Specifying Sulfate-Resisting Concrete

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Abstract The Sulfate-resisting concrete is traditionally specified by cement type and concrete mix proportions in terms of maximum water-cement ratio and/or minimum cement content. Cement Concrete & Aggregates Australia (CCAA) has recently completed a major research project on the performance and specification of sulfate-resisting concrete. The research examines the long-term dimensional stability and strength retention of nineteen concrete mixes in 5% sodium sulfate solutions maintained at pH 7 and 3.5. The concretes were made from 8 cements, six of these were sulfate-resisting cements (Type SR) in accordance with the Australian Standard AS 3972 [1]. The concretes were proportioned at water-cement ratios of 0.4, 0.5 and 0.65. The coefficient of water permeability and a new rapid sulfate permeability of the concretes were determined at the age of 28 days on 3 days moist-cured cylindrical discs. The rapid sulfate permeability is a 6-hour accelerated test, based on ASTM C1202 [2], and measures the sulfate permeability in term of coulombs. Sulfate-resisting concrete can be produced by specifying the use of a performance-based AS 3972 Type SR cement and a performance-based limit on either a water permeability coefficient of 2.0×10^{-12} m/s or a rapid sulfate permeability of 2000 coulombs. These concretes were found to be resistant to both neutral and acidic sulfate conditions.

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.

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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, e.g. 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. 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].

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 these 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.

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 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 [11]. In this research and in addition to water permeability, 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 [12] has been used to rapidly assess the ability of concrete to resist sulfate penetration. Long-term concrete performance tests have been 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 Portland Cement Association (PCA) in the US. It involved long-term exposure of concrete prisms in the laboratory and in the field. Findings have been reported by Verbeck [13] and Starks [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.

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 completed in 2010. In this research project, nineteen concrete mixes were proportioned using six Type SR sulfate-resisting cements: C1, C2, C3, C4, C5 & S1; and two non sulfate-resisting cements: S2 and S3; at water–cement ratios (w/c) of 0.4, 0.5 and 0.65. It is noted that a number of Type SR cements are GB cements incorporating supplementary Cementitious material (SCM) such as fly ash and slag. 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 75x75x285 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**.

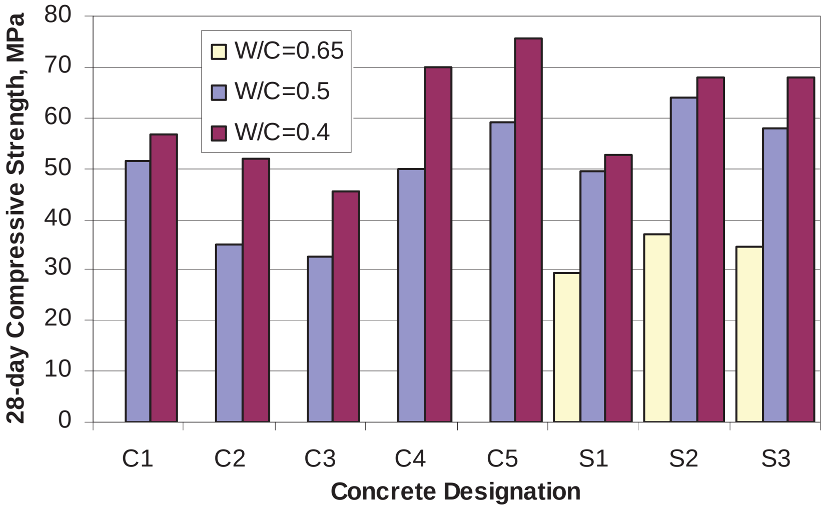

Figure 1 28-day compressive strength of the concretes at w/c of 0.4, 0.5 and 0.65

Performance of buried concrete

From previous CSIRO [11] and PCA [14] studies 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 their 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&3** and **Tables I&II**, these 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 could not be measured after two-year exposure as shown in **Plates 1&2**.

