TECHNICAL note

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Sulfate-resisting Concrete

Sulfate-resisting concrete

INTRODUCTION

This Technical Note discusses the mechanisms of external sulfate attack which include chemical reactions and the physio-chemical effects on concrete. It reports the outcome of a research project conducted by Cement Concrete & Aggregates Australia (CCAA). In this project the performance of Australian concrete mixes, proportioned using sulfate-resisting cements (AS 3972 Type SR[1]) and non sulfate-resisting cements were evaluated in both neutral and acidic sulfate conditions. The results were examined in relation to the long-term concrete exposure data from the US Portland Cement Association (PCA) and the 40-year non-accelerated exposure programme at the US Bureau of Reclamation (USBR). Current specifications for sulfate resisting concrete in relevant Australian Standards and some Road Authorities' specifications are reviewed in the context of CCAA research findings which are applicable to concrete structures in sulfate or acid sulfate soil conditions.

1 SULFATE EXPOSURE CONDITIONS IN AUSTRALIA

Sulfates may occur naturally in soil and groundwater, in industrial effluents and wastes from chemical and mining industries, as well as in sea water. Acid sulfate soils are associated with naturally occurring sediments and soils containing iron sulfides usually found in mangroves, salt marsh vegetation or tidal areas and low lying parts of coastal floodplains, rivers and creeks.

Very few cases of aggressive sulfate soil and groundwater conditions have been reported in Australia. In certain sections of the Parramatta Rail Link in the Lane Cove Valley in Sydney, aggressive sulfate and carbon dioxide in groundwater were found; concretes with and without protective membrane were therefore used to satisfy the 100 years design life. The concrete at the base of water cooling towers have been found to be exposed to high sulfate levels in the closed circuit cooling systems. In the case of cooling towers at Bayswater Power Station in NSW, the concrete was found[2] to show no sign of attack when inspected after 10 years of service. In the M5 East Motorway project at Cooks River Crossing near Kingsford Smith airport in Sydney, sulfate-resisting

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concrete was used for the piles and diaphragm wall constructed in areas where the groundwater was found to have very high sulfate contents, possibly caused by effluents from the industrial areas around the Cooks River.

According to the NSW Acid Sulfate Soils Management Advisory Committee[3], acid sulfate soils are soils containing highly acidic soil horizons or layers resulting from the aeration of soil materials that are rich in iron sulfides. The oxidation produces hydrogen ions in excess of the sediment's capacity to neutralise the acidity, resulting in soils of pH of 4 or less. The field pH of these soils in their undisturbed state is pH 4 or more and may be neutral or slightly alkaline. Organic acids are common in coastal ecosystems and can produce acid water and sediment. The pH of these sediments is usually around 4.5–5.5. As they do not have the ability to generate additional acid when exposed to air, they do not exhibit the same kinds of environmental risks that are associated with acid sulfate sediments.

In New South Wales, acid sulfate soil conditions have been reported by the Roads and Traffic Authority[4] in the Pacific Highway upgrading programme, eg at the Chinderah Bypass which involved the dredging and disposal of potential acid sulfate soil from a site near a major bridge over the Tweed River at Barneys Point. Other locations include the floodplains of many rivers including Clarence River, Clyde River, Hawkesbury River, Hunter River, Macleay River, Manning River, Myall River, Nambucca River, Richmond River and Shoalhaven River. In Queensland, acid sulfate soils have also been found in the coastal regions including sulfide-bearing source rock and sodic soils which cover 45% of Queensland[5]. This has led Queensland Main Roads to draw designers' attention to detailed analysis of the chemistry of the soil and groundwater, and the design of concrete to withstand these potentially harsh conditions.

2 MECHANISMS OF SULFATE ATTACK

The deterioration of concrete exposed to sulfate is the result of the penetration of aggressive agents into the concrete and their chemical reaction with the cement matrix. The three main reactions involved are:

- Ettringite formation – conversion of hydrated calcium aluminate to calcium sulphoaluminate,
- Gypsum formation – conversion of the calcium hydroxide to calcium sulfate, and
- Decalcification – decomposition of the hydrated calcium silicates.

