



SULPHATE RESISTANCE IN CONCRETES USING FLY ASH

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**FLY ASH
REFERENCE
DATA SHEET**

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“The effectiveness of bituminous coal fly ash in improving sulfate resistance increases as the severity of exposure to sulfates is increased.”

J.T. Dikeou in *Fly Ash increases Resistance of Concrete to Sulfate Attack*

INTRODUCTION

The benefits, in general terms, of using fly ash concrete in sulphate environments are discussed in Fly Ash Technical Notes No. 2., Sulphate attack on Concrete, What it is and how to stop it. The reference data herein is to provide formal technical backup, to confirm the basis of the earlier Notes.

AN HISTORICAL PERSPECTIVE

The use of natural pozzolans to combat sulphate attack was first reported by Jewett (1908) and has been fully explored in the technical literature. Abdun-Nur, in 1960, outlined the benefits of fly ash in prevention of sulphate attack but much of the detailed work was completed later by the US Bureau of Reclamation. Under Bureau cover, Dikeou's 1970 report fully described the main chemical reactions caused by the presence of the sulphate ion in concrete. Further Bureau work, was published by Kalousek et al (1976), recognised the benefits of fly ash and other pozzolans in providing sulphate resistance.

Most researchers seem to have worked with fly ash replacement levels of 20% and 40% by mass but Bureau workers von Fay and Pierce (1989) found that 30% fly ash was most effective for their specific materials. An additional finding of interest was that accelerated wetting and drying was a more severe test condition than continuous soaking.

The mechanisms of attack by sulphates on concrete are a little more complex than originally indicated by Dikeou. As a result, the optimum concrete proportions for resistance should not be generalised. In addition, while his report does not apply to the full range of fly ashes used world wide today, it certainly is valid for the fly ashes commercially available for use in concrete in Australia.

THE MECHANISMS OF ATTACK

The common sulphates available from soils and ground water are those of calcium, sodium and magnesium. Industrial sites can introduce others. As well as the sulphate concentration, the pH of the soil or water is critical. At low pH these destructive reactions proceed more rapidly, because both sulphate attack and acid attack are involved. The

various sulphate compounds attack concretes in different ways. Calcium sulphate is relatively insoluble in water. Its involvement is mainly as the expansive product of reaction between soluble sulphates and free lime in the concrete.

Sodium sulphate is readily soluble and causes rapid reaction with the aluminates forming expansive ettringite. Because of the sodium ion, it introduces the additional risk of producing alkali-silica reaction (dealt with in Fly Ash Technical Note No. 3 - Can you afford to risk an Alkali Aggregate Reaction?).

Magnesium sulphate also introduces a secondary effect from the presence of the magnesium ion. This ion is extremely aggressive and can attack concrete in its own right, forming Brucite and breaking down the strength of the calcium silicate hydrate gel by conversion to the equivalent magnesium salt which has no binding properties.

In an attempt to deal with these and other key factors, the Building Research Establishment (UK) published their Digest 363 in July 1991. This guide considers the pH and presence of magnesium ion as well as the sulphate. One of the recommended binder combinations is portland cement, blended at the mixer with fine fly ash (essentially as defined in AS 3582.1) as 25 to 40% of the total binder.

SUMMARY OF OVERSEAS WORK

The key issues identified through this work were that:

- a) there are many sources of free sulphate ions in the environment, soils and groundwaters.
- b) All or any of these sources may lead to various types of destructive reactions with hardened concrete.
- c) Fly ash, when used to replace approximately 30% of the portland cement, provides a high degree of resistance to sulphate attack.

RESEARCH IN AUSTRALIA

The use of fly ash in sulphate-rich environments is not new to Australia. In 1981, During the design of natural hyperbolic cooling towers for the Electricity Commission of NSW, BMG Laboratories undertook

extensive testing of the sulphate resistance of concrete using Munmorah fly ash.

