SULPHATE ATTACK AND CHLORIDE ION PENETRATION: THEIR ROLE IN CONCRETE DURABILITY

Concrete durability continues to be a subject of controversy among design professionals, specifiers, Government instrumentalities, builders and developers, despite the significant changes made in the 90s to the Australian Concrete Code. This paper addresses two aspects of concrete serviceability, which has been the subject of extensive recent discussion and research: sulphate attack and chloride ion penetration.

The basic chemistry involved in each of these processes is outlined and differentiated and their effects on concrete and reinforcing steel described. The paper reports the recent introduction of performance tests intended to provide a means of assessing the contribution to resistance to these chemical actions of various cementitious binder options now available for inclusion in concrete. Reference is made to the increasing significance of supplementary cementitious materials in Australian concrete technology.

The paper relies for actual test data, showing relative performance of binder options, on experimental work carried out by researchers at the CSIRO Division of Building, Construction, and Engineering. The paper includes reference to other key factors contributing to concrete durability, in particular water/cement ratio, cover to steel, compaction and curing.

INTRODUCTION

Up until the 1970s the durability of concrete was rarely a concern to the community at large, design professionals, builders, developers or Government specifiers in particular. All this changed through into the 80s with phrases such as “concrete cancer” becoming common place in the media and society.

The response to what was to become a furore in some areas in this country, and indeed in many other countries, was much analysis and research into occurrences and their causes. This led in Australia to significant changes in the Concrete Structures Code (Ref 1) and review of site practices contributing to the situation.

The emphasis in the upgrading of AS 3600 at that time was to differentiate between exposure conditions basically dependent upon proximity of particular concrete structures to the sea, and/or the conditions to which immersed or buried concrete structures or elements might be exposed. Dependent upon these conditions, the quality of the concrete was upgraded in terms of strength; this was correlated with the amount of concrete cover the reinforcing steel required, which was increased in many structures.

ANALYSIS

The basis of these Code changes was summed up by Dr George Somerville of the British Cement Association (Ref 2) in the mid 80s with his “Four Cs of Concrete Durability”:

- Constituents of the concrete mix;
- Cover to the reinforcing steel;
- Compaction; and
- Curing.

The key constituents of all concrete mixes in this context (and most others) are the binder system and the amount of water present, most importantly as they combine in the calculation of water/binder ratio. The AS 3600 upgrade reflects the fact that in achieving higher strengths the necessary water/binder ratio must be reduced as shown in Figure 1. With that reduction in water/binder ratio comes a reduction in permeability of the concrete as shown in Figure 2. This then results in enhancement of the resistance of the concrete to physical penetration by all liquids no matter what they might contain. As discussed later, good construction practices, most significantly compaction and curing, assist in enhancing resistance to liquid penetration. If that liquid should contain sulphate salts and/or chloride ions the chemistry of the binder system in the mix comes into play. The resistance of concrete to such chemical attack/penetration has been the subject of much research in recent years.

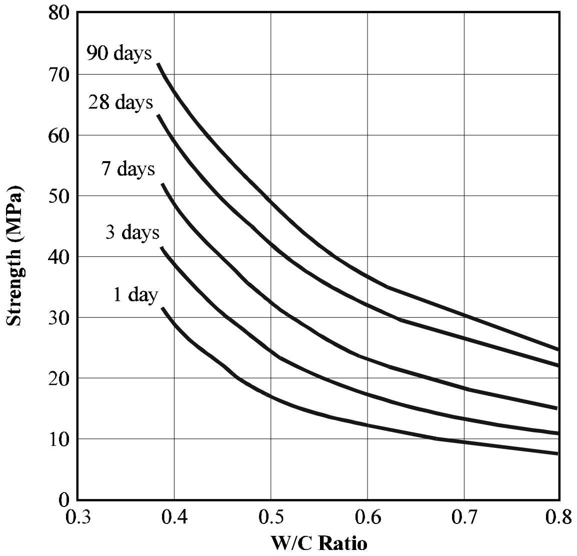

Figure 1: *Relationship between concrete strength and W/C ratio at various ages (Ref 3).*