These chemical reactions can lead to expansion and cracking of concrete, and/or the loss of strength and elastic properties of concrete. The form and extent of damage to concrete will depend on the sulfate concentration, the type of cations (eg sodium or magnesium) in the sulfate solution, the pH of the solution and the microstructure of the hardened cement matrix. Some cements are more susceptible to magnesium sulfate than sodium sulfate, the key mechanism is the replacement of calcium in calcium silicate hydrates that form much of the cement matrix. This leads to a loss of the binding properties. Formation of brucite ($Mg(OH)_2$) and magnesium silicate hydrates is an indication of such attack.

The presence of chloride in soil and groundwater may be beneficial since there is considerable evidence, from seawater studies[6,7], that the presence of chloride generally reduces expansion due to sulfate attack. The risk of corrosion of embedded metals in buried concrete in non-aggressive soil is generally lower than in externally exposed concrete. However, high chloride concentrations in the ground may increase the risk of corrosion since chloride ions may permeate the concrete, leading to a depassivation of the metal surface.

Above the soil or water table level in the soil profile where the concrete surface is exposed to a wetting and drying condition, the concrete will also be subjected to a physio-chemical sulfate attack. Folliard and Sandberg[8] reported that the physio-chemical process is more prevalent in the field, in which concrete is physically, rather than chemically attacked by sodium sulfate. The only reactions involved are within the sodium sulfate-water system; the phase changes from a solution to a solid, or from an anhydrous solid, thenardite (Na_2SO_4), to its hydrated form, mirabilite ($Na_2SO_4.10H_2O$). The amount of deterioration is a function of the potential crystallisation pressures or the volume increase associated with a given mechanism. Any of the mechanisms can potentially produce pressures that are an order of magnitude greater than the tensile strengths of the concrete. Further, the same pressures can be reached by any one of several crystallisation mechanisms by simply varying the temperature and concentration of the sulfate solution in the system. The volume increase could cause severe deterioration of the concrete but may be partially accommodated in air-entrained concrete.

3 PHYSICAL AND CHEMICAL RESISTANCE OF CONCRETE

Both the physical resistance of concrete to the penetration and capillary-induced migration of aggressive agents and the chemical resistance of the concrete to the deleterious reactions described above are important attributes of sulfate resisting concrete. Thus factors influencing the permeability and surface porosity of the concrete and the chemical resistance of cement are prime performance parameters of concrete exposed to sulfate attack.

The physical resistance of concrete is traditionally achieved by specifying mix design parameters such as maximum water–cement ratio and minimum cement content, while the

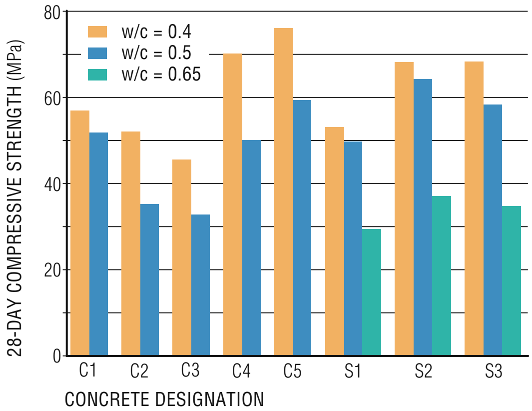

Figure 1 28-day compressive strength of the concretes at w/c of 0.4, 0.5 and 0.65

chemical resistance is by the use of sulfate-resisting cement. This is the approach adopted in codes and guideline such as ACI 318[9] and BRE Special Digest 1[10] and directly or indirectly in relevant Australian Standards. Recent research has focused on performance-based specification for sulfate resisting concrete. A specification based on water permeability was proposed by Sirivivatnanon and Khatri (1999)[11]. In this research, a rapid electrochemical test procedure similar to ASTM C 1202 *Indication of Concrete's Ability to Resist Chloride Ion Penetration* which was proposed by Tumidajski and Turc (1995)[12] has been used to rapidly assess the ability of concrete to resist sulfate penetration. Long-term concrete performance tests are evaluated by CCAA to substantiate the validity of these approaches.