The cooling water circulating within the towers reaches sulphate levels significantly higher than seawater and as such, selection of a resistant concrete was critical. As a result of the testing, 6 of these cooling tower structures, each 100 m in diameter and 130 m in height, were constructed using fly ash concretes. The performance of these structures has been excellent (as expected) and the research work has led to extensive use of fly ash concretes in sulphate-rich environments both in NSW and Queensland.

As reported in the companion technical note, the ADAA has sponsored research in progress at the CSIRO Division of Building, Construction and Engineering at North Ryde. The aim of the work is to assess the behaviour of Australian fly ash/cement blends in high chloride, sulphate and marine exposure conditions and to compare the performance with concrete containing other binder systems.

Stage 1 of the work (Cao et al 1994), reported below, assessed sulphate resistance both by the expansion of mortar bars and the degree of strength retention in mortar cubes stored in sodium sulphate solution under a range of conditions. Stage 2 of the work will involve tests on concrete specimens at two strength levels. These results will be reported when available.

The behaviour of fly ash blends in sulphate-bearing conditions was based on comparisons with portland cements: Type A (now GP)[A1,A2]; Type C (LH) and Type D (SR) produced to the superseded AS 1315-1982. The fly ashes studied were from power stations in NSW, SA & WA, designated FA1, FA2 and FA3.

The hypothetical mineralogical compositions of the portland cements are presented in the table.

| Composition (%) | Type "A1" | Type "A2" | Type "C" | Type "D" |
|-------------------|-----------|-----------|----------|----------|
| C ₃ S | 51 | 63 | 34 | 57 |
| C ₂ S | 22 | 10 | 39 | 17 |
| C ₃ A | 6.6 | 5.3 | 4.6 | 4.3 |
| C ₄ AF | 11 | 13 | 15 | 14 |

The expansion patterns, using essentially ASTM C 1012 test method, for mortars prepared with cement A1 and fly ash FA1 @ 0, 20 and 40% replacement (by mass) and Types C and D cements, are shown in figure 1.

The use of fly ash leads to reduction in the expansion of mortars compared with portland cement Types A, C and D. The portland cements show a rapid increase in expansion after 15 to 28 weeks of exposure. The fly ash blends show low expansions up to 52 weeks. Type C cement shows less expansion than Type D. The cements have similar C3A content but Type C has lower C3S.

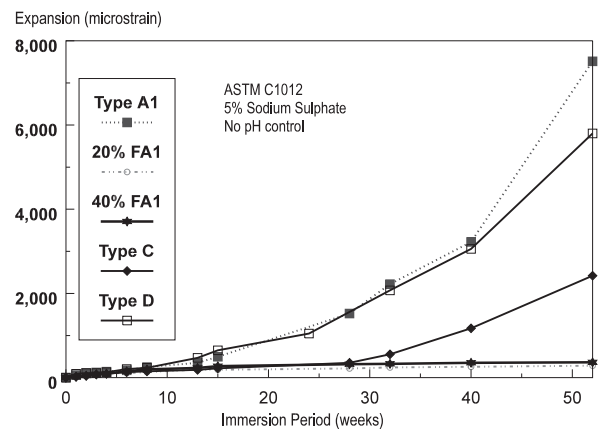


Figure 1 Expansion of mortar bars to ASTM C 1012.

The solution pH has been found to strongly influence the severity of sulphate attack. The pH of the solution is governed by the concentration of sulphate ions and other ions present. The pH of the 5% sulphate solution prepared to ASTM C 1012

(No pH control) changes from about 7 when freshly prepared to higher than 10 within a few hours of immersion of the specimens and has been found to be as high as 12. A solution at pH 7 better reflects that found in soil and sea water. Highly acid solutions, with a pH around 3 are found in some acidic soils, sewage water and industrial waste. Hence, expansions to ASTM C 1012 were also measured after storage in solutions maintained at constant pH of 7 and 3.

