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Sulfate resistance and carbonation of plain and blended cements

K.K. Sideris [a,*], A.E. Savva [a], J. Papayianni [b]

[a] *Democritus University of Thrace, Department of Civil Engineering, School of Engineering, P.O. Box 252, Xanthi 671 00, Greece*
[b] *Aristotle University of Thessaloniki, Department of Civil Engineering, P.O. Box 482, Thessalonki 540 06, Greece*

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Abstract

Results of an experimental investigation on the sulfate resistance and carbonation of plain and blended cement mortars are reported in this paper. In the sulfate resistance test all the specimens were immersed in a 5% Na_2SO_4 solution for 24 months. Two different types of lignite fly ashes and two natural pozzolans were used for the production of 13 blended cements. An ordinary portland cement and a commercially available blended cement were also used for reference. The effect of mineral admixtures on the carbonation depth of mortars was also investigated. Results show that the addition of pozzolanic admixtures in most cases had a positive effect on the sulfate resistance. The carbonation depth in all blended mortars was greater than that in portland cement mortar. However the rate of carbonation of blended mortars was reduced as hydration progressed.

Keywords: Carbonation; Durability; Fly ash; Mineral admixtures; Pozzolans; Sulfate attack; Sulfate resistance

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1. Introduction

The service life of concrete structures depends on the environmental conditions and on the quality of concrete. Durability of concrete to sulfate attack is one of the environmental problems. As a result of sulfate attack the cementitious matrix is damaged through the formation of ettringite ($C_6A\bar{S}_3H_{32}$), and gypsum ($C\bar{S}H_2$). According to one theory, the formation of ettringite is expansive (it has a density of 1.73 g/cm^3 compared with an averaged density of 2.50 g/cm^3 for the other products of hydration). Therefore expansion and cracking of concrete happen as a result of sulfate attack caused by Na_2SO_4 solutions [1]. Sulfate attack is a problem generally associated with buried concrete structures exposed to soils or ground waters containing soluble sulfates. Since usage of new type chemicals for agricultural purposes was extended during the last decades, underground water pollution has increased and sulfate attack is of great importance for the long term service life of such structures.

The principal method available to limit sulfate attack is the use of ASTM Type II or Type V portland cements instead of Type I portland cement [2] or the use of additives—such as natural pozzolanas, fly ashes or silica fume. Pozzolanic materials have an important role in the long term durability of mixtures exposed in sulfate environments because they contribute chemically and physically to their properties. Their effect is thought to be explained by two primary mechanisms [3]: the "dilution effect" (decrease of the C_3A content of the binder when they replace a portion of portland cement) and the "pozzolanic effect" (formation of secondary CSH). The latter results in a less permeable mortar, from which the excess calcium hydroxide has been consumed and rendered unavailable for the expansive formation of ettringite and gypsum compound [3–6].

Carbonation also affects the durability of reinforced concrete structures. This results from the interaction of atmosphere's carbon dioxide (CO_2) with the alkaline products of the cementitious matrix.

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[*] Corresponding author: Tel.: +30 25410 79862; fax: +30 25410 79864.
E-mail address: kksider@civil.duth.gr (K.K. Sideris).

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There is a large amount of solid $Ca(OH)_2$ in the hydration products of portland cement that can be dissolved in water. This helps to maintain the pH at 12–13. However, when all the available $Ca(OH)_2$ has reacted, the pH fall to a level below 11 which helps to promote corrosion [7]. Carbonation of cover concrete is a serious threat for decreasing the service life of concrete structures in most Mediterranean countries. This is due to the annual temperature and relative humidity of the local environments, which favor the fast progress of the carbonation reaction and further the corrosion of the steel reinforcement.

In this paper results of an investigation on the sulfate resistance and carbonation resistance of mortars prepared with 15 different cement types—one ordinary portland cement and 14 blended cements—are given. The sulfate resistance of binders was evaluated using expansion measurements of mortar prisms immersed in a 5% Na_2SO_4 solution, according to ASTM C1012 [8]. The carbonation resistance was evaluated by measuring the carbonation depth of mortar specimens at the ages of 6, 12 and 24 months according to RILEM specifications [9].

It is currently believed that pozzolan cements containing fly ashes with high SO_3 and high CaO content have deleterious effect on sulfate resistance [10–12]. This is one of the reasons that lignite fly ashes have initially been rejected for use in concrete by EN 450 [13]. The results of the investigation reported here show that the use of some lignite fly ashes is beneficial not only from the point of view of durability, but also from the point of view of cost and environmental protection, since millions of tones of lignite fly ashes are being land-filled every year [14].

2. Materials

Two Greek natural pozzolans of volcanic origin, Milos' Earth (ME) and Skydras' Earth (SkE) and two lignite fly ashes, Megalopoli fly ash (MFA) and Ptolemaida treated fly ash (PFA) were the pozzolanic materials used in this research. The chemical composition of the materials, including that of portland cement clinker and a commercial blended cement (II/B-M32.5N) are presented in Table 1.

PFA has been treated by the producer in order to increase it's fineness and to reduce the free CaO content of the material. MFA has a significant pozzolanic activity, whereas PFA has pozzolanic as well as hydraulic activity [15].

The mineralogical composition of the clinker used, as calculated according to ASTM C150 [2], comprises of 57.7% C_3S, 19.6% C_2S, 10.6% C_3A and 5.8% C_4AF.

