Effect of magnesium and sulphate ions on the sulphate resistance of blended cements in low- and medium-strength concretes

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Structural concrete components undergo degradation when exposed to sulphate-bearing environments. Diffusion of sulphate ions through concrete pores causes the formation of expansive products such as gypsum and ettringite in the internal microstructure of concrete. This chemical change leads to a significant reduction of strength in structural components. In the literature it has been reported that in blended cements, because of the reduction of calcium hydroxide, magnesium sulphate ions directly react with the cementitious calcium–silicate–hydrate (C–S–H) gel and convert this into non-cementititous magnesium–silicate–hydrate (M–S–H) gel. However, in the present investigation it was observed that, in low-strength concrete (20 MPa), blended cements show more resistance than ordinary Portland cement (OPC) because of the pozzolanic and dilution effect of added fly ash and slag. In this concrete, the expansive product, namely gypsum, densifies the porous pore structure and does not cause any cracking. In the case of medium-strength concretes (30 and 40 MPa), the pozzolanic and dilution effects of blended cements are not very significant and hence they did not show any increase in sulphate resistance compared with OPC cement. In these medium-strength concretes because of their pore structure, the expansive products cause micro-cracks. The inferior performance of concretes with blended cements due to magnesium ion attack is mainly attributed to the formation of ettringite and gypsum, as in the case of sodium sulphate, and these cause more micro-cracks in comparison with OPC cement. Thermal analysis also confirms this.

Introduction

Structural concrete components undergo degradation when exposed to sulphate-bearing environments. Seawater, soil, and groundwater contain high concentrations of calcium, sodium and magnesium salts of sulphates. Dissolved sulphates intrude into the concrete pore structure by diffusive or advective flow. This causes progressive precipitation of sulphate-bearing phases such as ettringite and gypsum in the internal micro structure of the concrete.[1–3] This change leads to swelling, spalling and cracking of concrete and causes a significant reduction in the cross-sectional area of the

structural components as well as decreasing the strength.[4–11] The intensity and rate of sulphate attack depends upon the mineralogical phases of cement, type of cation (Na_2SO_4 or $MgSO_4$) and concentration of the solution, quality of concrete and exposure conditions. Laboratory studies relating to sulphate attack continue to appear in the literature because of modifications to the physico-chemical characteristics of Portland cement, the increasing use of blending materials with Portland cement, the controversy over the influence of cement content and cement composition (i.e. C_4AF and C_3S/C_2S ratio) on sulphate attack. In comparison with sodium sulphate attack, magnesium sulphate attack on concrete is more severe.[11,12]
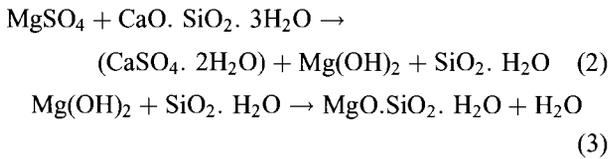
A characteristic feature of the magnesium ion attacks on Portland cement paste is that the attack is eventually extended to the calcium–silicate–hydrate (C–S–H) gel, which is the principal cementitious constituent. The reactions are as follows

$$MgSO_4 + Ca(OH)_2 + 2\,H_2O \rightarrow CaSO_4.2\,H_2O + Mg(OH)_2 \quad (1)$$
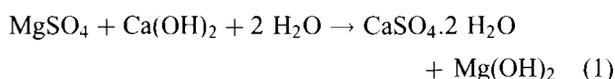
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$$MgSO_4 + CaO. SiO_2. 3H_2O \rightarrow$$
$$(CaSO_4. 2H_2O) + Mg(OH)_2 + SiO_2. H_2O \quad (2)$$
$$Mg(OH)_2 + SiO_2. H_2O \rightarrow MgO.SiO_2. H_2O + H_2O$$
$$(3)$$

The magnesium hydroxide (brucite) produced in equation (1) is only very slightly soluble and its saturated solution has a pH value of about 10·5.[13] Such a low pH destabilises both ettringite and C–S–H and because of this secondary ettringite will not form.[14] Then magnesium sulphate reacts with the C–S–H as shown in equation (2) thereby producing gypsum, brucite and silica gel (SiO_2H_2O). This gel is less cementitious than the original cementing C–S–H gel.[13] C–S–H tends to liberate more lime to raise the pH and to establish its equilibrium. This process is known as decalcification of C–S–H. The $Mg(OH)_2$ formed in equation (2) reacts further with hydrosilicates, thereby producing magnesium–silicate–hydrate (M–S–H), which is non-cementitious and has no binding properties.[13,15].

It is reported that when compared with Portland cement, blended cements perform better in a sulphate environment.[2,4,6] The advantages claimed are: (*a*) because of the pozzolanic reaction the consumption of portlandite [$Ca(OH)_2$] reduces the formation of gypsum; (*b*) the formation of secondary C–S–H leads to the densification of pore structure thus reducing the permeability of sulphate ions; and (*c*) ordinary Portland cement (OPC) is replaced by a pozzolanic material entailing a reduction of C_3A content (dilution effect) which reduces the aluminate-bearing phases by as much as 30% by weight of the cementitious material. Even if ettringite is formed it becomes less expansive because of the reduction of pH. Hence the sulphate resistance values of blended cements are due to both pozzolanic as well as dilution effects.