The relative expansion of the various binders after 52 weeks of exposure in 5% sodium sulphate at the three pH levels is shown in figures 2, 3 and 4.

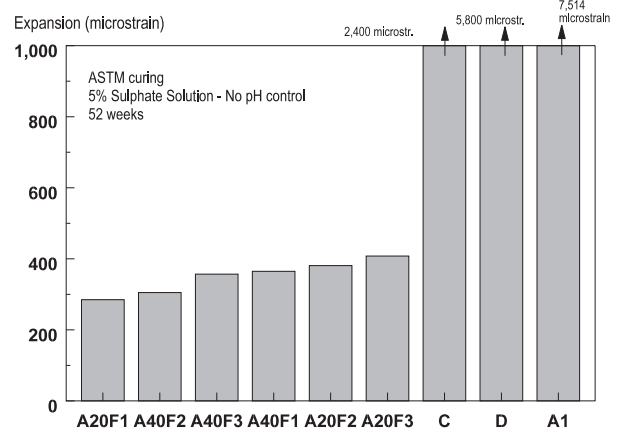


Figure 2 Expansion of mortars in 5% Na₂SO₄ solution to ASTM C 1012.

The results presented in these figures indicate that the binders containing fly ash show reduced expansion, compared to portland cements, at all three pH levels.

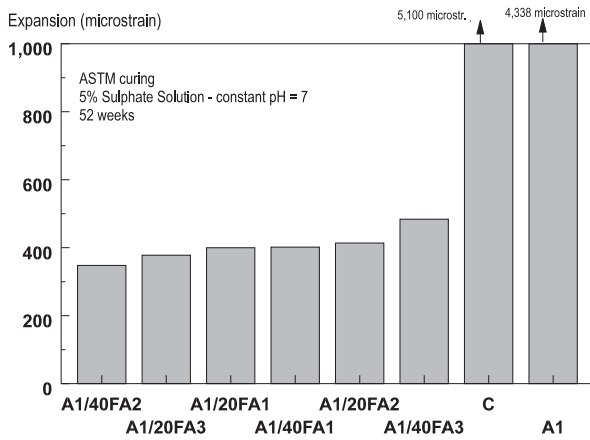


Figure 3 Expansion of mortars in 5% Na₂SO₄ solution at pH 7 to ASTM C 1012.

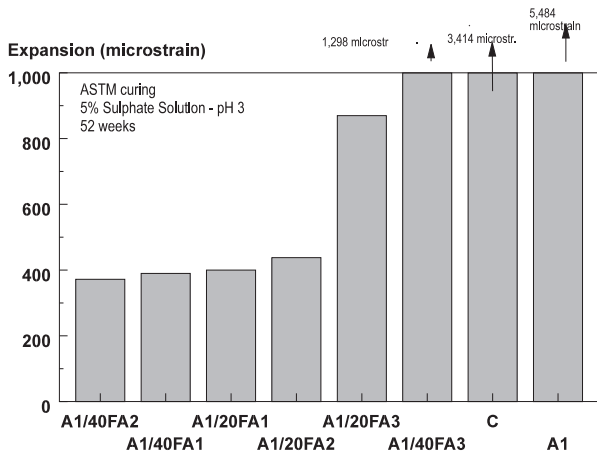


Figure 4 Expansion of mortars in 5% Na₂SO₄ solution at pH 3 to ASTM C 1012.

At pH 3, it should be noticed that sulphate resistance is significantly influenced by both the fly ash used and the replacement level.

Expansion is the most widely recognised mechanism of sulphate attack but, as was shown, the loss of binding and consequent loss of strength from decomposition of Ca(OH)₂ and C-S-H components should be considered an integral part of sulphate attack and the associated acid attack.