All cements used in this research were produced in the laboratory by mixing clinker, pozzolanic material and gypsum ($CaSO_4 \cdot 2H_2O$). The SO_3 content of the pozzolanic material was taken into consideration and the added gypsum was properly adjusted in order to keep the total SO_3 content of the binder (clinker + pozzolan) equal to 3.5%. This was not achieved for the mixtures with a large PFA content. The high SO_3 of PFA increased the total available amount of SO_3 of the mix (clinker + gypsum), although no gypsum was added.

The composition of the various cements prepared for this research, as well as the SO_3 content of the mix (clinker + gypsum) and the fineness of the binder, are presented in Table 2.

3. Preparation of mixtures—test procedure

Cement compositions presented in Table 2 were used for the preparation of mortars with a cement/sand ratio of 1:3 by weight. The aggregates used were standard sand (EN196-1) with maximum grain size equal to 2 mm. A different water/binder ratio was used in each case in order to keep the mixture's fluidity constant. No superplasticiser was added. The water/binder ratio as well as the fluidity measurements are presented in Table 3.

The specimens used for length change measurements were prisms 4 × 4 × 16 (cm). These specimens were immersed in a 5% Na_2SO_4 solution according to ASTM C-1012. Cube specimens 5 × 5 × 5 (cm) were also used. Two series of specimens were produced. Initially, specimens of the first series were cured in a room with relative humidity 95–98% and temperature of 35 ± 2 °C. Specimens remained in this room until their compressive strength,

Table 1
Chemical composition of the materials used

Oxide content (% wt)	Clinker	II32.5N cement	Milo's Earth (ME)	Skydra's Earth (SkE)	Megalopoli's fly ash (MFA)	Ptolemaida's fly ash (PFA)
SiO_2	22	28	65.9	61.7	47.08	45.15
Free SiO_2	–	–	23.21	21.13	15.69	22.58
Al_2O_3	5.2	9	15.7	19.6	18.62	17.50
Fe_2O_3	1.9	5.5	3.95	4.1	6.72	8.18
CaO	65.4	48.0	4.0	4.62	17.50	14.87
Free CaO	1.53	–	–	–	2.96	1.64
MgO	2.0	2.2	1.4	2.6	3.81	3.44
SO_3	1.3	3.2	–	–	3.28	4.72
Na_2O	0.5	0.5	2.90	2.78	0.68	–
K_2O	1.0	1.5	2.75	3.22	1.52	–
Blaine	3380	4250	–	–	–	–
Fineness (%, +45 μm)	12.9	14.5	18.9	21	25.5	16

Table 2
Composition, SO_3 content and fineness of cements

Mix. no.	Mixture	Cement type	SO_3 content of the mixture clinker + gypsum (%)	Fineness (retained %, 45 μm)
1	45 I	95.13% clinker + 4.87% gypsum	3.5	12.3
2	II32.5N	CEM II32.5 (commercial blended cement)	3.2	14.5
3	10% ME	10% ME + 85.62% clinker + 4.38% gypsum	3.5	12.9
4	20% ME	20% ME + 76.13% clinker + 3.87% gypsum	3.5	13.6
5	30% ME	30% ME + 66.59% clinker + 3.41% gypsum	3.5	14.3
6	10% SkE	10% SkE + 85.62% clinker + 4.38% gypsum	3.5	13.1
7	20% SkE	20% SkE + 76.13% clinker + 3.87% gypsum	3.5	14
8	30% SkE	30% SkE + 66.59% clinker + 3.41% gypsum	3.5	14.9
9	10% MFA	10% MFA + 86.35% clinker + 3.65% gypsum	3.5	13.7
10	20% MFA	20% MFA + 77.57% clinker + 2.43% gypsum	3.5	15.1
11	30% MFA	30% MFA + 68.78% clinker + 1.22%gypsum	3.5	16.5
12	30% PFA	30% PFA + 69.73% clinker + 0.27%gypsum	3.5	13.8
13	40% PFA	60% clinker + 40% PFA	3.2	14.1
14	50% PFA	50% clinker + 50% PFA	4.72	14.5
15	60% PFA	40% clinker + 60% PFA	7.08	14.8

Table 3
Water to binder ratio and flow of the prepared mixtures

Mixture	w/binder ratio	Flow meter (%)
45 I	0.46	114.75
II32.5N	0.53	114.5
10% ME	0.48	111.5
20% ME	0.50	120.5
30% ME	0.52	113.5
10% SkE	0.47	117
20% SkE	0.48	107
30% SKE	0.50	113.5
10% MFA	0.48	105
20% MFA	0.52	113.5
30% MFA	0.57	110
30% PFA	0.50	79.75
40% PFA	0.55	94.25
50% PFA	0.58	100
60% PFA	0.60	102.75

measured on 5 cm cubes became equal to or greater than 20 MPa. Thereafter they were immersed in the Na_2SO_4 solution at a temperature of 23 °C. Length change measurements were taken up to the age of 2 years or the final deterioration of specimens, whichever happened first. Measurements were performed at 1, 2, 3, 4, 8, 12, 16, 24, 36, 52, 65, 78, 91 and 104 weeks after immersion in the test solution. The Na_2SO_4 solution was changed after each measurement. These measurements are presented in Figs. 1–5. After the end of length change measurements the prismatic specimens were used for measuring their flexural strength, according to EN 196-1 [16]. Specimens of the second series were placed in a curing room with relative humidity 95–98% and temperature 21 ± 2 °C until the time of testing. Compressive strength measurements were performed at the ages of 3, 5, 7, 14, 21, 28, and 60 days on specimens of the second series. The measured values of compressive strength for all mixtures are presented in Table 4. Each value is the mean of three measurements.

