

Influence of Some Admixtures in Mitigating the Effects of Sodium and Magnesium Sulphate Attack in Cement Mortars

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ABSTRACT

In this paper, results from the efforts to improve the sulphate resistance of cement mortars by incorporating chemical and mineral admixtures are described. The experiments reported in this paper include physico-mechanical tests, thermal analysis by DSC, and backscatter SEM. The first section of the paper compares the performance of the air-entrained and pozzolanic mortars to the PC mortar. The second part of this paper deals with the effects of sodium citrate on the properties of the PC mortar subjected to sulphate attack. Entrained air voids resulted in reduction of the expansive stress and corresponding deterioration. Silica fume at 10% replacement was effective in reducing the extent of attack even in magnesium sulphate solution, but the performance with metakaolin replacement was not favourable. The use of sodium citrate reduced the extent of damage in the attack, which was attributed to the effect of retardation caused by sodium citrate.

Keywords. Sulphate; silica fume; metakaolin; air entrainment; sodium citrate

INTRODUCTION

Sulphate attack of concrete results in its deterioration by numerous mechanisms, including softening, loss of strength, and expansion (Bonen and Cohen, 1992). The role of chemical and mineral additives in mitigating the damage has been explored by several researchers in the past (Cohen and Bentur, 1988).

The use of air entrainment to counter or resist sulphate attack was first attempted in a long-term study conducted by the Portland Cement Association (PCA) (Tyler, 1960). Although the benefits of air entrainment could be clearly observed, future studies have not used this information to develop suitable solutions to the sulphate attack problem. This is because most cases dealing

with sulphate-related damage are reported from warm climates, where the use of entrained air is not prevalent.

Gypsum and ettringite arising from the sulphate attack reactions are known to cause expansive stresses in concrete. Several mechanisms have been suggested for the expansion, but there have not been significant efforts to change the nature of the crystalline product to reduce the expansion. Lea and Nurse (1949) reported on the influence of sodium citrate in the modification of crystal habit of gypsum crystallizing from hemihydrate. Normally, gypsum precipitates in a needle-like form, with numerous inter-crystal voids. However, in the presence of sodium citrate, gypsum is precipitated in a stubby and short form. The precipitation of gypsum in a needle form presumably causes an overall increase in volume due to the increased porosity, which leads to expansion. The use of sodium citrate, which causes gypsum to grow in a stubby form, could lead to a reduction in expansion caused by gypsum. However, it should be stated that no data is available regarding the pore structure that is formed in the presence of sodium citrate.

Silica fume, fly ash and other mineral additives can improve the resistance to sodium sulphate attack, while reducing the resistance to magnesium sulphate attack (Bonen and Cohen, 1992). In the first case, the pozzolanic reaction is beneficial, and in the latter case, it leads to complications. However, even for magnesium sulphate solutions, the reduction in permeability caused by mineral additives could reduce the rate of attack, provided the dosage of the admixture is optimum.

The study described in this paper explores the use of air entrainment, sodium citrate, silica fume and metakaolin as additives in cement mortar subjected to sodium and magnesium sulphate attack.

MATERIALS, MIXES, AND EXPERIMENTAL CONDITIONS

The chemical compositions of the binders used in the study (all from commercial sources) are shown in Table 1. Mortars were prepared using mixtures of binders and ASTM C778 standard sand as per the ratios in Table 2. While the water to binder ratio was 0.485 for the PC mixtures and 0.460 for the air entrained PC mixtures, it was increased to 0.600 for the mixtures with silica fume and metakaolin, to compensate for the reduction in workability.

The air-entraining admixture (AEA) used was a synthetic sodium salt of a tall oil resin with a solids content of 11.1%. The dosage of the air-entraining admixture was kept constant at 0.08% by weight of cement. Reagent grade sodium citrate powder was used as an admixture for one of the mortar mixtures. The dosage used was 0.4% by weight of cement.

