

# The Effect of Cement Composition and pH of Environment on Sulfate Resistance of Portland Cements and Blended Cements

H. T. Cao,<sup>a</sup> L. Bucea,<sup>a</sup> A. Ray<sup>b</sup> & S. Yozghatlian<sup>a</sup>

<sup>a</sup>CSIRO, Division of Building, Construction and Engineering, PO Box 310, North Ryde, NSW 2113, Australia

<sup>b</sup>Department of Materials Science, University of Technology, Sydney, NSW, Australia

(Received 17 October 1996; accepted 25 January 1997)

## Abstract

*This paper presents an investigation into the sulfate resistance of Portland cements and blended cements. Four Portland cements of different characteristics and blended cements containing fly ash, ground granulated blast furnace slag and silica fume were used in this work. The performances of binders were evaluated in sulfate solutions maintained at different pH levels ranging from 3 to 12 using expansion of mortar prisms (ASTM C 1012) and strength development of mortar cubes. The results indicate that sulfate resistance of cementitious materials is dependent on its composition and on the pH of the environment. Portland cement with low  $C_3A$  and low  $C_3S$  performed well in all sulfate solutions. Blended cements containing silica fume and fly ash (particularly at 40% replacement) showed a more superior performance than any of the Portland cements used. For slag blended cement, this can be achieved when the replacement percentage is higher than 60%. © 1997 Elsevier Science Ltd.*

**Keywords:** Concrete durability, sulfate resistance, Portland cements, blended cements, chemical composition, pH, testing.

## INTRODUCTION

It has been known for many years that sulfate-bearing soils and waters attack mortars and concrete. Research reports on sulfate attack can readily be found in the literature. In a comprehensive review, Mehta<sup>1</sup> noted that there are

several gaps in the knowledge, i.e. in the kinetics and mechanisms of sulfate attack; in the specification and test methods for sulfate resistance; and in the formulation of measures used to prevent sulfate attack. Furthermore, with the introduction of mineral additives, the range of materials available as binders in concrete has become very diversified. The experience regarding sulfate resistance of the new binders is relatively limited and not very transportable, due to variation in characteristics and compatibility of components.

At the CSIRO, North Ryde, a research program on sulfate attack on mortars and concretes was initiated in 1992. This research program was set-up as an attempt to provide data bases on sulfate resistance of local materials and to fill in some of the gaps of knowledge mentioned by Mehta.<sup>1</sup>

In this paper, some data obtained from this research program are presented. They were obtained from an investigation into the influence of binder types and (sulfate) solution pH on the expansion and compressive strength development of mortars. The range of binders reported in this paper includes four Portland cements and blended cements containing fly ash, silica fume and ground granulated blast furnace slag.

## MATERIALS AND EXPERIMENTAL PROCEDURES

The chemical compositions of the Portland cements and mineral admixtures used in this

work are shown in Table 1. The blended cements reported in this paper were all made with cement 1. Data presented in this paper include expansions of prisms prepared according to ASTM C 1012<sup>2</sup> and compressive strength monitoring of mortar cubes of 50 × 50 mm dimension. The mortar cubes were made with water-to-binder ratio (W/B) of 0.6, sand-to-binder ratio of 2.75 and cured for 7 days (1 day in mould plus 6 days in water) prior to immersion in sulfate solutions. Data related to different curing regimes, W/Bs and microstructures will be reported at a later date. Three types of sulfate solutions were used in this work. The 'standard' 5% Na<sub>2</sub>SO<sub>4</sub> solution was prepared and changed as prescribed in ASTM C 1012. Since this is an 'uncontrolled' environment, the pH of this solution is variable depending on the binder. Generally, after a short period of immersion of samples, the pH of the solution is raised to 12 or above. In this paper, this sulfate solution is referred to as either pH 12 solution or normal sulfate solution. The other two sulfate solutions were prepared with 5% Na<sub>2</sub>SO<sub>4</sub> and maintained at nominal pHs of 7 and 3 by automatic titration with 10% H<sub>2</sub>SO<sub>4</sub> at regular set intervals. The tanks of low pH sulfate solutions were kept constantly circulated. The set-up of the low pH sulfate tanks is very similar to that described by Brown.<sup>3</sup> The SO<sub>4</sub><sup>2-</sup> concentrations in the low pH tanks were regularly checked by ICP-AES analysis and kept at an 5% Na<sub>2</sub>SO<sub>4</sub> equivalent (33.8 g/l SO<sub>4</sub><sup>2-</sup>). Data reported in this paper were the averages of five measurements for expansion and three for compressive strength.

## RESULTS

### Expansion of portland cement mortar (ASTM C 1012)

Figure 1 shows the expansion patterns of Portland cement mortars in normal sulfate solution. As expected, this figure denotes that the composition of the Portland cement is an important factor affecting its expansion pattern. Portland cement with highest C<sub>3</sub>A content such as cement 1 shows the highest expansion. The interesting implication obtained from these results is that a Portland cement with a C<sub>3</sub>A content less than 5% may not be as sulfate resistant as might have been expected based on the expansion pattern (e.g. cement 2). In fact, the lowest expansion was observed for cement 4 which has low C<sub>3</sub>A and low C<sub>3</sub>S (low heat).

Figures 2 and 3 show the expansion patterns of Portland cements when subjected to sulfate solutions of pH of 7 and 3, respectively. The trends observed in these figures are similar to that observed in Fig. 1. Cement 1 showed the highest expansion pattern in all sulfate solutions. The difference in behavior of the other cements was less noticeable in low pH sulfate solution. Generally, the acid type attack on hardened cement pastes is associated with erosion and softening due to leaching of Ca and decalcification of C–S–H.<sup>4</sup> Hence, expansion might be expected to be less with reducing pH level. In this work, the trend is relatively consistent. Expansion decreased when the pH of the sulfate solution was reduced from 12 to 7 and increased from 7 to 3. This suggests that