The role of concrete quality on the resistance to both the chemical and physio-chemical attack by sulfates has been studied by researchers at the PCA. It involved long-term exposure of concrete prisms in the laboratory and in the field. Findings have been reported by Verbeck (1967)[13] and Starks (2002)[14]. Interestingly, it was found that a continuous immersion in sulfate solution was a relatively mild condition compared with cyclic wetting and drying. The physical resistance of the concrete to the physio-chemical sulfate attack was achieved by limiting the maximum water–cement ratio and minimum cement content of the concrete, and the application of a sealer to the surface of concrete.

4 AUSTRALIAN RESEARCH ON SULFATE-RESISTING CONCRETE

In 2002, CCAA initiated a research project to develop a performance–based specification for sulfate-resisting concrete. The research was undertaken and completed in 2010. In this research project, nineteen concrete mixes were proportioned using six Type SR sulfate-resisting cements and two non sulfate-resisting cements, at water–cement ratios (w/c) of 0.4, 0.5 and 0.65. The concrete was proportioned with a fixed dosage of water–reducing admixture and a variable dosage of superplasticiser to produce concrete with a slump of 120 ± 20 mm. The minimum cement contents were 415, 335 and 290 kg/m^3 for the mixes with w/c of 0.4, 0.5 and 0.65 respectively. The concrete specimens were moist cured for three days and kept in the laboratory until testing at 28 days. (Hence there was a limited depth of carbonation at the surface of the concrete at the commencement of sulfate exposure.) Compressive strength, water permeability and rapid sulfate permeability of the concretes were determined at 28 days.

At 28 days, the concrete specimens were exposed by full immersion in 5% (50,000 ppm) sodium sulfate solutions maintained at pH of 7±0.5 and 3.5±0.5. The performance of the concrete was measured in terms of expansion of 75 x 75 x 285 mm duplicate prisms and strength retention of 100 mm x 200 mm duplicate cylinders throughout the exposure period of three years.

The 28 day compressive strength of the concrete varied widely from 45.5–75.5 MPa, 32.5–64.0 MPa and 29.5–37.0 MPa for w/c of 0.4, 0.5, and 0.65 respectively reflecting the influence of different cements. Results are shown in **Figure 1**.

4.1 Performance of buried concrete

From previous CSIRO and PCA studies[11,14] of long-term expansion of concrete immersed in sodium sulfate solution, an expansion performance limit of 220 microstrain per year within the first three years of exposure has been found to indicate long-term dimensional stability of the concrete. Small concrete specimens which maintain its 28-day strength within the first three years are indicator of good long-term strength retention. After three years of exposure, all Type SR cement concretes with water-cement ratios of 0.4 and 0.5 performed well both in terms of expansion and strength retention. As shown in **Figures 2 and 3** and **Tables 1 and 2**, all the concretes were stable in both neutral and acidic sulfate solutions with increases in expansion rate within the performance limit of 220 microstrain per year, and with strength retentions above 100% of the 28-day compressive strength. The results suggest that all concretes of 0.4 and 0.5 water–cement ratio, irrespective of the strength, will provide good resistance to sulfate attack in the long-term and could be classified as sulfate-resisting concretes.

In both pH 3.5 and 7 sulfate solutions, S2C and S3C (w/c 0.65) showed expansion rates significantly exceeding 220 microstrain per year during the first two years of exposure. Some S3C prisms were found to be badly cracked and expansion cannot be measured after two-year exposure as shown in **Plates 1 and 2**.