While reviewing the literature, it was found that the studies on the sulphate resistance of blended cements had been carried out in sodium and magnesium sulphate solution using paste, mortar and concrete.[3–7,16–18] These studies have varied replacement level of mineral admixture, chemical composition of fly ash, sulphate concentrations, test conditions and evaluation criteria. The chemical analysis of composite cement does not yield a satisfactory estimate of its sulphate resistance. In addition to this, the pore structures of different concrete mixes have different effects on their resistance to sulphate when compared with paste and mortars. Hence there is a need to understand the mechanism of magnesium attack on blended cement-added concretes under laboratory test conditions.

In the present investigation, the effect of w/c ratio and the influence of cement type and cement content of concrete on magnesium attack were investigated in 10% $MgSO_4$ solution. The rate of deterioration was assessed by measuring the change in resistivity and compressive strength. The ettringite and gypsum for-

mation was identified using differential thermal analysis (DTA). The overall porosity of the concretes was determined by measuring the coefficient of water absorption.

Materials

Ordinary Portland cement (OPC; grade 43) conforming to IS 8112[19] (equivalent to ASTM C150 Type I cement), Portland pozzolana cement (PPC; fly ash based) conforming to IS 1489–Part I[20] and Portland slag cement (PSC) conforming to IS 455[21] were used. In pozzolana and slag cements, Portland cement was blended with 25% fly ash and 50% slag respectively. Well-graded river sand and good quality crushed blue granite were used as fine and coarse aggregates respectively. The different size fractions of coarse aggregate (20 mm down-graded and 12·5 mm down-graded) were taken in order to get a dense concrete. The sand was sieved through 4·75 mm to avoid the presence of pebbles. The physical characteristics of the coarse and fine aggregate used are given in Table 1. Potable water was used for the casting concrete specimens. The 20, 30 and 40 MPa concretes were designed as per the recommendations of ACI.211-91.[22] The detailed mix proportions used in this investigation are given in Table 2. In each of the grades, the proportions were kept constant for OPC, PPC and PSC concretes.

Specimen preparation and method of exposure

Concrete specimens (100 mm cubes) were cast. After 24 h, the specimens were demoulded and kept immersed in the curing tank for 28 days. After 28 days, the specimens were removed from the curing tank and were kept immersed in 10% $MgSO_4$ solution in such a way that they should not touch each other. The ratio of the volume of the solution to the volume of the specimen was kept at 4 : 1. During exposure the pH of the solution was between 7 and 8·5. The solution was renewed once in 3 months. At the end of 6, 9, 15 and 21 months, the specimens were tested for change in resistivity and compressive strength.

Measurements

Visual appearance

The progress of deterioration due to sulphate was assessed by visually examining the surface of the

Table 1. Physical properties of aggregates

Type of aggregate	Maximum size of the aggregate: mm	Fineness modulus	Specific gravity
Fine aggregate	4	2·43	2·55
Coarse aggregate	20	7·50	2·78

Table 2. Details of mix proportions

Strength	Type of cement	W/C ratio	Cement: kg/m³	Water: kg/m³	Fine aggregate: kg/m³	Coarse aggregate: kg/m³
20 MPa	OPC	0·67	284	190	770	1026
	PPC	0·67	284	190	770	1026
	PSC	0·67	284	190	770	1026
30 MPa	OPC	0·54	352	190	739	1026
	PPC	0·54	352	190	739	1026
	PSC	0·54	352	190	739	1026
40 MPa	OPC	0·42	452	190	655	1026
	PPC	0·42	452	190	655	1026
	PSC	0·42	452	190	655	1026

concrete specimens at the end of each exposure period for the presence of cracks, softening, corner attack and edge failure.

Electrical resistivity

The electrical resistivity of concrete is an important parameter, which can be related to various other aspects such as strength, porosity and deterioration. The reason is that resistivity is the parameter characterising pore connectivity. Hence its measurements are an interesting way to assess concrete durability from the point of view of assessing the transport properties.[23] The advantage of this method is that it is non-destructive. It is well-known that a concrete cover offers protection from deterioration because of its high electrical resistance.[24,25] Stratfull investigated in detail the variation of resistivity with deterioration of concrete.[26] It has also been reported that the resistivity of concrete decreases as the deterioration increases. In the present study, a four-probe resistivity meter based on the wenner-probe principle was used.[27 29] This produces frequency-independent resistivity measurements. The electrodes of the resistivity meter were in the form of spring-loaded 3 mm dia. probes of copper rod surrounded by wetted sponge. The spacing between the electrodes was adjustable; however, for the present study, the spacing (a) was maintained at 25 mm. A known current I is impressed on the outer probes and the resulting potential drop V between the inner probes was measured. The resistance R is given by V/I. From this, the resistivity can be calculated as

$$\text{Resistivity of concrete } (\rho) = 2\pi a R$$

Four measurements were taken on each side of the cube (avoiding the cast and bottom faces of the cube), and then averaged to obtain a mean value. During the measurements, the contact surfaces of the probes were maintained in a moist state to ensure good electrical contact with the concrete surface. By applying the four probes to the concrete surface, the resistivity of concrete up to 25 mm was displayed on the meter. The resistivity was measured at the end of 6, 9, 15 and 21 months.

Compressive strength

To assess the deterioration due to sulphate attack, the change in compressive strength of the cubes after a scheduled immersion period in 10% $MgSO_4$ was carried out in conformity with IS specification 516.[30] The rate of deterioration at the end of 6 and 9 months in sulphate solution was assessed by comparing the corresponding compressive strength of cubes kept immersed in water at the end of 6 and 9 months. For 15 and 21 months, the compressive strength at the end of 12 months in water was used for comparison. Duplicate specimens were tested and values obtained for each time period.