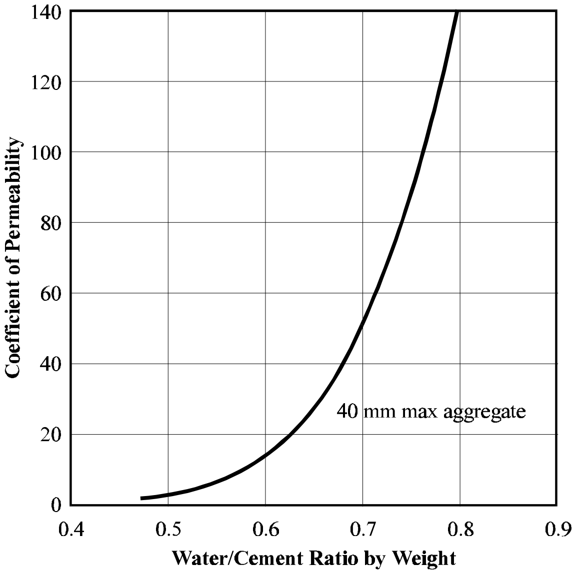

Figure 2: *Relationship between coefficient of permeability and water/cement ratio (Ref 4).*

THE CHEMISTRY OF SULPHATE ATTACK

The end result of sulphate attack can be excessive expansion, delamination, cracking, and loss of strength. The degree to which this attack can occur depends on water penetration (as referred to above), the sulphate salt and its concentration and type (eg sodium or magnesium), the means by which the salt develops in the concrete (eg is it rising and drying causing crystallisation), and the chemistry of the binder present in the concrete. These processes and factors have been the subject of intense study across the world in recent years and outcomes are reported widely, for example, the CSIRO work relating to Australian studies (Ref 5).

From these studies it can be summarised that at a concentration of about 0.2% sulphate content in the ground water, concrete may suffer sulphate attack; that magnesium sulphate can be more aggressive than sodium; and that there are three key chemical reactions between sulphate ions and hardened cement pastes. These reactions are:

- recrystallisation of ettringite;
- formation of gypsum; and
- decalcification of the main cementitious phase (C-S-H).

In the presence of the calcium hydroxide formed in cement paste, when the latter comes in contact with sulphate ions, the alumina containing hydrates are converted to the high sulphate form ettringite. These ettringite crystals grow, expand, or swell by mechanisms, which are still the subject of controversy among researchers. While there is agreement that most (but not all) ettringites will expand in this formation, the exact causes are not agreed.

The formation of gypsum as a result of cation exchange reactions is also capable of causing expansion but is normally linked to loss of mass and strength (Ref 5). CSIRO work shows that gypsum can cause considerable local expansion and cracking especially when formed in large masses.

The decalcification of the C-S-H has not received as much discussion as the other two types of sulphate attack, but can be just as important, particularly where the sulphate solution is lower in pH (ie more acidic). This particular reaction, with more gypsum formation, leads to both strength loss and expansion. This is a particular situation in which blended cements with lower initial calcium/silica (C/S) ratios in the C-S-H gel are shown to be less susceptible to this type of attack.

THE EFFECTS OF CHLORIDE ION PENETRATION

Once again, the first step in considering this process is the physical resistance to penetration into the concrete of all liquids, by reducing the water/binder ratio, and adequately consolidating and curing the concrete. By contrast with the complex chemistry of the sulphate attack process, chloride ion penetration is more physics in action with ion bonding and reduction, if not elimination, of these ions reaching the reinforcing steel. While the subject of much debate, the chloride threshold for corrosion is believed to be in the range 0.2 to 0.4%.

Once these ions reach the steel they depassivate the area surrounding the steel and in the presence of air/water, the steel commences to corrode. The products of corrosion are greater in volume (up to 600%) than the original steel resulting in an expansion and later spalling of the concrete.

However, in terms of the role of the binder, the objective is to come up with options, which will prolong the time to initiation of the corrosion and cracking. The development of this process has been graphically summarised in Figure 3 (Ref 6).