The expansion performance limit was derived from a long-term study by the PCA of concretes exposed to accelerated field and laboratory-simulated sulphate environments reported by

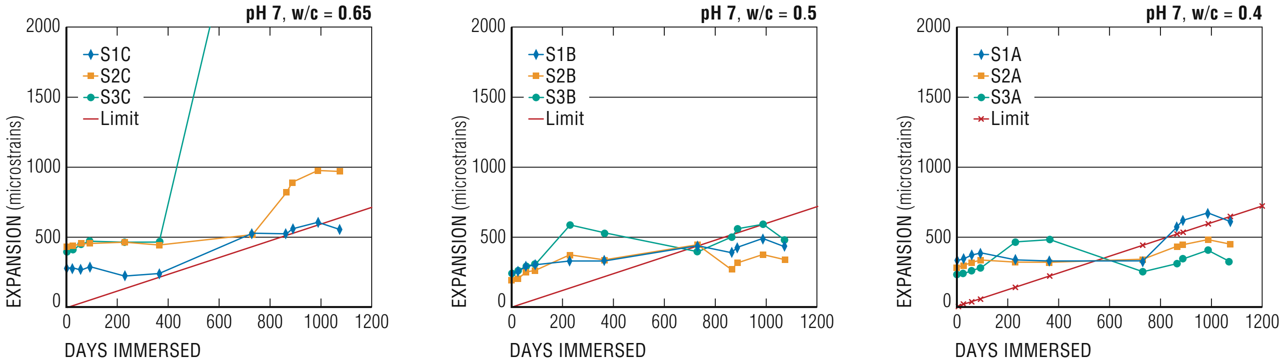

Figure 2 Expansion of concrete prisms in 5% Na_2SO_4 solution at pH 7

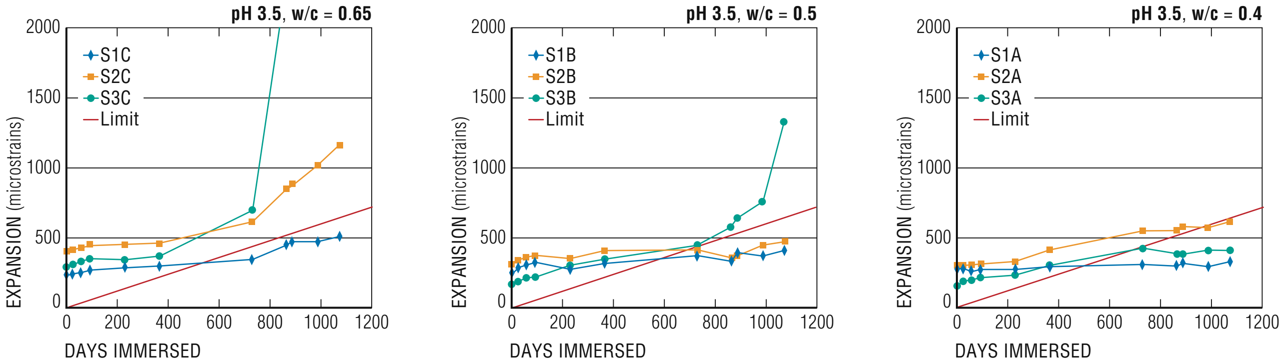

Figure 3 Expansion of concrete prisms in 5% Na_2SO_4 solution at pH 3.5

Plate 1 Failure of S3C (w/c 0.65) prisms after 570 days in 5% Na_2SO_4 at pH 7

Plate 2 Failure of S3C (w/c 0.65) prisms after 570 days in 5% Na_2SO_4 at pH 3.5

Plate 3 Cylinders after 3 years exposure prior to compression test. Grey in neutral sulfate solution *(left)*. Rustic red in acidic sulfate solution *(right)*

Stark[14]. In Sacramento, California concrete prisms from 50 concrete mixtures were partially buried in sodium sulfate-rich soils, maintained at about 6.5% or 65,000 ppm sodium sulfate concentration, and exposed to cyclic immersion and atmospheric drying condition since 1989. The performance of the prisms was rated visually from 1.0 to 5.0 with a rating of 1.0 indicating excellent performance with virtually no evidence of deterioration, while a rating of 5.0 represented major loss of paste matrix and widespread exposure and loss of coarse aggregate particles. It was found that the main deterioration mechanism of concrete in this wetting and drying condition was due to the physio-chemical process of sulfate attack.