DTA analysis

After testing the compressive strength at the end of 9 and 15 months, the samples from the top layer up to 3 mm depth of the specimen were taken and powdered in silica mortar and sieved through a 75 μm sieve for DTA analysis. DTA was done using a Polymer Laboratories (UK), Thermal Science Division, STA 1500 thermal analyser. It has a balance with a resolution of 0·01 mg. A Type 'R' thermocouple (Pt–13% Rh/Pt) was used for temperature measurement. The sample was taken in a ceramic crucible and heated from room temperature to 600°C at a heating rate of 20°C/min using air as the medium under static conditions.

Water permeability studies

The permeability of concrete is a measure of the rate at which a liquid will pass through it. It depends upon its pore network, which arises from the excess water used during mixing and the initial hardening process. The permeability can be measured by conducting water permeability test as per standard, percentage of water absorption test and initial surface absorption tests.[31,32] In the present study, the overall porosity was determined by the percentage of water absorption. It measures the pore space in the material indirectly. This was done as per procedure given in ASTM C 642-90 by oven-drying method.[33] For this test, 100 mm × 100 mm × 100 mm size concrete cubes were cast in duplicate. After demoulding, the specimens were kept immersed in water. The experiment was conducted at

the end of three curing periods; namely 7, 28 and 90 days to evaluate the effect of curing on overall porosity. At the end of each curing period, the specimens were taken from the curing tank and air-dried to remove the surface moisture. They were then dried in an oven at a temperature of $100 \pm 10°C$ for 48 h and allowed to cool to room temperature. At this stage, the weights of the specimens were measured to an accuracy of 1 g using a digital balance. The specimens were then kept immersed in water for 1 h and the increase in weight was measured. The coefficient of water absorption was calculated from this using the following formula

$$K_a = (Q/A)^2/t$$

where K_a is the coefficient of water absorption (m^2/s); Q is the quantity of water absorbed by the oven-dry specimen (m^3); A is the total surface area of the concrete specimen through which water penetrates (m^2) and t is the time (s).

The coefficient of water absorption was calculated for each curing period.

Results and discussion

Visual appearance

The progress of deterioration, which was assessed by visual appearance, indicated that at the end of 6 months, slight attack on the corners and edges was only observed on 40 MPa-PSC concrete. Subsequently at the end of 9 months of exposure, small cracks were observed at the edges for a length of 8–10 cm. In the 30 MPa-OPC and PPC-added concrete, moderate attack on the corners and edges was observed. Extensive cracks along the edges throughout the length of the specimen were observed in the 40 MPa concrete at the end of 15 months of exposure but their cores were still intact. The 20 MPa concrete did not show any sign of deterioration even up to 21 months of exposure whereas the 30 and 40 MPa concretes showed severe cracking on all edges.

Electrical resistivity

Figure 1 compares the change in resistivity of three cements in 20 MPa concrete with exposure period. It can be seen that in OPC concrete, the resistivity value increased from 27 kΩ cm up to 9 months and thereafter it decreased to 20 kΩ cm at the end of 21 months. The decrease in resistivity value indicates the deterioration of concrete due to sulphate. In the case of PPC concrete, initially the value was 38 kΩ cm and this increased to 48 kΩ cm and this value was maintained until the end of the exposure. Similarly in PSC concrete, the resistivity increased from 38 to 56 kΩ cm. The increase in resistivity value indicates the concrete had not deteriorated very much due to sulphate. In PPC and PSC concrete the resistivity values are more than the value for OPC concrete. An increase in resistivity
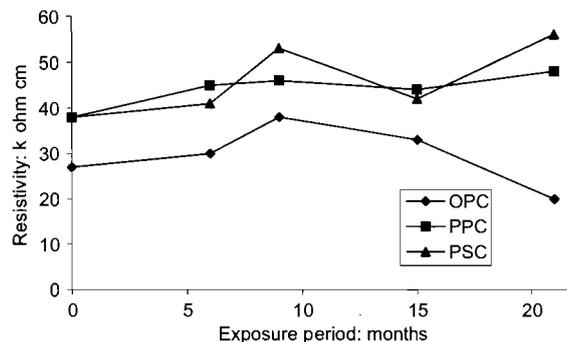

Fig. 1. Variation of resistivity of 20 MPa concrete immersed in 10% MgSO₄ solution

has been reported in fly ash, slag, blended concretes with curing and the values were greater than the plain cement concrete.[34,35]

In 30 MPa concrete (Fig. 2) the value for OPC decreased from 51 to 24 kΩ cm with exposure indicating that the concrete had shown deterioration from the beginning of the exposure. In PPC concrete initially the value was 33 kΩ cm and it increased to 55 kΩ cm up to 15 months and thereafter decreased to 42 kΩ cm at the end of 21 months. In PSC concrete, the value increased from 40 kΩ cm and attained a value of 59 kΩ cm at the end of the exposure. The results indicate that the decrease in value was more in OPC concrete than in PPC and PSC concrete.
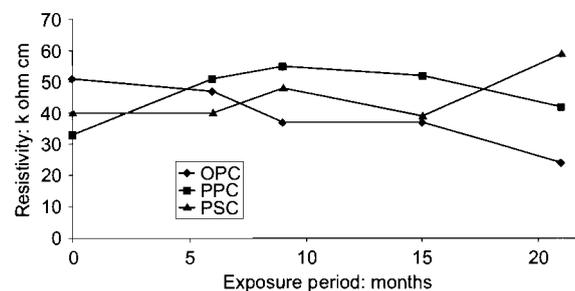
Similarly in 40 MPa concrete (Fig. 3) in OPC the