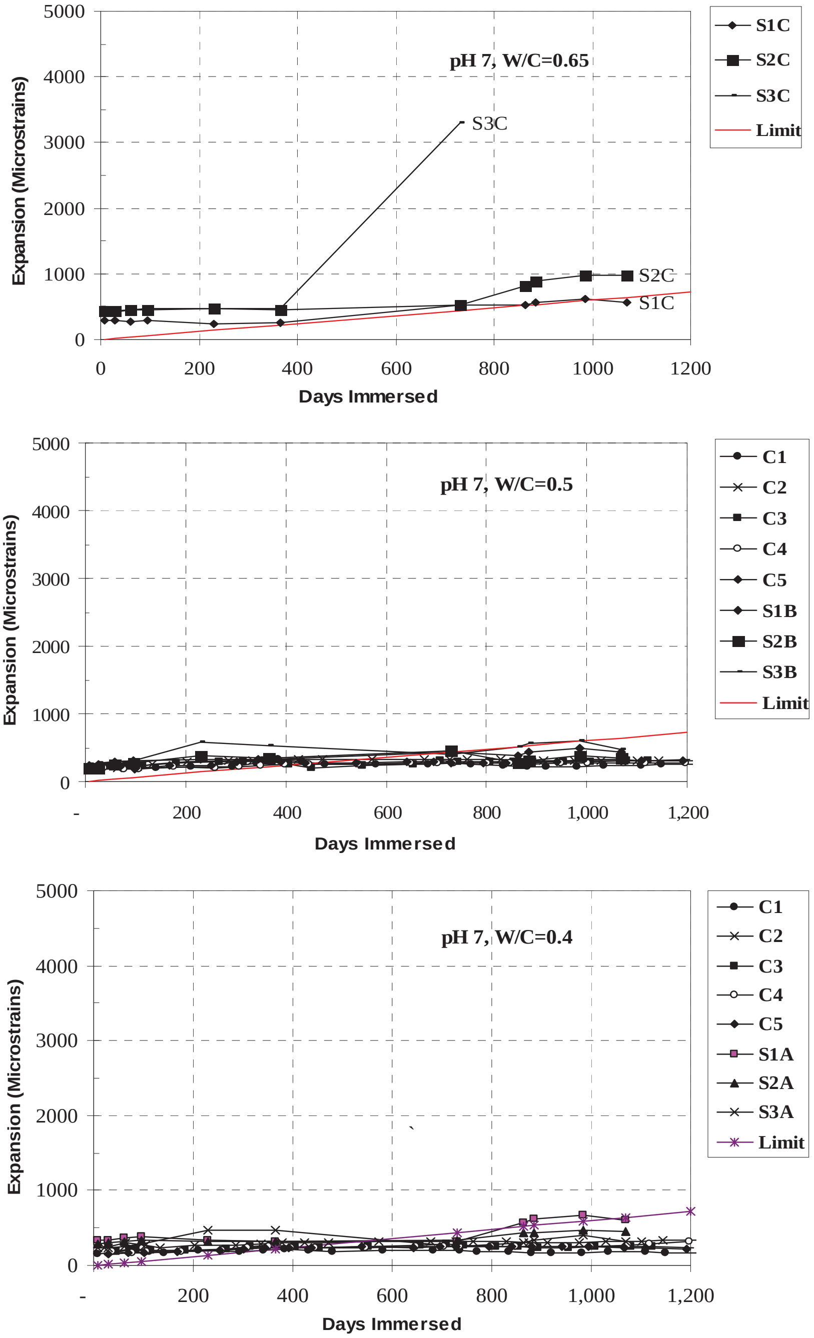

Figure 2 Expansion of concrete prisms in 5% Na_2SO_4 solution at pH7

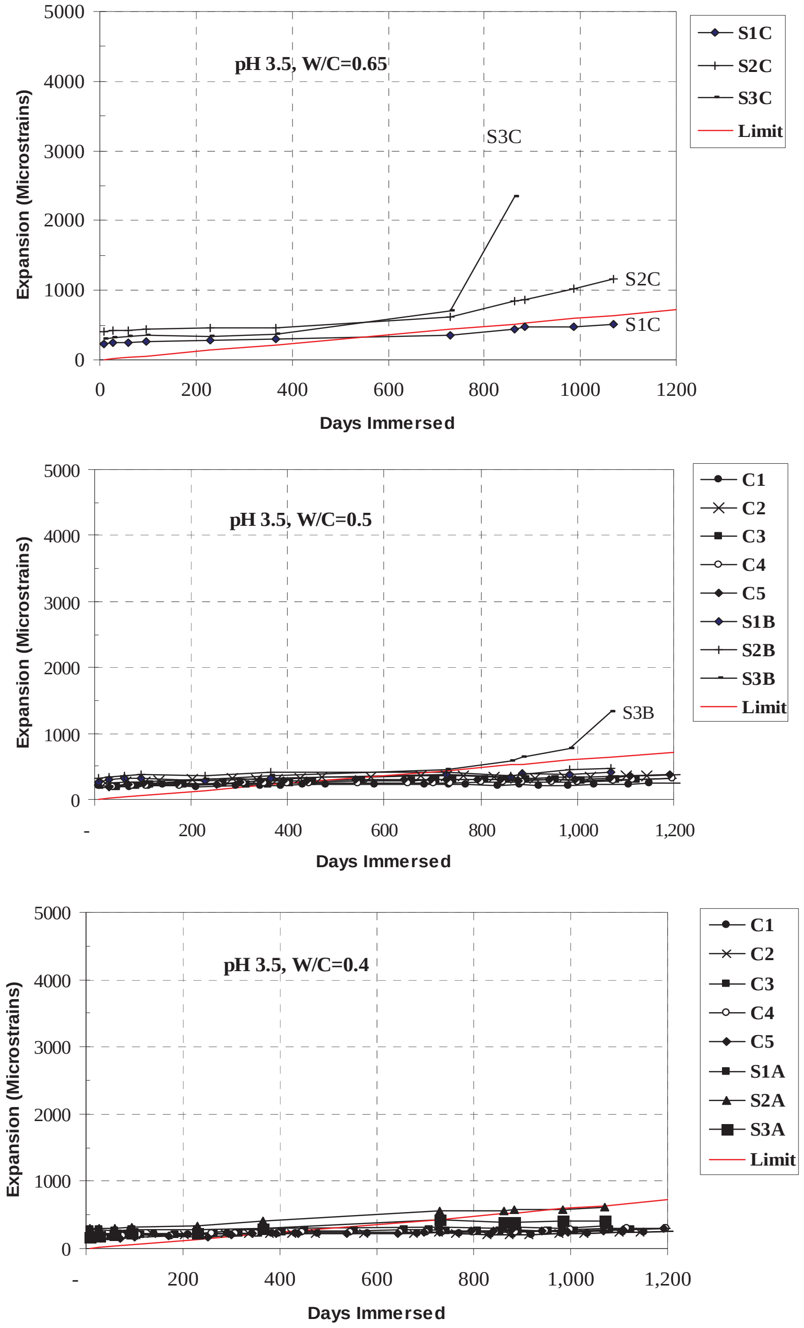

Figure 3 Expansion of concrete prisms in 5% Na_2SO_4 solution at pH 3.5

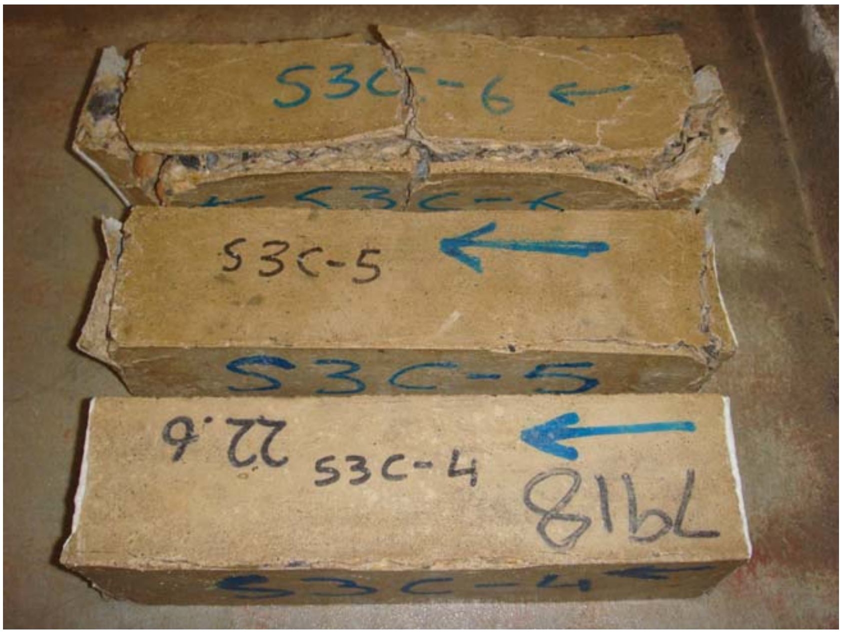

Plate 1 Failure of S3C (w/c 0.65) prisms after 570 days in 5% Na_2SO_4 at pH 7

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

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 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.

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.

Table I 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