The following types of mortar specimens were prepared:

- 23 mm diameter x 80 mm height cylinders for mass change and scanning electron microscopy (SEM)
- 4 mm x 14 mm x 60 mm prisms for differential scanning calorimetry (DSC)
- 6 mm x 15 mm x 80 mm prisms with plastic end pieces (the design of these acrylic pieces has been described by Richards and Helmuth (1977) and Kerdegari (1978)), for length measurements

Table 1. Composition and properties of binders used in the study

Property	Type I PC	Silica Fume	Metakaolin
CaO (%)	64.60	0.15	-
SiO ₂ (%)	20.63	98.25	53.79
Al ₂ O ₃ (%)	5.03	Trace	46.15
Fe ₂ O ₃ (%)	2.80	Trace	Trace
C ₃ S (%)	62.00	-	-
C ₃ A (%)	9.00	-	-
SO ₃ (%)	2.67	-	-
Alkalis (%)	0.50	-	-
Fineness (m ² /kg)	360	20000	5500
Specific Gravity	3.15	2.20	2.45

Table 2. Proportions of cementitious mortar mixtures

Designation	% Composition			Water to binder ratio	Admixture
	Type I PC	Silica Fume	Metakaolin		
PC	100	-	-	0.485	-
PC-N	100	-	-	0.485	Na-Citrate
AE-PC	100	-	-	0.460	AEA
SF	90	10	-	0.600	-
MK	80	-	20	0.600	-

After demoulding, the specimens were transferred to a saturated limewater solution, where they were stored for an additional 12 days (thus the total period of initial curing is 14 days). Following the initial cure, the physical properties (length and mass) were measured, and the specimens were transferred to various control and sulfate solutions. The storage solutions (all at 23 °C) were: (i) saturated limewater (control), (ii) 4.5% Na₂SO₄ (SO₃ = 25000 ppm), and (iii) 3.8% MgSO₄ (SO₃ = 25000 ppm; Mg²⁺ = 7600 ppm). The total period of exposure was 41 weeks, with the exception of the PC-N mortar, which was only studied for 21 weeks.

Mortar samples for DSC were obtained from the 4 x 14 x 60 mm specimens. Pieces of mortar from these prismatic specimens were stored in acetone for a period of at least one day, after which they were ground to a fine powder using mortar and pestle. At this level of grinding, it was assumed that only the paste fraction got ground to the powder, while the sand particles were not ground. The powder was then passed through a #200 (75 µm) sieve, and the material passing the sieve was stored in airtight containers to be used later for testing. For quantification, calibration curves were prepared for (i) ettringite, (ii) gypsum, (iii) brucite, and (iv) portlandite, as per the method described by Santhanam (2001).

The specimens for SEM were obtained after 32 weeks of immersion in the respective solutions. A 0.5" thick section was cut using a saw, and this section was then dried at 70 °C for at least 12 hours. This dried specimen was then impregnated by a low modulus epoxy, inside a cylindrical plastic mold, by evacuating to a low vacuum for two to three hours. The epoxy was then cured in an oven at 70 °C for at least eight hours. The hardened epoxy polymer was then cut with a fine diamond-tipped saw to expose the cross-section of the specimen. This was followed by grinding of the exposed surface on a series of plates ranging from 45 µm to 15 µm. Fine polishing was then performed using diamond pastes of varying sizes, up to 1 µm. The adequacy of polishing was confirmed after each step using an optical microscope. After polishing, the surface was coated with a layer of gold-palladium. The prepared specimens were then stored in desiccators until testing.

For secondary electron microscopy, fractured specimens, obtained from the cylindrical mortars, were mounted on aluminum stubs using a mixture of silver paste and glue. These were then coated with a layer of gold-palladium.