Fig. 2. Variation of resistivity of 30 MPa concrete immersed in 10% MgSO₄ solution

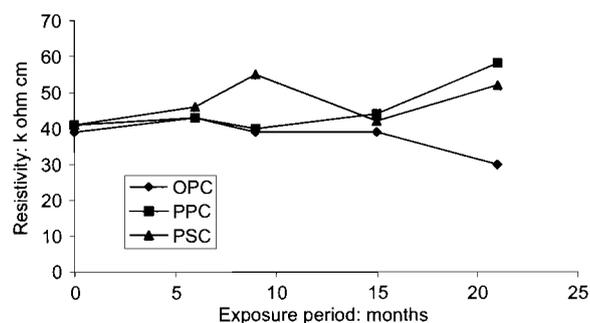*Fig. 3. Variation of resistivity of 40 MPa concrete immersed in 10% MgSO₄ solution*

value was reduced to 30 kΩ cm from an initial value of 43 kΩ cm whereas in the case of PPC and PSC concrete the value increased to 58 kΩ cm at the end of the exposure having increased from an initial value of 40 kΩ cm.

From the above discussion it can be inferred that the decrease in resistivity value indicates the process of deterioration in concrete and this was only observed in OPC concrete. It can also be seen that the deterioration started earlier in the 30 and 40 MPa concrete than in the 20 MPa concrete.

Compressive strength

Table 3 compares the variation of compressive strength of 20, 30 and 40 MPa concrete in water and 10% MgSO₄ with exposure period. The percentage increase/decrease in compressive strength in the sulphate solution was calculated relatively by comparing with the strength in water.

In 20 MPa concrete, it can be seen that up to 15 months all the three cements show a greater increase in compressive strength in those immersed in sulphate solution than in water. The initial increase in compressive strength was mainly contributed by the densification of the pore structure by the precipitation of hydrated cement products as well as expansive products such as gypsum and ettringite within the voids and micropores. Hekal *et al.* have also reported a similar observation in cement pastes due to magnesium sulphate.[36] At the end of 21 months, OPC cement showed an 8% reduction in compressive strength whereas PPC and PSC cement showed increases in compressive strength of 13 and 6%, respectively. This indicates that after 15 months, sulphate attack had become more dominant, leading to the formation of micro-cracks and this decreased the strength in the OPC concrete. In the case of blended cement concrete, sulphate attack was not initiated because of the reduced diffusion of sulphate ions. The increase in resistivity value in PPC and PSC concrete also confirms this.

In 30 MPa concrete, OPC cement showed 11·32% reduction in compressive strength in specimens immersed in sulphate solution compared with water at the end of 6 months and deteriorated further before improving to finally show a reduction of 11·32% at the end of 21 months. In PPC cement an increase in strength was observed up to 6 months followed by a reduction to a value of 11·76% at the end of 21 months. PSC cement showed an increase in compressive strength up to the end of the exposure. It is well known that all the deterioration phenomena are directly related to the permeability of concrete, which is inversely proportional to the w/c ratio. However, the results indicate that reducing the w/c ratio tends to aggravate the sulphate attack. That is, if the w/c ratio reduces from 0·67 to 0·54 the percentage reduction of compressive strength increases from 8·11 to 17·8%. The inferior performance of low w/c ratio concrete is mainly

Table 3. Variation of compressive strength with exposure conditions/period

Strength of concrete	Type of cement	At the end of 6 months			At the end of 9 months			At the end of 15 months			At the end of 21 months		
		Water	10% MgSO₄	Relative strength: %	Water	10% MgSO₄	Relative strength: %	Water	10% MgSO₄	Relative strength: %	Water	10% MgSO₄	Relative strength: %
20 MPa	OPC	36	38	(+) 5·60	36	39	(+) 18·35	37	43	(+) 16·22	37	34	(−) 8·11
	PPC	34	37	(+) 8·80	33	38	(+) 15·00	38	41	(+) 7·90	38	43	(+) 13·16
	PSC	28	34	(+) 21·43	30	33	(+) 10·00	33	31	(−) 6·06	33	35	(+) 6·06
30 MPa	OPC	53	47	(−) 11·32	54	46	(−) 14·40	53	52	(−) 1·96	53	47	(−) 11·32
	PPC	51	52	(+) 2·00	50	49	(−) 2·00	51	48	(+) 2·13	51	45	(−) 11·76
	PSC	31	43	(+) 38·71	38	53	(+) 39·00	45	50	(+) 11·11	45	47	(+) 4·44
40 MPa	OPC	72	58	(−) 19·40	73	60	(−) 6·00	73	69	(−) 5·48	73	63	(−) 13·70
	PPC	65	60	(−) 7·70	67	59	(−) 12·00	67	61	(−) 8·96	67	59	(−) 11·94
	PSC	48	41	(−) 14·58	54	41	(−) 24·00	56	44	(−) 21·43	56	57	(+) 1·79

Compressive strength: MPa

attributed to the dense micro-structure, which could not accommodate the formation of expansive reaction products such as gypsum and ettringite as the concrete has a high w/c ratio and this causes cracks at a very early stage. Similar results indicating the poor performance of low w/c ratio concrete in magnesium sulphate have been reported in the literature.[11,37–41] The trend observed in compressive strength was also confirmed by a decrease in resistivity values obtained in the resistivity measurements. However, the results of long-term exposure of low and high w/c ratio concretes in MgSO$_4$ solution can only reveal the ultimate behaviour.