Carbonation depth was also measured using a phenolphthalein indicator solution. Specimens used for those measurements were also kept in the curing room mentioned above until the age of 28 days. After this time they were placed in the laboratory environment with relative humidity of 50–65%, temperature of 21 ± 2 °C and CO_2 concentration of 354 ppm. Carbonation measurements are presented in Table 5. Each value is considered as the mean value of 10 measurements.

4. Test results and discussion

4.1. Compressive strength development

In spite the fact that PFA mixtures were produced with high w/binder ratios (Table 3) they developed high compressive strength from the early stage of their hydration. Natural pozzolans did not develop high compressive strength values and in no case did they reach values higher than the control. Thirty and fourty percent of PFA mixtures had at any age the highest compressive strength values among all blended cement mixtures tested whereas the 30% PFA mixture performed better than the control, especially after the age of 14 days. This finding confirms results by other researchers [3,12,17] who attribute this fact to the development of smaller diameter pores as well as at the greater amount of C–S–H produced from the hydration of blended cements [1]. Among the pozzolanic materials tested in this research, PFA was found to be more active. This is attributed to the increased finesse of the material in combination with its high free SiO_2 content.

4.2. Sulfate resistance

Mixtures produced with natural pozzolans had a relative good sulfate resistance performance only when the pozzolan replaced cement at high proportions. Among them the 10% SkE mixture is the one which first deteriorated between 6 and 8 months (180 and 240 days) (Fig. 1), without showing signs of cracking at earlier ages. This mixture had from the age of 4 months (120 days) a very fast

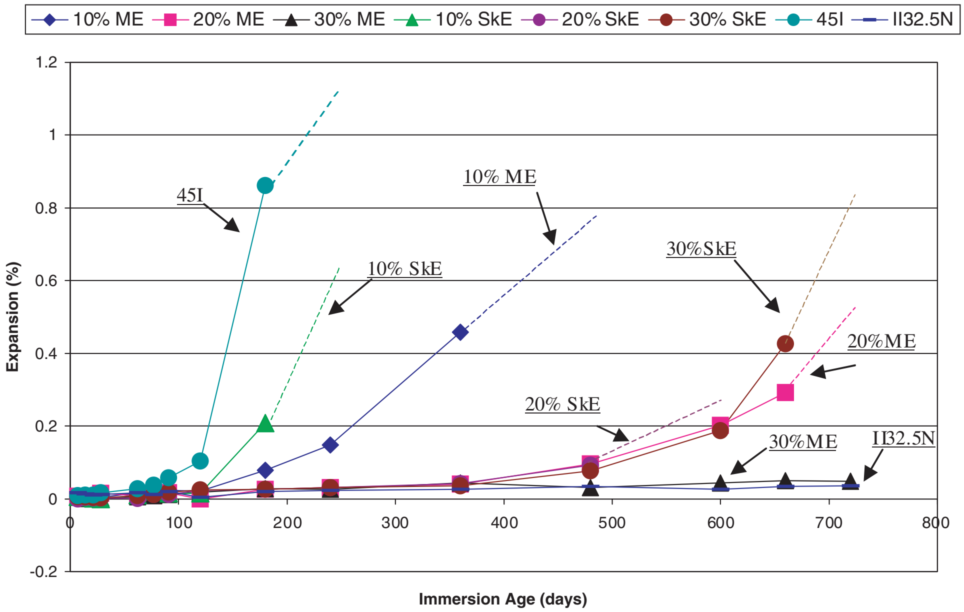

Fig. 1. Length change of specimens prepared with ordinary portland cement (45I), commercial cement (II32.5N), Milo's Earth (ME) and Skydra's Earth (SkE).