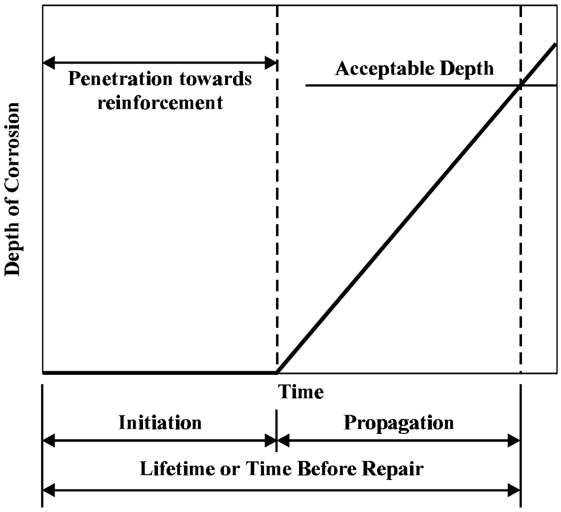

Figure 3: *Lifetime model (from Tutti).*

Corrosion is, in effect, an electrochemical process necessitating the formation of corrosion cells, with the formation of an anode and a cathode, either on one piece of steel or between two dissimilar metals. The anode reaction involving ionisation of metallic iron will not go far unless there is electron flow at the cathode: to achieve this there must be air and water at the surface of the cathode.

Thus the importance of reducing permeability of the concrete by mix design and construction practice become vital factors in reducing chloride ion penetration, steel corrosion and “concrete cancer”.

TEST METHODS FOR ASSESSMENT OF PERFORMANCE

Over the last decade there have been increasing pressures from the community and the construction industry to change standard Codes and specifications from a prescription to a performance base. This for example is manifest in the Building Code of Australia.
The challenge for specification writers and users in this context in relation to concrete has been the lack of applicable and appropriate performance tests. This has resulted in extensive research and subsequent test development, followed by introduction of performance criteria in at least some areas. This process has not been without controversy and even today debate continues about some of these tests, none perhaps more so than with regard to assessment of sulphate resistance and chloride ion penetration.

Resistance to Sulphate Attack

Review of world practice shows that there are two current standards in operation; in the order in which they were developed they came from the American Society for Testing and Materials (ASTM) (Ref 7) followed in 1996 by Standards Australia (Ref 8). It must be noted immediately that both these tests relate to mortar and not concrete and therefore focus on the binder system. While the basic concepts of the two test methods are similar there are some differences. For example, while they are both expansion assessment tests, the sample configurations, sand types, mortar mix designs, and curing regimes are different, as are the performance assessment criteria.

The overall objective with these tests is to assess the relative sulphate resistance of various binder options from traditional (basically low C_3A content) sulphate resistant cements, to the various blended cements which are now found to have excellent properties in this particular aspect of concrete technology. At this point in time the Australian test is being widely used in rating various binder options although as provided for in the Preface to the test method some refinements of the procedure may be agreed after its first two years of operation. At the present time the key issue seems to be the duration of the test (presently 16 weeks), the permeability of the mortar, and the degree to which a longer test will make it easier to differentiate the binder options.

Chloride Ion Penetration

At this time there is no applicable Australian Standard test. There are two American tests in use, with two very widely different approaches, each subject to controversy. Each test has had a range of variations to the procedure suggested by researchers. From ASTM (Ref 9) was developed a rapid chloride permeability test with an electric charge being used to accelerate chloride ion penetration through a thin section of concrete.

The American Association of State Highway and Transportation Officials (AASHTO) (Ref 10) developed the other approach. This involves a chloride ponding test of much longer duration.

Each of these procedures has their advocates and also their critics. For example, the ASTM test is the subject of much debate (Refs 11 & 12). The key issues here appear to be associated with pore chemistry and heat generated. The end result is of concern, in particular with regard to the test data obtained when there are materials such as fly ash, slag or silica fume in the mix. In the meantime, some organisations in Australia, such as CSIRO, have developed their own test methods. The chloride ion data reported in this Paper from CSIRO are based primarily on chloride profiles obtained on test specimens submerged in salt water.

