate attack

3.2.1. Compressive strength reduction

The results of the sulfate resistance tests carried on blended cement and PPC specimens are shown in Table 3. These results show that there is an obvious increase in the sulfate resistance of the mortars with an increase in the percentage of the additives. Other researchers have reported similar observations mentioning that both natural and artificial additives could contribute to the enhancement of the chemical resistance of concrete [17]. GBBS cement concretes are also acknowledged to have high resistance to the aggressive action of sulfates and seawater [18].

Blaine specific surface area is the most significant property causing interground specimens to have longer dormant periods (the period in which sulfates have no important effect) than their separately ground counterparts. It is observed from Table 3 that there is no relation between sulfate resistance of the mortars and the grinding process.

The compressive strength of the mortars decreases roughly 50% showing the significance of sulfate attack. Some selected specimens are given in Fig. 5. The sulfate attack is a layer by layer chemical reaction starting on the surface and moving inwards. Thus, the initial external signs of deterioration continue with loss of compressive

Table 3
Compressive strength of PPC and blended cement specimens immersed in 5% sulfate solution (MPa)

Specimens	For 28 days in pure water	For 6 months in sulfate solutions		For 12 months in sulfate solutions		For 24 months in sulfate solutions		For 36 months in sulfate solutions	
		Na_2SO_4	$MgSO_4$	Na_2SO_4	$MgSO_4$	Na_2SO_4	$MgSO_4$	Na_2SO_4	$MgSO_4$
A_1	49.7	45.6	47.1	26.8	29.2	0	0	0	0
A_2	58.9	52.1	53.4	31.1	33.5	0	17.3	0	0
B_1	46.6	37.1	41	33.7	35	19	19.4	0	0
B_2	45.2	40.7	43.6	35.3	38.3	20.7	21.3	0	0
B_3	42.5	40	41.6	37.8	40.4	18.2	19.7	0	0
Average of B	44.7	39.2	42	35.6	37.9	19.3	20.1	0	0
C_1	58.8	56.2	57.8	45.3	47.6	30.3	32.5	18.7	19.9
C_2	59.7	57.4	58.6	47.6	50.2	31.1	33.7	20.6	21.2
C_3	60.2	58.5	59.6	48.3	51.4	32.2	34.7	21.1	22.3
Average of C	59.5	57.3	58.6	47	49.7	31.2	33.6	20.1	21.1
D_1	46.3	41.7	43.3	35.2	37.6	21	25.4	0	0
D_2	44.6	40.2	41.2	36.7	38.1	22.1	26.1	0	0
D_3	42.3	35.9	37.3	30.3	33.0	22.7	23.5	0	15.1
Average of D	44.4	39.2	40.6	34	36.2	21.9	25	0	5
E_1	56.9	53.0	52.2	46.2	49.1	31.3	33.6	19.1	20.7
E_2	57.2	52.9	54.1	48.3	50.5	32.7	35.8	20.2	21.8
E_3	58.4	53.1	56.4	47.1	51.4	31.1	33.1	20.9	21.5
Average of E	57.5	53	54.2	47.2	50.3	31.7	34.1	20	21.3

strength (see Fig. 5). As seen in Fig. 5a, specimens A_1, exposed to Na_2SO_4 and Fig. 5b specimens A_2, exposed to $MgSO_4$, have suffered a lot of expansion, cracking and fractures on whole surface. However, it is seen in Fig. 5c and d that specimens C_3 and E_3, respectively, both exposed to $MgSO_4$, showed no significant signs of deterioration.

Figs. 4 and 5 show the reduction of the relative compressive strength (the ratio of the compressive strength in sulfate to the compressive strength in pure water). The curves in the figures show that the relative compressive strengths of all mortars decrease with increasing exposure to Na_2SO_4 and $MgSO_4$ solutions. However, their amplitudes of decrease are different. For PPC, the relative compressive strength decreases rapidly and dispersion takes place by 24 months, whereas, all blended cement mortars preserved their integrity till then.

In all specimens, the compressive strength reduction was higher in sodium sulfate solution compared to magnesium sulfate solution. Blended cement C exhibited greater sulfate resistance than any of the other specimens (Table 3).