Similarly in 40 MPa concrete, which has a lower w/c ratio (0·42) than the other two concretes, all the cements showed a reduction of compressive strength from 6 months onward. When compared with OPC cement, PPC and PSC cement showed greater deterioration at the end of 9 and 15 months. The reduction in compressive strength was greater in PSC than PPC. This was not observed in the 20 and 30 MPa concrete. In the literature it is reported that this was not observed when concrete was subjected to sodium sulphate attack.[42] However, Stark[43] reported little or no improvement or lesser durability of fly ash-added concrete at higher cement content when concrete was exposed to sodium sulphate-contaminated soil. Rasheeduzzaffar[13] also reported that under magnesium sulphate attack silica fume and slag-added concrete showed inferior performance in terms of strength reduction in comparison with plain cement. However, in the resistivity measurements the value increased in PPC and PSC concrete, which indicates that the deterioration was only on the top surface and progresses with time into the core matrix of the concrete.

From the above discussion it can be inferred that in 30 and 40 MPa concrete, which have a greater cement content and low w/c ratio, the pozzolanic and dilution effect of blended cements are not very significant and for this reason they behaved in a similar manner to OPC cement. Vedalakshmi et al.[44] reported that in comparison with 20 MPa concrete, the higher cement content and low w/c ratio, which densifies the pore structure in 30 and 40 MPa concretes, might also be restricting the pozzolanic reaction.

Thermal analysis

After 9 months of exposure. The formation of expansive products such as ettringite and gypsum was identified by DTA curves at the end of 9 and 15 months. Figs 4–6 compare DTA curves of three cements after 9 months of exposure for 20, 30 and 40 MPa concrete, respectively. The DTA plots show endothermic peaks at 80–100°C and 110–130°C which denotes the dehydration of ettringite and gypsum respectively.[4,45–47] An endothermic peak around 460°C indicates the dehydration of Ca(OH)$_2$.

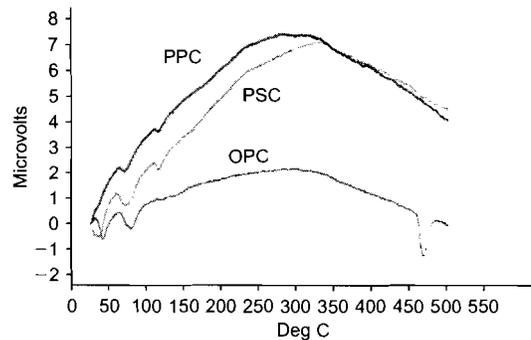From Fig. 4, it can be observed that in 20 MPa concrete, OPC cement only shows an ettringite peak

Fig. 4. DTA curves of three cements in 20 MPa concrete after 9 months of exposure in 10% MgSO$_4$ solution
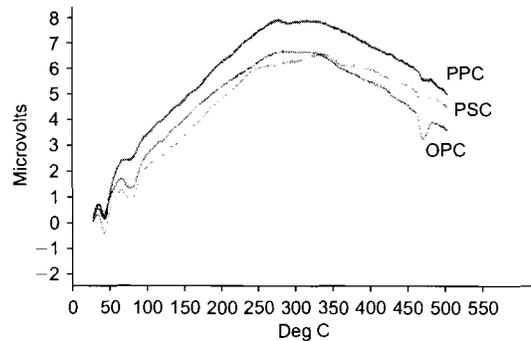

Fig. 5. DTA curves of three cements in 30 MPa concrete after 9 months of exposure in 10% MgSO$_4$ solution
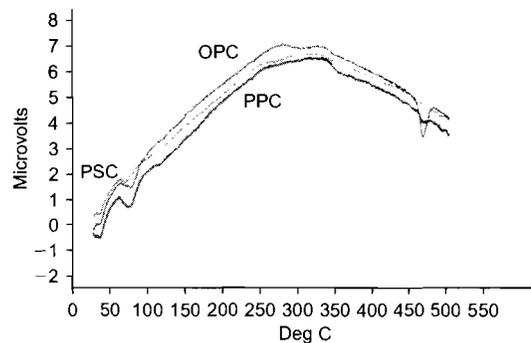

Fig. 6. DTA curves of three cements in 40 MPa concrete after 9 months of exposure in 10% MgSO$_4$ solution

whereas PPC and PSC cements show both ettringite and gypsum peaks. In OPC, which has a higher C$_3$A content, all the gypsum formed is converted into ettringite and this is denoted by the high intensity of the peak. In the case of blended cements the intensity of the ettringite peak is weak in comparison with OPC concrete because of reduction of C$_3$A content (dilution effect), but the gypsum peak is strong.

In 30 MPa concrete (Fig. 5) only an ettringite peak is observed for all the cements. In this concrete, the cement content was greater and hence the available C$_3$A content was also greater. Thus, the expansive

product was only ettringite. In the 40 MPa concrete (Fig. 6), the intensity of the ettringite peak was greater in PPC than OPC. In PSC both ettringite and gypsum peaks were present. The intensity of both peaks was less in the 30 and 40 MPa concretes than in 20 MPa concrete indicating that the formation of gypsum and ettringite was less in these concretes. Although these products could not be accommodated in the dense pore structure they lead to more micro-cracks. This causes a greater reduction in compressive strength in 30 and 40 MPa concrete than in 20 MPa concrete.