RESULTS

Physical properties. The results comparing the performance of Type I PC mortar (PC), air entrained PC mortar (AE), sodium citrate – added PC mortar (PC-N), silica fume mortar (SF) and metakaolin mortar (MK) in sodium sulphate solution have been shown in Figures 1 and 2. The air-entrained mortar was able to resist a much higher degree of expansion (~2.5%) compared to the PC mortar (~1.1%). The SF mortar showed an increase in expansion only at a very late stage (after 32 weeks). A similar trend was observed for the MK mortars. Specimens from PC, AE-PC, and MK mortars fractured at the ages beyond 12, 21, and 32 weeks respectively. In comparison to PC, the PC-N mortar exhibited significantly lower expansion at 12 weeks, and even at 21 weeks, the expansion was lower compared to PC at 12 weeks.

The mass change behavior of PC, SF, and MK mortars was similar. The AE mortars showed a very high degree of mass change, a result that is expected because of the filling up of pore spaces. The PC mortars exhibited a steady mass increase before fracturing after 12 weeks of immersion. The AE-PC mortars fractured after 21 weeks of exposure. The PC-N mortars showed marginally lower change in mass compared to PC mortars.

Figures 3 and 4 depict the comparison of physical properties for the mortars immersed in magnesium sulphate solution. The AE mortar exhibited highest expansion, followed by PC, MK, and SF. The PC and AE mortars were both able to resist high degree of expansion (2.4% and 3.1% respectively), and did not fail as in the case of sodium sulphate solution. The MK mortar specimens deteriorated rapidly after 32 weeks and completely disintegrated. The best performance was obtained from the SF mortar, which expanded less than 1% at 41 weeks. The expansion behavior of the PC-N mortar was also similar to the SF mortar. It showed significantly lower expansion than the PC mortar.

Mass change patterns for AE and PC mortars were very similar, while the SF and MK mortars exhibited a similar behavior up to 21 weeks, after which the MK mortars showed a substantial

mass increase. Once again, the PC-N mortars exhibited lower mass increase compared to PC mortars.