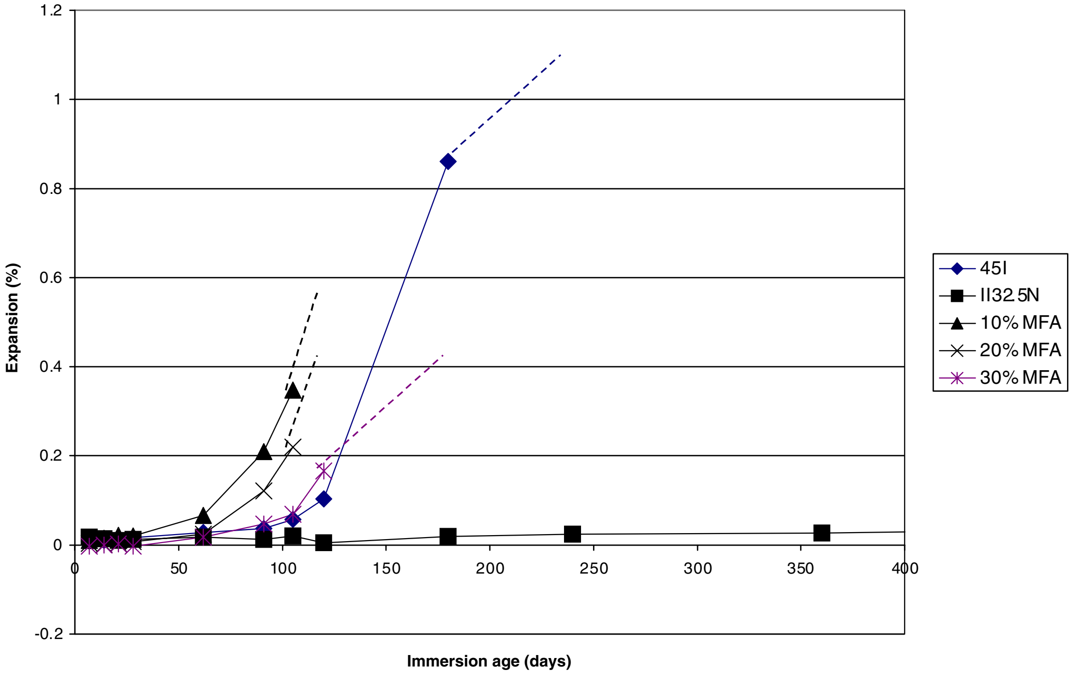

Fig. 2. Length change of specimens prepared with ordinary portland cement (I45), commercial cement (II32.5N) and Megalopoli's fly ash (MFA).

expansion (Figs. 1 and 4). The 10% ME mixture started also to expand from this age, but its length change was significantly smaller (Figs. 1 and 4). Cracks appeared at 8 months (240 days) and it deteriorated between 12 and 16 months (360 and 480 days). The 20% SkE mixture showed cracks from the age of 8 months (240 days) and deteriorated between 16 and 20 months (480 and 600 days) (Fig. 4). Thirty percent of SkE and 20% ME deteriorated between 22 and 24 months (660 and 720 days). The 30% ME mixture did not deteriorate during the period of the test. This mixture also suffered the smaller expansion whereas it showed its first crack at the age of 20 months (600 days).

Different results were obtained when the sulfate resistance of MFA mixtures is examined. The 10% MFA mixture showed greatest expansion from the age of 2 months (60 days), whereas all MFA mixtures started to deteriorate after exposure of 4–6 months (120–180 days) (Figs. 2 and 6). Deterioration was very sudden. Only the 20% MFA

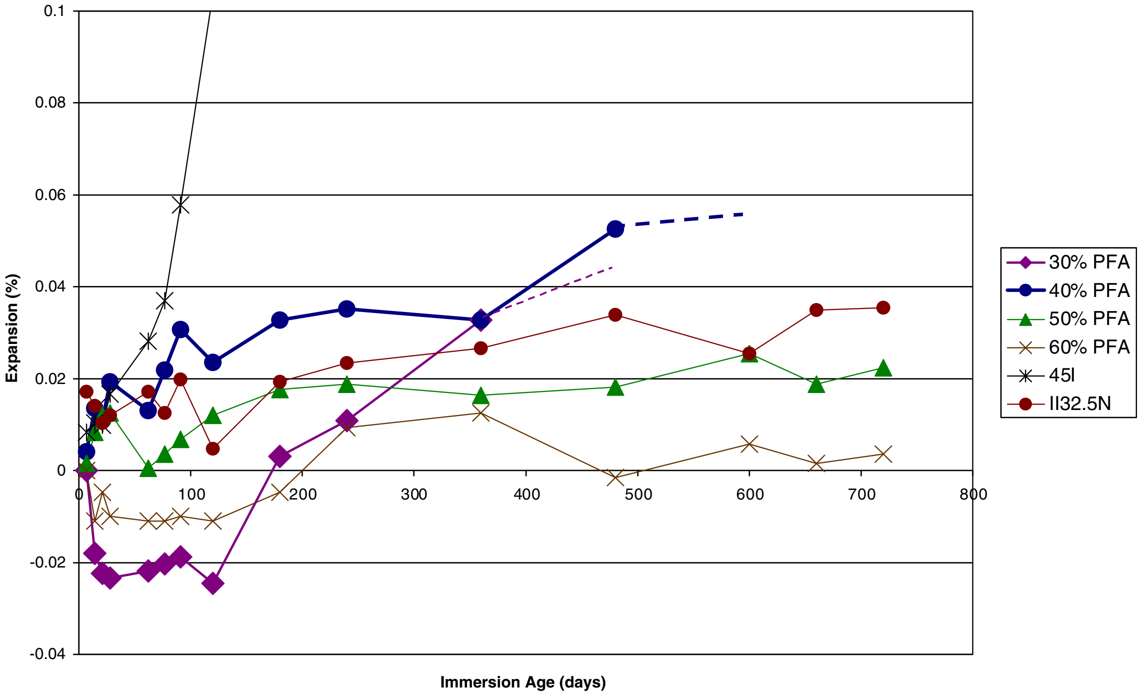

Fig. 3. Length change of specimens prepared with ordinary portland cement (45I), commercial cement (II32.5N) and Ptolemaida's treated fly ash (PFA).