A second set of companion concrete prisms were immersed in a 6.5% or 65,000 ppm sodium sulfate solution in PCA's Construction Technology Laboratories (CTL) in Skokie, Illinois and their expansion monitored for over 12 years. All the concrete prisms were reported to perform very well after a 12-year exposure period. More importantly, all concrete with low expansion rate (within 220 microstain) per year in the first three years of exposure did not exhibit rapid increase in the rate of expansion in subsequent years nor did their maximum expansion reach 3000 microstrain – an elastic strain limit for most concrete. This PCA study concluded that sulfate resistance of concrete was mainly governed by water-cement ratios at w/c of 0.4 and below, whereas cement composition would influence the performance of concrete with intermediate w/c of 0.4 to 0.55.

TABLE 1 Retention of cylindrical compressive strength as % of 28-day strength in pH 7

Exposure period (days)	C1		C2		C3		C4		C5	
	0.4	0.5	0.4	0.5	0.4	0.5	0.4	0.5	0.4	0.5
0	100	100	100	100	100	100	100	100	100	100
514	126	126	129	164	129	161	125	131	116	116
776	134	135	125	159	131	158	124	132	115	115
939	128	130	121	152	145	158	116	126	112	105
1240	118	123	122	161	136	159	117	130	111	101

Exposure period (days)	S1			S2			S3		
	0.4 S1A	0.5 S1B	0.65 S1C	0.4 S2A	0.5 S2B	0.65 S2C	0.4 S3A	0.5 S3B	0.65 S3C
0	100	100	100	100	100	100	100	100	100
365	132	139	154	103	103	112	93	110	87
570	130	133	149	99	99	111	95	90	10
1075	125	127	152	97	93	65	110	45	0

TABLE 2 Retention of cylindrical compressive strength as % of 28-day strength in pH 3.5

Exposure period (days)	C1		C2		C3		C4		C5	
	0.4	0.5	0.4	0.5	0.4	0.5	0.4	0.5	0.4	0.5
0	100	100	100	100	100	100	100	100	100	100
514	125	130	136	151	146	158	117	137	125	123
776	120	116	141	153	136	151	109	128	118	109
939	120	122	138	151	135	146	113	129	115	106
1240	123	127	136	163	131	149	111	136	115	108

Exposure period (days)	S1			S2			S3		
	0.4 S1A	0.5 S1B	0.65 S1C	0.4 S2A	0.5 S2B	0.65 S2C	0.4 S3A	0.5 S3B	0.65 S3C
0	100	100	100	100	100	100	100	100	100
365	119	123	156	87	97	112	90	102	90
570	120	128	136	77	95	97	102	86	6
1075	101	116	135	90	91	87	93	24	11

The conditions of the concrete cylinders after 3-years exposure were quite varied with most retaining their integrity but some were badly cracked especially around the top edges. See Plate 3 showing contrast in colour of cylinders after 3-year exposure.

The US Bureau of Reclamation (USBR) non-accelerated sulfate testing programme, on concrete cylinders partially submerged in 2.1% or 21,000 ppm sodium sulfate solution at ambient temperature, showed concrete with w/c ratio of 0.45 and lower to be intact even after 40-year exposure period[15]. The Bureau defined failure when expansion reached 0.5% or 5000 microstrain. The results also showed the importance of permeability and cement composition for concrete with w/c exceeding 0.45. USBR results support the validity of current service life performance specification.