AUSTRALIAN USE OF SUPPLEMENTARY CEMENTITIOUS MATERIALS (SCMs)

Fly ash and finely ground granulated iron blast furnace slag have been used in concrete in Australia since the mid 60s (Ref 13) and currently 800,000 to 1,000,000 tonnes of each are being used in concrete around Australia. Their use varies with geographic area, primarily dependent upon the location of the black coal fired power stations and steelworks in relation to the markets. The State of Queensland is well endowed with quality fly ash sources over much of the State but because it must rely on steelworks in New South Wales for slag, there is only limited use of this material outside the south eastern corner of the State.

Condensed silica fume, a by-product of the manufacture of silicon metal or ferro silicon alloy, is manufactured from only one source in Australia (south of Perth). Much has been imported from countries such as Norway. It is a very fine powder which is a powerful pozzolan but carries with it a significant cost premium.

The use of these SCMs has been found to impart a range of benefits to plastic and/or hardened properties of concrete, provided they are used properly.

The key to the successful use of these materials is knowing the technology of both the materials themselves and of the cements with which they are being associated. Mix designs, proportions of binder components, curing needs, relative rates of strength gain are all factors which must be remembered when using SCMs to provide the many benefits which can be derived. These include the well-established improvements in workability and pumping, reduction in generation of heat, and control of alkali silica reaction. To these must now be added improvement in resistance to chemical attack.

While consuming what are otherwise industrial wastes in a value-adding approach, the use of SCMs makes another significant contribution to the community. The high temperature cement clinker manufacturing process and subsequent cement milling processes can produce up to one tonne of greenhouse gas per tonne of clinker. The use of SCMs to reduce the amount of clinker per tonne of cement used can thus significantly reduce greenhouse gas emissions from the cement industry. Indeed the cement industry's target of reducing greenhouse gas emissions by the year 2005 to 17% below those in 1989 would be extremely difficult if not impossible to achieve without the ever increasing use of SCMs.

DATA DERIVED ON RELATIVE PERFORMANCE

In this decade, there has been intensive activity in a wide spectrum of laboratories throughout Australian assessing the relative performance of various binder options in resisting sulphate attack and chloride ion penetration.

Data derived in CSIRO research is reported below and indicates the particular attractions of using fly ash and slag in enhancing these critical aspects of concrete durability.

Sulphate Resistance Test Data

The effect of fly ash on mortar specimens prepared as per AS 2350.14 and cured in what quickly becomes an alkaline environment are shown in Figure 4. Introduction of 20% fly ash immediately and significantly reduces expansion. Indeed, this addition rate is marginally better than both 30 and 40% fly ash, but in any event, from 16 weeks, the fly ash mixes far outperform the GP cement mix.

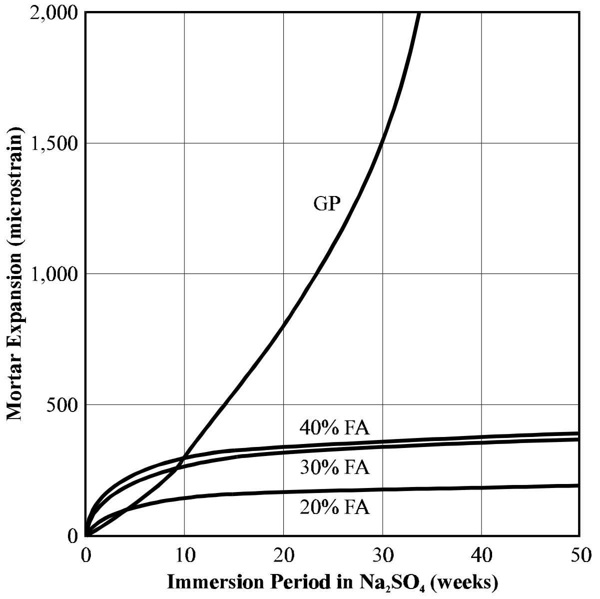

Figure 4: *Effect of fly ash on expansion - AS 2350.14 (ultimate alkaline environment - pH 12).*

In Figure 5, similar relative results are obtained with fly ash using the ASTM C1012 method.