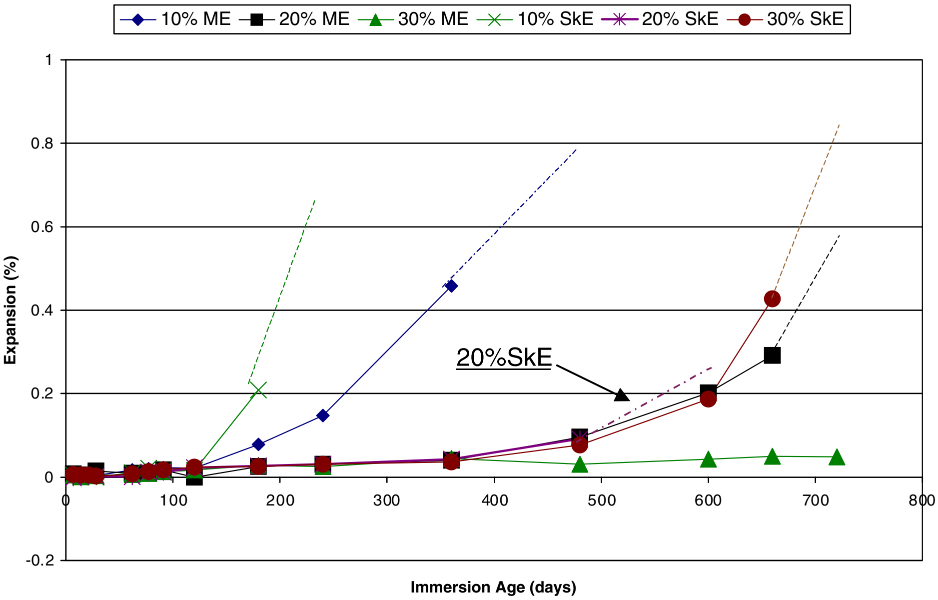

Fig. 4. Length change of specimens prepared with Milo's Earth (ME) and Skydra's Earth (SkE).

mixture showed cracks at the age of 8 weeks. The control mixture showed cracks at the age of 6 months and from that point onwards deteriorated very fast, between 6 and 8 months (Fig. 2). Mixture produced with commercial cement (CEM II32.5N) did not deteriorate until the age of 2 years (720 days). The increased finesse of this cement (Table 1) as well as the combination of the pozzolanic additives used had a beneficial effect.

Sulfate resistance of PFA mixtures was satisfactory. Those mixtures underwent small expansions through the first year of immersion whereas the 30% and 60% showed signs of shrinkage during the first months (Figs. 3 and 5). Deterioration occurred first on the 30% PFA mixture, between 12 and 16 months (360 and 480 days). No cracks were observed at earlier ages. The 40% PFA specimens deteriorated next, between 16 and 20 months (480 and 600 days). Specimens produced with 50% and 60% mixtures did not deteriorate until the end of the test (Figs. 3 and 5).

In spite of the fact that PFA mixtures had the highest w/binder ratio and the highest SO_3 content among all tested

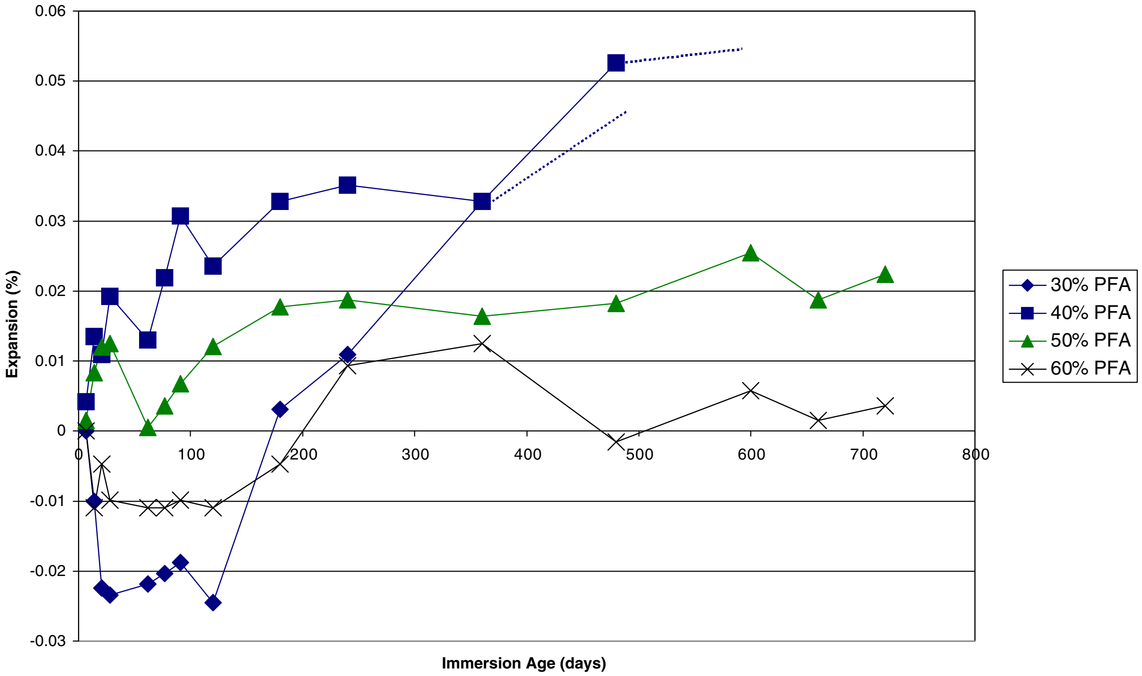

Fig. 5. Length change of specimens prepared with Ptolemaida's treated fly ash (PFA).