It can be observed from **Tables 1 and 2** that the compressive strength of the concrete increased well above the 28 day strength in the first 1–2 years of immersion, followed by a gradual reduction in strengths. After three-year exposure in both neutral and acidic sodium sulfate solutions, the strengths remained at or above the 28-day strength level for Type SR cement concretes with water-cement ratios of 0.4 and 0.5. This clearly showed the integrity of the concrete and its mechanical resistance to sulfate attack.

4.2 Performance of partly buried concrete

While most buried concrete elements such as piles and footings are likely to be kept moist throughout their service life, parts of some of them (eg the top of footings and pile caps) may be exposed to periodic wetting and drying conditions. The PCA study confirmed that the exposure to alternate immersion and atmospheric drying in the sodium sulfate-rich soil was a more severe exposure condition than continuous immersion in the same solution. Attention must therefore be given to the sulfate resistance of concrete under such exposure conditions. Stark[14] found a consistently improved trend in the rating of the surface deterioration of concrete with increased cement content irrespective of the type of cement. In the PCA's 17 concrete mixtures with a cement

TABLE 3 Strength and cover requirements for sulfate soils
(Summarised from Tables 4.8.1 and 4.10.3.2 in AS 3600—2009)

SO_4 In groundwater (mg/L)	SO_4 In soil (%)	**Exposure classification**	**Characteristic strength** (MPa)	**Minimum cover** (mm)
<1000	< 0.5	A2	25	50
1000–3000	0.5–1	B1	32	50[1]
3000–10,000	1–2	B2	40	50[1,2]
>10,000	> 2	C1 and C2	≥ 50	65[1,2,3]

Notes:

1 *It is recommended that cement be Type SR.*

2 *Additional protective coating is recommended.*

3 *The cover may be reduced to 50 mm if protective coating or barriers are used.*

TABLE 4 Additional requirements
(*From Table 8 of QDMR MSR11.70*)

Exposure classification	**Minimum cementitious content** (kg/m^3)	**Maximum water–cementitious ratio**	**Strength grade** (MPa)
B1	320	0.56	32
B2	390	0.46	40
C	450	0.40	50

content of 390 kg/m^3, most concretes had a rating between 1.4 and 3.8 after 12–years exposure in the sulfate-rich soil ground in Sacramento. This is considered to be a good performance of the concrete under such an aggressive sulfate environment. Stark found that the observed severe deterioration in the outdoor exposure was due largely to cyclic crystallisation of $NaSO_4$ salts after sufficient evaporation of moisture from the outdoor soils exposure as postulated by Folliard and Sandberg[8]. This is probably the reason for the effectiveness of a sealer, such as silicon and linseed oil, in limiting the capillary-induced migration of sulfate, and thus improving the performance of concrete including concrete with higher w/c of 0.49–0.52.

With all Type SR cement concrete mixes performing exceedingly well under full immersion in sodium sulfate solutions at both neutral and acidic conditions, and a minimum cement content of 415 kg/m^3 in the 0.4 w/c series, it is likely that the low water–cement ratio concretes will also perform very well in the severe wetting and drying condition. With appropriate surface protection, the 0.5 w/c series of concrete with a minimum cement content of 335 kg/m^3 would also be expected to perform well in the more aggressive wetting and drying condition.

5 SPECIFYING SULFATE-RESISTING CONCRETE

Sulfate-resisting concrete has traditionally been specified prescriptively by the type of cement and mix proportion limits in terms of maximum water-cement ratio and minimum cement content. In highly acidic and permeable soils where pH is below 3.5, additional protective measures are required to isolate the concrete from direct contact with the aggressive ground condition. ACI 318[9] and BRE SD1[10] are examples of these specifications. BRE SD1 is particularly progressive in recommending specifications for sulfate-resisting concrete for intended working life of 50 years for building works and 100 years for civil engineering structures.

