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Durability of the hydrated limestone-silica fume Portland cement mortars under sulphate attack

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Abstract

The effect of silica fume, emerging as a by-product in production of ferrosilicon, on corrosion resistance to sulphate attack of Na_2SO_4 and $MgSO_4$ solutions has been studied in Portland cement mortars containing limestone and mortars containing no limestone. Expansion and changes in the elasticity modulus of mortars as a function of silica fume content have been investigated. The phases formed and the microstructural changes in the mortar exposed to sulphate corrosion have been determined by differential thermal analysis (DTA), X-ray diffraction, scanning electron microscopy, and transmission electron microscopy. The presence of monocarbonate and the absence of monosulphate were detected in the mortars containing limestone. The addition of silica fume results in less CH formed by the hydration process and consequently less gypsum and ettringite during the sulphate immersion of mortars. Mortars containing more than 5 mass% of SiO_2, or simultaneously limestone and more than 2 mass% of SiO_2, are characterised by a good sulphate resistance and show lower expansion than the control, the sulphate-resisting mortars independent of the type of the sulphate solution.

Keywords: Durability; Sulphate attack; $CaCO_3$; Silica fume; Mortar

In order to improve the properties of cement/concrete relative to the effect of aggressive environments, their production has been increasingly directed towards blended cements. To this purpose, various natural or artificial additions of inorganic origin are added to cements. One of these additions, silica fume, has been rather prominent recently. The research so far has proved that addition of silica fume to cement as pozzolan improves mechanical properties of cement and thereby improves the resistance of cement stone to activity of corrosion agents, which can be explained by the pozzolanic reaction between calcium hydroxide and amorphous silicon dioxide [1–4]. On the other hand, controversial diverse opinions can be found in the literature on addition of limestone as an inert filler to cement and its effect. Some authors consider the effect of limestone on cement to be only physical, taking into account the increase in strength and resistance to seawater [5]. The improvement is ascribed to reduced porosity or to formation of calcium-carboaluminate-hydrate, which is responsible for increased strength and resistance in cement/concrete [6,7]. Addition of finely ground $CaCO_3$ to cement affects the hydration rate for individual components (C_3S, C_2S) of cement and modifies the properties of the paste and mortars [8,9]. However, recent literature supported that the limestone acts as an active participant and some $CaCO_3$ during hydration of Portland cement (PC) is taken up into system and reacts with C_3A or ferrite phases to form hemicarbonate, monocarbonate, or a mixture of both [10–14].

The present work simultaneously examines the effects of limestone and silica fume on corrosion resistance and durability of PC mortars. In the samples, 15 mass% of cement was substituted with finely ground limestone and the results obtained were compared to those obtained for cement mortars containing no limestone.

1. Experimental procedure

1.1. Materials

1.1.1. Cement

Commercially blended PC that was produced by grinding of cement clinker and mixing with up to 5% of gypsum

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and 30% of a blast furnace slag, made in Croatian cement works (Dalmacijacement Co., Solin, HR) and marked PC 30z 45s, was used in examinations. The sulphate-resisting cement, marked SPC 45, Type V according ASTM C-150, was used as control (referent) cement.

1.1.2. Silica fume

Silica fume was obtained from filters in production of ferrosilicon, containing 89 mass% SiO_2, and had extremely fine spherical and amorphous particles. The specific surface is on the order of 18 m^2/g, measured by nitrogen adsorption method according to Brunauer, Emmett and Teller (BET).

1.1.3. Limestone

Limestone containing 99.00 mass% of $CaCO_3$, fineness 1.30 m^2/g according to BET method, was used.

Chemical analyses of materials used and the potential mineralogical composition of PC (neat), marked PC 45, a blended PC, PC 30z 45s, and the sulphate-resisting cement, marked SPC 45, are given in Tables 1 and 2, respectively.

1.1.4. Mortars

Mortars were prepared from a mixture of blended cement, standard quartz sand, and 2–15 mass% of silica fume. The water/cement ratio varied from 0.50–0.67; the samples had been prepared to have the same flow table consistency. Two series of samples were prepared. The first series (P) contained mortars with addition of 0, 2, 5, 8, 11, and 15 mass% of silica fume at the expense of cement. The samples were designated P-0, P-2, P-5, P-8, P-11, and P-15, respectively. In the second series (PK) 15 mass% of cement was substituted with finely ground limestone, and silica fume was added in the same way as in the P-sample series. Designations used for the PK-series were PK-0, PK-2, PK-5, PK-8, PK-11, and PK-15, respectively.