Table 4
Development of the compressive strength (in MPa) of the prepared mixtures

Mixture	Hydration age (days)						
	3	5	7	14	21	28	60
45 I	23.5	28.3	32.8	37.0	41.6	43.9	50.5
II32.5N	18.3	24.5	28.0	36.1	39.2	42.2	47.0
10% ME	15.0	–	24.8	36.2	36.6	39.6	42.6
20% ME	–	22.1	22.8	27.3	28.7	31.6	34.0
30% ME	10.9	–	17.3	22.7	23.7	26.3	31.0
10% SkE	21.0	–	31.5	37.4	–	41.5	44.8
20% SkE	21.7	23.4	–	24.0	29.6	33.0	42.5
30% SkE	10.0	15.6	–	22.9	25.1	26.2	29.7
10% MFA	25.8	30.0	30.9	31.5	37.4	41.7	52.0
20% MFA	20.5	21.7	26.8	31.0	33.4	35.4	41.0
30% MFA	15.1	18.9	–	24.8	25.8	28.7	34.3
30% PFA	23.1	25.3	31.1	38.0	46.0	47.8	51.0
40% PFA	22.9	–	31.9	38.7	40.3	43.5	47.5
50% PFA	19.1	–	31.2	38.3	–	40.2	42.7
60% PFA	14.4	21.7	23.9	30.6	–	34.2	36.7

mixtures (Tables 2 and 3) they demonstrated a better sulfate resistance and developed high compressive strength values. This is in agreement with other works [12,18] that support the conclusion that mixtures rich in SO_3 may have good sulfate resistance.

Most of the mixtures produced with blended cements showed better sulfate resistance than the control mixture, although they had higher w/binder ratios. It also seems that as the proportion of the replacement of clinker by pozzolanic material increased, the sulfate resistance of the mixture also increased. This conclusion, which is in accordance with other research results [18–20], indicates that the decrease of C_3A content of the mixture in combination with the reduction of large pores caused by the pozzolanic reaction, are more critical than the total porosity alone (which increases as the w/binder ratio also increases) when sulfate resistance is of primary interest. OPC mixture, as well as mixtures prepared with low pozzolan content cement, had the smallest sulfate resistance. Those mixtures also had the lowest w/binder ratio and the lowest total porosity [21]. On the other hand, blended cement mixtures with high pozzolan content were less permeable due to pore refinement [21].

It is noticeable that although the ashes used in this research had similar chemical composition (Table 1) they performed differently against sulfates. Several attempts have been made in order to predict the sulfate resistance of a fly ash based on its chemical composition. Among

Table 5
Carbonation depth of plain and blended cements

Mix. no.	Mixture	Carbonation depth (mm)		
		6 months	12 months	24 months
1	Portland cement (ASTM type I)	1	3	4.5
2	II32.5N (commerc. Blended cem.)	2	4	5.5
3	10% ME	1.5	3	5
4	20% ME	2.2	4	6.5
5	30% ME	2.6	5.5	8.5
6	10% SkE	1.5	4	4.7
7	20% SkE	1.7	4	6.6
8	30% SkE	3.5	7.5	9.0
9	10% MFA	1.6	3.5	5.5
10	20% MFA	2	4	6.2
11	30% MFA	3	5	8.3
12	30% PFA	2.5	4	6.3
13	40% PFA	2.7	5	9.0
14	50% PFA	4	6	9.5
15	60% PFA	4.8	8	13.5

them the first is that of Dunstan [10]. He introduced the "resistance value" which was $R = \frac{\text{CaO}-5}{\text{Fe}_2\text{O}_3}$. According to Dunstan, a fly ash improves the sulfate resistance of the mixture if $R < 1.5$, whereas this decreases if the R-value of the ash is greater than 3. In a later research Dunstan [22] reported that the sulfate resistance of mortars tested according to ASTM C-1012 will be improved, if fly ash with $R \leqslant 3.5$ is used. The R-value for the two ashes used were $R_{\text{MFA}} = 1.86$ and $R_{\text{PFA}} = 1.21$. Despite the fact that in both cases the R-value is much less than 3.5, their contribution to the sulfate resistance of the mixtures is totally different: MFA has a deleterious effect, whereas PFA has a beneficial one. This is attributed to the different mineralogical composition of the two fly ashes [23]. Mehta [12] also confirmed with laboratory data and theoretical consideration that R-value is not a valid criterion for evaluation of the ability of a fly ash to improve sulfate resistance of blended cements.

In other research [24] the ratio CaO/SiO_2 of the fly ash was introduced as an indicator of their contribution to the sulfate resistance of mixtures. According to the researchers, fly ash with CaO/SiO_2 ratio less than 0.25, contained no detectable C_3A and provided a level of resistance to sulfate attack equal or greater than that of cement Type II alone. When fly ash had a CaO/SiO_2 ratio greater than 0.60, it reduced the sulfate resistance of the mixtures. The CaO/SiO_2 ratio of the ashes used was equal to 0.33 for PFA and 0.37 for MFA.

Erdogan et al. [25] reported that the (free CaO)/Fe_2O_3 and (C_3 + free alumina)/(free CaO) ratios of the cement-high lime fly ash mixtures can be used to determine their sulfate susceptibility. According to the authors, there is a clear relationship between these ratios and the sulfate resistance of the mixtures: sulfate resistance increases when the (free CaO)/Fe_2O_3 ratio decreases and the (C_3A + free alumina)/(free CaO) ratio increases. The (free CaO)/Fe_2O_3 ratios of the 10% MFA, 20% MFA, 30% MFA, 30% PFA, 40% PFA, 50% PFA and 60% PFA are 0.70, 0.63, 0.58, 0.41, 0.35, 0.31 and 0.28, respectively. The (C_3A + free alumina)/(free CaO) ratios of the mixtures are 6.25, 5.47, 4.93, 6.04, 5.77, 5.49 and 5.23, respectively. Mixtures with 60% PFA and 50% PFA suffered small expansions during the two year test period, whereas the MFA mixtures were the first which deteriorated. The

