Moving from Chemically Resistant Cement to Chemically Resistant Concrete

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1. Introduction

The history of sulphate resisting cements provides an insight into the changing situation of measures to prevent sulphate attack	
@1890	Le Chatelier suggests substitution of C_4AF for C_3A
@1900	Germany manufactures "Erz cement" a very low alumina:iron oxide ratio cement
1920	Ferrari produce cement with Al_2O_3:Fe_2O_3 <1. Type comes known as Ferrai cement
1921	American Portland Cement Ass. extensive testing.
1930	Canada produces first low C_3A cement standard
1940's	Low C_3A cements introduced in USA and UK
1951	US dept of agriculture extensive tests in sodium and magnesium sulphate solutions. Obtain broad correlation between performance and C_3A content
1965	BS4027 - 3.5% C_3A max in sulphate ground water
1968	ASTM C150 - 5% C_3A in sulphate ground water
1990	First paper on poor performance of low C_3A cements in low sulphate concentrations
1990's	Extensive documentation on the good performance of fly ash, slag and Microsilica but some concern regarding use of Microsilica and slag at magnesium sulphate concentrations
1998	Australian standard reverts to a performance based (expansion) for sulphate resistance

The title of the paper is not technically correct. Chemical resistance has always been considered as a combination of the chemical reactivity of the binder and the concrete penetrability of the paste as determined by w/c ratio. The old paradigm was to specify low C_3A cement as the predominant requirement and a low w/c ratio was often considered as secondary. Historically very low w/c ratios have not been possible and most in ground concrete, the predominant area of chemical attack, would have had w/c ratios of 0.45 and above. At these w/c ratio the concrete is quite penetrable and w/c ratio would have a low overall effect. Hence it is not surprising that research focused on chemical resistance. Over the last 20 years very low w/c ratios have become possible and use of Supplementary Cementitious Materials (SCM's) common place. At the same time shortcomings in the use of low C_3A cements has led to a radical revision to the approach to concrete's chemical resistance. The outcome of this change is that there is now greater emphasis on the concrete's chemical resistance rather than relying on the chemistry of the cement.

2. Preliminary Considerations

Before discussing the chemical attack mechanisms it is important to consider some factors that impact the durability analysis.

Chemical Resistance Tests

Chemical attack of concrete is a confusing area for designers not least because of these radical changes and the lack of a clear explanation of the mechanisms of attack in all cases.

All deterioration processes are controlled by a combination of the rate of penetration of the aggressive element and the reaction rate once penetrated. Hence, to assess how a mix will perform, account has to be taken on concrete's penetrability and chemical properties. This is often overlooked in accelerated tests where, in order to get rapid results, the aggressive concentration is increased to speed the chemical reaction while nothing is done to influence the penetrability. This will favour the chemically resistant rather than impermeable materials i.e. low C_3A cements will look better than in practice, and Microsilica concrete will look worse than in practice.

> ***"No single theory exists for predicting the sulphate resistance potential of blending components or blended cements, although from limited laboratory and field test attempts have been made to develop empirical guidelines for evaluating the suitability of individual blending materials". PK Mehta 1988.***

Where cement pastes and mortars are used rather than concrete the influence of permeability is even more markedly reduced. Mars notes *"Sulphate media penetrate mainly through interfacial zone"*. However the interfacial zone is strongly influenced by the concrete's cohesion. In high bleed mixes the interfacial zone could be 50 micron thick with aggregate only 100 micron apart. These channels form a virtual network through which contaminated water can rapidly permeate. Where mortars are used in tests these channels do not exist and the effectiveness of microsilica in eliminating these channels will not be established.

Other important factors in a test are:

- The sample size. One inch mortar cubes are frequently used. While these accelerate the rate of attack as six surfaces and many edges/corners are available for attack rather than the one surface and no edges/corners in real world concrete.
- The replenishment rate of the chemicals. This is taken into account in ground exposures by considering the permeability of the ground but no tests have been undertaken at different replacement rates.
- The chemical reactions that take place may lead to a protective layer on the concrete (or at least in the surface concrete pores). The formation of this layer, and its potential deterioration in certain circumstances needs to be accounted for.

These aspects, and the different rankings given by different tests, leads to no performance test being free from criticism. Hence while tests remain the best way to compare performances they are not absolute measures of performance. For example 1 inch mortar cubes with a w/c of 0.45 are attacked relatively quickly in seawater exposure tests but concrete with a w/c ratio of 0.45 and in real world seawater is not. Hence all chemical resistance tests should be undertaken with samples of known performance used as a point of reference. Santhanam 2001 reports on brine (2 x seawater concentration) attack on 25mm mortar cubes. Although the rate of attack seemed high it was less than twice the rate of attack on samples in seawater. The seawater tests provided an essential reference point for the high concentration test results.

Where an assessment of actual insitu performance is required both penetrability and chemical resistance must be taken into account. Many contend the cement system is all important while others suggest that if the concrete is sufficiently impermeable chemical attack will be limited. Mehta 1988 states "*Sulphate attack is limited to the surface and is usually of no consequence when the concrete is impermeable. Therefore the reduction in permeability alone that occurs as a result of the use of pozzolanic material becomes a major factor".* The views of the former may have been determined by the lack of testing at low w/c ratio while those of the latter may be influenced by testing of chemical of low aggresivity.

When considering penetrability of the concrete it is important to bear in mind there are various penetration mechanisms involved, i.e.:
Permeability – penetration due to a pressure head
Sorptivity – penetration due to capillary rise
Diffusion – penetration due to ionic concentration differences

Penetrability is further compounded by the differences that can occur in a concrete's pore structure.

Design Life

Use of Lowest Economic Lifecycle Cost (LELC) is the most suitable durability design approach but has to place a financial value on all aspects of initial costs, maintenance expenditure, replacement cost, operational cost, public costs, disposal cost and residual value. Its introduction causes considerable discussion on replacing items at intervals rather than designing them to last the life of the structure. The concept of replacement interval has been introduced to reduce unnecessary expenditure on design for long life where it is cheaper to replace at intervals. This was a consideration for a salt mine bridge deck where it was most economic to design using replaceable precast concrete panels with a design life of 20 years rather than designing using alternative materials with a longer life.

Using discounted cash flow with typical public expenditure rates, it can be shown that if cost of construction for a 100 year replacement interval is 10% greater than the cost of construction for a 50 year replacement interval, it is cheaper to design for 50 year replacement intervals. For practical concrete designing, three replacement intervals have been found appropriate as shown in Table 1.

Table 1: Replacement Intervals for Concrete Durability Design

Replacement Interval	Typical Element Type
20 years	Easily replaced items which come as standard items (i.e. high cost to upgrade) such as precast pit covers.
50 years	Moderate replacement cost (e.g. replacement cost less than 5 times initial cost). For example many elements of civil structures.
100 years	Very high replacement cost, e.g. parts of bridges where replacement interrupts traffic; major structural supports such as diaphragm walls and piles.

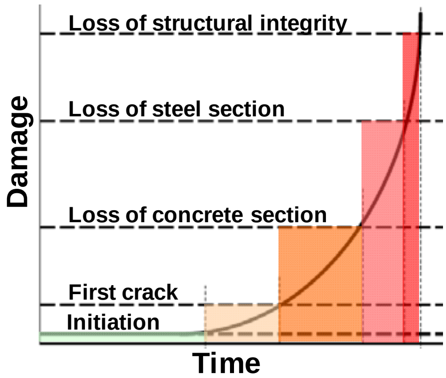
At higher discount rates, eg for industrial plants, designing for shorter replacement intervals becomes economic.

Allowable Damage

In corrosion studies the concept of defining the allowable damage as part of the durability design is well accepted (Figure 1). The same concept should be applied to all durability analysis including chemical attack. Codes and standards suggest allowable concrete mix designs for different exposures but give no guidance on what level of damage is allowable.

On one project where the concrete was subject to brine the structural engineer initially suggested a damage allowance of 20 mm but changed this to 0 mm when loads increased. This change meant that unlined concrete would no longer be suitable. A change in design later increased the allowable loss of section to 30 mm and made unlined concrete possible.