**Table 1.** Chemical compositions of raw materials

(%)	Cement 1	Cement 2	Cement 3	Cement 4	Fly Ash	S/fume	Slag
CaO	62.3	63.2	64.2	61.9	1.3	0.2	40.0
Si <sub>2</sub> O	20.8	20.6	20.0	22.6	65.1	98.7	34.3
Al <sub>2</sub> O <sub>3</sub>	4.8	4.6	4.8	4.8	25.9	0.1	14.9
Fe <sub>2</sub> O <sub>3</sub>	3.6	4.6	4.8	4.8	3.0	0.1	0.9
K <sub>2</sub> O	0.52	0.05	0.5	0.47	1.65	0.27	0.43
Na <sub>2</sub> O	0.02	0.06	0.01	0.01	0.06	0.02	0.02
SO <sub>3</sub>	2.7	2.3	2.6	2.4	0.2	0.1	1.8
TiO <sub>2</sub>	0.4	0.4	0.3	0.3	1.1	0.1	0.8
L.O.I.	—	—	—	—	1.5	—	—
Fineness (m2/kg)	345	340	355	320	350	—	450
C <sub>3</sub> S	51	57	63	34	—	—	—
C <sub>2</sub> S	22	17	10	39	—	—	—
C <sub>3</sub> A	6.6	4.3	5.3	4.6	—	—	—
C <sub>4</sub> AF	11	14	13	15	—	—	—

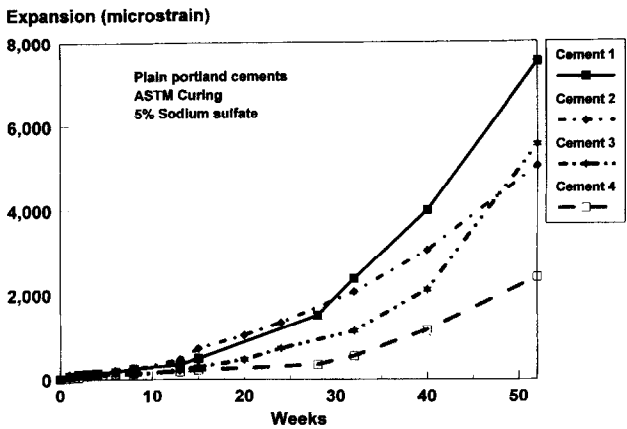


Fig. 1. Expansion of portland cement mortars in normal 5%  $\text{Na}_2\text{SO}_4$  solution.

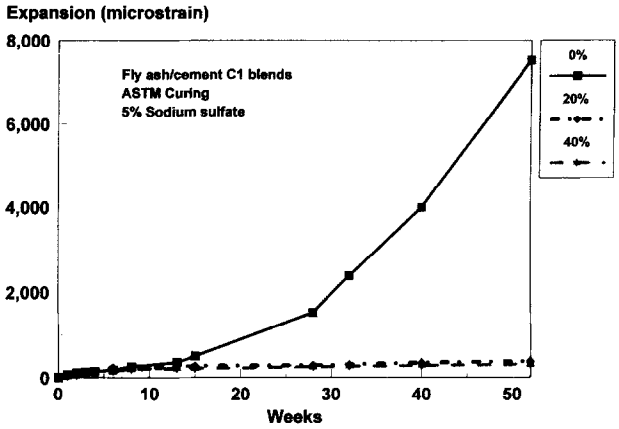


Fig. 4. Expansion of fly ash blended cement mortars in normal 5%  $\text{Na}_2\text{SO}_4$  solution.

expansion type reactions between hardened cement pastes and sulfate solutions are still important factors at all pH levels considered.

#### Influence of fly ash on expansion of blended cement mortar

The effects of fly ash on expansion of blended cement mortars are shown in Figs 4–6 for normal sulfate solution and sulfate solutions kept at pH 7 and 3, respectively. The important feature of these figures is that for the particular fly ash used, significant reductions in expansion of mortars were achieved by the incorporation of fly ash in the range of 20–40% replacement. Furthermore, contrary to the behaviors shown by Portland cements, no time-dependent accelerating pattern of expansion was shown by fly ash blended cements in any of the pH conditions. The expansions of fly ash/cement 1

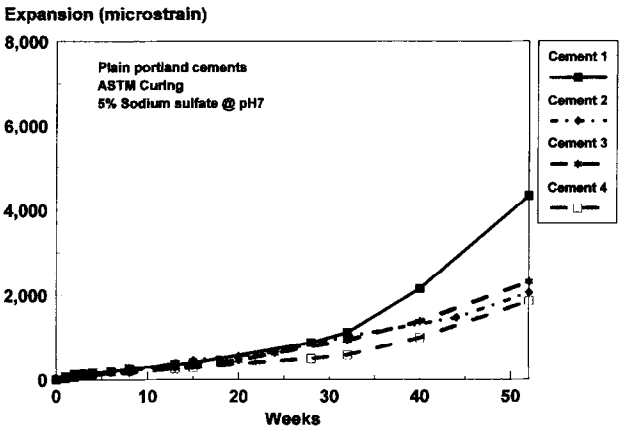


Fig. 2. Expansion of Portland cement mortars in pH 7 sulfate solution.

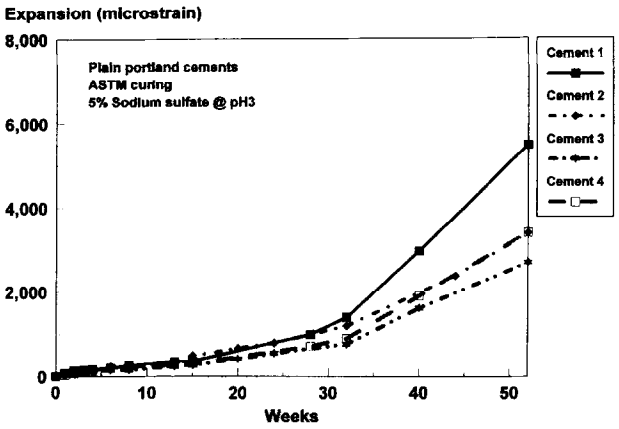


Fig. 3. Expansion of Portland cement mortars in pH 3 sulfate solution.

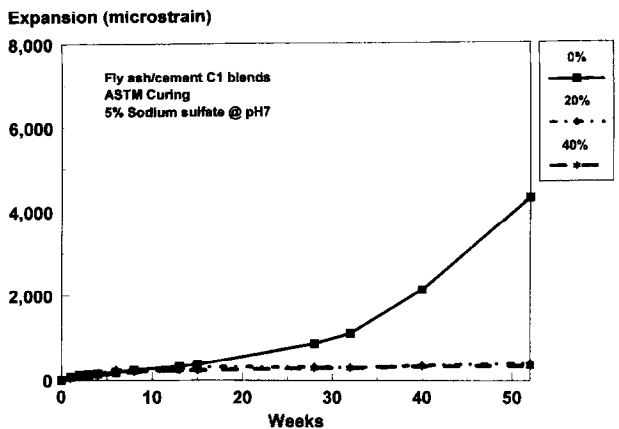


Fig. 5. Expansion of fly ash blended cement mortars in pH 7 sulfate solution.