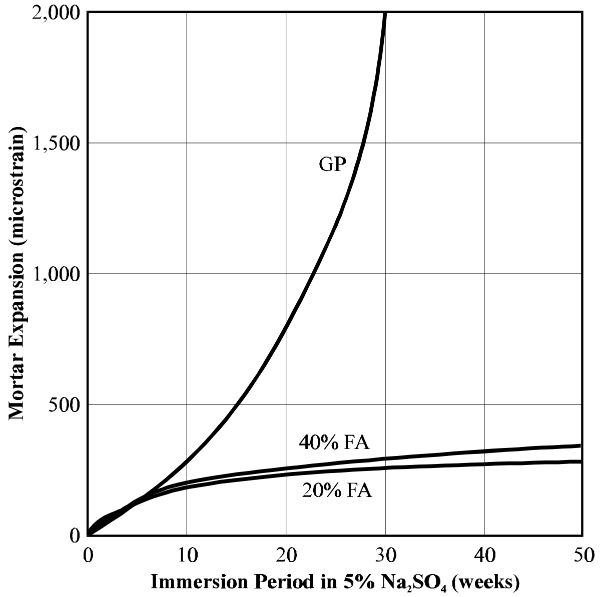

Figure 5: *Effect of fly ash on expansion - ASTM C1012 (ultimate alkaline environment - pH 12).*

In Figure 6, ASTM C1012 data is shown using a range of levels of slag replacement. However, while the benefits at ages up to 20 weeks are similar to those obtained with fly ash, at ages after 30 weeks the 40 and 60% slag replacement specimens start to expand. This highlights that key area of controversy with AS 2350.14. A strong case is being argued at present to extend the length of test from the present 16 weeks. In applying the Australian Standard data it should be remembered that the specification limit for sulphate expansion is 900 microstrain after those 16 weeks.

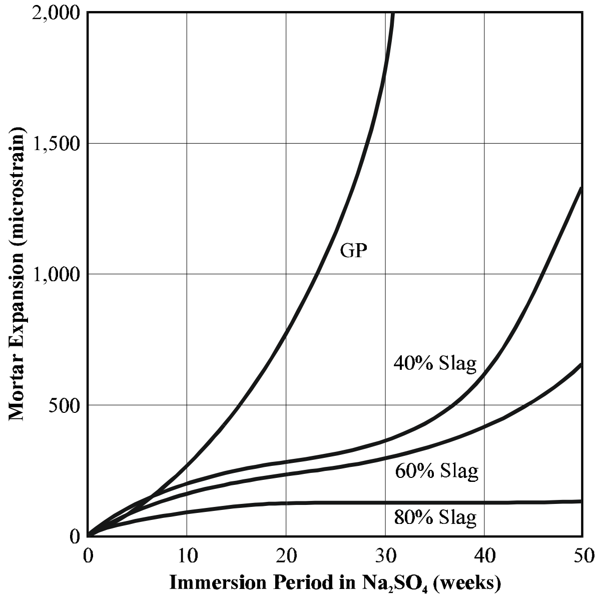

Figure 6: *Effect of slag on expansion - ASTM C1012 (ultimate alkaline environment - pH 12).*

Chloride Ion Penetration Data

As indicated earlier, the CSIRO research team working in this area has preferred to use an absorption based laboratory test and measured chloride profile with time. At the same time they have been carrying out field studies on chloride profiles and the data obtained are set out below.