Figure 1 : Allowable damage concept used for rebar corrosion



Where there is no other structural analysis the cover to reinforcement can be taken as the limiting factor. Sufficient cover must remain to ensure the reinforcement stress is transferred to the concrete. However other damage criteria might include colour, cracking, expansion, loss of fibre performance, rebar corrosion risk and thickness. Expansion is particularly important as it can induce cracking and may disturb operations.

Risk Assessment

The concept of risk assessment for durability assessment is not new. It is a standard method in Alkali Silica Reaction assessment. Australian and New Zealand requirements include the structures significance in the assessment of protection requirements. A more formal approach to risk assessment can be used based on AS 4360's two dimensions as shown in Table 2.

The process of identifying risk, evaluating and minimising the likelihood and/or consequences of potential element failure ensures financial and performance requirements of built assets are controlled.

Table 2 : AS 4360 Risk Assessment

Likelihood of failure		Consequence of Failure				
		Neg.	Low	Mod.	Very High	Extreme
Rare	Only in exceptional circumstances	Neg.	Neg.	Very Low	Low	Mod.
Unlikely	Could occur at some time	Neg.	Very Low	Low	Mod.	High
Possible	Might occur at some time	Very Low	Low	Mod.	High	Extreme
Likely	Probably occurs in most circumstances	Low	Mod.	High	Extreme	Extreme
Almost certain	Expected in most circumstance	Mod.	High	Extreme	Extreme	Extreme

Risk assessment for durability planning involves assessment of the likelihood of failure and the consequence of failure. Where the consequence of failure is high the likelihood of failure must be suitably low.

Table 3: Assessing Consequence of Failure

Rating	Ability to repair (consider disruption and access difficulty)	Cost of repair	Deterioration if left unchecked
1	No disruption to operations and access by normal maintenance equipment.	Rectification would be part of normal maintenance.	Deterioration likely to be self stifling.
2	Minimal disruption to operations or some low cost specialist access equipment required.	Repair could be undertaken by modest increase in normal maintenance budget.	Deterioration would continue at a slow rate.
3	Access possible with expensive specialist equipment or repair would lead to obvious disruption.	Repair costs would be significantly outside a normal maintenance budget.	Deterioration would continue at a accelerating rate.
4	Access is possible but cause significant disruption to operations.	Repair costs would require significant additional project funding.	Deterioration would accelerate rapidly but would not cause major increase in cost of repair.
5	Access is not possible without removing the element or repair would lead to major disruption.	Repair cost would approach or be greater than the cost of original cost of construction.	Deterioration would rapidly accelerate and then lead to major increase in cost of repair.

The Durability Consultant cannot consider all parts of the risk assessment in isolation. Safety and cost to operation must be considered with the designer and possibly the client. For example, for buried structures on the Perth Metro the Durability Plan assessed each element for consequence of failure based on a combination of the ratings in Table 3.

Early warning signs given by testing can eliminate or reduce the risk of catastrophic failure. Where testing and monitoring is not feasible the only way of reducing the risk to an acceptable level may be to increase the durability of the element. Whereas durability design of elements whose performance can be monitored might be undertaken to the 95% confidence level, buried elements may need to be designed at a 99% confidence level. Higher levels may be appropriate depending on the critical nature of the element and the outcome of the durability risk assessment.

Exposure Assessment

The requirements for chemical exposure assessment are not defined in any standard and this leads to considerable misinterpretation. This problem can be envisaged from the common problem of in ground assessment.

Specifications for geotechnical assessment do not provide details of the extent and type of testing required. Hence the geotechnical engineer is forced to be competitive and do the absolute minimum he considers will fulfil the subjective brief of providing data on the ground aggressiveness. This often means that the geotechnical report provided to the Durability Consultant contains insufficient information on which to base an exposure assessment and additional testing is called for. Hence, to save time and cost the design engineer needs to ensure the specification contains sufficient details that a reliable assessment of ground exposure severity can be made.

For small projects the assessment might be simply based on a few test results to show the general exposure but on a large project the specification might comprise something like:

1) The previous use of the land shall be assessed to identify any chemical exposure that needs to be considered in the durability design. Where industrial contamination is expected then the ground shall be specifically tested for the chemicals involved. The area involved shall be divided into zones of likely equivalent contamination and in each zone a minimum of 3 samples shall be tested at each depth increment to be considered. The design exposure for each depth in each zone shall be taken as the characteristic concentration. The results of the assessment shall be included in an exposure section in the geotechnical report.

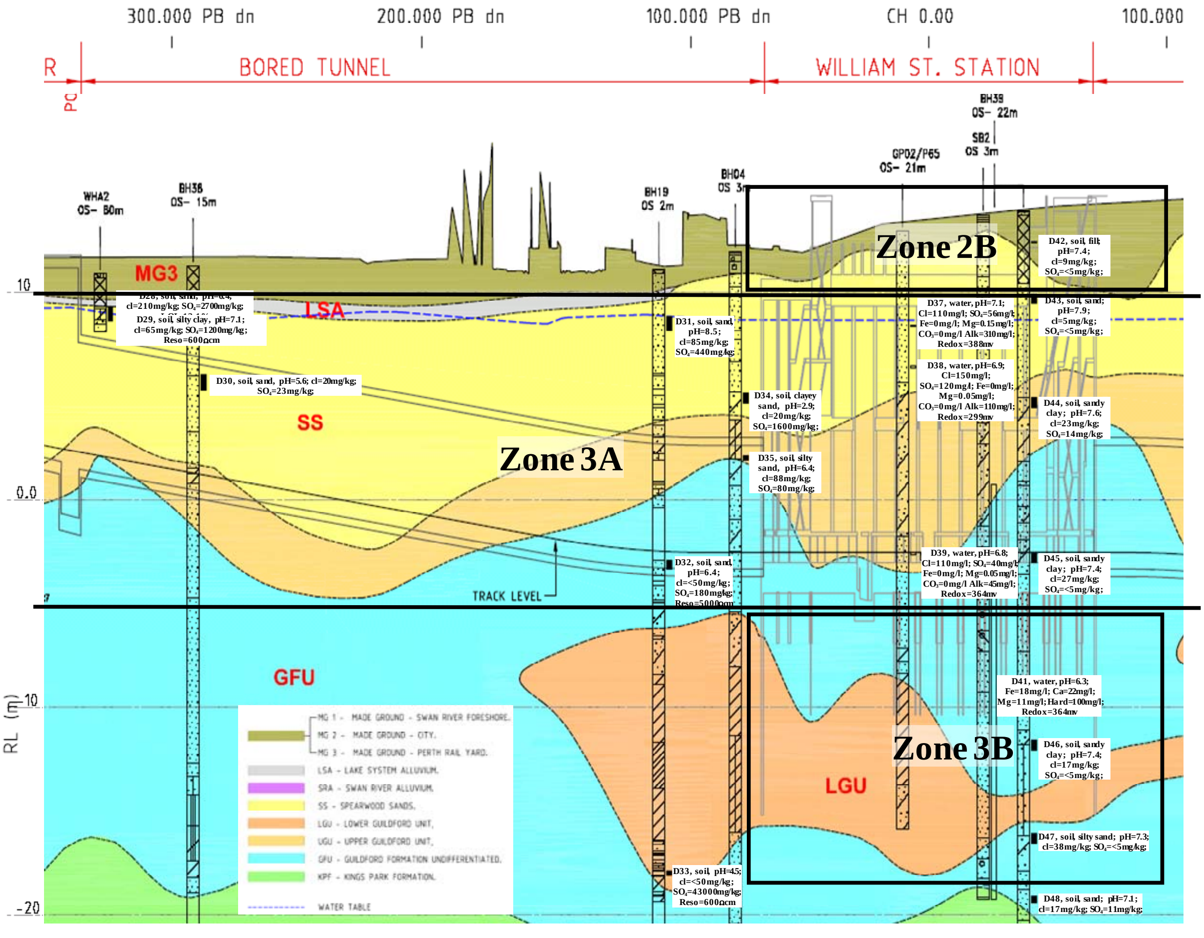
2) The ground shall be divided into durability strata that might contain significantly different exposures. These durability strata shall be determined from the borehole logs of geotechnical investigations for this project and previous assessments and from government geological plans. The geotechnical engineer may use standard geotechnical strata to define the durability strata where appropriate but shall not where exposure may differ with depth or proximity to other geophysical features. The durability strata shall be described in an exposure section in the geotechnical report.