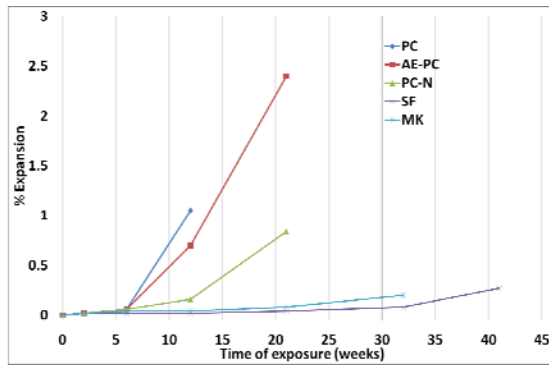


Figure 1: Expansion of mortars in sodium sulphate solution

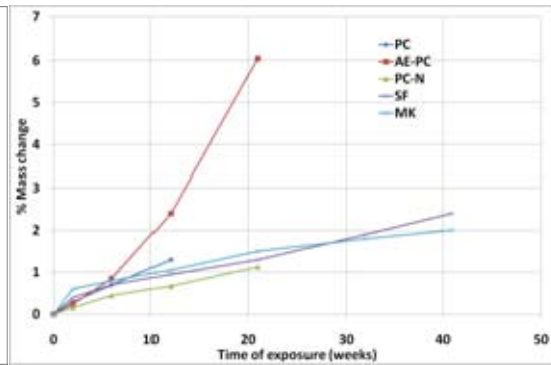


Figure 2: Mass change measurements for mortars in sodium sulphate solution

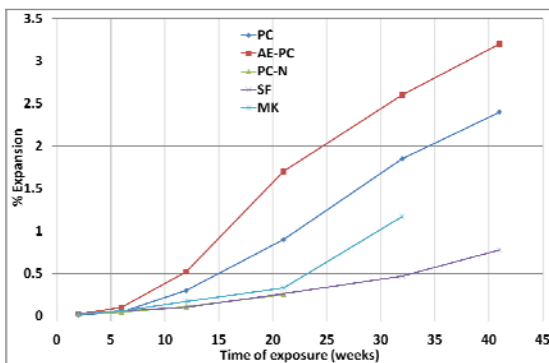


Figure 3: Expansion of mortars in magnesium sulphate solution

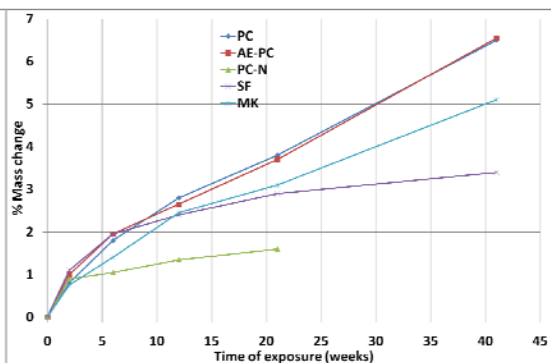


Figure 4: Mass change measurements for mortars in magnesium sulphate solution

Thermal Analysis by DSC. The relative amounts of the compounds formed at 12, 21, and 32 weeks of exposure in different systems as a result of sodium and magnesium sulphate attack are presented in Tables 3 and 4 respectively.

The results in Table 3 for sodium sulphate solution indicate that the formation of ettringite is favoured in the PC mortar. In the case of the AE-PC mortar, significantly higher proportion of gypsum is formed, and as the voids provide sites for nucleation and growth of gypsum, its subsequent conversion to ettringite does not take place as easily as in the PC mortar. For the PC-N mortar, lower amounts of ettringite were formed, in spite of larger production of gypsum. In the systems with mineral admixtures, both ettringite and gypsum were significantly lower than for PC mortars, which is expected owing to the lower calcium hydroxide availability. In fact,

almost no gypsum remains in the MK mortar at 32 weeks. When compared with the data in Figure 1, there is a good correlation of the change in length with the total quantities of the attack products (gypsum and ettringite).

From Table 4, it is evident that lower quantities of ettringite are formed in the magnesium sulphate attack. However, there is almost complete depletion of calcium hydroxide and large deposition of gypsum by 32 weeks of exposure possibly due to the deposition of secondary gypsum (from the reaction with C-S-H), which is in agreement with published literature (Bonen and Cohen, 1992; Santhanam 2001). While PC and AE-PC mortars exhibit nearly identical behavior (which also matches the expansion and mass increase trends in Figures 3 and 4), lower amounts of attack products are formed in the PC-N system, which is supported well by the lower expansion and mass change. In the case of the mortars with MK, very large amounts of gypsum are seen (while there is almost no ettringite remaining in the system), and this is indicative of a major attack of the C-S-H. Indeed, the specimen for length change fractured beyond 32 weeks of exposure.

Table 3. Results of thermal analyses for sodium sulphate attack

Designation	% Ettringite			% Gypsum			% Calcium hydroxide		
	12	21	32	12	21	32	12	21	32
PC	8.4	-	9.5	2.0	-	2.0	1.0	-	0.9
AE-PC	7.6	6.2	8.1	3.8	3.7	3.1	0.5	0.1	0
PC-N	5.9	6.1	-	1.6	3.6	-	2.4	1.1	-
SF	2.8	3.5	4.7	0.4	0.6	1.4	1.4	0.6	0.3
MK	1.5	3.8	4.7	0.1	0	0	0.4	0.2	0

Table 4. Results of thermal analyses for magnesium sulphate attack

Designation	% Ettringite			% Gypsum			% Calcium hydroxide			% Brucite		
	12	21	32	12	21	32	12	21	32	12	21	32
PC	5.5	-	3.6	3.0	-	5.6	1.4	-	0.0	1.5	-	1.7
AE-PC	5.0	2.5	3.0	3.5	5.2	6.5	1.0	0.0	0.0	2.4	2.4	1.6
PC-N	4.2	4.2	-	1.6	2.2	-	2.8	1.7	-	1.2	1.7	-
SF	2.5	2.9	4.0	2.5	2.5	4.8	0.8	0.4	0.0	1.1	0.8	1.1
MK	1.8	2.2	0.0	3.2	8.0	19.0	0.0	0.0	0.0	0.6	0.0	0.0