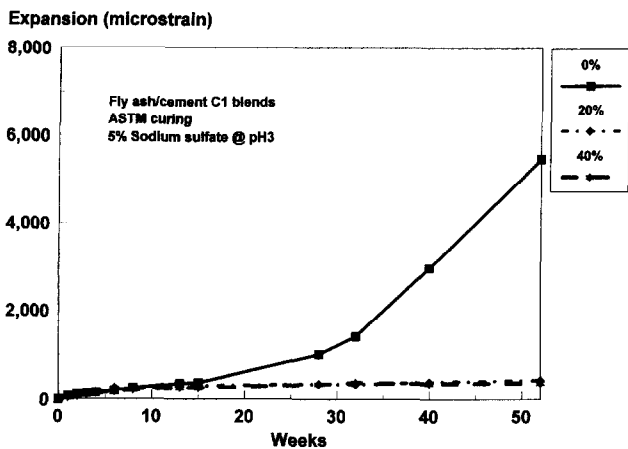


Fig. 6. Expansion of fly ash blended cement mortars in pH 3 sulfate solution.

blended cements were much less than those shown by cement 4 (portland cement with best overall performance). This was achieved even when the fly ash blended cements were made with the least sulfate resistant cement (cement 1).

**Influence of silica fume on expansion of blended cement mortar**

Silica fume blended cements show very low expansions in all sulfate solutions (Figs 7–9). Similar to the expansion patterns shown by fly ash blended cements, silica fume blended cements showed no noticeable accelerating expansion even after 1 year of immersion in a variety of sulfate solutions. As in the cases of fly ash blends, the expansion patterns showed that

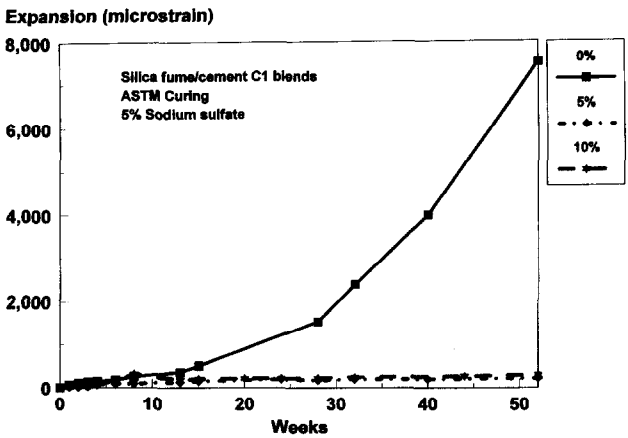


Fig. 7. Expansion of silica fume blended cement mortars in normal 5% Na<sub>2</sub>SO<sub>4</sub> solution.

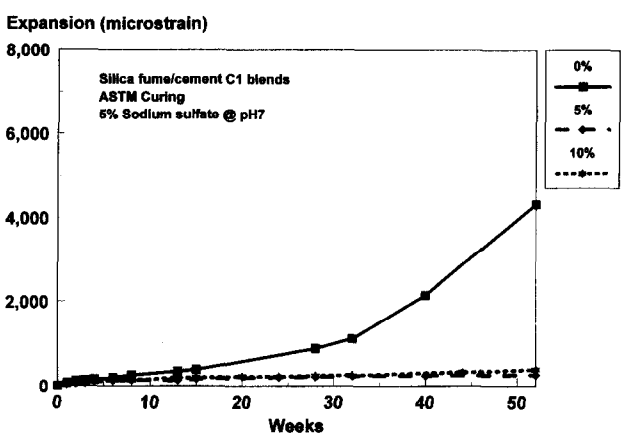


Fig. 8. Expansion of silica fume blended cement mortars in pH 7 sulfate solution.

silica fume blends were unaffected by changes in pH of the sulfate solution.

**Influence of ground granulated blast furnace slag on expansion of blended cement mortar**

In normal sulfate solution (Fig. 10), marked reductions in expansion of mortars were observed with slag blended cements in comparison to those shown by plain Portland cements. With the exception of the 80% slag blended cement which showed negligible expansion, some accelerating expansions were observed with the 40 and 60% slag blends after about 30 and 40 weeks, respectively.

In pH 7 sulfate solution, the expansions of the 40 and 60% slag blends noticeably increased (Fig. 11). The 40% slag blend mortars failed at about 40 weeks in this solution. High expansion was observed with the 60% slag blend.

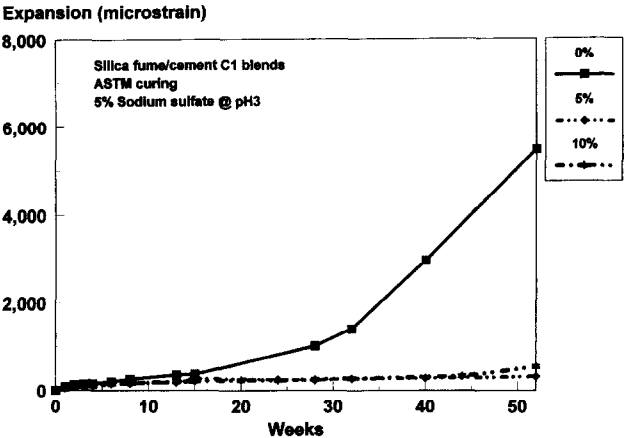


Fig. 9. Expansion of silica fume blended cement mortars in pH 3 sulfate solution.

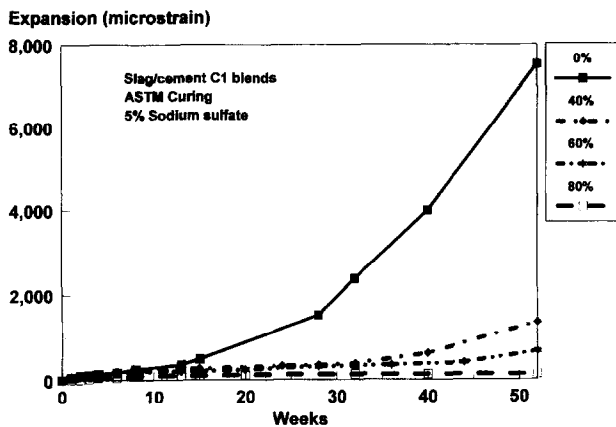


Fig. 10. Expansion of slag blended cement mortars in normal 5%  $\text{Na}_2\text{SO}_4$  solution.

Although there was some reduction in expansion in comparison to cement 1, the 60% slag blend did not perform as well as cement 4. The 80% slag blend still showed little expansion in this solution.