3) The exposure of each durability strata shall be defined by the characteristic concentration from a minimum of 3 samples.

4) The durability strata, test data and general arrangement of the structure shall be overlain and from this various durability strata may be combined by an experienced Durability Consultant to define exposure zones (Figure 2). The concentrations assumed for each exposure zone shall be the highest concentration of the durability strata contained.

5) The likely mechanisms of attack shall be defined by the Durability Consultant based on the chemical exposure and the rate of attack determined by the attack mechanism, replenishment rate of attacking medium, the protection afforded by the reaction products and the mechanical aggressiveness of the exposure.

Figure 2 : Example of overlaying geological strata, the structures general arrangement and test results to define the exposure zones



3. Sulphate Resistance

The use and deterioration of concrete in environments containing sulphates has led to the development of special sulphate resisting cements. It has also spawned significant research into the use of supplementary cementitious materials to improve sulphate resistance.

The major problem in assessing materials is that the form of attack in sulphate environments is variable and the mechanistic theory is complex and uncertain. For most specifiers concrete mix design is a small part of a project and they may have no experience in the chemistry of cement. Hence, they often opt for the easy answer i.e. the industry norms. The old ‘industry norm’ was to use low C_3A cement in sulphate environments. Today this is recognised as both expensive and generally inappropriate.

The case against low C_3A cements

Low C_3A sulphate resisting cements (Type V) have a low C_3A content to minimise the risk of sulphate attack. However, this does not necessarily provide immunity and can provide other problems, i.e.:

a) Sulphate resisting cement provide less protection than expected:
There are two mechanisms that cause deterioration due to sulphates i.e. ettringite formation and an acid form of attack. The acid form of attack is predominant at high concentrations, i.e. the concentrations used in accelerated tests, while ettringite formation is predominant at low sulphate concentration, ie more typical of in ground conditions (Figure 3). Hence accelerated tests may not even represent the mechanism of attack that occurs in real world exposures.

Fidjestols 1989 undertook tests over an extended period in low sulphate concentrations (Figure 4). He showed that low C_3A cements might have a lower performance than OPC cements. Hence low C_3A cements should not be used in low sulphate concentrations.

b) Low C_3A cements are more susceptible to reinforcement corrosion:
Early work by Page (Figure 5) showed that chloride diffusion is dependent on the cement paste chemistry. As chlorides penetrate some chlorides complex with the chloro-aluminates to form Friedal Salts. It is the free chlorides (i.e. those not complexed) that penetrate to the steel to initiate corrosion. The extent of chloride binding, and hence the diffusion results depend on:-

- C_3A content. High C_3A cement concrete complexes more chlorides than low C_3A cement concretes. Hence, sulphate resisting cements exacerbate corrosion initiation. High C_3A (>12%) may lead to other problems, hence moderate C_3A cement, ideally 8-10%, for chloride structures is preferred.
- Chlorides diffuse through the water in the pores. Dry and low penetrability concretes have low diffusion rates. Microsilica 600 concretes have very low diffusion rates due to a combination of a high chloride complexing (using moderate C_3A cements) and low penetrability (Figure 6)

c) low C_3A cement may have to be stored as it may not be readily available

d) low C_3A cements provide lower 28 day strengths and slower strength gains.

e) *low C_3A cements may be expensive*

f) it may be difficult to make silos available for low C_3A cement and cement for other applications

In Australia and New Zealand low C_3A cements are not stipulated but overseas there are still specifications where low C_3A content is the basis of achieving sulphate resistance. Where overseas designers specify low C_3A cements the basis for the specifications should be questioned. Unless there is a sound reason for the requirements it is likely to be advisable to change the requirements to use of SCM's and controlled penetrability.

Cation Effect

It is well recognised that the cation has a major effect on the severity of chemical attack. The cation determines the nature of the attack on the cement paste and the final reaction products (Figure 7)

Figure 3 : Change in type of attack with increasing sulphate concentration

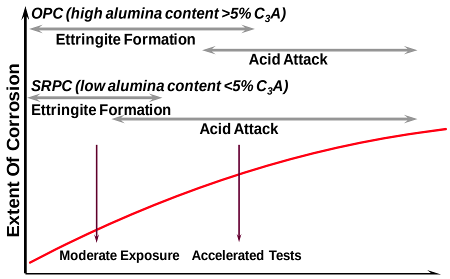


Figure 4 – Deterioration in low sulphate concentrations

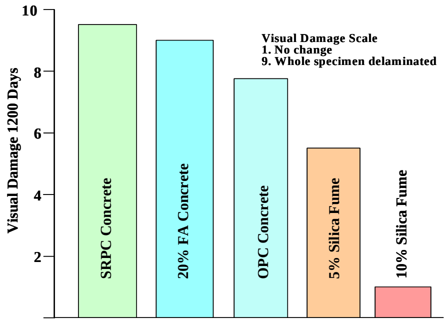


Figure 5 - Affect Of C_3A On Chloride Complexing and Chloride Ingress

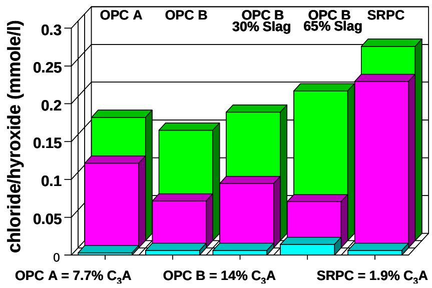


Figure 6 – Time to initiation for various binder types

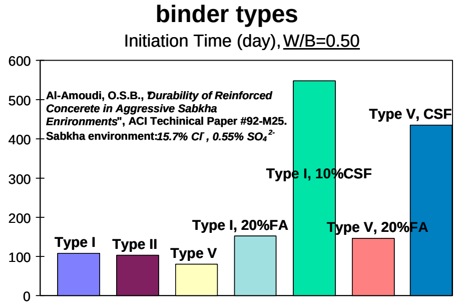
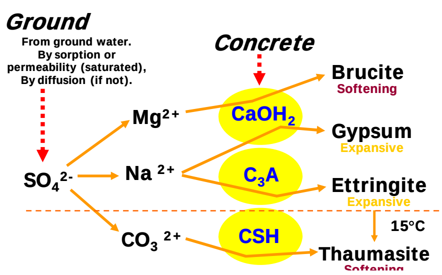


Figure 7 : The cation determines the attack mechanism and rate



Magnesium Sulphate : Magnesium sulphate, reacts with the lime to form gypsum and magnesium hydroxide. However, the magnesium hydroxide that is formed has a lower pH than that of the lime it is displacing. The CSH is unstable at this low pH and decomposes with release of lime. Thus, more lime becomes available to react with the attacking sulphate solution resulting in the formation of more magnesium hydroxide. The process continues with loss of CSH and concomitant loss of structural strength.

Aluminium Sulphate : Aluminium sulphate, which is widely used in fireproofing and waterproofing fabrics as well as in waterproofing concrete, is more acidic than magnesium hydroxide, and so can be expected to be even more aggressive than magnesium hydroxide. It is not clear whether the presence of the aluminium may also play an accelerating role by contributing to ettringite formation.

Ammonium Sulphate : Ammonium sulphate is the most damaging of the sulfate salts, possibly because gypsum is soluble in ammonia solutions and so may be rapidly leached away, allowing the reaction between the sulfate and the lime to proceed at a faster rate.

Sulphuric Acid : The most aggressive sulphate is sulphuric acid which reacts rapidly with the lime and has the potential to significantly reduce the pH and so promote the decomposition of the CSH.

Calcium Sulphate : Calcium sulphate that is either present in the attacking medium, or that is formed by the reaction of other sulphates with the lime in the cement paste, may react with the tricalcium aluminate in the cement paste to form ettringite. Ettringite is not stable in the presence of alkali sulfates, so it seems the reaction to form gypsum is an essential first step to ettringite formation.

This can be seen from the old paradigm where low C_3A cements were the primary means of specifying sulphate resistance.