Microstructural Investigations by SEM. The microstructural alterations caused by sodium and magnesium sulphate have been explained by various researchers (Bonen and Cohen, 1992; Gollop and Taylor, 1992; Santhanam et al. 2002). For brevity, only the distinguishing features of the other types of mortars are presented in this section. A detailed treatment may be found in (Santhanam, 2001).

The inclusion of air in the mortars provides sites for nucleation of attack products like ettringite and gypsum, as is evident from the micrograph shown in Figure 5 (a) for attack by sodium

sulphate solution. Extensive deposition of attack products is found in attack by both types of solutions, which is consistent with the large mass increase reported earlier. Further, the extent of cracking was not as much as in the PC mortar. The typical features of magnesium sulphate attack, i.e., a brucite-gypsum double layer at the surface, and abundant gypsum deposits in air voids, are observed in AE mortars subjected to attack by magnesium sulphate solution, as shown in Figure 5 (b). M-S-H formation was also observed at later stages of the attack.

In the case of SF and MK mortars, the damage due to sodium sulphate was only limited to regions very close to the surface, but in the case of magnesium sulphate attack, extensive decalcification of C-S-H and its conversion to M-S-H (particularly in MK mortar – see Figure 6(b)), along with abundant deposits of gypsum were observed. This is consistent with the greater extent of damage of MK mortar in magnesium sulphate solution.

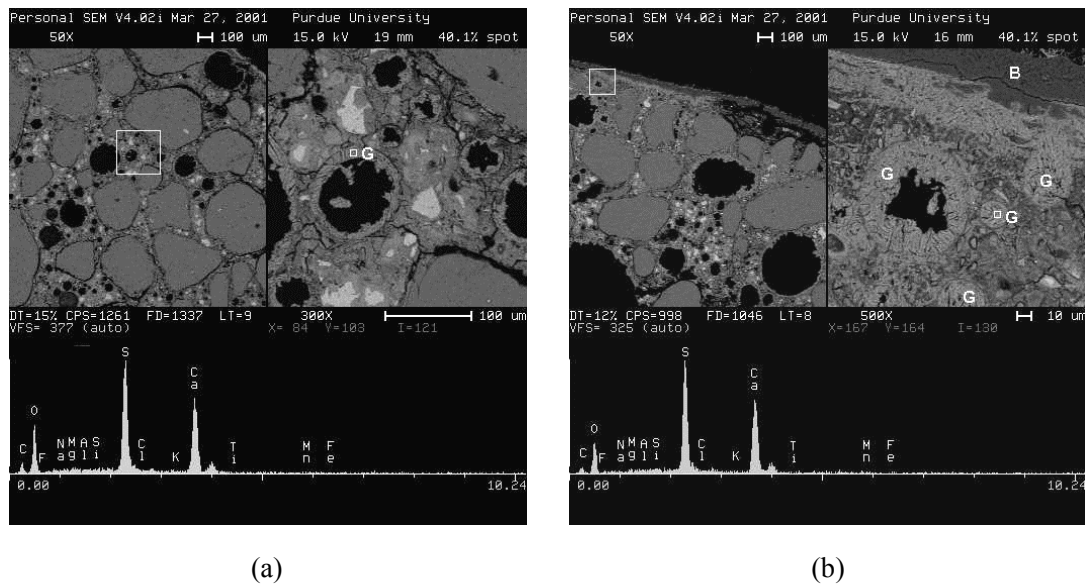
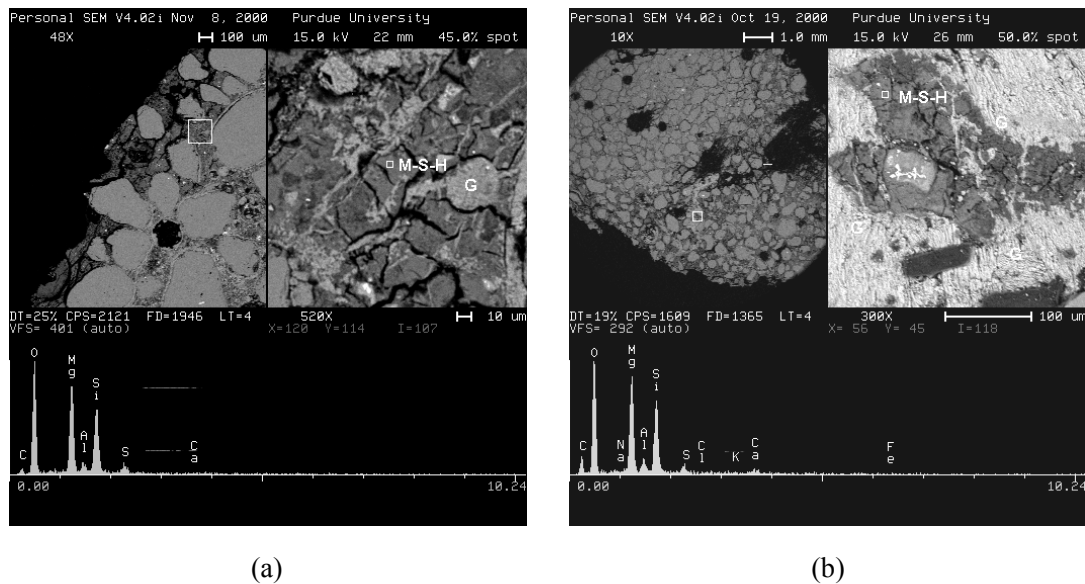