In pH 3 sulfate solution, very high accelerating expansions were observed for both 40 and 60% slag blends after about 16 weeks (Fig. 12). They failed after 30 and 40 weeks, respectively. Whereas little expansion was observed for the 80% slag blend.

These results denote that contrary to silica fume blended cement and fly ash blended cement, the potential for reducing expansion of slag blended cement depends markedly on the pH of the solution. Apparently in low pH sulfate solutions, a slag blend with more than 60% slag is needed to provide the required low expansion characteristics.

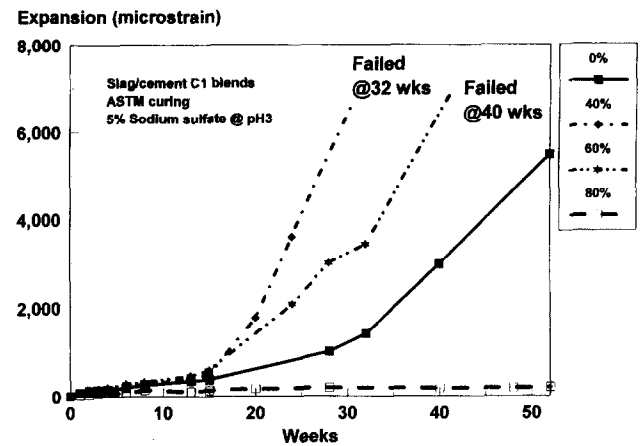


Fig. 12. Expansion of slag blended cement mortars in pH 3 sulfate solution.

### Compressive strength development of mortars in sulfate solutions

The behavior of different binders are compared with data of mortars prepared with W/B of 0.6; S/B of 2.75 and 7 days of initial curing.

#### Normal sulfate solution

The compressive strength developments of the Portland cement mortars in normal sulfate solution are shown in Fig. 13. In this solution, all Portland cements showed strength regression within 1 year of immersion. Cements 1–3 showed similar strength regression patterns with a gradual strength drop after about 90 days in sulfate solution. (Curve of cement 2 falls in between those of cements 1 and 3.) Cement 4 with least expansion in normal sulfate solution (Fig. 1), showed better strength retention characteristics. There is an indication that the

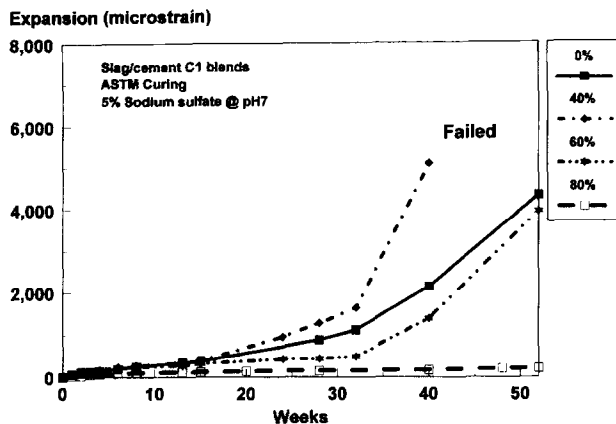


Fig. 11. Expansion of slag blended cement mortars in pH 7 sulfate solution.

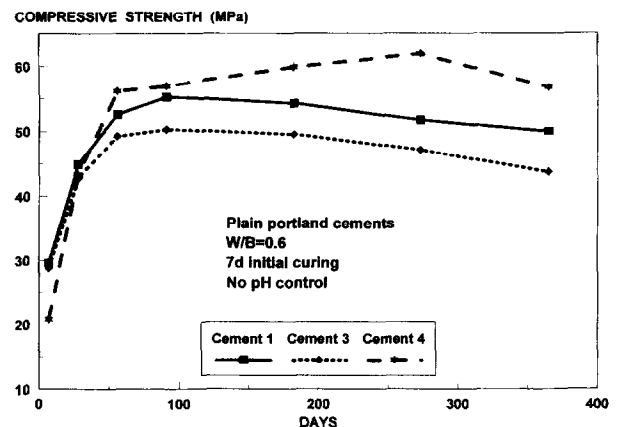


Fig. 13. Strength development of portland cement mortars in normal sulfate solution.

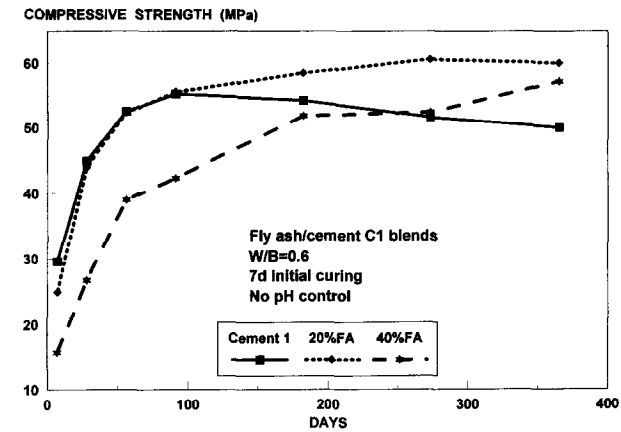


Fig. 14. Strength development of fly ash blended cement mortars in normal sulfate solution.

strength regression started with this cement after about 300 days of immersion.

The influence of fly ash and silica fume on compressive strength development of mortars is shown in Figs 14 and 15, respectively. Figure 14 shows that the incorporation of fly ash results in better strength development pattern. The 20% fly ash blend showed little or no strength loss. While the strength development in the 40% fly ash blend continued in sulfate solution. The use of silica fume also clearly resulted in improvement in the strength development patterns in normal sulfate solution. The data shown in Fig. 15 suggest that the 5% silica fume blend performed better than the 10% blend which started to show some strength loss within 1 year.

In the case of slag blends in normal sulfate solution (Fig. 16), the 40% slag blend failed very early in comparison to Portland cement. This was quite unexpected since the expansion of the 40% slag in normal sulfate solution

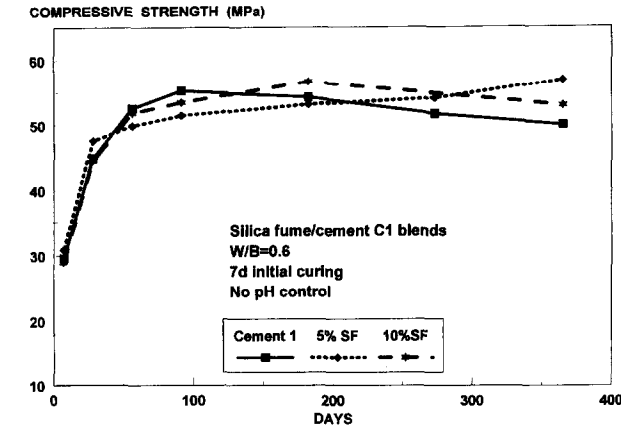


Fig. 15. Strength development of silica fume blended cement mortars in normal sulfate solution.