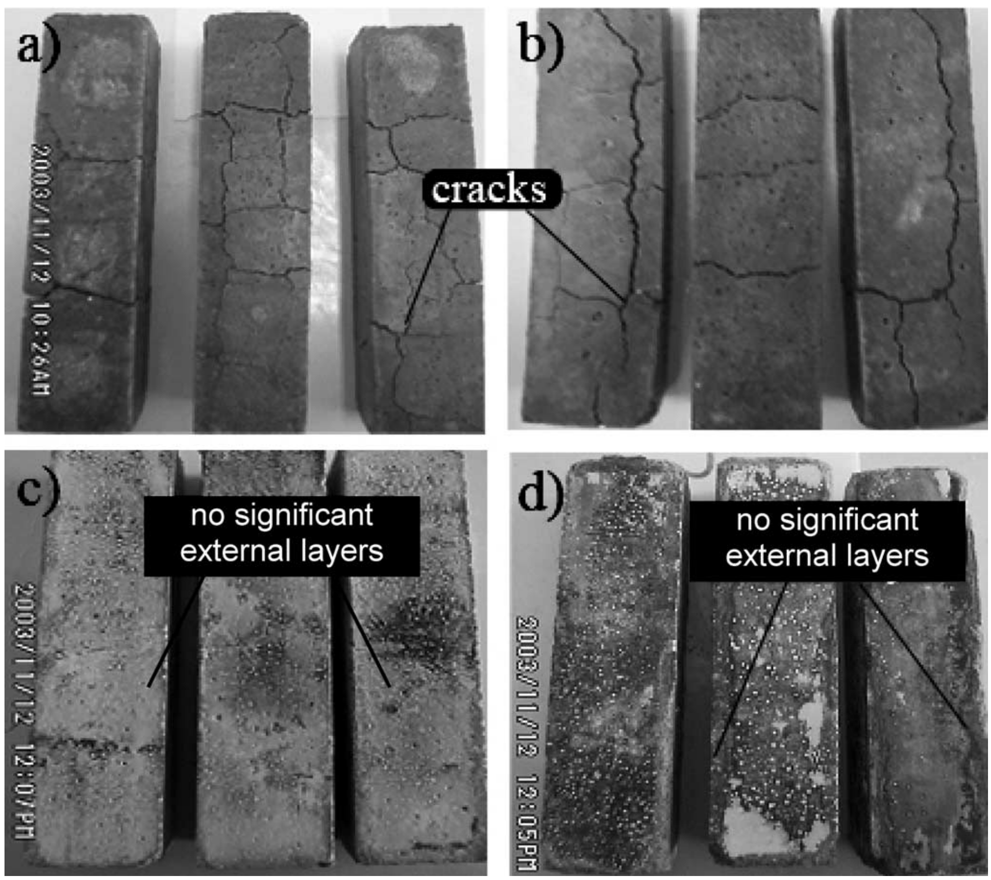

Fig. 5. PPC and blended cement prismatic mortars exposed to sulfate solutions for 24 months: (a) Specimen (A_1), (b) Specimens (A_2), (E_3), (c) Specimens (C_3), (d) Specimens (E_3).

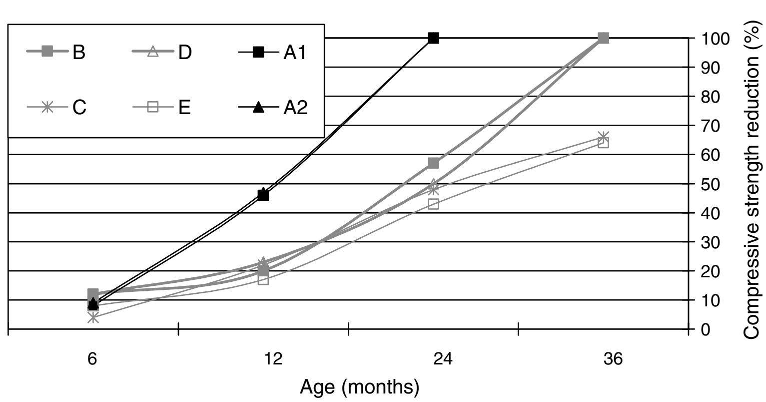

Fig. 6. Reduction of compressive strength in Na_2SO_4 solution.