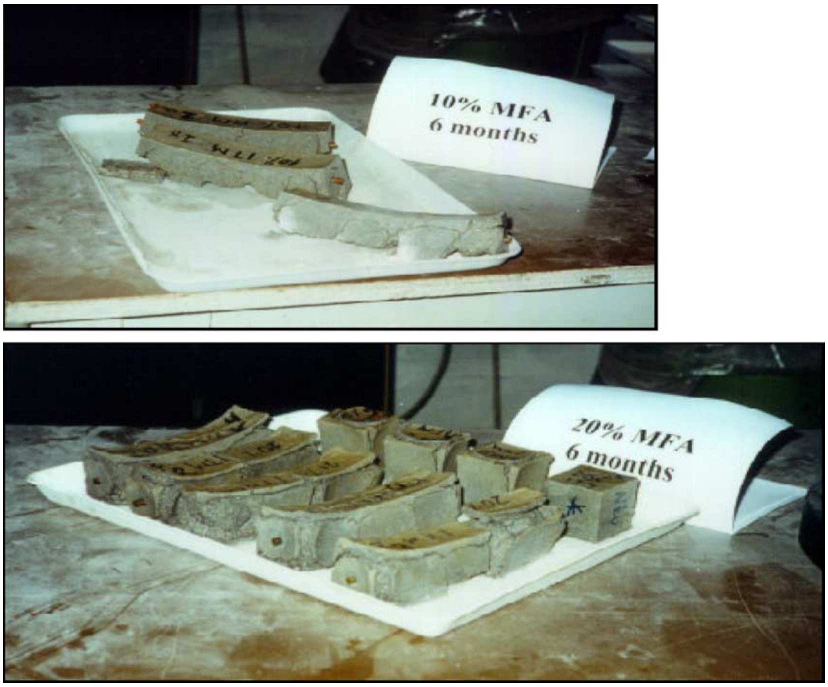

Fig. 6. Typical failure mode of mortar prisms and cubes.

sulfate susceptibility of the mixtures is well predicted only by the first criterion (free CaO)/(Fe_2O_3 ratio). The second criterion ((C_3A + free alumina)/(free CaO) ratio) was not able to predict the sulfate resistance of the mixtures prepared with different cement replacement by the same fly ash (i.e 10–30% MFA and 30–60% PFA). On the other hand it managed to compare the resistance of mixtures prepared with different fly ashes replacing cement at the same ratio (30% MFA and 30% PFA mixtures had ratios of 4.93 and 6.04, respectively).

Similar results regarding the effect of pozzolanic materials on the sulfate resistance of mixtures are obtained if the length change measurements until the age of one year only (Table 6) are taken into consideration. The 50% PFA and 60% PFA mixtures suffered the smallest expansion, followed by the II32.5N cement mixture, the 40% PFA and the 30% PFA cement mixture.

This data confirm Mehta's [12] conclusion that it is not the chemical but the mineralogical composition of the ash that makes the difference in the sulfate resistance of fly ash cement mixtures. The free SiO_2, the free CaO and the fineness of the material are of great importance [16,23,25]. PFA has a greater amount of free SiO_2 than the MFA (Table 1). PFA showed hydraulic as well as pozzolanic reaction [4]: The free CaO reacts with water to form $Ca(OH)_2$. This reacts with SiO_2 to form C–S–H. Compressive strength increases very fast due the formation of additional C–S–H and the parallel reaction of alumina (it has the form of C_3A and $C_4A_3\bar{S}$) with water and portlandite [26]. On the other hand pozzolanic activity is prolonged due to the internal source of CaO. The secondary C–S–H produces a film or a coating on the alumina-rich and other reactive phases thereby hindering the formation of secondary ettringite [6]. Secondary C–S–H also reduces the total porosity and leads to the formation of pores with smaller diameter [20,27]. Increased finesse of PFA is an additional explanation for the material's superior sulfate resistance. PFA was finer than MFA, whereas it also contained higher amount of free SiO_2. The combination of those two properties resulted to faster formation of hydration products and therefore to lower porosity and increased sulfate resistance.

4.3. Strength reduction

Regarding strength reduction of mixtures due to sulfate attack, it appears that the use of blended cements is generally effective (Table 6). The compressive strength loss of most blended cements was lower than the loss of the strength of OPC, whereas they were deteriorated at later ages. In the case of 20% ME the loss in strength was higher than the one of the control, but this was measured at the age of 20 months instead of 8 months (deterioration age). The same conclusion is valid for the flexural strength (except the flexural strength of 10% and 20% ME mixtures). All MFA specimens were totally deteriorated. This happened very suddenly, so the strength at the deterioration age could not be measured.

The 50% and 60% PFA mixtures did not show any strength loss at all. On the contrary, the final compressive strength of those mixtures measured after 2 years of immersion in the Na_2SO_4 solution slightly increased, as compared with the one measured on specimens cured in the curing room. The increase of the final flexural strength values was much higher. Those specimens also demonstrated the smallest expansion (Table 6) whereas they did not deteriorate, and developed no cracks during the whole immersion period. According to other researchers [28], compressive

Table 6
Compressive and flexural strength loss (%), final expansion (%), deterioration age and first crack observed age (months) for all mixtures