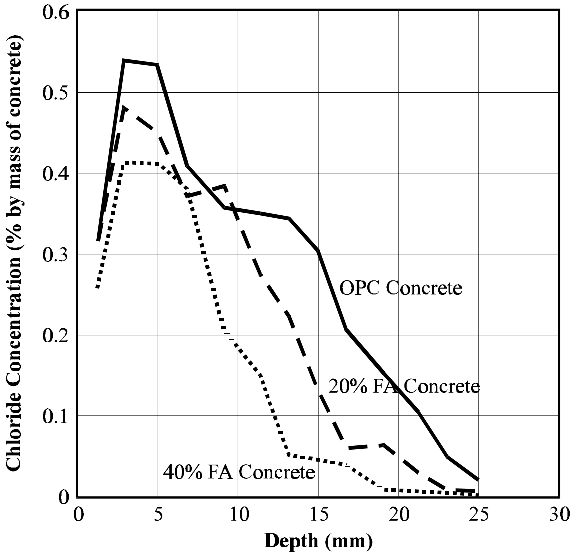

Figure 7: *Chloride profiles - Laboratory results: 32 MPa concretes, 80 mm slump, 3 days moist curing, 6 months of half immersion (tidal zone exposure) in ocean water.*

Figures 7 and 8 show chloride concentrations at different depths on 32 and 60 MPa concretes with ranges of fly ash contents. The significant improvement generated by inclusion of fly ash in both mixes is clearly apparent.

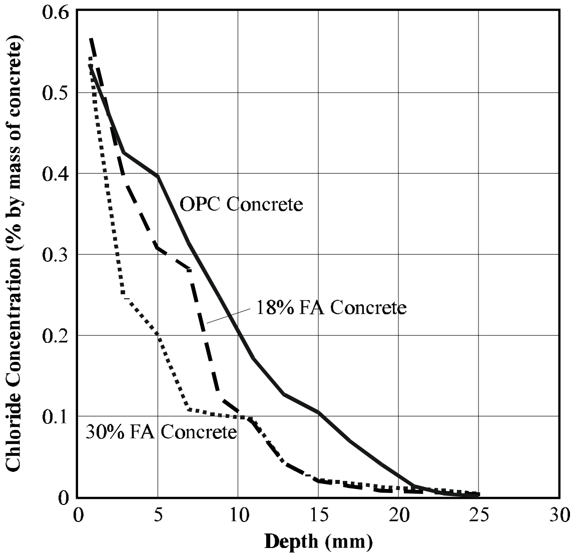

Figure 8: *Chloride profiles - Laboratory results: 60*

MPa concretes, 100 mm slump, 3 days moist curing, 6 months of half immersion (tidal zone exposure) in ocean water.

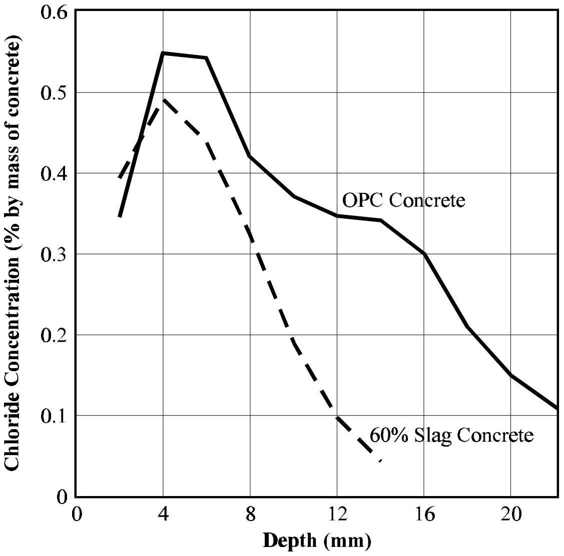

Figure 9: *Chloride profiles - Laboratory results: 32 MPa concretes, 80 mm slump, 3 days moist curing, 6 months of half immersion (tidal zone exposure) in ocean water.*

The corresponding data for 60% slag replacement of GP cement in 32 and 60 MPa concrete mixes are shown in Figures 9 and 10. However, it is most noticeable that in the higher strength, lower water/binder ratio (and therefore lower permeability) mixes, there is less difference between the OPC and fly ash and slag modified concrete.