5.1 Australian Standards

In the revision of the Australian Standard for concrete structures AS 3600[16], specifications for concrete in sulfate soils with a magnesium content of less that 1000 mg/L have been introduced. For each exposure classification, concrete is specified in terms of concrete grade and minimum concrete cover, see **Table 3**. The current Australian Standards for piling, AS 2159[17] and for concrete structures for retaining liquids, AS 3735[18], recommend the specification of certain concrete grades and corresponding covers for a design life 40–60 years in a range of exposure classifications. The exposure classification is defined by the magnitude of sulfate in the soil or in groundwater, pH level and the soil conditions in term of its permeability. In severe and very severe conditions, where sulfate levels exceed 2000 ppm in groundwater or 1% in soil, AS 3735 Supplement[19] recommends a minimum cement content of 320 kg/m^3 and a maximum water–cement ratio of 0.5 and the use of Type SR cement.

The findings from CCAA research, described in the previous section, supported the specification of sulfate resisting concrete by strength grade and cover (AS 2159 and AS 3600), and in particular, confirmed the expected performance of the sulfate resisting concrete in the moderate (B2) and severe to very severe (C1 and C2) exposure classifications shown in **Table 3**.

It should be noted that the Australian Standard for bridge design AS 5100[20] provides no specific guidance on specifying concrete for 100 years design life in sulfate conditions.

5.2 Other specifications

Road authorities, such as the RTA in New South Wales and the Queensland Department of Main Roads, are specifying sulfate-resisting concrete based on exposure classifications in Austroads Bridge Design Code (superseded by AS 5100), but with additional limits on maximum w/c and minimum cement content. Queensland Department of Main Roads refers to MRS11.70 with the additional requirements shown in **Table 4**.

TABLE 5 Summary of long-term performance and possible specifications

Concrete properties	C1–C5		S1			S2			S3		
	0.4	0.5	0.4	0.5	0.65	0.4	0.5	0.65	0.4	0.5	0.65
Water permeability ($\times 10^{-12}$ m/s)	0.07–0.28	0.34–1.70	0.16	1.5	70.3	0.14	0.35	13.4	0.13	0.44	16
Rapid sulfate permeability (coulombs)	940–1260	1180–1450	1475	1965	2260	2580	3225	4010	1780	2265	3060
Water-to-cement	0.40–0.41	0.50	0.39	0.50	0.63	0.39	0.5	0.66	0.40	0.50	0.66
28-day compressive strength (MPa)	47.5–75.5	32.5–59.0	52.5	49.5	29.5	68.0	64.0	37.0	68.0	58.0	34.5

As can be noted, the findings from CCAA research project also support the above specifications.

5.3 Performance-based specifications

Sulfate resisting concrete has traditionally been specified prescriptively by the maximum water–cement ratio and a specific type of SR cement. This is to ensure good physical resistance of the concrete to limit the penetrating sulfate ions, and good chemical resistance of the cement matrix to the deleterious sulfate reactions. A performance specification based on water permeability of the concrete has been proposed by Sirivivatnanon and Khatri [11]. As part of CCAA research, a further attempt has been made to develop a performance-based specification for sulfate resisting concrete based on the physical resistance of the concrete (eg water permeability, rapid sulfate permeability) and the chemical resistance of the cement (sulfate expansion). A six-hour accelerated test method for a rapid sulfate permeability determination was developed and is shown in **Figure 4**.

The dimension stability and strength retention properties of the nineteen concrete mixes were evaluated in accordance with the criteria established in Section 4.1. Concrete passing both expansion and strength retention criteria is considered sulfate-resisting concrete. The

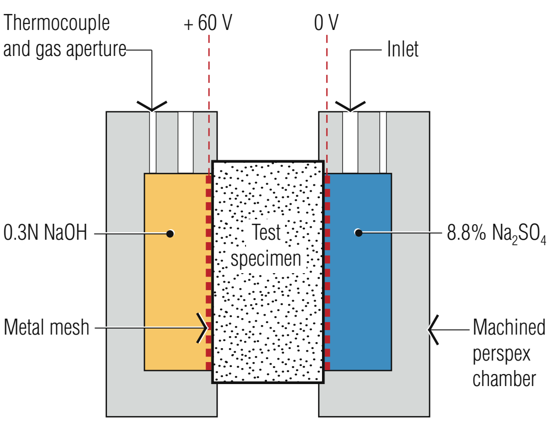

Figure 4 An accelerated test set-up for the rapid sulfate permeability determination