Penetrability

The Portland Cement Association research shows that in general terms concrete deterioration was controlled when exposed to sodium sulphate concentrations up to 65,000 ppm provided that the w/c ratio was below 0.4 but at w/c ratios above 0.4 cement type was significant. These 12 year studies tested over 50 mixes and also showed that wet dry cycling was far more aggressive than continuous immersion and that if expansion was less than 200 µs at 3 years there was no subsequent rapid expansion. The US Bureau of Reclamation showed that after 40 years exposure to 21000ppm concrete with a w/c below 0.45 had little deterioration.

Testing for sulphate resistance

Many different methods based on various criteria have been developed to assess sulphate resistance. No method has emerged which is free from criticism, possibly because different methods lead to a different ranking order for various binder types.

Most testing is undertaken on mortar samples as concrete introduces additional variables and makes testing more labour intensive. However testing on mortar samples introduces a number of problems:

Penetrability plays is a major part in the deterioration process, particularly penetration of the sulphate solution around the interface layer between aggregate and paste. This layer does not exist in mortars or small concrete samples but does become a major factor in real concrete pours. As mortar sample do not pick up this effect it will also mask improvements in permeability reducing remedies such as Microsilica 600.

All test methods expose a sample to a solution of sulphates. Variables include:

- Concentration of sulphate
- Type of sulphate

There are two different type of deterioration. The one thought to be most predominant is due to the formation of ettringite which is expansive. Hence, its not surprising that the most common form of testing is to measure expansion. All expansion tests are undertaken on mortar bars but variable include:

- Size and shape
- Cementitious content
- Water:binder ratio

Standards

Table 4 shows the exposure criteria of various standards for different sulphate exposures. The current version of AS 3600 is particularly unhelpful requiring the designer to determine requirements for anything over 1000ppm sulphate. AS 3735 uses the same exposure classes as BRE digest 1 and the DIN code while NZ 3101 follows EN 206-1. All are remarkably similar and are little changed from older British Standard requirements (Table 5). The concrete requirements from British and Australian Standards of the 1980's are given in Table 5 & 6. What is remarkable is that the lowest w/c ratio specified is 0.45 although it had been recognised for many years before that that lower w/c ratios will give far better protection and hence higher concentrations would be tolerated without protection.

Table 4 – Comparison of Exposure Classes From Different Codes (Groundwater SO_4 mg/l)

Class	BRE D1 Din 4030 AS 3735	Class	AS3600	AS3600 Draft	Class	NZ 3101 EN206-1
DS1	<400	A2	<1000	<1000	XA1	200-600
DS2	400-1400					
DS3	1400-3000	B1		1000-3000	XA2	600-3000
DS4	3000-6000	B2		3000-10000	XA3	3000-6000
DS5	>6000	C		>10000	U	>6000

Table 5 –Circa 1980 British Standard Requirements For Sulphate Environments

Class	SO_4	Mg	Cement Type	Cement Content	w/c
1	<400	(1)	Type 1 OK	Refer to Design Exposure Class	
2	400-1400	(1)	Type1, FA,Slag or Type V	330 300 280	0.5 0.55 0.55
3	1400-3000		FA,Slag or Type V	340 320	0.5 0.5
4a	3000-6000	<1000	FA,Slag or Type V	360 380	0.45 0.45
4b	3000-6000	>1000	Type V	360	0.45
5a	>6000	<3000	As Class 4 + surface protection		
5b	>6000	>3000	As Class 4 + surface protection		

Notes:

1. Where the SO_4 is less than 1.4 the solubility of the various salts suggest that sodium and magnesium salts are absent.
2. Silica fume is not referred to. Probably because it was not generally available in the UK.
3. In basements subject to hydrostatic pressure, requirements of each class should be increased by one level.
4. In static water class requirements may be dropped one level.

Table 6 – Circa 1980 Australian Standard Requirements

	Sulphate (mg/l)			w/b	
Class	Total SO_4 +	$MgSO_4$	$AlSO_4$	Type V Cement	30% FA or 70% Slag
1	<300			None	None
2	300-1200+	<1000	<250	0.55	0.5
3	1200-2500	<1000	<250	0.50	0.45
4a	2500-5000	>1000	250-1000	0.45	⊥
4b	2500-5000	<3000	>1000	0.45	⊥
5a	<5000	>3000	>1000	0.45	⊥
5b	>5000			NA	NA

* Total SO_4 including $MgSO_4$ and or $AlSO_4$.
* Minimise cement content for best performance provided workability and segregation do not become problematical.
\+ Below 1200mg/l sodium, magnesium and aluminium sulphate unlikely to be present. Sulphates most likely calcium
⊥ Requires specific checks
In deep basements increase requirements by one grade.

It is clear that in the 1980's and 1990's that the use of SCM's were overtaking the use of low C_3A (type V) cements. Although the influence of w/c ratio and SCM's has been demonstrated the current codes are still very restrictive on the limit of sulphate concentration. The draft of AS 3600, reliably predicted to be released by December 2009, now contains the highest provisions for uncoated concrete at sulphates of 10,000 ppm (Table 7). This is particularly notable as it does not differentiate between the form of sulphate or the replenishment rate.

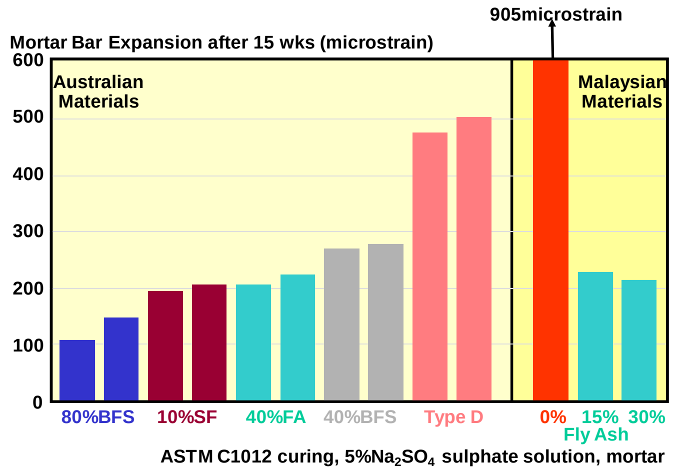
Table 7 : Requirement of the Draft of AS3600

Class	In water mg/L	Strength (MPa)	Cement	Cover	Coating	Protection over that normally required
A2	400-1000	25	-	50	-	+20mm
B1	1000-3000	32	SR	50	-	+10mm+SR
B2	3000-10000	40	SR	50	-	+5mm+SR
C1	>10000	50	-	65	Required	+coating

Table 7 shows that an SR cement is required for higher levels of sulphate. This is not a low C_3A cement but rather any cement that will pass the expansion requirements of the Australian Standard.

The research undertaken in Australia to establish the performance of various cement systems (Sirivivatnanon 1997) showed that SCM can give much higher performance than low C_3A cements (Figure 8) using the expansion test used to define sulphate resistance in Australia. In these tests expansion of mortar bar samples in 5% sodium sulphate must not exceed 600 microstrain at 15 weeks. Malaysian materials were also tested and these showed that 15% FA performed better than 30% FA. This is not inconsistent with other data and makes the point that the normal fly ash dosages used in concrete (25-30%) may be excellent for heat reduction and economics but may not be optimum for sulphate resistance. Although optimisation may not matter in many cases it is important to consider it in extreme cases.

Figure 8: Sulphate resistance of various cement blends (ref Sirivivatnanon 1997)



Influence of SCM's

Fly Ash

The performance of Fly Ash in concrete is directly proportional to its composition and its composition is dependent on the type of coal burnt at the power station and the collection process. Tikalisty and Dunstan found that high calcium oxide and low ferro oxide lead to increased expansion. They defined an R factor as (% CaO-5)/(% Fe_2O_3). They suggest the influence of the R factor is

R<1.5	Improved Performance
R=1.5-3.0	Low influence
R>3.0	Detrimental if sulphates react with calcium hydroxide or aluminates

The R factor for Huntly Fly Ash is 1.6.

Mehta (1988) concluded that the sulphate resisting cement behaviour of blended cements depends on the cement-fly ash interaction products, rather than on any arbitrary factor based on the fly ash chemistry alone. Based on Mehta's analysis of the chemical factors influencing the sulphate resistance of portland cement-fly ash mixtures, Manz et al proposed the use of two parameters, namely the Calcium Aluminate Potential (CAP) and the Calcium Sulphate Equivalent (CSE), from which the effectiveness of a fly ash in combating the sulphate attack may be predetermined. Fly ashes with high CAP and low CSE are not expected to provide satisfactory sulphate resistance to blended cements.