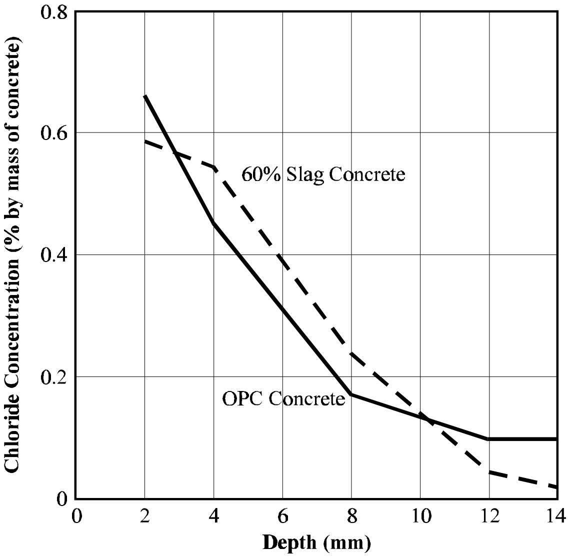

Figure 10: *Chloride profiles - Laboratory results: 60 MPa concretes, 100 mm slump, 3 days moist curing, 6 months of half immersion (tidal zone exposure) in ocean water.*

Further CSIRO data relating to 2 year ocean water immersion studies on concretes with total binder contents of 280 and 420 kg/m^3 are shown in Figures 11 and 12. Here the benefits of slag replacements are shown, while fly ash field performance data in a concrete seawall over 30 years old are shown in Figure 13. Further data on fly ash effects in a 2 year tidal zone test is shown in Figure 14.

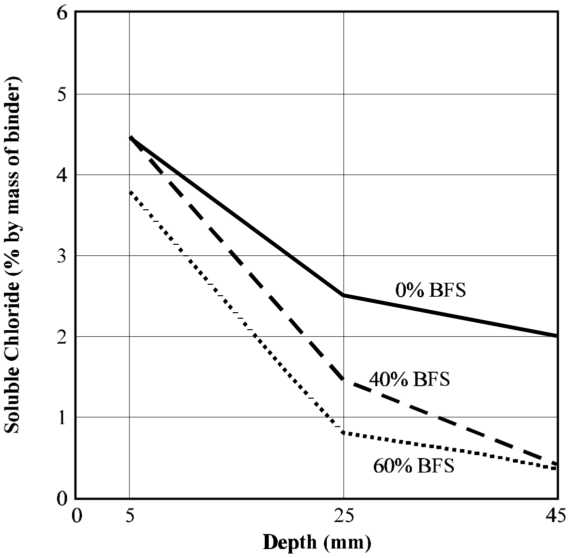

Figure 11: *Chloride profiles after 2 years immersion in ocean water - binder content 280 kg/m^3.*

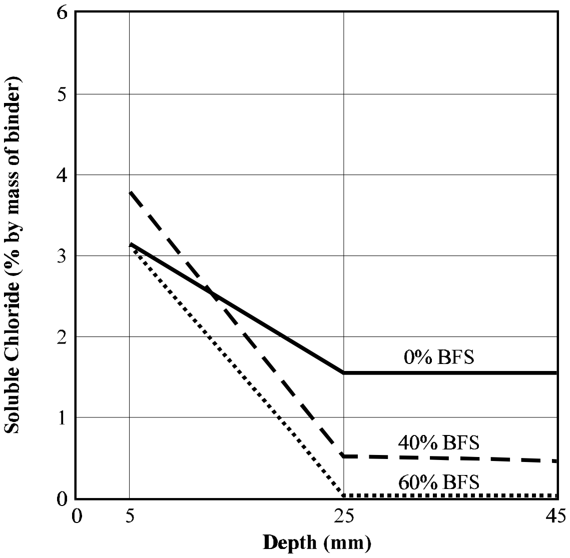

Figure 12: *Chloride profiles after 2 years immersion in ocean water - binder content 420 kg/m^3.*