Mixture	Compressive strength loss (%)	Flexural strength loss (%)	One year expansion (%)	Final expansion (%)	Deterioration age (months)	First crack (months)
45 I	30	67.5	1.10	1.10	6–8	6
II32.5N	15.4	−3.5*	0.026	0.035	Not deteriorated	16
10% ME	26.3	79.7	0.458	0.79	16–20	8
20% ME	31.6	84.6	0.040	0.546	22–24	12
30% ME	0.4	44.3	0.044	0.048	Not deteriorated	20
10% SkE	13	69.3	0.650	0.650	6–8	No cracks
20% SkE	17	41.7	0.042	0.220	20–22	8
30% SkE	21	−216*	0.036	0.824	22–24	12
10% MFA	–	–	0.544	0.544	3–4	No cracks
20% MFA	–	–	0.428	0.428	3–4	2
30% MFA	30	–	0.408	0.408	4–6	No cracks
30% PFA	19	17	0.033	0.049	12–16	No cracks
40% PFA	15.3	14.7	0.033	0.055	16–20	16
50% PFA	−0.8*	−153*	0.016	0.022	Not deteriorated	No cracks
60% PFA	−8*	−179*	0.012	0.016	Not deteriorated	No cracks

Compr. strength loss = reduction of the compr. strength measured at the deterioration age due to sulfate attack as compared with the one of normal curing specimens of the same mixture measured at the same age.

Flexural strength loss = reduction of the flexural strength measured at the deterioration age due to sulfate attack as compared with the one of normal curing specimens of the same mixture measured at the same age.

–: totally deteriorated, not measured. *: strength increased.

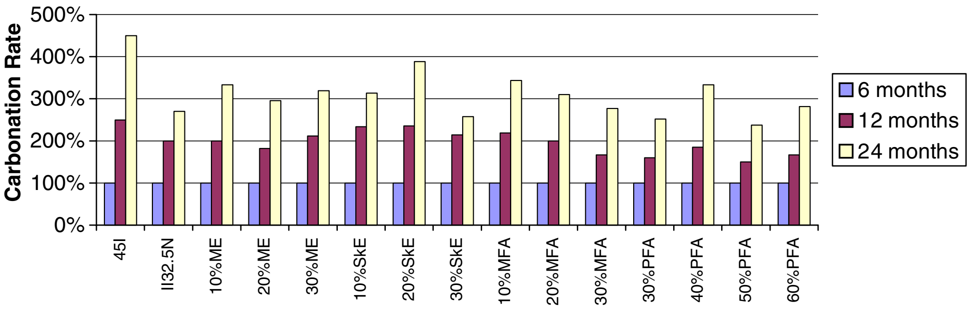

Fig. 7. Carbonation rate of plain and blended cements.

strength of immersed specimens initially increases beyond that of the control due to the pore filling by the reaction products of sulfate attack. Subsequently, the disruption of the cement matrix by the reaction products resulted in a strength decline. This means that in these cases, deterioration due to sulfate attack is much prolonged, since the phenomenon is still in the first stage. It is also noticeable that those mixtures were produced with the higher w/binder ratio and the 50% and 60% PFA cements had the highest SO_3 content (Tables 2 and 3).

4.4. Carbonation rate

Carbonation depth of all blended cement mixtures was greater than the one of the plain cement mixture (Table 5). This finding was also reported by Papadakis et al. [29]. On the other hand, the carbonation rate, i.e., the increase in carbonation depth at older ages as compared with the one at the initial measurement (6 months), was greater with the plain cement mixture. Carbonation rate generally reduced, as the pozzolanic content increased (Fig. 7). It is well documented [30,31] that pores with radius less than 450 Å are not permeable to CO_2. During the hydration of blended mixtures, the $Ca(OH)_2$ available in the pore solution is consumed by the pozzolanic reaction, yielding this way to smaller pH values. This results in higher carbonation depth at the early stages of hydration. As hydration proceeds in blended cements, the total porosity increases but it also consists of pores with smaller diameter, therefore the CO_2-permeable porosity decreases [21]. Carbonation rate is therefore reduced. Among the pozzolanic materials tested, PFA had the smallest carbonation depth at any age (Table 6, mixtures Nos. 5, 8, 11, 12), mainly due to the internal source of CaO in the material as well as due to the increased finesse of the material. This latter was responsible, in combination with the high amount of free SiO_2, for the faster formation of secondary CSH to fill the pores and decrease the CO_2-permeable porosity of PFA blended cement mixtures.

5. Conclusions

Using pozzolanic admixtures increased in most cases the sulfate resistance of the blended cements. As the pozzolan content increased, the sulfate resistance also increased, even with somewhat higher w/binder ratio used in this research.

Lignite fly ashes, with high CaO and SO_3 content may have a positive effect on the sulfate resistance of blended cements. Specimens containing PFA fly ash blended cements gave the smallest expansion among all cement mixtures tested in this research and developed high compressive strength from early ages. These specimens also gave the least reduction in compressive and flexural strengths due to sulfate attack. On the other hand specimens containing MFA fly ash blended cements gave the worst performance since they were very fast totally deteriorated. The two examined lignite fly ashes had similar chemical composition but they had totally different performance regarding the sulfate resistance of the mixtures. This indicates that is the mineralogical composition what really counts and makes the difference.

Carbonation depth of blended cement mixtures at any age was greater than that of the control portland cement mixture. On the other hand, the rate of carbonation of the portland cement mixture was greater than that of blended cement mixtures, due to the formation of secondary C–S–H and reduction in the pore structure. Among all mixtures tested, PFA fly ash blended cements gave the lowest carbonation rate.

Among the pozzolanic materials tested in this research, PFA had the best total performance. It is suggested that 50% PFA blended cements may be used instead of portland cement for the construction of sulfate resistant concrete structures with almost equal compressive strength. Although in this case the carbonation rate was very slow, extra protection against carbonation should be taken at early age by means of extended curing period until the hydration will progress and the diameter of the pores will be therefore reduced.

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