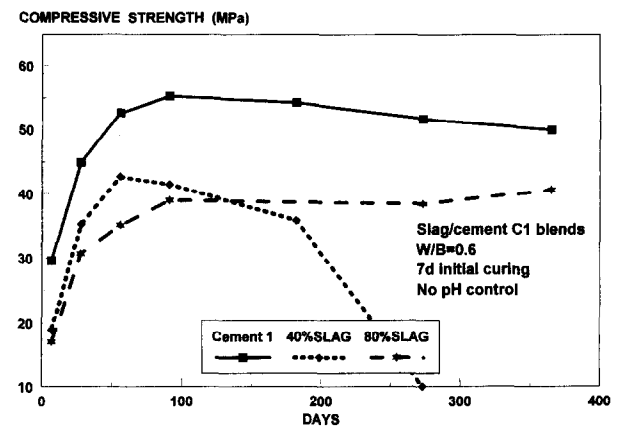


Fig. 16. Strength development of slag blended cement mortars in normal sulfate solution.

would suggest an improvement in sulfate resistance. Whereas, the 80% slag blend did not show any indication of strength loss.

*ph 7 sulfate solution*

Figure 17 shows the strength development of Portland cement in pH 7 sulfate solution. This figure shows that all Portland cements show strength regression in this solution within 200 days of immersion. Cement 4 remains the best performer in terms of strength retention characteristics. The rate of strength loss in this solution was not that much different from that observed in normal sulfate solution for cements 1 and 4. A limited initial strength development was observed with cement 3.

Figure 18 shows the influence of fly ash in the strength development at pH of 7. There was

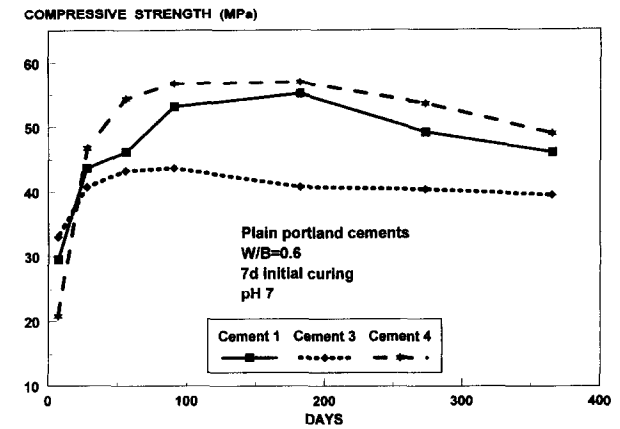


Fig. 17. Strength development of portland cement mortars in pH 7 sulfate solution.

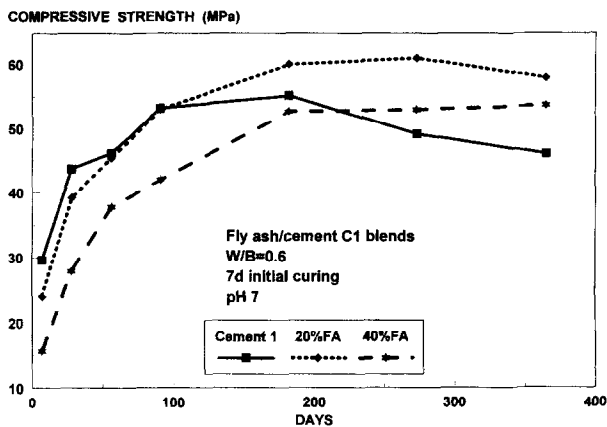


Fig. 18. Strength development of fly ash blended cement mortars in pH 7 sulfate solution.

little difference in the strength development of fly ash blends in this solution as compared to that in normal sulfate solution. This suggests that the fly ash blends were quite insensitive to the drop of pH from 12 to 7. Similar comments can be made with respect to silica fume blends (Fig. 19). The improvement in strength retention characteristics observed in normal sulfate solution persists in pH 7 sulfate solution.

In the cases of slag blends, the trends observed for the 40 and 80% slag blends were similar to those in normal sulfate solution, i.e. the 40% slag blend failed within 200 days of immersion and the 80% slag blend showed little or no strength drop. However, in pH 7 (Fig. 20) the 60% slag blend also failed after about 300 days. This trend denotes that the sulfate resistance of slag is fairly sensitive to the pH level (as observed in expansion measurement).

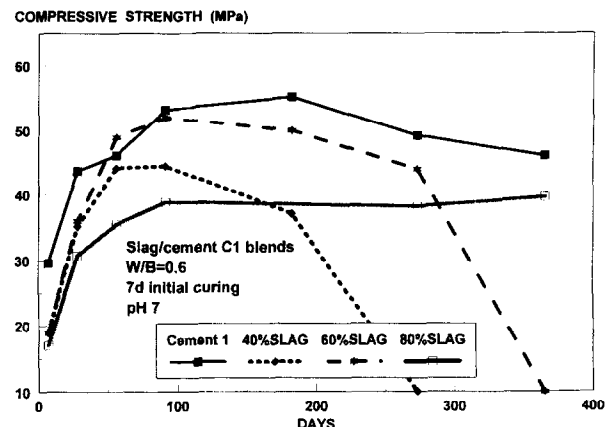


Fig. 20. Strength development of slag blended cement mortars in pH 7 sulfate solution.

### ph 3 sulfate solution

Figure 21 shows typical strength development patterns of Portland cements in pH 3 sulfate solution. All Portland cements showed strength drops after about 90 days in this acidic environment. The strength drop was significant after 1 year of immersion. As in the cases of normal sulfate solution and pH 7 sulfate solution, cement 4 (low C3S and low C3A) showed the best strength development pattern.