Figure 5: Features of AE-PC mortars attacked by (a) sodium and (b) magnesium sulphate (Note: G = gypsum)

Unlike what was reported in literature, there were no distinct differences in the type of gypsum or ettringite deposits for the PC-N mortar, and the same was confirmed by secondary electron imaging.



**Figure 6: Features of magnesium sulphate attack of (a) SF and (b) MK mortars
(Note: G = gypsum; M-S-H = Magnesium silicate hydrate)**

DISCUSSION

The presence of entrained air in the mortars provided sites for the nucleation and deposition of attack products. As a consequence, the AE mortars were able to withstand the expansive stresses better than the PC mortars. Complete deterioration of the specimens was delayed in the case of AE mortars, although the variation in physical properties was comparable to the PC mortars. It is possible that the air voids could arrest the growth of cracks, and thus slow down the cracking and the ultimate deterioration. Indeed, microstructural observations indicate a lesser degree of cracking for the AE mortars. Chemically, the major difference was seen in the quantity of gypsum formed, which was greater for the AE mortars as compared to the PC mortars. Once again, this could be attributed to the tendency for gypsum to nucleate in air voids. Thaumasite is detected by SEM in small inclusions in both mixtures.

Silica fume and metakaolin lead to a quick consumption of the CH due to the pozzolanic reaction. In sodium sulphate, the consumption of CH is good, since it reduces the formation of gypsum. Indeed, the damage to the pozzolan-substituted mortars was much lesser than the PC mortars. However, in the case of magnesium sulphate attack, where the main effect is the formation of brucite, the consumption of CH leads to a direct attack on the C-S-H. When all the available CH is consumed, the C-S-H releases some CH into the paste, and thus gets progressively decalcified. The formation of non-cementitious M-S-H is triggered by the direct attack on the C-S-H. This was especially true in the case of the MK mortars, where almost the entire paste at 32 weeks was seen to be composed of M-S-H and secondary gypsum. The absence of the surface layer of brucite also contributed to the extensive deterioration. There was marked deterioration in the SF mortar also, but not as much as the MK mortars.