After 15 months of exposure. Figs 7–9 shows the DTA curves of the three cements at the end of 15 months of exposure for the 20, 30 and 40 MPa concretes, respectively. Fig. 7 shows that only a gypsum peak was observed in all three cements for the 20 MPa concrete. The intensity of the peak is greater in comparison with that observed at the end of 9 months of exposure. This indicates that all the C_3A phases reacted and gypsum formation was the only expansive product, and this densifies the pore structure and causes an increase in compressive strength. In OPC concrete there was no endothermic peak at 462°C, which indicates that, with exposure, all the $Ca(OH)_2$ that was formed reacted with the sulphate ions.

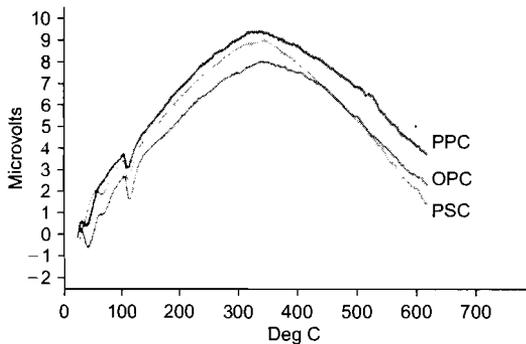In the case of 30 and 40 MPa concrete (Figs 8 and 9)

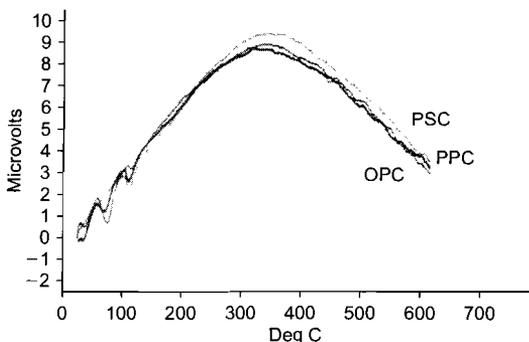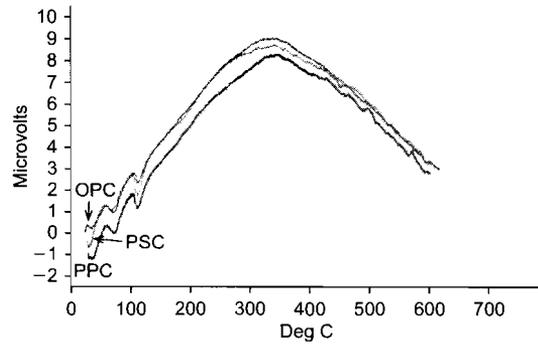*Fig. 9. DTA curves of three cements in 40 MPa concrete after 15 months of exposure in 10% MgSO$_4$ solution*

both ettringite and gypsum peaks were observed. As there was a higher cement content in these concretes, the C_3A content was greater and this caused the formation of both expansive products. These could not be accommodated in the dense pore structure and caused a greater reduction in compressive strength. It has been reported in the literature[36,43] that in blended cements, due to the absence of calcium hydroxide, which is consumed by the pozzolanic reaction, magnesium ions reacted directly with the C–S–H leading to the formation of M–S–H and this contributed to the aggravated deterioration. However, in the present study the expansive products were only ettringite and gypsum and this was confirmed by DTA analysis. Hence the mechanism of attack by magnesium sulphate ions is similar to that of sodium sulphate ions in both the blended and plain cements. The inferior performance of blended cements is mainly because they have a denser pore structure than OPC cement. The curves also reveal that as the exposure period increases, the intensity of the gypsum becomes more than ettringite and this indicates that, with prolonged exposure, gypsum formation will be the only expansive reaction.

From the above discussion it can be inferred that the reduction of compressive strength in low w/c ratio concrete is more than in high w/c ratio concrete and this is mainly because of its dense pore structure.

Fig. 7. DTA curves of three cements in 20 MPa concrete after 15 months of exposure in 10% MgSO$_4$ solution

Water permeability studies

The coefficients of water absorption in 20, 30 and 40 MPa concretes are given in Table 4. In general, the PPC and PSC concretes had lower coefficients of water absorption than OPC concrete, and the coefficient also decreased with increasing strength of the concrete. Thus in all the curing periods, the coefficient of water absorption in blended cement concrete was less than in OPC concrete. Hence the reduced permeability of PPC and PSC concrete was mainly due to densification of pore structure by the formation of additional calcium hydrates.

Fig. 8. DTA curves of three cements in 30 MPa concrete after 15 months of exposure in 10% MgSO$_4$ solution

Table 4. Comparison of coefficient of water absorption

Type of cement	Period of curing	Coefficient of water absorption: m^2/s ($\times 10^{-10}$)		
		M20 grade	M30 grade	M40 grade
OPC	7	16·6	9·17	6·76
PPC	7	9·86	5·64	4·46
PSC	7	8·27	4·88	5·71
OPC	28	15·1	7·81	8·43
PPC	28	7·71	5·0	4·46
PSC	28	5·80	5·32	5·06
OPC	90	7·64	6·68	1·72
PPC	90	4·94	5·13	2·24
PSC	90	3·32	4·40	1·93

Conclusions

(a) The decrease in resistivity value indicates the deterioration of concrete due to sulphate attack. The measurements were very well correlated with the compressive strength measurements and so this could be used in the field as a non-destructive method to measure the deterioration of structural components.

(b) In low-strength concrete (high w/c ratio), which accommodates gypsum formation in its pore structure, this densifies and causes an increase in compressive strength with exposure period. In this concrete, blended cements show more resistance than OPC cement because of the pozzolanic and dilution effect.