The influence of fly ash on sulfate resistance at low pH is shown in Fig. 22. The effectiveness of the 20% fly ash replacement was much reduced at pH 3. The improvement of the strength retention characteristics was only marginal in comparison to cement 1 and was not as good as that shown by cement 4. The 40% fly ash blend, however, showed no evidence of

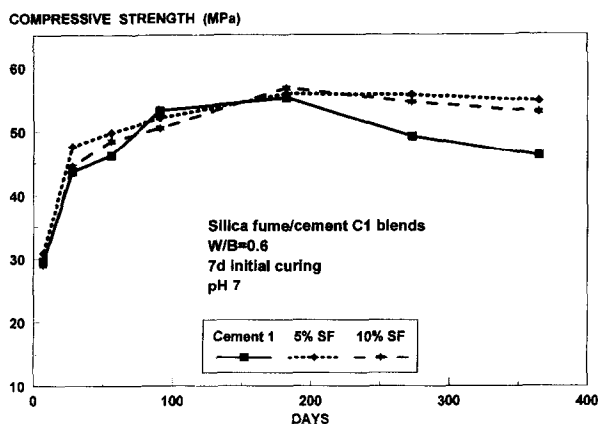


Fig. 19. Strength development of silica fume blended cement mortars in pH 7 sulfate solution.

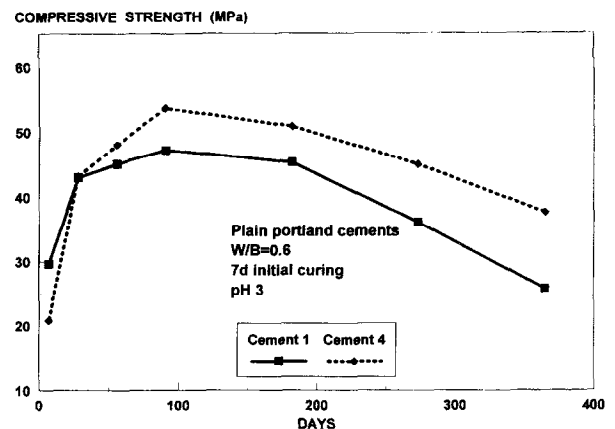


Fig. 21. Strength development of portland cement mortars in pH 3 sulfate solution.

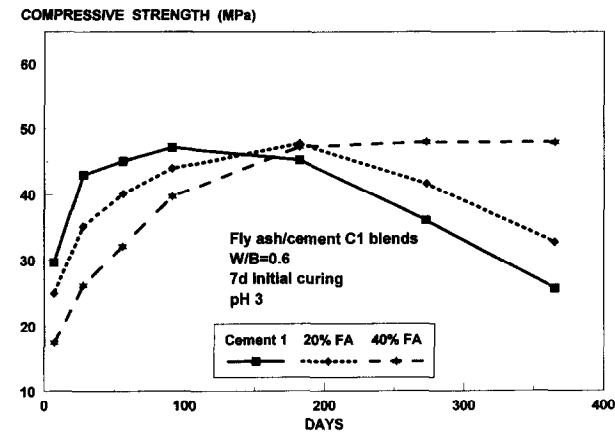


Fig. 22. Strength development of fly ash blended cement mortars in pH 3 sulfate solution.

strength regression, The strength development pattern of the 40% fly ash blend was similar to those in normal and pH 7 sulfate solution. This suggests that this particular mix is unaffected by pH level and should be considered for concreting applications in harsh sulfate environment.

For silica fume blends (Fig. 23), strength regression was observed for both 5 and 10% blends. The strength drop of silica fume was much more gradual than any of the portland cements. This indicates that the use of silica fume will lead to long term benefit. As in the previous cases, there was indication that the 5% silica fume blend was a better mix than the 10% silica fume blend.

The strength development of slag blends in pH 3 solution (Fig. 24) was similar to that found at pH 7. Both the 40 and 60% slag blends failed. The time to failure of these two blends

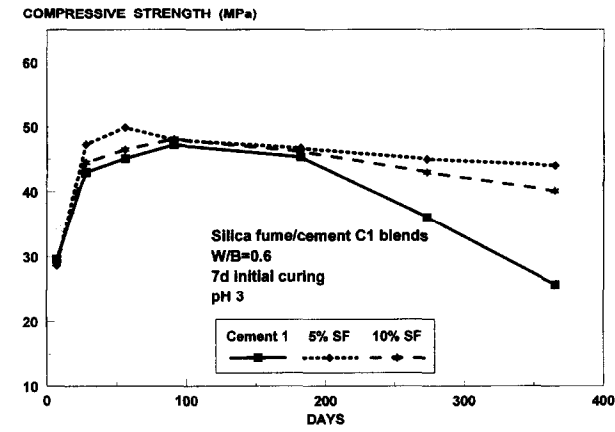


Fig. 23. Strength development of silica fume blended cement mortars in pH 3 sulfate solution.

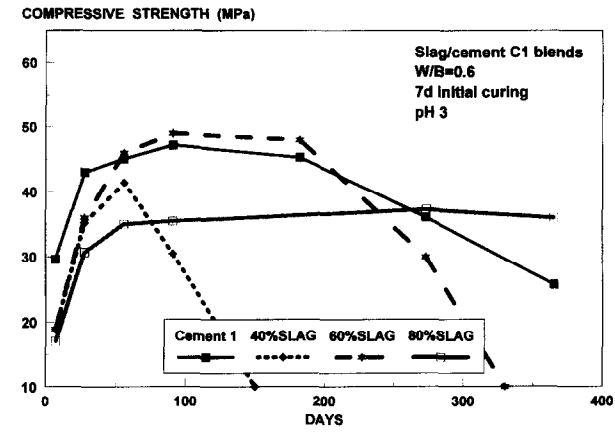


Fig. 24. Strength development of slag blended cement mortars in pH 3 sulfate solution.

was shortened as the pH decreased. As in other sulfate containing solutions, the 80% slag blend showed remarkable strength retention characteristics. This suggests that for harsh acidic environments, the use of slag blend can lead to improved performance if the level of replacement is close to 80%.

## DISCUSSION

Data obtained from expansion tests and compression tests confirm that the compositions of the binder have a major influence on the sulfate resistance of mortar. As expected, the expansion data indicate that with portland cements, higher expansions are associated with cement with higher  $C_3A$  content (Fig. 1). However, at short term exposure, e.g. 16 weeks, it is very difficult to classify the behavior of cements. Even after 32 weeks, there is little difference in expansions of cement 1 (6.6%  $C_3A$ ) and cement 2 (4.3%  $C_3A$ ). The differences in performance between Portland cements are much more distinguishable after long term exposure to sulfate solution of 1 year. This suggests that the assessment of sulfate resistance of Portland cement using expansion of mortar should be based on long term data. Although, the data presented are generated using ASTM C 1012 sample configuration and procedure, it is likely that this trend would persist for other sample configurations and procedures. This has been noted in the literature.<sup>5</sup> Using a single test (e.g. expansion) in conjunction with a short term exposure (e.g. 16 weeks) does not appear to be an appro-



priate method for the purpose of classification or selection of binder for sulfate resistance.