The strength retention of mortar cubes containing the binders studied in this work indicates that all portland cements used show strength loss after 6 to 12 months of immersion. All fly ash blends, particularly 40% blends, held or increased strength with time. A similar trend was observed in the case of mortar prism expansion at low pH and the attack of mixed sodium and magnesium sulphates on mortar cubes. These findings are shown in figures 4, 5, 6 and 7.

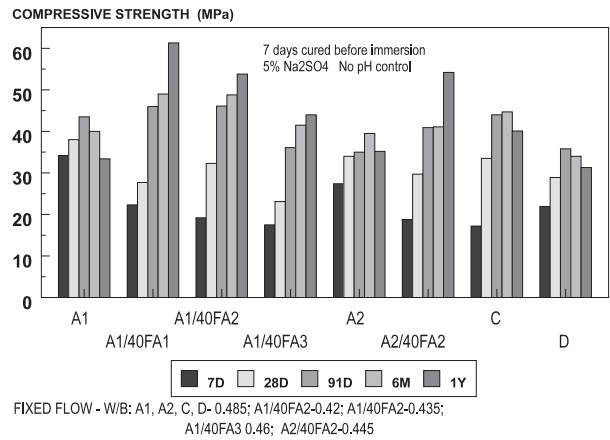


Figure 5 Compressive strength of mortars in 5% Na₂SO₄ solution.

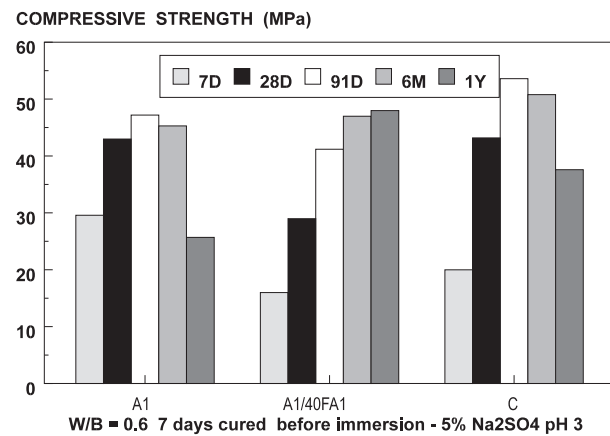


Figure 6 Compressive strength of mortars in a 5% Na₂SO₄ solution at pH 3.

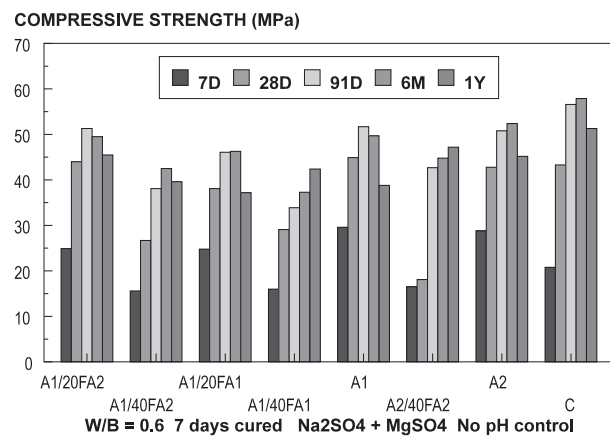


Figure 7 Compressive strength of mortars in a Na₂SO₄ and MgSO₄ solution.

The results indicate that the the type of fly ash, percentage replacement and fly ash/cement combination are all extremely important.

Compressive strength is a good indicator of the degree of attack when non-expansive, decomposition reactions are involved. Such reactions occur in low pH solutions (acid attack) and when magnesium ion exchange is involved.

The results indicate that the use of fly ash in concrete exposed to sulphate environments will significantly extend its service life. The optimum proportion is between 20 and 40% by mass of binder and is dependent on:

- the source and Grade of fly ash;
- the source and Type of cement;
- the blend proportions;

and most importantly:

- the types of sulphate (sodium, magnesium or combination)and
- the pH of the environment.

Ash Development Association staff are happy to assist in determining the most suitable combination for specific conditions.

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