Table 1
Chemical analyses of materials used

	Mass %			
Constituents	Blast furnace slag	PC30z45s	Silica fume	Limestone
SiO_2	36,07	21,03	89,68	0,115
Al_2O_3	10,69	6,58	1,15	0,220
Fe_2O_3	1,18	2,68	1,54	0,230
CaO	41,36	58,10	1,40	55,440
MnO	0,55	–	–	–
MgO	7,20	2,57	1,45	0,970
SO_3	0,98	2,54	0,17	–
P_2O_5	0,20	–	–	–
P	–	–	–	0,011
S	–	–	–	0,034
K_2O	0,82	0,73	–	–
Na_2O	0,45	0,29	–	–
L.O.I.* (1000°C)	–	1,04	2,99	42,980
C	–	–	1,83	–

* L.O.I. = loss on ignition.

1.1.5. Aggressive solutions

Salts $Na_2SO_4 \times 10\ H_2O$, p.a., and $MgSO_4 \times 7\ H_2O$, p.a., were used in preparation of sulphate solutions. The SO_4^{2-} ion concentration in both solutions was 0.26 mole/dm^3 and was kept constant during examinations.

1.2. Test methods

Sulphate attack on PK-series cement mortars containing various additions of silica fume was examined as follows:

- The cement stone potential sulphate resistance was determined according to the ASTM.C.452-68 standard. Sample expansion was measured. Prisms with dimensions 25.4 × 25.4 × 285.75 mm were cured for 24 h in a humid environment (20°C, 90% relative humidity) and then kept in water storage for the remaining time. The first test was carried out 28 days after sample preparation, and then the samples were exposed to aggressive environment and measurements. The linear changes in samples due to expansion were measured every 30 days and were compared with sample length before exposure to a sulphate solution ($\Delta L/L$).
- Changes in the elasticity modulus in mortars immersed into sulphate solutions were determined by dynamic resonance frequency measurements after 28 days and every 28 days thereafter within a 260-day period. An electrosonometer [15] was used for that purpose. Prisms of dimensions 25 × 25 × 350 mm were prepared for this test.
- The quantity of calcium hydroxide (CH) in hydrated mortar of P and PK samples during sulphate attack was determined by differential thermal analysis (DTA-DTG-TG; Derivatograph MOM, Budapest, Hungary, with Pt-crucibles and corundum inert substance).
- Structural changes in samples during sulphate attack were identified by X-ray diffraction (XRD; X-ray diffractometer, Philips PW 1010, Eindhoven, Netherlands) with CuKα radiation and with the scan rates of 0,5° 2Θ/min in the ranges of Bragg's angles of 3–60°. The following abbreviations will be used: CH = $Ca(OH)_2$; E = $C_3A \cdot 3CaSO_4 \cdot 32\ H_2O$; G = $CaSO_4 \cdot 2H_2O$; Hc = $C_3A \cdot 1/2CaCO_3 \cdot 1/2Ca(OH)_2 \cdot 11{,}5\ H_2O$; Mc = $C_3A \cdot CaCO_3 \cdot 11H_2O$; Ms = $C_3A \cdot CaSO_4 \cdot 12H_2O$.
- The scanning electron microscopy (SEM; Leitz AMR 1600T, Wetzlar, Germany) method was used to exam-

Table 2
The potential mineralogical composition, mass % (the Bogue calculation) of the sulphate-resisting cement, SPC 45, neat cement, PC 45, and a blended portland cement, PC 30z 45s*

Minerals	C_3S	C_2S	C_3A	C_4AF	CaO free
SPC 45	55,65	19,98	2,24	13,64	–
PC 45	70,00	15,00	6,00	8,00	1,00
PC 30z45s	62,10	17,60	11,20	8,20	0,90

* Calculated according to Bogue for the neat cement, PC 45.

ine the morphology of mortars in freshly fractured surface of samples. The same samples (carbon-single, stage replica) were submitted to transmission electron microscopy (Philips 301 Transmission EM, Eindhoven, Netherlands). The samples for SEM were gold-coated before examinations.

2. Results and discussion

After 28 days of hydration, mortars containing limestone and 2–15 mass% of silica fume were exposed to sulphate attack of the Na_2SO_4 and $MgSO_4$ solutions, $c(SO_4^{2-})$ being 0.26 mole/dm^3. Fig. 1 presents the results obtained for sample expansion.

The positive effect of limestone is observed (Fig. 1). The expansion in the Na_2SO_4 solution [Fig. 1(*A*)] decreases with the increase in the silica fume content. The highest expansion was observed in the sample without silica fume (sample PK-0). In other PK-series samples similar or even better behaviour was observed than in the referent cement mortar sample prepared from sulphate-resisting cement, designated SPC. Mortars immersed in the $MgSO_4$ solution [Fig. 1(*B*)] behaved in a similar manner. Sample without silica fume (PK-0 one) broke down after 150 days, while samples with more than 2 mass% silica fume (the PK-5, PK-8, PK-11, and PK-15 samples) underwent less expansion than the referent SPC sample, due to corrosion. It is important to remark that data on volume change due to expansion indicate better sulphate resistance in all PK-series samples than in the P-series ones [4]. Relative to the sample without limestone (sample P-0), this one shows higher resistance to sulphate attack, as the P-0 sample disintegrated after only 60 days while the PK-0 one endured 150 days of immersion in the Na_2SO_4 and $MgSO_4$ solution before breakdown.