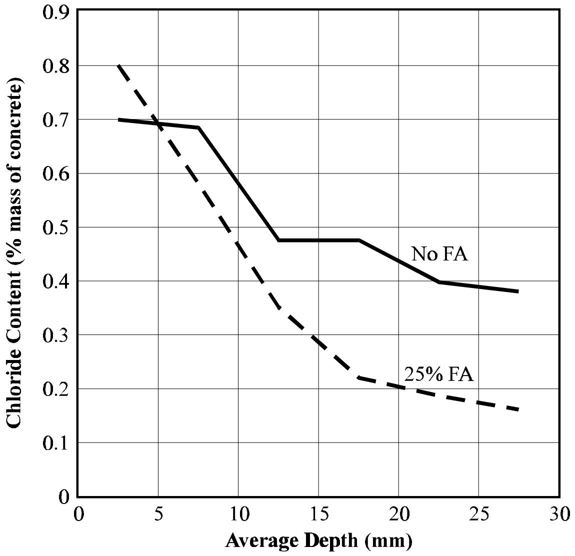

Figure 13: Influence of fly ash on chloride penetration - field data (concrete seawall + 30 years).

These test data, and those from many other researchers, highlight the benefits to be obtained in terms of reducing sulphate attack and chloride ion penetration from incorporating SCMs in concrete exposed to these aggressive conditions. However, in order to minimise such attacks, attention must be given to ensuring good construction practices.

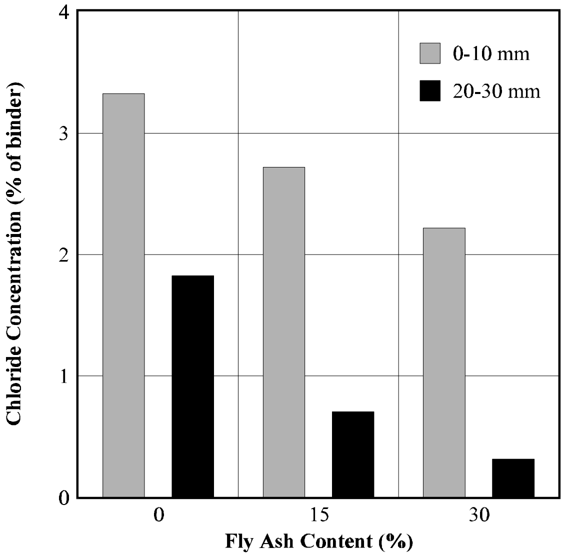

Figure 14: *Chloride profiles - Field results: 40 MPa concretes, 80 mm slump, 3 days of moist curing, 2 years of marine tidal zone exposure.*

CONSTRUCTION PRACTICES

The key issues in all forms of concrete construction, but in particular where durability is a concern most notably when exposed to aggressive environments, are compaction and curing. The achievement of dense impermeable concrete, no matter what the binder system, is fundamental to maximising concrete durability. Elimination of voids by good consolidation and full hydration of the binder to achieve a high quality concrete structure and least possible permeability by curing are objectives well known to concrete practitioners but all too rarely achieved in practice. Optimum use of SCMs to achieve maximum resistance to sulphate attack or chloride ion penetration typically uses mix proportions which can be vulnerable to premature termination (if started at all) of curing.

CONCLUSION

Resistance to sulphate attack and chloride ion penetration are two of the latest areas of durability concern to specifiers and users of concrete. Traditionally they were addressed by specifying cements of particular chemical composition, which were not always compatible (eg low C_3A for sulphate resistance, a higher C_3A for marine chloride resistance). The advent of quality assured SCMs capable of being evaluated using a range of performance tests is providing a sound base for revisiting the specification of concrete to achieve these particular durability objectives. While economic constraints may place some limits on the range of SCMs available in different areas of Queensland, data is being obtained which indicate that there is great potential for the use of SCMs to address these and other challenges in achieving durable concrete structures. Based on data reported from the CSIRO research project above, it would appear that in specifying concrete to resist sulphate attack or chloride ion penetration, a suitable approach would be as follows:

1. f’c of 40 MPa (to achieve a maximum water/cement ratio of 0.45 to reduce permeability); and
2. incorporation of at least 20% fly ash or 60% slag (either of which would also be beneficial in reducing any tendency for alkali silica reaction).

The technological developments reported in this paper, while significant in themselves, do not obviate the ongoing challenges to the concrete construction industry of the world, in particular ensuring full compaction of concrete in situ and provision of adequate curing.

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