The expansion data also suggest that the  $C_3A$  content is not the only factor influencing the performance of Portland cement in sulfate solutions. The cement showing the least expansion is cement 4 which has a very low  $C_3S/C_2S$  ratio in comparison with the other cements. This has been noted elsewhere<sup>6</sup> in an investigation using Portland cements of higher  $C_3A$  contents than those used in this work. Data presented in this paper show that low expansion was observed for the cement with low  $C_3A$  and low  $C_3S$  contents over the pH range of 3–12 (normal  $Na_2SO_4$  solution). The compressive strength development of mortar cubes ( $W/C = 0.6$ ; 7 d initial curing) showed the same trend, i.e. cement 4 showed the highest strength retention pattern. This indicates that for better overall sulfate resistance, particularly in environment where pH is low, a Portland cement with a low  $C_3A$  and  $C_3S$  should be preferred.

The role of alumina (from hydrates deriving from  $C_3A$ ) on the formation of ettringite in sulfate solution has been discussed elsewhere.<sup>1,7–9</sup> This has been associated with high expansion. On the other hand, the effect of  $C_3S$  content on expansion is not very clear. Formation of gypsum (from CH) and decomposition of C–S–H (hydration products of  $C_3S$ ) are often linked to loss of adhesion and strength rather than to expansion.<sup>9</sup> Initial examination of the microstructure of the mortar (by SEM and microprobe) indicates that gypsum formation in cement with high  $C_3S$  content tends to be in large lenses parallel to exposed surfaces. Whereas in low  $C_3S$  cement, the formation of gypsum is more dispersed in smaller masses. In all cements, both gypsum and ettringite were found with ettringite more pronounced in deeper layer. Ettringite was observed even in samples kept in pH 3 sulfate solution. In most cases, ettringite was found in the rod or fiber forms and appeared to form on crack faces or in voids. It appears that a 'skin' consisting of porous C–S–H, gypsum and carbonate was sufficient to sustain a high internal pH condition for ettringite formation since ettringite is unstable at pH lower than 10.<sup>10</sup> The information obtained from the examination of microstructures will be published at a later date. At this stage, it is suggested that the role of  $C_3S$ , through formation of gypsum and supplier of  $Ca^{2+}$  for ettringite formation, can be quite

important in the overall sulfate resistance as observed by expansion and mortar cubes compressive strength over a wide range of pH levels.

It is expected that Ca leaching and decalcification of C–S–H become more dominant as pH is lowered.<sup>4</sup> The strength loss is hence expected to be faster at lower pH. The compression strength data confirm this. The expansion patterns, however, did not show a consistent trend with regard to the pH level. Similar data have been published in the literature.<sup>3</sup> This suggests that the kinetics of sulfate attack on Portland cement particularly in regard to expansion is dependent on the pH level. The implication of this is that the selection of binder should be based on data obtained from test conditions similarly to service conditions, especially concerning pH level. Mehta<sup>1</sup> noted that 'from both a theoretical and a practical standpoint, immersion tests, involving continuous control of the pH of the sulfate solution, would be a more suitable adoption as accelerated laboratory tests for evaluation of sulfate resistance of cements'.

The use of fly ash as cement replacement leads to reduction of expansion and improvement in compressive strength retention characteristics in sulfate solutions over the pH range of 3–12. Although, the expansions of fly ash blended cement mortars were significantly less than all Portland cements used in this work, the improvement in compressive strength retention characteristics depended on the pH of the sulfate solution. In pH 12 sulfate solution, both the 20 and 40% fly ash blends shown little or no strength reduction after 1 year of immersion. In pH 7, there was indication of strength regression in the 20% fly ash blend. In pH 3, the strength regression of the 20% fly ash blend was evident. The 40% fly ash blend was the only mixture that consistently showed no apparent strength reduction. This indicates that as the severity of the sulfate environment increases (i.e. lower pH), the use of high volume fly ash concrete (e.g. 40% replacement) should be considered. In a less severe sulfate environment, the incorporation of fly ash even at the normally used dosage of 20% replacement will provide improved sulfate resistance. It should be noted that the 'effectiveness' of a fly ash in increasing sulfate resistance has been reported to be dependent on its compositions.<sup>9,11</sup> Work on low calcium Australian fly ashes (CaO in the

range of 1.3–5.4) indicates that the 'dependence' of sulfate resistance of fly ash blend on its compositions is more noticeable at low replacement percentage (20%). At a high replacement level of 40%, most Australian fine fly ashes significantly improve sulfate resistance of blended cement, particularly in low pH conditions.<sup>12</sup>

Similar to the fly ash blends, silica fume blends showed little expansion in all sulfate solutions. There was little strength reduction with silica fume blends in sulfate solutions at pH values of 12 and 7. At pH 3, there is a trend of gradual strength reduction. However, as in the cases of fly ash blends, the rate of strength reduction was much slower than that observed with Portland cements. The compressive strength development patterns suggest that better performance was obtained with the 5% silica fume blends.

The improvement in sulfate resistance of blended cements containing pozzolanic materials such as low calcium fly ash and silica fume, can generally be attributed to the combined effects of reduced permeability and reduction in CH in the hardened cement paste. A reduction in CH will lessen the effect of gypsum formation and the tendency of ettringite recrystallisation. This explains the very low expansion observed in fly ash and particularly silica fume blends. The compressive strength patterns, however, suggest that the sulfate attack on fly ash and silica fume blends, at lower pH range, would not be based solely on reactions involving expansion. It is likely that the deterioration of the C–S–H gel (low C/S) has a more important role for these blended cements in sulfate attack. It appears that although the improvement in sulfate resistance of blended cements using fly ash and silica fume can be detected by expansion, their effectiveness would be better observed with strength measurement. In some cases, the differences in expansion behavior can be very substantial, (e.g. between Cement 1 and 10% silica fume in pH 3 solution) while the differences in compressive strength behavior may not be remarkable between mixes. It is suggested that complementary tests (instead of a single test) would be more valuable in the assessment of sulfate resistance of binders and concretes.