The mineralogical analysis of the PK-0 paste after 120 days of hydration by XRD (Fig. 2) in comparison with the P-0 paste indicates the presence of monocarbonate, Mc (d-spacing = 0,760; 0,380; 0,286 nm), and absence of monosulphate-12 hydrate, Ms-12 (d-spacing = 0,892; 0,446; 0,287 nm), indicating that the reaction had occurred between the remaining C_3A, $CaCO_3$, and the CH [12,13]. The presence of both hemicarbonate, Hc ($2\Theta = 10{,}8°$, d-spacing = 0,820 nm), and calcite ($2\Theta = 29{,}5°$, d-spacing = 0,303 nm) was observed for both samples, perhaps indicating that contamination of the sample by atmospheric CO_2 occurred. Gypsum may also appear together with calcite as a result of carbonation of calcium sulphoaluminates [16]. Gypsum peaks at d-spacing = 0,762; 0,428; 0,287; 0,268 nm were identified in the hydrated cement mortars of the PK-series [7]. The existence of ettringite was detected with different intensity of the principal peak at 9,00° 2Θ, d-spacing = 0,980 nm for all P and PK samples exposed to water or sulphate solutions [7]. However, in the PK-series only, besides the existence of the first principal peak of ettringite, the second reflection of ettringite was detected also. The second one was shifted by about $2\Theta = 0{,}2°$ to higher Bragg angles ($2\Theta = 9{,}20°$, d-spacing = 0,962 nm), the marked peak (*) as shown Fig. 2, perhaps indicating that SO_4^{2-} was partially replaced by other anions in the ettringite structure. Mixed ettringite-like species containing CO_3^{2-} or OH^- substituting for SO_4^{2-} have also been observed by other authors [11–13]. Further results obtained with thermal analysis of the PK-0 samples confirm that carbonate had been taken up to system. The amount of CO_2 (remaining carbonate) decreases during hydration. The higher value of 1,77 mass% CO_2 was obtained after 28 days of hydration, and the lower value of 1,62 mass% CO_2 was obtained in the latter stages of hydration. It means that 1,65–2,93 mass% of $CaCO_3$ was incorporated during 28 and 120 days of hydration, respectively. The quantity of $CaCO_3$ incorporated had been affected by the silica fume content [7,17]. This is compatible with previous reports that the conversion of $CaCO_3$ in cement paste/mortar sufficient for the formation of monocarbonate depends on the amount of aluminate and ferrite phases available, as well on the presence of CH [12–14].

Development and course of corrosion was traced by changes in the elasticity modulus through ultrasonic measurement of dynamic resonance frequency. Fig. 3 shows the changes in the elasticity modulus relative to the quantity of silica fume in samples after 120 days of immersion in the Na_2SO_4 (N) and $MgSO_4$ (M) solutions. The data on changes in the elasticity modulus clearly indicate that corrosion resistance to the Na_2SO_4 and $MgSO_4$ solutions increases with the content of silica fume in the sample [i.e., the PK-11 and PK-15 samples behave in the same manner when exposed to the effect of the N or M solution, or to water storage (W)].

The thermal analysis established the dependence of change in the CH concentration in the P- and PK-series samples after 120 days of immersion in the Na_2SO_4 or $MgSO_4$ solution on the concentration of silica fume added. Fig. 4 presents the results. The same diagram shows the change in the CH concentration for the same samples after 120 days of hydration in W. The addition of up to 5 mass% silica fume to the P-series samples reduces the quantity of CH in cement mortar samples due to leaching during the corrosion activity of Na_2SO_4. In samples with more than 5 mass% silica fume added, no further reduction in the quantity of CH occurs in mortar samples, and the plot of the change in the CH concentration for samples treated in Na_2SO_4 completely corresponds to the plot of the CH concentration in samples treated in W.

In the PK-series samples the corrosion activity (i.e., leaching of lime) was observed only in samples containing no silica fume or 2 mass% silica fume, while in samples with a higher content of silica fume there was no difference in the quantity of CH between those treated in N or W.