Apart from the pozzolanic reaction, the use of mineral admixtures causes a reduction in the permeability because of their 'filler' effect. The benefits of reduced permeability were clearly observed when silica fume was used in this study. A dosage level of 10% of silica fume produced enough positive effects due to reduced permeability to counter the negative effects of the pozzolanic reaction during MgSO_4 attack. At higher dosages, silica fume substitution has been reported to be harmful to the performance (Cohen and Bentur, 1988). On the other hand, metakaolin, which is only a little finer than the cement, is not able to sufficiently reduce the permeability. Hence the MK mortars suffer a high degree of damage in MgSO_4 attack.

The benefits of using sodium citrate as an admixture are evident from the decreased rates of deterioration observed in the PC-N mortars compared to the PC mortars. The results up to 21 weeks of immersion clearly showed that the expansion and mass change were reduced for the PC-N mortars as compared to the PC mortars. The use of sodium citrate resulted in a delay in the onset of expansion in sodium sulphate, while reducing the rate of expansion in magnesium sulphate. The rate of mass increase was reduced in both the solutions with the use of sodium citrate. The use of sodium citrate also resulted in a retardation of the setting time of the mixture. However, the compressive strength after the initial curing period of 14 days was comparable to the PC mortar mixture.

DSC results confirm the formation of a smaller quantity of ettringite in sodium sulphate. Although the amount of gypsum forming at 12 weeks is almost similar to the PC mortars, the measured expansion for the PC-N mortars is less than one-fifths of the PC mortar. The quantity of ettringite at this stage is around 6%, compared to 8% for PC mortars. However, with subsequent storage in the solution, there is hardly any change in the quantity of ettringite, while the quantity of gypsum steadily increases. A link between gypsum formation and expansion is evident.

The PC-N mortar specimens appear to be damaged to a very small extent compared to the PC mortars from the SEM observations. The damage is also limited to the near-surface regions. The overall effect of the use of sodium citrate appears to be a retardation of the sulphate-related damage, due to a reduction in the rate of dissolution of CH to form gypsum and ettringite. From the trends at 21 weeks, the damage seems to be increasing at a steady rate, comparable to the PC mortars. Hence, the use of sodium citrate can only be to slow down the onset of damage, and not actually prevent it from happening. The use of other retarding admixtures could possibly have a similar effect on the performance of cement mortars during sulphate attack.

CONCLUSIONS

- Air entrainment did not change the variation in physical properties of the PC mortars. The time to complete disintegration of the mortars, was, however, prolonged. The stresses in the paste due to the formation of expansive products were reduced in the air-entrained mortars, since the air voids acted as sites for nucleation of the products.
- The use of sodium citrate caused a delay in the onset of deterioration of the mortars subjected to both sodium and magnesium sulfate solutions. The delay was primarily caused by the slower formation of attack products such as gypsum and ettringite, owing to the low

solubility of Ca^{2+} . No evidence could be found for the hypothesis that sodium citrate causes a change in the crystal growth habit of gypsum.

- The use of mineral admixtures such as silica fume and metakaolin improved the performance of mortars in sodium sulfate solution. The reduced damage could be directly linked to the formation of a lower amount of gypsum and ettringite due to the low availability of calcium hydroxide in the pozzolanic mortars. At the dosage rate used (10% substitution), silica fume substitution was found to improve the performance of the mortars in magnesium sulfate solution. The beneficial effects of a reduced permeability probably overcame the disadvantage of the lower availability of calcium hydroxide (which renders the C-S-H susceptible to a direct attack). On the other hand, the substitution by metakaolin reduced the resistance of the mortars to magnesium sulfate. The microstructure of the metakaolin mortars was seen to be completely altered, with most of the C-S-H having been converted to M-S-H and secondary gypsum.

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