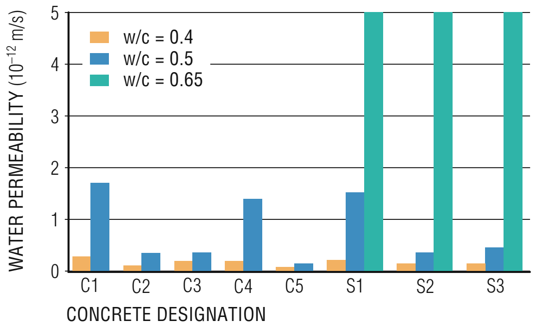

Figure 5 Water permeability of the concretes at w/c of 0.4, 0.5 and 0.65

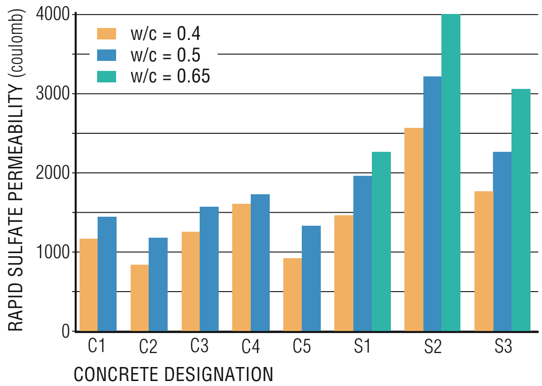

Figure 6 Rapid sulfate permeability of the concretes at w/c of 0.4, 0.5 and 0.65

mix prescription in water-cement ratio, and performance properties: water permeability coefficient and rapid sulfate permeability; are summarised in **Table 5** and shown in **Figures 5 and 6**.

Based on these properties, a semi-prescriptive and performance-based specifications for sulfate-resisting concrete are proposed as follows.

1 Type SR cement and water-cement ratio ≤ 0.5, and
2 Type SR cement and a water permeability coefficient $\leq 2\times10^{-12}$ m/s or rapid sulfate permeability ≤ 2000 coulombs.

The result also showed that concrete with Type SR cement at w/c greater than 0.5 or non sulfate-resisting cement at very low w/c no greater than 0.4 can perform well especially in neutral sulfate condition.

6 CONCLUSIONS

Sulfate resistance of the concrete is a function of its physical and chemical resistance to penetrating sulfate ions. Good physical resistance of the concrete is directly related to the water-cement ratio and the cement content. Good chemical resistance is related to the resistance of the cement matrix to the deleterious sulfate reactions.

Sulfate-resisting concrete can be achieved using a sufficient quantity of a sulfate-resisting cement (Type SR complying with AS 3972) and a low water–cement ratio to obtain a concrete with low water permeability. For fully buried concrete structures in saturated soils, a sulfate-resisting concrete can be achieved from Type SR cement at a cement content of 335 kg/m^3 and a water–cement ratio of 0.5. For partially buried structures exposed to a wetting and drying condition, the same sulfate-resisting concrete can be used but with additional protective measure such as the application of an appropriate sealer to the surface of the exposed concrete. Alternatively, a sulfate-resisting concrete can be achieved from Type SR cement at a cement content of 415 kg/m^3 and a water–cement ratio of 0.4. The AS 3600 specifications for concrete structures in acid sulfate soils, based on minimum compressive strength and Type SR cement, is shown to produce adequate sulfate-resisting concrete for the exposure condition indicated. Alternatively, performance-based specifications based on Type SR cement and a concrete with a limit on either water permeability or rapid sulfate permeability can be used.

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