Fig. 4 shows the CH concentration in the P- and PK-series samples treated for 120 days in the $MgSO_4$ solution relative to addition of silica fume. In this case, the P-series samples containing more silica fume (more than 8 mass%) show resistance to attack, although the environment is a more aggressive one (the effect of Mg^{2+} ions and sulphates). Samples containing limestone (the PK-series) behave in the

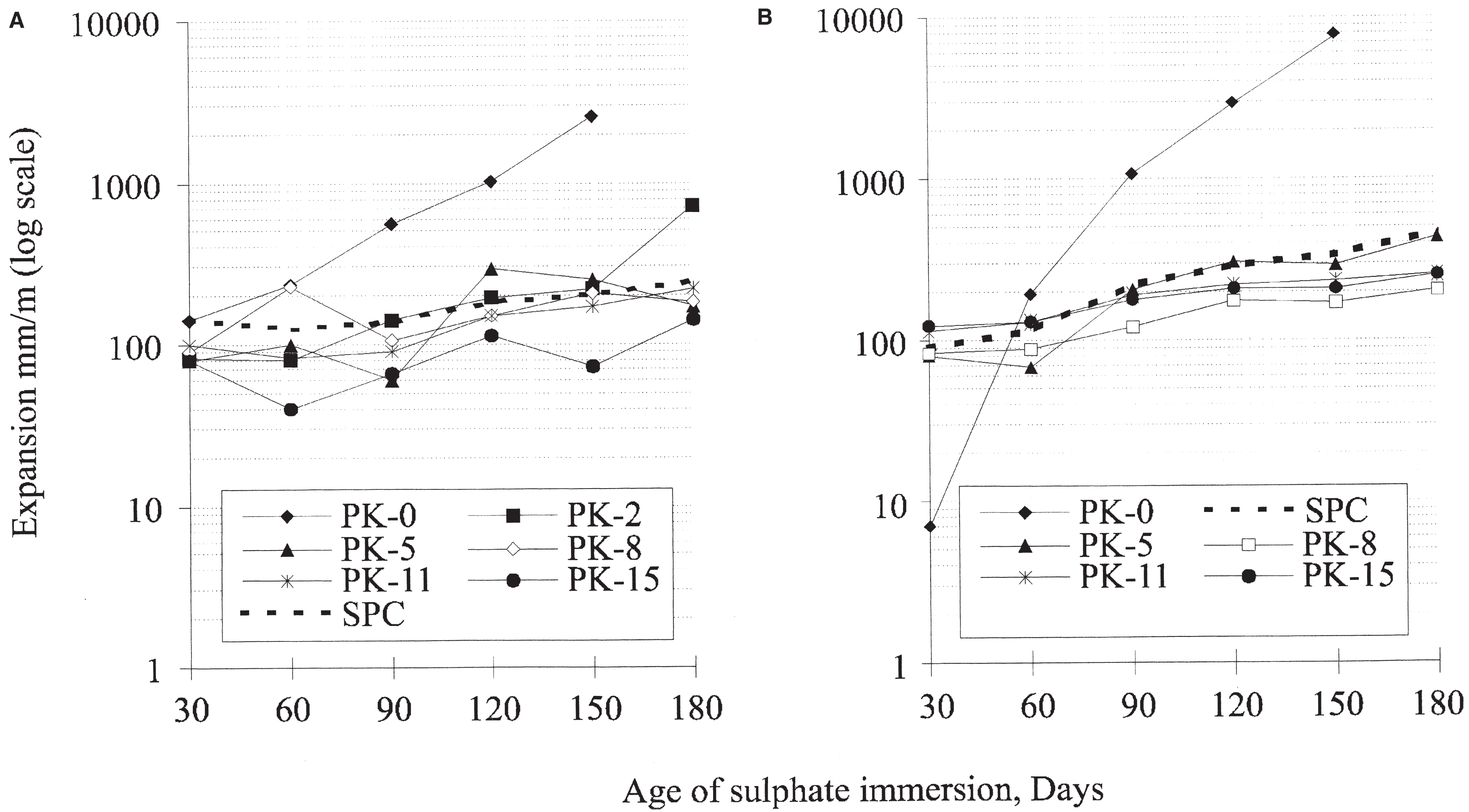

Fig. 1. Expansion of the PK-series mortars vs. duration of sulphate immersion for samples exposed to *(A)* the Na_2SO_4 solution and *(B)* the $MgSO_4$ solution.

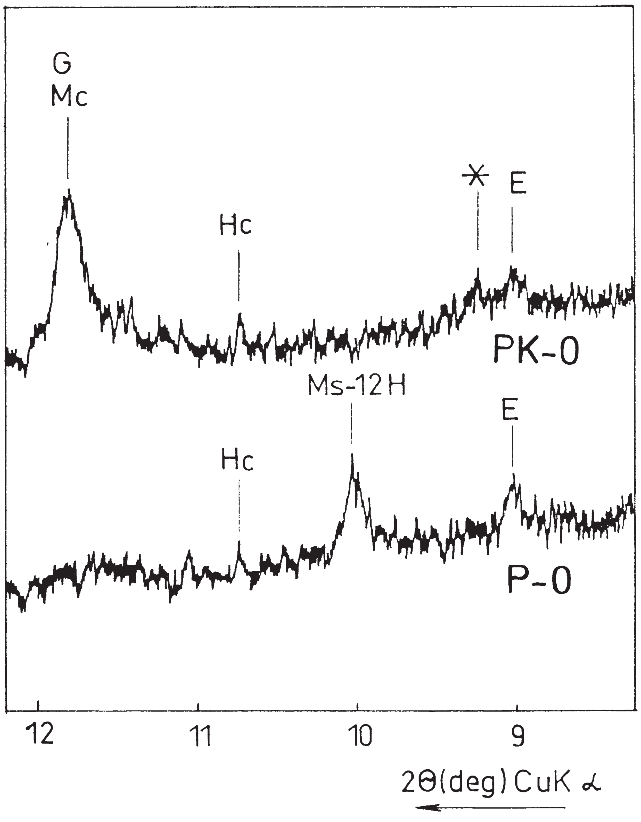

Fig. 2. XRD patterns of the P-0 and PK-0 mortars after 120 days of hydration. The scan rates of 0,25° 2θ/min.