Using an estimate of oxides present in the reactive (soluble) form, the two parameters are defined as follows:

$$CAP = \underline{(CaO + Al_2O_3 + Fe_2O_3)/}\ SiO_2 = 1.2 \text{ for Huntly Fly Ash}$$

$$CSE = \text{anhydrite} + 1.69S = 6.9 \text{ for Huntly Fly Ash}$$

The approach suggested by Manz et al is definitely more scientific than Tikalisty & Dunstan's because the former authors take into consideration the reactive Al_2O_3 and soluble SO_3 which are key factors in sulphate resistance. However, it ignores the fundamental issue raised by Mehta that the sulphate resisting behaviour of blended cements depends on the cement-fly ash interaction products and not on the fly ash chemistry alone. An added complexity is the requirement of semi-quantitative X-ray diffraction analysis data for the fly ash involved.

If anything becomes clear it is that it is the concrete's sulphate resistance that is important not the performance of the individual components.

Blast Furnace Slag
ASTM C989-1985 summarises the status as:-

"The use of ground slag will decrease the C_3A content of the cementing materials and decreases the permeability and calcium hydroxide content of the mortar or concrete. Tests have shown that the alumina content of the slag also influences sulphate resistance, and that high alumina content can have detrimental influence at low slag-replacement levels. The data from laboratory exposure of mortars to sodium and magnesium sulphate solutions provided the following general conclusions:

> *The combination of ground slag and portland cement in which the slag content was greater than 60 to 65%, had high sulphate resistance always better than the portland cement alone, irrespective of the Al_2O_3 content of the slag. The improvement in sulphate resistance was greatest for the cements with the high C_3A contents.*
>
> *The low alumina (11%) slags tested, increased the sulphate resistance independently of the C3A content of the cement. To obtain adequate sulphate resistance, higher slag percentages were necessary with the higher C3A cements.*
>
> *The high alumina (18%) slag tested, adversely affected the sulphate resistance of portland cements when blended in low percentages (50% or less). Some tests indicated rapid decreases in resistance for cements in the 8 and 11% C3A ranges, with slag percentages as low as 20% in the blends".*

From the chemistry of reactions in the sulphate attack it is obvious that the presence of free calcium hydroxide is needed for the expansion and strength loss associated with the formation of ettringite and gypsum. Since with the 70% slag cement, before exposure to the sulphate solution, all the calcium hydroxide formed by hydration of the 30% portland cement present had been consumed by chemical reactions with the slag, this explains why in spite of the availability of large amount of reactive alumina from the slag there was no sulphate attack.

An important difference between factory produced slag cement and site blended is the control of SO3. In factory produced this is normally kept to less than 1%.

Kolleck notes "in the case of slags the probability of change (chemical and physical) with time may be significant as they are dictated by the efficient running of a blastfurnace". The changes may be small but could have a significant impact on sulphate resistance.

Microsilica
Microsilica is becoming increasingly well known for its ability to provide concrete with high strength, high durability and improved placement. Microsilica 600 (Figure 9) is a New Zealand Material and has significant advantages in some applications relative to silica fume. Most often it is used with OPC although use with fly ash, slag and specialty cements is not uncommon. Dosages can vary from 2-15% by weight of cement, but are commonly around 8%.

Figure 9 : Microsilica 600 is a naturally occurring Geosilica

Berke (1991) postulates the chemical mechanisms by which Microsilica increase sulphate attack resistance as:-

- Dilution effect - The amount of lime and C_3A present in a given volume of the concrete is reduced by the presence of the silica fume, so the amount of gypsum and ettringite that can be formed per unit volume of paste is also reduced.
- Lime consumption - Some of the lime that is formed during hydration reacts with the silica fume to form CSH. This further reduces the amount of lime that is available for gypsum formation. Unless the attacking sulphate is itself gypsum, the prevention of gypsum formation can eliminate

expansive ettringite formation, which is probably the most important cause of structural failure due to sulphate attack

To clarify the role of gypsum formation in sulphate attack, Mehta conducted a laboratory study comparing the sulphate resistance of two cements. One of the cements was a white portland cement with about 20% C_3A and the other was made by blending 80 parts by weight of the white cement with 20 parts Microsilica. Small specimens of neat cement paste (0.55 water/cement ratio) were moist cured for 7 days at 50^oC before immersion in a 4% Na_2SO_4 solution, held at constant pH and sulphate concentration. Prisms were used for measurement of length changes and cylindrical specimens for changes in the elastic modulus.

From X-ray diffraction analyses of powdered specimens, both before and after the sulphate immersion, semi-quantitative estimate of the phases present, was obtained. Before the sulphate immersion, the hydrated paste from the reference cement (without the Microsilica) showed the presence of considerable calcium hydroxide and monosulphate hydrate, but no ettringite. The corresponding paste containing the Microsilica contained not only much less calcium hydroxide, but also a silica analog of monosulphate hydrate which, like the iron analog, is believed to be resistant to sulphate attack.

The relative XRD peak intensity data from specimens exposed to the sulphate solution showed that with the reference cement paste a large amount of ettringite was formed rapidly during the first 7 days of sulfate immersion, however only a small linear expansion was observed in the prismatic specimens. As for the cement paste containing the Microsilica, the samples showed only negligible expansion throughout the entire sulphate immersion period, no loss in the elastic modulus, and very small amounts of ettringite and gypsum.

High Magnesium Sulphate Solutions

Cohen 1988 reviewed the resistance to magnesium and sodium sulphate of thin cement discs comprising 15% silica fume, a w/c of 0.3 and portland cement with 10.52% C_3A (ASTM Type 1) and 2.26% C_3A (ASTM Type U). The authors note that testing undertaken does not reflect in service performance as the tests regime does not allow for performance enhancement due to low permeability (this may be the predominant factor). The high silica fume content is also not typical and amplifies the normal conversion of $CaOH_2$ to silica fume. The results were intended to indicate the difference in concretes chemical reactions to magnesium and sodium sulphate.

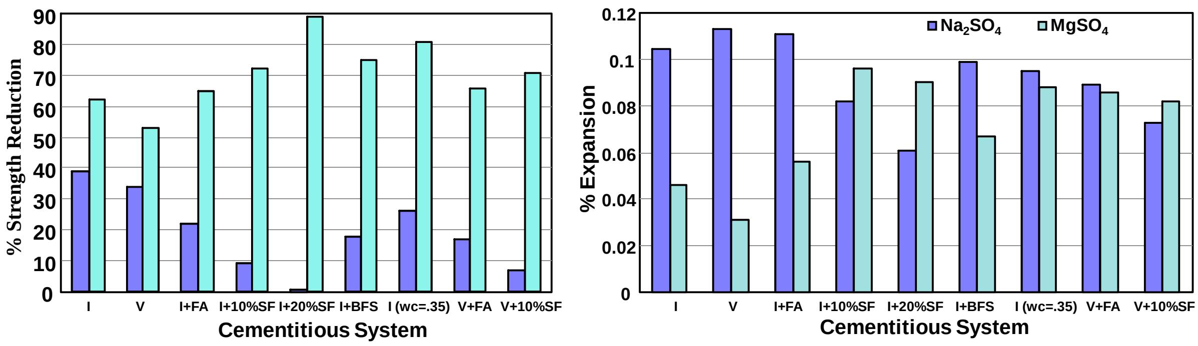
The reaction between silica fume cement pastes and magnesium sulphate produced silica hydrate, magnesium hydrate and gypsum. The latter reacted with calcium aluminate to produce expansive ettringite while the silica and magnesium hydrates reacted together to produce a non-cementitious material. This has implications for any cementitious system that reduces the $CaOH_2$ and produces a higher than normal percentage of CSH. Under similar conditions fly ash and slag could be expected to give similar results.

In magnesium sulphate reactions brucite is also formed. This tends to provide a protective layer on the concrete surface. In situations where the brucite layer is not damaged by the environment significantly greater protection is afforded and some results show an increase in life of around two times.