(c) In medium-strength concretes (low w/c ratio) which, because of their dense pore structure, could not accommodate the ettringite and gypsum formation this leads to micro-cracks. This causes a decrease in compressive strength with exposure period. In these concretes the pozzolanic and dilution effect of blended cements were not very significant and so they did not show any greater increase in resistance than OPC cement.

(d) DTA analysis confirms that in low-strength concrete, which has low cement content (low C_3A content), the expansive product is initially ettringite and gypsum and later it is only gypsum.

(e) The coefficient of water absorption is less in blended cement concrete than in OPC concrete and is reduced further with increasing curing period and strength of concrete.

References

1. LAWRENCE C. D. Sulphate attack on concrete. *Magazine of Concrete Research*, 1990, **42**, No. 153, 249–264.
2. MANGAT P. S. and KHATIB J. M. Influence of fly ash, silica fume and slag on sulphate resistance of concrete. *ACI Materials Journal*, 1995, **92**, No. 5, 542–552.
3. MARCHAND J., SAMSON E., MALTIS Y. and BEAUDOIN J. J. Theoretical analysis of the effect of weak sodium sulphate solutions on the durability of concrete. *Cement and Concrete Composites*, 2002, **24**, 317–329.
4. WEE T. H., SURYAVANSHI A. K., WANG S. F. and ANISUR RAHMAN A. K. M. Sulphate resistance of concrete containing mineral admixtures. *ACI Materials Journal*, 2000, **97**, No. 5, 536–549.
5. RU M. U., MIAO C. and LIU J. Properties of concrete subjected to freezing and thawing under sulphate attack. *The Indian Concrete Journal*, 2001, **75**, No. 7, 451–454.
6. IRASSER E. F., DID MAIO A. and BATIO O. R. Sulphate attack on concrete with mineral admixtures. *Cement and Concrete Research*, 1996, **26**, No. 1, 113–123.
7. AL-AMOUDI, O. S. B., RASHEEDUZZAFAR, MASLEHUDDIN M. and ABDULJAWAD S. N. Influence of chloride ions on sulphate deterioration in plain and blended cements. *Magazine of Concrete Research*, 1994, **46**, No. 167, 113–123.
8. BROWN P. W. An evaluation of the sulphate resistance of cements in controlled environment, *Cement and Concrete Research*, 1981, **11**, No. 11, 719–727.
9. TIKALSKY P. J. and CARROSQUILLO R. L. Influence of fly ash on the sulphate resistance of concrete, *ACI Materials Journal*, 1992, **89**, No. 2, 69–75.
10. MATHEWS M. S., SOMAYAJI S. and AMBEDKAR G. S. B. Effects of fly ash on strength an durability of hydraulic structures with various grades of cement and concrete. *Proceedings of the 7th CANMET/ACI International Conference of Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete*, SP-199, ACI, Detroit, Vol. 1, 2001, pp. 127–146.
11. AL-AMOUDI O. S. B. Performance of fifteen reinforced concretes in magnesium-sodium sulphate environments. *Construction of Building Materials*, 1999, 9, No.1, 25–33.
12. MEHTA, P. K., PAULO, J. M. and MONTERIO. *Concrete Micro Structure, Properties and Materials*. Indian Concrete Institute, Chennai, 1999, pp. 146–154.
13. RASHEEDUZZAFAR, AL-AMOUDI O. S. B., ABDULJAWAD S. N. and MASLEHUDDIN M. Magnesium-sodium sulphate attack in plain and blended cements, *ASCE Journal of Materials in Civil Engineering*, 1994, **6**, No. 2, 201–222.
14. LEA, F. M. *The Chemistry of Cement and Concrete*. Edward Arnold, London, 4th edn., 1974, pp. 347–348.
15. BROWN P. W. and DOERR A. Chemical changes in concrete due to the ingress of aggressive species, *Cement and Concrete Research*, 2000, **30**, No. 3, 411–418.
16. GONZALEZ M. A. and IRASSAR E. F. Ettringite formation in low C_3A Portland cement exposed to sodium sulphate solution. *Cement and Concrete Research*, 1997, **27**, No. 7, 1061–1072.
17. IRASSAR E. F., BONAVETTI V. L. and GONZALEZ M. Microstructural study of sulphate attack on ordinary and lime-stone Portland cements at ambient temperatures. *Cement and Concrete Research*, 2003, **33**, No. 1, 31–41.
18. SORRENTINO D., LACROIX M., GINES S. and CHABANIS F. Behaviour of a wide series of mortar bars (20 to 120 MPa) stored in $MgSO_4$ or in sea water solution. In: *Corrosion of Cement Paste* (Kurdowski W. (ed.)), Polish Ceramic Society, Warsaw, 1994, pp. 13–32.
19. BUREAU OF INDIAN STANDARDS. *Specification for 43 Grade Ordinary Portland Cement*. BIS, New Delhi, 1989, BIS 8112:1989.
20. BUREAU OF INDIAN STANDARDS. *Specification for Portland Pozzolana Cement (Fly ash based)*. BIS, New Delhi, 1991, BIS 1489 (Part I):1991
21. BUREAU OF INDIAN STANDARDS. *Specification for Portland Slag Cement*. BIS, NewDelhi, 1989, BIS 455:1989.
22. ACI COMMITTEE 211·1. Standard Practice for Selecting Proportions for Normal, Heavy Weight and Mass Concrete. ACI, Detroit, 1991.
23. CASTELLOTE M., ANDRADE C. and ALONSO M. C. Standardization, to a reference of 25°C, of electrical resistivity for mortars and concretes in saturated or isolated conditions. *ACI Materials Journal*, 2002, **99**, No. 2, 119–128.
24. WHITINGTON H. W. The conduction of electricity through

concrete. *Magazine of Concrete Research*, 1981, **33**, No. 114, 48–60.