same way in the $MgSO_4$ solution as in the Na_2SO_4 solution; a reduction in the CH concentration in mortar samples due to corrosion activity was observed only in samples containing no silica fume or 2 mass% silica fume.

XRD patterns of the P-0 and P-8 mortars exposed to Na_2SO_4 solution for 120 days (Fig. 5) confirm the behaviour observed in the P-series samples. Formation of gypsum and a higher quantity of ettringite due to sulphate corrosion was detected in the sample containing no silica fume (the P-0 one), while no gypsum was detected in the P-8 sample and its ettringite content corresponded to that formed during cement hydration. However, although the best mechanical properties [4] and the best corrosion resistance were observed for the mortar containing 8 mass% of silica fume (P-8 sample), even with this sample, after its 120 days of immersion in the Na_2SO_4 solution, SEM detected the large, long-needle ettringite crystals in pores about 200 μm remote from mortar surface, as shown in Fig. 6. No corrosion activity was detected elsewhere in the structure. As the P-8 mortar contained ettringite and had the best corrosion resistance (i.e., showed no expansion) it may be concluded according to the Mehta theory [18] that this type of ettringite, formed at lower CH concentrations, is not expansive. Addition of silica fume evidently improves the cement mortar durability as the pozzolanic reaction of CH formed hydration and amorphous SiO_2 from silica fume reduces the lime content in cement mortars, which prevents higher leaching of CH and disintegration of cement mortars/stone, as well as for-

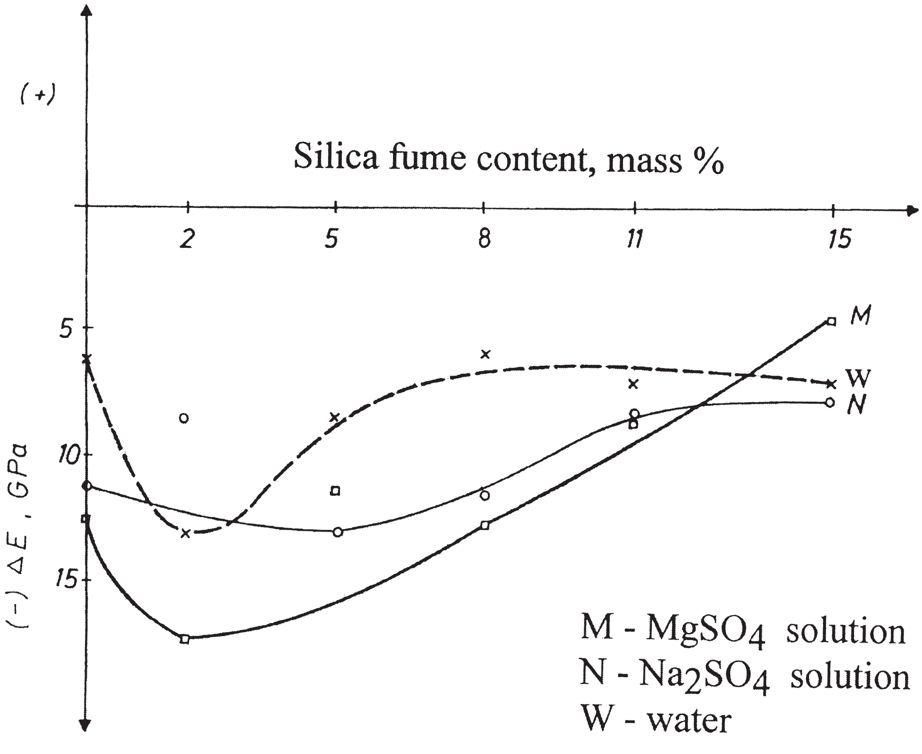

Fig. 3. The change of dynamic elasticity modulus (E-modulus) for the PK-series mortars exposed to sulphate attack of the N and M solutions vs. silica fume content. Control mortars were stored in W.