Since Cohen’s early work there have been several research studies on the relative attack rates of sodium and magnesium sulphate solutions. Al-Amoudi 1995 results showed that at the same concentrations magnesium sulphate was less aggressive than sodium sulphate in regard expansion but significantly more aggressive in regards strength loss (Figure 10). This reflects the different mechanisms occurring.

They also showed that SCM’s all assisted in reducing the sodium sulphate rate of attack but expansion and strength loss were increased using SCM’s. Like Cohen’s work these small mortar cubes do not reflect the improvements that SCM’s give to permeability and do not represent real world concrete due to their shape. The 20% silica fume levels are also unrepresentative of the real world.

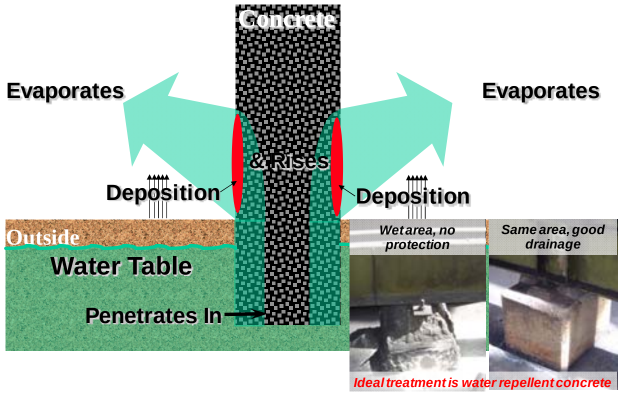
Figure 10 : Performance of 25mm mortar specimens exposed to 2.1% SO_4^- for 360 days



4. Salt Etching

Wet dry cycling is generally considered as the severe form of sulphate attack. This is because the salts get left behind in the concrete as it dries and the next wetting cycling brings a new dose of salts. The cycling leads to a build up of concentration greater than that in the contaminating water.

Figure 11 :Schematic of the evaporation pump leading to salt crystalisation and examples of two plinths where one is subject to ponding and the other is not.



A particular case of this salt build up is in capillary rise (Figure 11). Water with salts rises through the concrete by capillary forces and evaporates off where the concrete is exposed to air. The continuous evaporation pump leads to a salt build up in the concrete surfaces and these high salt levels lead to chemical attack of the concrete. A specific mechanism is crystalisation of the salts in the concrete pores. The pressure in the pores as the crystals grow causes the surface of the concrete to fret off.

A similar mechanism occurs in tunnels where water penetrates under high pressure and where it evaporates off the inside face it deposits the salts carried with it. Permeability calculations can be used to assess the time for water to penetrate the concrete and the subsequent flow rate. The flow rate can be used to assess the amount of salts deposited and diffusion used to calculate the rate at which salts at the surface will diffuse back to the reinforcement. In this way the likelihood of sulphate attack, salt crystalisation and reinforcement corrosion can be assessed.

5. Acid Resistance

Fattuhi studied the performance of OPC and SRPC with silica fume and fly ash subject to sulphuric acid. They conclude:-

"Concrete cubes made with sulphate-resisting cement (SRPC) suffered considerable loss in weight when subjected to acid attack. The rate of attack increased with an increase in cement content.

These results indicate that the generally accepted recommendation to use a relatively high cement content for durable concrete does not apply and is surprisingly counter-productive, when concrete is subjected to water containing sulphuric acid. When comparing the performance of low C_3A and OPC concretes, the results appear to indicate that there is little advantage in recommending low C_3A cement for this type of application.

Concrete cubes made with Densit mortar (Microsilica based) suffered much smaller losses in weight when subjected to acid attack. Therefore Microsilica concretes appear to offer a longer service life than OPC or low C_3A cement concretes."

Standards

AS 2159, AS 3600 and AS 3735 all deal with acid exposures but unfortunately they all have different provisions. For example for a pH of 4 and using 50MPa concrete the cover requirements are 70mm, 25mm and 55mm respectively. It may be assumed that these cater for different levels of damage but there is no statement on allowable damage levels. Hence, little reliance can be placed on the guidance in current Australian Codes.

Carbon dioxide

Carbonation of concrete is often thought to only be a process of carbon dioxide in the atmosphere reacting with the concrete. However carbon dioxide dissolved in water is also aggressive.

In immersed concrete the layer of calcium carbonate that forms in the pores surfaces close to the concrete surface as a result of dissolved CO_2 and $CaOH_2$ reaction breaks down to form $Ca(HCO_3)_2$ which is soluble and easily leached out. Following the depletion of calcium hydroxide the calcium from the calcium silicate hydrate is also broken down leaving a weak gel of hydrous silicon dioxide.

Australian standards do not refer to dissolved carbon dioxide but guidance is given in DIN 4030 and by the Australian Concrete Pipe Association technical. DIN 4030 provides only one criteria, ie if CO_2 is less than 40mg/l then it is not problematic. ACPA gives guidance on the allowable maximum aggressive CO_2 contents related to replenishment rate which is more useful i.e. : Stagnant – 150ppm, Medium – 50ppm and Flowing - 15ppm. Clearly DIN 4030 is unconservative in some circumstances. The designer is left to make his own conclusion on the damage level but it is assumed these apply to a 100 year life.

6. Aggregates

Alkali Silica Reaction

Alkali Aggregate Reaction (AAR) occurs between sodium and potassium ions in solution with certain types of aggregate. AAR can be divided into several reactions associated with the type of aggregate. Alkali Silica Reaction (ASR) occurs with various silica based aggregate and is the reaction between alkali hydroxides and reactive silica. It is a result of the increased solubility of amorphous, disordered or poorly crystalline forms of silica materials in high pH solutions.

"New Zealand has been fortunate that despite the use of reactive aggregates in concrete, there have been few cases where damage due to alkali aggregate reaction (AAR) has necessitated extensive remedial repairs. This has largely been due to the early recognition of the potential for reaction and careful use of low alkali cements in areas where there was the greatest risk." TR3 'Alkali Silica Reaction'.

New Zealand were fortunate to be involved with those that were the first to identify AAR in the USA. Early recognition of the mechanism and the evidence of AAR in New Zealand has led to world class research of the local problem and solutions. This is summarised in CCANZ's TR3 2003, the document referred to by NZS 3191 for control of ASR if concretes alkali content exceeds 2.5kg/m^3. In Australia SAA HB79-1996 and in the UK the Concrete Society's "Alkali-Silica Reaction: Minimising the Risk of Damage to Concrete" are similar documents summarising the local approaches to ASR prevention. It is clear that AAR is a significant durability risk with certain aggregates but it can be avoided if appropriate assessment measures are taken.

Most researchers agree that the main ASR reaction is between certain forms of silica present in the aggregates and the hydroxide ions (OH^-) associated with calcium, potassium and sodium alkalis in the pore water of a concrete. The process, as shown schematically in Figure 12, comprises three essential ingredients as described in TR3:

1. ***Alkali***. Very early in the hydration of cement, calcium ions are incorporated in the hydration products but potassium and sodium stay in solution. The extent to which these alkalis are

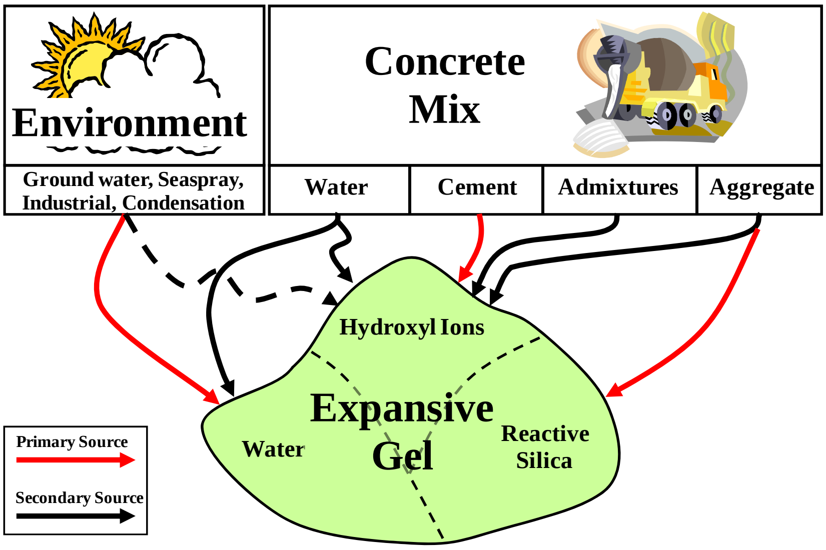
eventually made harmless by incorporation into the paste is dependent on the cement system, notably the use of Supplementary Cementitious Materials (SCM).The alkalies released by the cement can be supplemented by alkalis from other sources e.g. aggregates, admixtures and SCM's. All alkali hydroxide sources must be taken into account when assessing a structure's susceptibility to ASR.