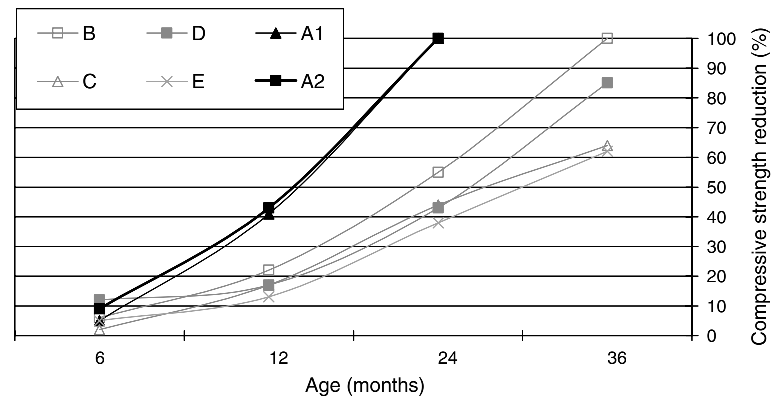

Fig. 7. Reduction of compressive strength in $MgSO_4$ solution.

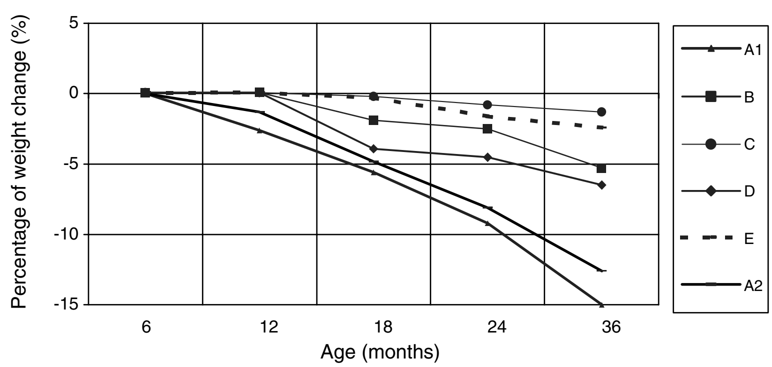

Fig. 8. Mass variation of blended cement and PPC immersed in Na_2SO_4 solution.

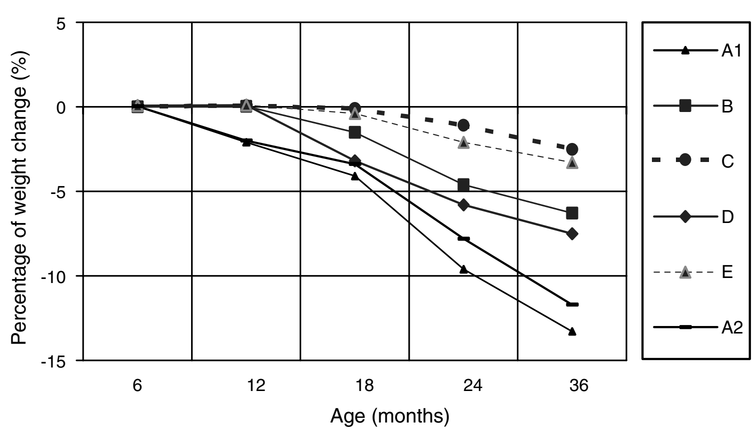

Fig. 9. Mass variation of blended cement and PPC immersed in $MgSO_4$ solution.

3.2.2. Mass loss

Figs. 6 and 7 depict the test results of mass loss versus time for the mortars. There is a relatively large amount of mass loss associated with PPC, compared to blended cement. The total mass loss of PPC and blended cement after 12 months exposure to sulfate solution is about 4% and 1%, respectively. Then, these values increase gradually and reach the value of 10% and 5%, respectively, by the end of 24 months. It can be said that blended cement mortars present an excellent behavior in both short and long term mass loss due to sulfate attack (Figs. 8 and 9).

4. Conclusions

The following conclusions can be drawn based on the test results of this study:

1. The blended cement specimens (C_3) exhibited greater sulfate resistance than any of the other specimens.
2. No particular relation has been observed between the sulfate resistance of mortars and the grinding process.
3. At 36 months, the strength reduction for mixes C and E in $MgSO_4$ is marginally lower than in Na_2SO_4. For specimen D tested in sulfate solutions, the compressive strength reduction was higher in sodium sulfate than in magnesium sulfate.
4. The results show that PPC specimens were disintegrated at the age of 24 months. However, some of the blended cement mortars (C and E) preserved their integrity in sulfate solutions throughout the test.
5. Since GGBS and NP are available in vast amounts in Turkey, taking into account the results of the present study, these materials should preferably be used as additives in the Turkish cement industry as a precaution against sulfate attack.

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