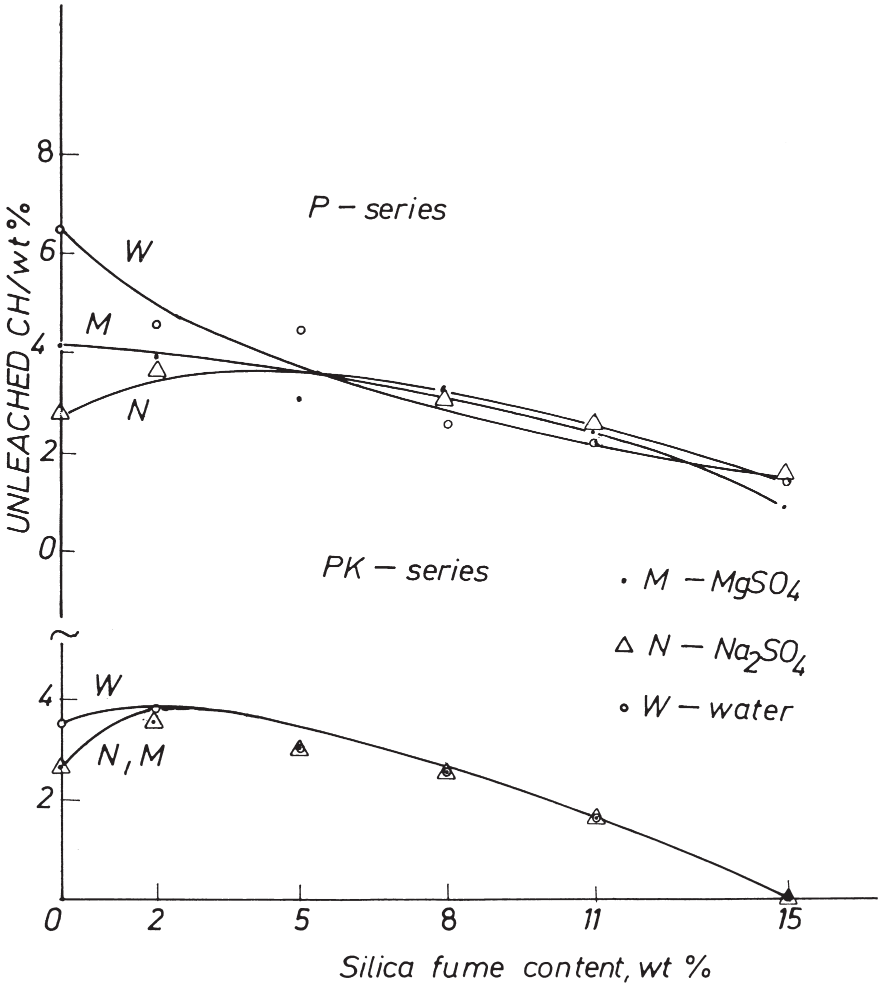

Fig. 4. Unleached CH in the P- and PK-series mortars exposed to sulphate attack of the N and M solutions for 120 days vs. silica fume content. The control mortars were started at the same time in W.

mation of a greater quantity of gypsum and ettringite during sulphate corrosion. Thereafter, TEM image of the deteriorated P-0 mortar showed both well-grown gypsum and ettringite crystals (Fig. 7). The average length of the small rodlike ettringite crystals is about 2 μm [Fig. 7(*B*)]. According to Mehta [18], this type of ettringite crystal, formed under conditions of high CH concentration, increases the water-adsorption capacity that causes expansion and damages of mortars.

The improvements in the sulphate resistance observed in the PK mortars exposed to Na_2SO_4 solution for 120 days have been supported by the change in phase composition of mortars. X-ray patterns, as shown in Fig. 8, reveal that the CH peaks decrease with increasing of silica fume content. Both typical compounds associated with sulphate attack (gypsum and ettringite) were detected in spite of an abundant presence of CH. The corrosion activity was observed only in samples with no silica fume or 2 mass% silica fume (the PK-0 and PK-2 samples), as it was only in them that an increased quantity of ettringite was detected, relative to the PK-0 sample treated in water storage. For mortars/concrete in contact with the sulphate solution, the attack is attributed to the chemical reaction between sulphate ions and hydrated PC compounds to form the more insoluble ettringite and gypsum. Because the sulphate attack is centered on hydrated calcium aluminates, the transformation of it into a more stable compound, such as monocarbonate, during hydration of cement containing limestone contributes to better stability of the PK-series mortars to sulphate attack. With the addition of limestone a reaction occurs upon hydration between it and tricalciumaluminate and ferrite phases to form monocarbonate, suppressing the crystallisation of monosulphate. The solubility of the aluminate hydrate phases is reduced as other ions are incorporated into their structure [19]. Knowing this, the solubility of the hydrated calcium aluminates is very low in saturated lime solutions, but increases as the lime in solution falls, so that according to this theory the removal of the free CH established conditions under which sulphate reaction can occur without expansion [20]. The previous works [4,7] supported that the presence of silica fume reduced the quantity of the CH in hydrated cement mortars. The quantity of the CH present is reduced,