25. HOPE B. B., PAGE J. A. and ALAN K. K Corrosion rates of steel in concrete. *Cement and Concrete Research*, 1986, **16**, No. 5, 51–59.

26. STRATFULL R. F. The corrosion of steel in reinforced concrete bridges. *Corrosion*, 1957, **13**, No. 3, 43–48.

27. MILLARD S. U., GHASSEMI M. H., BUNGEG J. H and JAFAR M. L. Assessing the electrical resistivity of concrete structures for corrosion durability studies. In: *Corrosion of Reinforcement in Concrete* (PAGE C. L., TREADWAY K. W. J. and BAMFORTH P. B. (eds)). Elsevier Applied Science, London, 1990, pp. 303–313.

28. RENGASWAMY N. S., BALASUBRAMANIYAN T. M., SRINIVASAN, S., MAHADEVA IYER Y. and SURESH BABU R. H. Corrosion survey of bridges. *The Indian Concrete Journal*, 1987, **61**, No. 6, 147–160.

29. GJORV O. E., VENNESLAND O. and EL-BUDSAIDY A. H. S. Electrical resistivity of concrete in oceans. In *Proceedings of the Offshore Technology Conference, OTC paper No. 2*, Texas, 1977, pp. 581–588.

30. BUREAU OF INDIAN STANDARDS. *Method of Test for Strength of Concrete*. BIS, New Delhi, 1959, BIS 516:1959.

31. WEE T. H., SURYAVANSHI A. K. and TIN. S. S. Evaluation of rapid chloride permeability test (RCPT) results for concrete containing mineral admixtures. *ACI Materials Journal*, 2000, **97**, No. 2, 221–232.

32. HUSSAIN S. H. and RASHEEDUZZAFAR. Corrosion performance of fly ash blended cement concrete. *ACI Materials Journal*, 1994, **91**, No. 3, 66–74.

33. SARICIMNE H. and MASLEHUDDI M. Permeability and durability of plain and blended cements cured in field and laboratory conditions, *ACI Materials Journal*, 1995, **92**, No. 2, 111–115.

34. KHATRI R. P., SRIVIVATNANON V. and LAM K. Y. Effect of curing on water permeability of concretes prepared with normal Portland cement with slag, silica fume, *Magazine of Concrete Research*, 1997, **49**, No. 180, 167–172.

35. ASTM C 642-80. *Standard Test Method for Specific Gravity, Absorption and Voids in Hardened Concrete.* ASTM Standards, V.04-02, 1995, p. 318

36. HEKAL E. E., KISHAN E. and MOSTAFA H. Magnesium sulphate attack on hardened blended cement pastes under different circumstances. *Cement and Concrete Research*, 2002, **32**, No. 10, 1421–1427.

37. BEN-YAIR M. The effect of chlorides on concrete in hot and arid regions. *Cement and Concrete Research*, 1974, **4**, No. 3, 405–416.

38. AL-AMOUDI O. S. B., MASLEHUDDIN M. and SAADI M. M. Effect of magnesium sulphate and sodium sulphate on the concrete durability performance of plain and blended cements. *ACI Materials Journal*, 1995, **92**, No. 1, 15–24.

39. MANGAT P. S. and EL-KHATIB J. M. Influence of initial curing on sulphate resistance of blended cement concrete. *Cement and Concrete Research*, 1992, **22**, No. 6, 1089–1100.

40. KALOUSEK G. R., PORTER L. C and BENTON E. J. Concrete for long-term service in sulphate environment. *Cement and Concrete Research*, 1972, **2**, No. 1, 79–89.

41. HUGHES D. C. Sulphate resistance of OPC, OPC/Fly ash and SRPC pastes; Pore structure and permeability. *Cement and Concrete Research*, 1985, **15**, No. 6, 1003–1012.

42. AL-AMOUDI, O. S. B. Attack on plain and blended cements exposed to aggressive sulphate environments, *Cement and Concrete Composites*, 2002, **24**, Nos 3–4, 305–316.

43. STAR. K. D. Long term study of concrete durability in sulphate soils. In *George Verbeck Symposium on Sulphate Resistance of Concrete*, SP-77, ACI, Detroit, 1982, pp. 21–40.

44. VEDALAKSHMI R., SUNDARARAJ A., SRINIVASAN S. and GANESH BABU K. Quantification of hydrated cement products of blended cements in low and medium strength concrete using TG and DTA technique. *Thermochimica Acta*, 2003, **407**, Nos 1–2, 49–60.

45. MANU SANTHANAM, COHEN C. D. and OLEK J. Effects of gypsum formation on the performance of cement mortars during external sulphate attack, *Cement and Concrete Research*, 2003, **33**, No. 3, 325–332.

46. LI D., CHEN Y., SHEN J. and WU X. The influence of alkalinity on activation and micro structure of fly ash. *Cement and Concrete Research*, 2000, **30**, No. 6, 881–886.

47. CHANG H., Huang P. J. and HOU S. C. Application of thermo-Raman spectroscopy to study dehydration of $CaSO_4.2\ H_2O$ and $CaSO_4.0·5\ H_2O$. *Materials Chemistry and Physics*, 1999, **58**, No. 2, 12–19.

Discussion contributions on this paper should reach the editor by 1 October 2005