In the cases of slag blends, a clear trend is that the improvement of sulfate resistance depends greatly on the replacement percentage and more importantly on the pH level of the

sulfate solution. Even in pH 12 sulfate solution, the 40% blend showed rapid deterioration of compressive strength in comparison to Portland cements. Mehta<sup>9</sup> noted that high alumina slag (18%) when used with cements with moderate to high C<sub>3</sub>A (8–11%), at a level of 50% or less, showed decreased sulfate resistance. The slag used in this work had a fairly high alumina level (~15%) and was blended with cement of about 6% C<sub>3</sub>A. It appears that Mehta's findings are also applicable for this particular slag/cement combination.

In pH 3 sulfate solution, the expansion data and the strength data indicate that even at 60% replacement, the slag blend did not show any improvement in sulfate resistance. In contrast, the 80% slag blend showed excellent sulfate resistance in all sulfate solutions as shown by very low expansion and no strength reduction.

The obtained data indicate clearly that for sulfate environment with high pH, the use of 60% slag blend would provide improved sulfate resistance compared to portland cement. For harsh environments of acidic sulfate solution, the use of high replacement of slag (70–80%) is recommended as advocated in BRE Digest 363.<sup>14</sup> Similar trends have also been reported in the literature.<sup>5,15</sup>

These results highlight the importance of the relevance between testing conditions for sulfate resistance and intended applications. The findings show that selection of materials based on sulfate testing in normal sulfate solution may not be relevant if the application involves acidic sulfate attack.

It must be stressed that the sulfate solutions used in this work had high sulfate ion concentrations (~34 g/l SO<sub>4</sub><sup>2-</sup>) for accelerated testing. At a lower sulfate concentration of 3 g/l SO<sub>4</sub><sup>2-</sup>, which is more typical in groundwater, slag blend concretes in the range of 45–72% replacements showed no deterioration, whereas Portland cement concretes (3.5–12.3% C<sub>3</sub>A) showed varying degrees of damage.<sup>13</sup>

In this work similar trends were shown by expansion and compressive strength of slag blends in sulfate solutions. This suggests that the expansion-related mechanisms of sulfate attack are predominant with slag blends.

It is worth noting that from case histories of deteriorated concrete in structures subjected to long term sulfate exposure, Mehta<sup>1</sup> mentioned that permeability of concrete is the primary factor in sulfate attack, i.e. the sulfate ions must

first diffuse into the concrete. Hence, the rate of sulfate attack on concrete can be slowed down by ensuring good compaction, sufficient curing and good mix design including low water-to-binder ratio. Requirements for concrete exposed to sulfate attack under different environments can be found in the literature.<sup>14</sup> Since the diffusion rate of  $\text{SO}_4^{2-}$  appears to be relatively insensitive to the binder type,<sup>7</sup> low permeable concrete should be the important factor regardless of the type of binder used.

## CONCLUSIONS

The work presented in this paper indicates that sulfate resistance of a cementitious material is dependent on its composition and the pH of the environment. Portland cement with a low  $\text{C}_3\text{A}$  content and a low  $\text{C}_3\text{S}$  content would provide a better performance in sulfate containing environments. The use of mineral admixtures such as fly ash, silica fume and slag would generally provide an improved performance. However, the selection of the mineral admixture and its replacement dosage becomes more critical as the pH of the sulfate solution decreases. It was found that 40% fly ash blend, 5% silica fume blend or a high slag blend (80%) provided a good overall performance related to resistance to sulfate attack over a wide pH range. The data presented in this paper also suggest that the behavior of a binder can be wrongly assessed if the test solution is not relevant to the application or when a single test is used. The findings are limited to the materials used in this work.

## ACKNOWLEDGEMENTS

Some data presented in this paper were obtained from an investigation sponsored by the Ash Development Association of Australia. The authors are grateful for their support.

## REFERENCES

1. Mehta, P. K., Sulfate attack on concrete—a critical review. In *Materials Science of Concrete*, Vol. III, ed. Jan Skalny. American Ceramics Society, 1992, pp. 105–130.
2. ASTM C 1012-95a—Standard test method for length change of hydraulic cement mortars exposed to a sulfate solution, *1995 Annual book of ASTM Standards*, Section 4 — Construction, Vol. 04.01 Cement; lime; gypsum, pp. 450–456.
3. Brown, P. W., An evaluation of the sulfate resistance of cements in a controlled environment. *Cement and Concrete Research*, **11** (1981) 719–727.
4. Revertgat, E., Richet, C. & Gegout, P., Effect of pH on the durability of cement pastes. *Cement and Concrete Research*, **22** (1992) 259–272.
5. Osborne, G. J., Determination of sulfate resistance of blast furnace slag cements using small-scale accelerated methods of test. *Advances in Cement Research*, **2** 5 (1989) 21–27.
6. Rasheeduzzafar, Dakhil, F. H., Al-Gahtani, A. S., Al-Saadoun, S. S. & Bader, M. A., Influence of cement composition on the corrosion of reinforcement and sulfate resistance of concrete. *ACI Materials Journal*, **87** 153 (1990) 114–122.
7. Lawrence, C. D., Sulfate attack on concrete. *Magazine of Concrete Research*, **42** 153 (1990) 249–264.
8. Taylor, H. F. W., *Cement Chemistry*, 2nd edn. Academic Press, New York, 1992.
9. Mehta, P. K., Sulfate resistance of blended cements. *Proceedings of the International Workshop on the Use of Fly Ash, Slag, Silica Fume and Other Siliceous Materials in Concrete*, Concrete 88, ed. W.G. Ryan, Sydney, July 1988, pp. 337–351.
10. Gabrisova, A., Havlica, J. & Sahu, S., Stability of calcium sulphoaluminate hydrates in solutions with various pH values. *Cement and Concrete Research*, **21** (1991) 1023–1027.
11. Dunstan, E., Sulfate resistance of fly ash concretes — the R-value. *Proceedings of the Katherine and Bryant Mather International Conference on Concrete Durability*, Atlanta, SP-100, Vol. 2, 1987, pp. 2027–2036.
12. Cao, H. T., Bucea, L., Yozghatlian, S. and Wortley, B. A., Influence of fly ash on sulfate resistance of blended cements, CSIRO DBCE Report BRE 023 to the Ash Development Association of Australia, June 1994.
13. Hooton, R. D. & Emery, J. J., Sulfate resistance of a Canadian slag cement. *ACI Materials Journal*, **87**(6) (1990) 547–555.
14. BRE Digest 363, Sulfate and acid resistance of concrete in the ground, CI/SfB q (R8), January 1996.
15. Osborne, G. J., The sulphate resistance of portland and blastfurnace slag cement concrete. *Proceedings of the Second CANMET/ACI Int. Conference on The Durability of Concrete*, August 1991, Montreal, Canada.