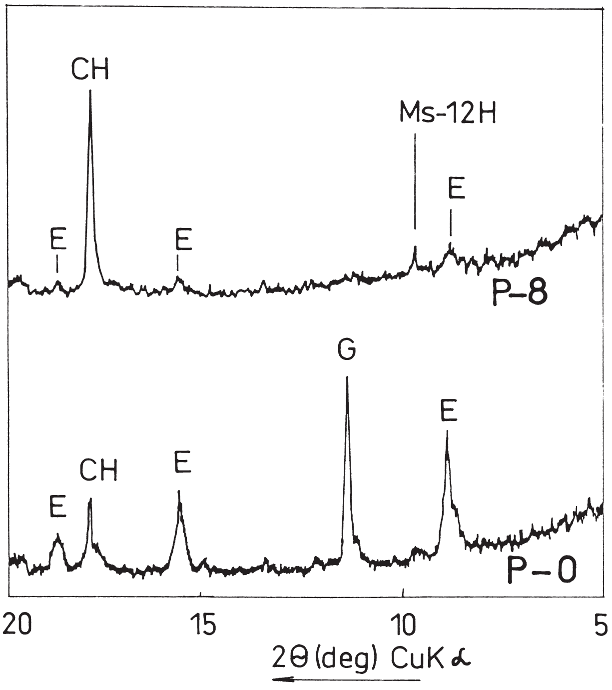

Fig. 5. XRD patterns of P-0 and P-8 mortars exposed to the N solution for 120 days.

thereby increasing the solubility of ettringite and making it unstable and less or not expansive.

Based on the experimental data (expansion of mortars, leaching of lime, change of dynamic modulus, X-ray analysis) it is evident that a simultaneous addition of finely ground limestone and silica fume contributes to a higher corrosion resistance of mortars exposed to sulphate attack. It means that durability of cement mortars exposed to sulphate attack should be improved to favour monocarboaluminate formation during hydration of cement containing the finest ground limestone in the presence of silica fume as a pozzolanic addition.

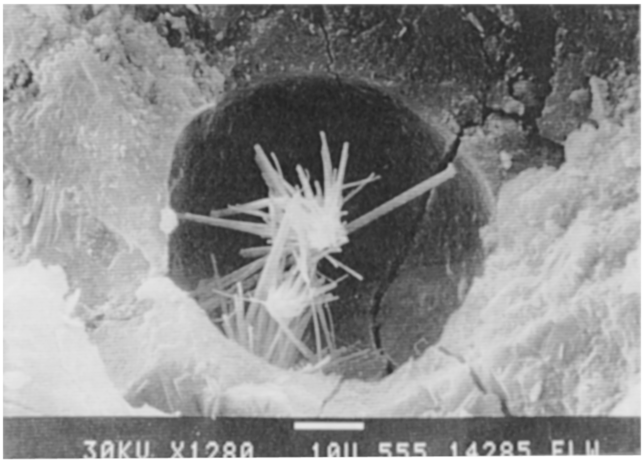

Fig. 6. SEM of the fractured surface of the P-8 sample showing the large, long-needle ettringite crystals produced by sulphate attack during 120 days of immersion in the N solution.

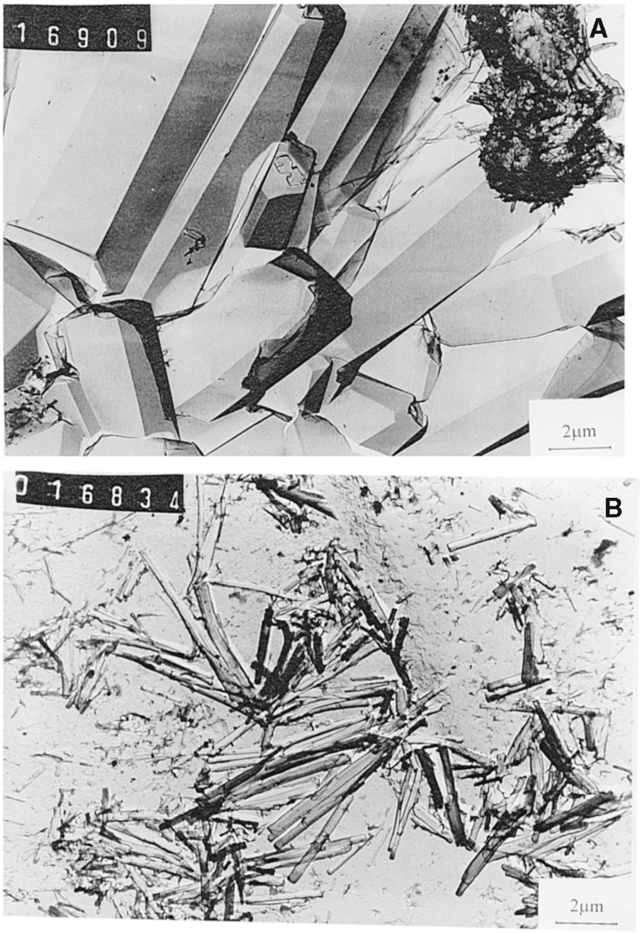

Fig. 7. TEM image of the fracture surface of the corrosion deteriorated P-0 mortar showed well-grown crystals of *(A)* gypsum and *(B)* the small rod-like ettringite crystals.