2. ***Reactive aggregate.*** Aggregates may be rapidly or slowly reactive. Primarily, alkali-reactive aggregates were related to various heterogeneously structured, porous, and sometimes hydrous silica minerals such as opal, chert, chalcedony, flint, and some sorts of volcanic glass, which were found to be extremely reactive under the right conditions. More recently well crystallised and more dense quartz-bearing rock types (e.g. meta-greywacke, metasandstone, argillite, phyllite, cataclastic rocks and various other types of rock exhibiting signs of deformation) have been observed to show reactions in concrete as well, by a slower mechanism which leads to a delayed expansion and damage. Microcrystalline quartz and/or quartz with crystal lattice defects (strained quartz) caused by some sort of deformation, are assumed to be one of the reasons for the alkali-reactivity for such slow/late alkali-reactive aggregate.

3. ***Water***. The expansive ASR reaction requires the presence of water. This water generally comes from the external environment but, in thick elements, mix water remains can be sufficient alone. Relative humidity over 75% within the bulk of concrete is generally required to give ASR expansions that wil cause cracking at the concrete surface.

The reaction produces a gel that can produce sufficient swelling pressure to cause extensive concrete cracking. These cracks can open the reinforcement to the environment and can lead to freeze thaw damage, reinforcement corrosion and additional distress to the concrete.

Figure 12 : Mechanism of Alkali Silica Reaction



TR3's process for preventing ASR are:

1) Petrographic section to determine if the aggregate is potentially reactive.
2) If aggregate potentially reactive from 1) then assess by field experience, tests data or ASTM C289 expansion tests
3) If aggregate not innocuous from 2) then test aggregate in mortar or concrete.
4) If aggregate not innocuous from 3) then
   Test SCM's in a mortar or concrete test or
   a. For Normal concrete limit concrete alkalis to 2.5kg/m^3
   b. For special concrete assess risk

The objective of this paper is not to detail all aspects of ASR but to highlight the option of using SCM's as an ASR preventative measure. For further information on reactive aggregates and ASR strategies in NZ refer to CCANZ's TR3. Table 4 of TR3 lists preventative measures for the various ASR Precaution Levels. Use of SCM is given as a preventive measure for low, standard and extraordinary precaution levels.

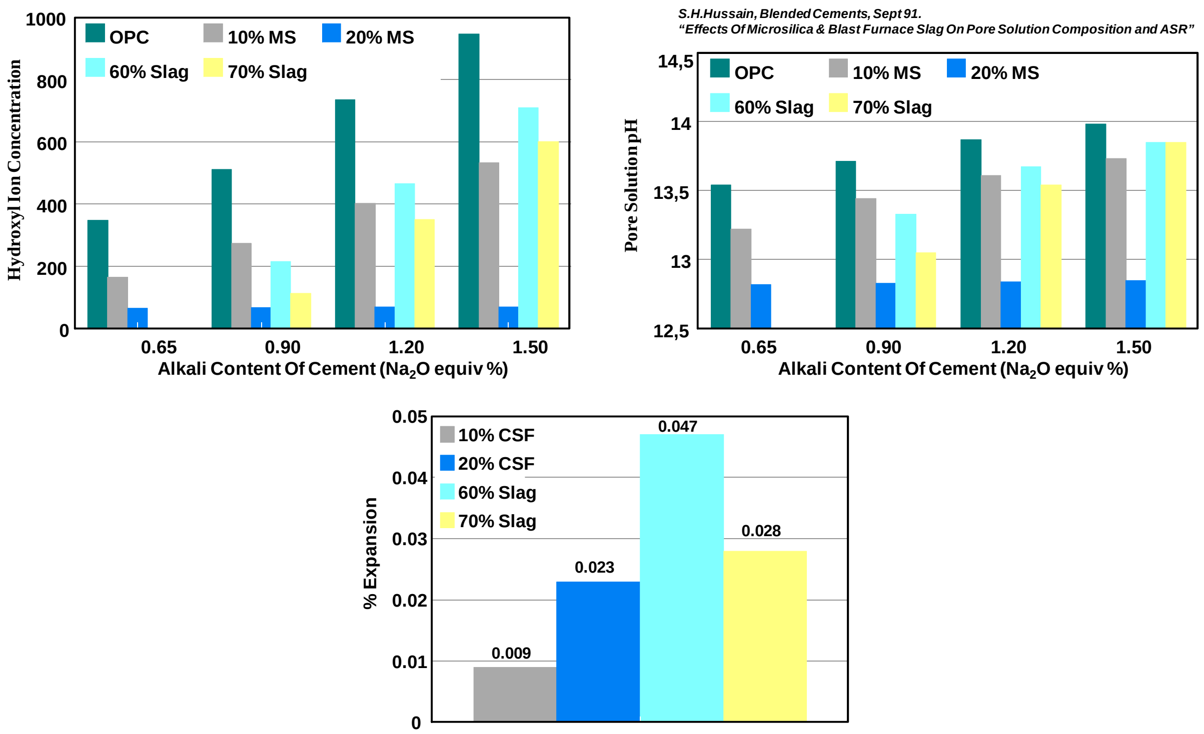
Section 5.4 of TR3 deals with SCM's in some detail. SCM's can dilute the alkalis from cement, bind the alkalis making them unavailable for reaction, make the concrete impermeable thereby reducing water available, reduce calcium hydroxide and pH.

TR3 is the only document that deals specifically with Geothermal silica (Microsilica 600) and notes the advantages relative to silica fume as:

- Particle size is controlled to ensure full reaction
- Particle are un-agglomerated to ensure no risk of the ASR of agglomerates
- Low alkali content relative to some silica fumes

Apart from that geothermal silica reacts in a similar way to silica fume to provide the long term benefits. The reduction in available alkalis and pH is shown in Figure 13 together with the resultant ASR expansion at 6 months. At all cement alkali levels the 10% microsilica the CSH locks in more alkali than the dilution effect of 70% slag and leads to a reduced expansion.

Figure 13 : Effect of Microsilica on Alkali Content, pH and ASR 6 Month Expansion of Concrete



Fly ash and slag performance in ASR mitigation depends on their physical and chemical composition. Slag is imported into NZ and its performance will depend on the source and age of material. One issue found elsewhere is that imported slag may age significantly during transport and storage giving a highly variable performance. NZ's fly comes from Huntly power station and has been shown to reduce ASR reaction. It has a low alkali content.

An economic means of providing ASR protection and early age strength would be to use a combination of fly ash and Microsilica 600. A popular means of assessing the protection afforded in mortar bars is the ASTM C1260 14 day expansion test.

Pyrites

Care is also required with Pyrites in the aggregate. For a large reservoir in Kalgoorlie the inclusion of pyrites meant that aggregates had to be transported 300 km from Esperance. Pyrites oxidises insitu and expands. This causes popouts at the surface but also expansion of the concrete in bulk. Stresses can lead to major cracking. The main risk area is in concrete subject to high humidity.

Although the local aggregate had been used for low risk, non water retaining structures with a 40-60 year life for many years there was evidence of cracking in some old culverts. It was assessed that the local aggregates were unsuitable for a 100 year design life major water retaining structure (holds all of Kalgoorlie's water for one year's supply) where expansion or cracking would be problematic.

7. Applications

Geothermal Power Stations

Chemical attack of concrete at geothermal power stations is of particular concern in New Zealand. The reported acidic ground water could potentially lead to severe and rapid attack of concrete. The temperatures of ground water are reported to be at temperatures of up to 300°C, water is reported to have salinities in excess of 300,000 ppm and the dissolved gases reported to contain sulphuric acid, ammonia and carbon dioxide.