3. Conclusions

Reviewing the experimental results, the following may be concluded:

- Addition of silica fume, because of the pozzolanic reaction, reduces the content of CH formed during hydration, which consequently reduces the leaching of lime and the content both of gypsum and ettringite during sulphate corrosion of mortars, and hence increases the mortar durability.
- Formation of expansion ettringite crystals in cement mortars depends on the lime content, which affects the morphology and size of the ettringite crystals.
- Limestone acts as an active participant in hydration of PC. The presence of limestone favours formation of calcium monocarboaluminate-hydrate and prevents formation of calcium monosulphate-12 hydrate.
- Mortars containing more than 5 mass% of silica fume, or simultaneously both limestone and more than 2 mass% of silica fume, show good sulphate resistance

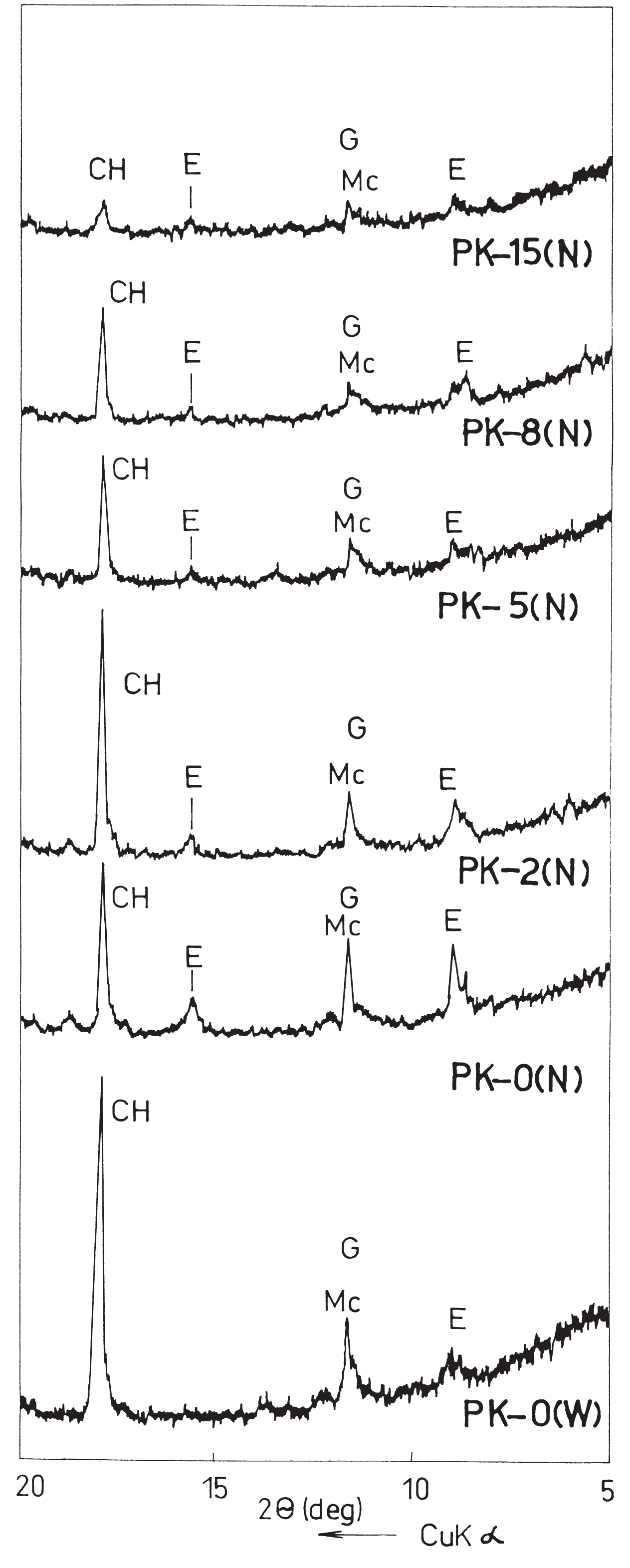

Fig. 8. XRD patterns of the PK-series mortars exposed 120 days into the N solution. The control PK-0 mortar was stored in W.

and less expansion than the control, sulphate-resisting mortar, regardless of the type of sulphate solution.

- Durability of cement mortars exposed to sulphate attack should be improved to favour monocarboaluminate-hydrate formation during cement hydration by the addition of finest ground limestone in the presence of silica fume as pozzolana.
- The optimum addition of limestone and silica fume should be previously determined experimentally for each cement type and each aggressive environment.

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