However, this is a prime case where it is important to carefully determine the severity of exposure of the various elements to be constructed. Oxidation of reduced hydrogen sulphide and elemental sulphur occurs near the spring surface to produce sulphuric acid and ground in these areas could be very aggressive where the spring water has high salinity. However, this high salinity is not necessarily the case and even when it is reduction and oxidation may not occur sufficiently quickly in the process to cause acidic conditions.

Analysis of the spring water is also not sufficient to determine the exposure severity as the process may lead to concentrations and reactions that could be detrimental. The process of assessment needs to involve the geotechnical engineer to determine what the current ground conditions are and the process engineer to determine what different areas of the plant will be exposed to. On one plant where the exposure was thought likely to be severe the water analysis gave low sulphates and ammonia and neutral pH. If the assessment was correct the exposure would be quite benign.

Sewage

In the case of sewage there are two different types of attack that must be considered, the direct attack of the sewage and the attack due to sulphuric acid formation on surfaces above the liquid.

The direct attack of liquid sewage is only mildly aggressive due to the sodium sulphate. The use of an SCM of appropriate quality and strength and a w/c ratio of less than 0.45 will provide adequate protection if the acceptable damage is less than 5mm in 50 years. Higher levels of protection may be required if less damage is permitted. Microsilica was used shortly after its introduction to Australia in the early 90's at Black Rock and Anglesea Sewage Works (Figure 14).

Figure 14 : Black Rock (left) and Anglesea (eight) sewage works where Microsilica was used for durability

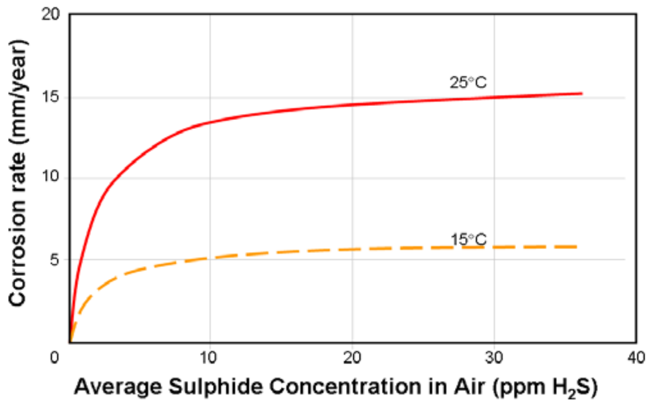
For a major sewage project BCRC were given the brief to review the durability of concrete pipes cast in place, precast, with and without HDPE liner.

The process of acid attack is:

- Anaerobic microbial sulphate reduction on submerged sewer walls
- Sulphides oxidise to hydrogen sulphide in sewage or on released to the sewer atmosphere
- Hydrogen sulphide in air space adsorbed in the thin film of water on sewer walls
- Hydrogen sulphide oxidized to sulphuric acid by bacteria
- Concentration & replenishment depends on hydrogen sulphide generated (hydrogen sulphide control by chemical dosing or air replacement) and bacteria cycle

- Minimum pH limited to 0.2 biologically
- Sulphuric acid reacts with the concrete (rate depends on concrete mix)

Figure 15 : Corrosion rate of concrete as a function of hydrogen sulphide concentration in the air space



Pomeroy 1990 developed empirical formula for the build up of hydrogen sulphide and conversion to sulphuric acid and these have been used for 20 years. The formula have been developed and adapted by Matos 1995 but more recently Neilson 2005 developed the WATS model which considers the sulphide production, water phase biological and chemical oxidation, the biofilm sulphide oxidation and any re-aeration. It provides the flux of sulphuric acid on the walls. The corrosion rate of the concrete is taken as a linear function of acid exposure without allowance for the type of concrete other than the aggregate. This recognises that the cement system alkalinity is not significantly affected by the cement system. However Aesoy 2002 measured the corrosion rate and found it was not linear with hydrogen sulphide concentrations (Figure 15) as suggested by Pomeroy.

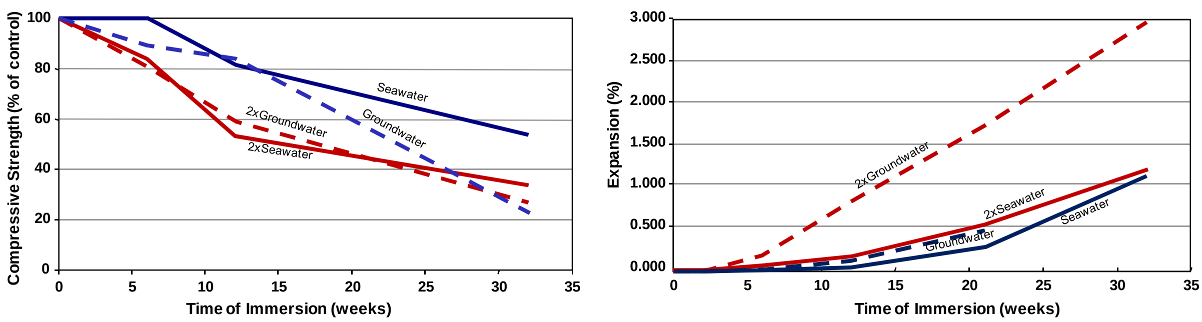
Brine Exposure

Santhanam's 2001 research is valuable to brine outfall assessment as it shows the effect of increasing sulphate concentration and the presence of chlorides on sulphate attack.

Expansion and strength loss of 25mm mortar cubes was measured when subject to seawater and 2x seawater concentrations (Figure 16). There was little difference in expansion as might be expected by the predominant attack mechanism. The strength loss of the high concentration was 30% higher than the seawater concentration. As we know that in the real world seawater attack on concrete with a w/c ratio of less than 0.45 is negligible over a 100 year life an attack rate of even 2 x seawater is not of major concern. The 2 x seawater concentration (around 10000ppm) is typical of brine channels in desalination plants and suggests that these concentrations are not highly aggressive in fully saturated conditions.

It is notable that at the high sulphate concentration but without chloride the expansion was significantly higher (Figure 16) than with chlorides. This sulphate water without chloride is more typical of groundwater.

Figure 16 : Comparison of sulphate waters with and without chloride at moderate and high concentrations



Santhanam's work suggests that the Draft of AS 3600 may not adequately cater for all sulphate conditions (Table 7). Separate provisions may be beneficial for sulphate solutions with and without chlorides and with and without magnesium sulphate.

These issues are significant. If current requirements in AS 3735 are followed any concrete in magnesium sulphate solutions with concentrations over 7000ppm SO_4^- must be lined. Desalination plant brine has sulphates over 9000ppm and following AS 3735 would add millions of dollars to the cost and months to the construction programme. Yet research indicates the exposure is only moderate if care is taken over the selection of cement system to achieve optimum results.

Santhanam's research is supported by the author's experience. 25 years ago a 0.4 w/c ratio concrete with fly ash was specified for bridge decks and culverts at a salt mine. The concrete was subject to very high levels of brine that included magnesium sulphate and chlorides. A recent check with the owner identified that the bridge was demolished after 20 years service as it was no longer required. At the time of demolition the deck was still in excellent condition. The culverts are pristine after 20 years service.

Based on research and experience the authors recommendations for desalination brine channels is to use a low w/c ratio (0.35max) and Microsilica and FA. The combination of FA and Microsilica should be optimised based on cement and FA composition but a maximum of 15% FA and 3% Microsilica is likely. Quality assurance of the concrete is important and the concrete mix should be assessed for threshold pore diameter and sorptivity used as a QA test.

8. Conclusions

Research and experience shows that concrete can be an extremely durable material in very severe exposures but great care is required in defining the problem. The replacement interval, allowable damage, the actual exposure and the consequence of failure are all important inputs to the durability assessment. Low C_3A cements should not be used in general as SCM's generally give higher chemical resistance. IN very severe exposures there may be advantages in combining low C3A cements, SCM's and low w/c ratios. Care is required to select the appropriate cement system particularly when fly ash or slag are used, however in New Zealand the availability of Microsilica 600 is a valuable resource that is likely to provide the most suitable SCM in many cases. Above all it is the concrete performance that is important, as determined by chemical resistance and penetrability of the paste.

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