Introduction
Concrete exposed to sulfate solutions can be attacked and may suffer deterioration to an extent dependent on the concrete constituents, the quality of the concrete in place and the type and concentration of the sulfate.
Knowledge of the sulfate resisting characteristics of concrete is necessary so that the appropriate steps can be taken to minimise the deterioration of concrete exposed to sulfate solutions.
For many years, sulfate resisting cement was specified in terms of its chemical constituents. In recent years, sulfate resisting cement has been characterised by its sulfate resisting performance and has been included in AS 3972.
This article reviews the factors affecting sulfate resistance of concrete, seeking to put in perspective their varying influences and thus enabling practical and effective measures be taken to produce sulfate resisting concrete.

Sulfate Attack on Concrete
Occurrence – Naturally occurring sulfates of sodium, potassium, calcium or magnesium are sometimes found in soil or dissolved in ground water or present in aggregates (eg pyrite). Sulfate may be present in industrial effluents and wastes such as in industries associated with the manufacture of chemicals, batteries, aluminium and in the mining industry. The water used in cooling towers may also contain sulfates because of the gradual build-up of sulfates from evaporation.

Mechanism – There are two chemical reactions involved in sulfate attack on concrete:
1. Reaction of the sulfate with calcium hydroxide liberated during the hydration of the cement, forming calcium sulfate (gypsum).
2. Reaction of the calcium sulfate with the hydrated calcium aluminate, forming calcium sulfoaluminate (ettringite).

Both of these reactions result in an increase in the volume of solids which is the cause of expansion and disruption of concretes exposed to sulfate solutions.
It should be pointed out that sulfates and chemicals in general rarely, if ever, attack concrete if they are in a solid or dry form. To result in significant attack on concrete, sulfates must be in solution and above some minimum concentration.
The severity of sulfate attack on concrete depends on the following:
- Type of sulfate; magnesium and ammonium sulfates are the most-damaging to concrete.
- Concentration of the sulfate; the present of more-soluble sulfates is more damaging to concrete.
Most recommendations take into account the amount of sulfate present in classifying the severity of the attack Table 1.

- Whether the sulfate solution is stagnant or flowing; severity of the attack increases in the case of flowing waters. Thus, the nature of the contact between the sulfate and the concrete is important. More intensive attack takes place on concrete which is exposed to cycles of wetting and drying than on concrete which is fully and continuously submerged in the solution.

- Pressure; severity of the attack increases because pressures tend to force the sulfate solution into the concrete.

- Temperature; as with any chemical reaction, the rate of the reaction increases with temperature.

- Presence of other ions; other ions present in the sulfate solution affect the severity of the attack. A typical example is seawater which contains sulfates and chlorides. It is generally found that the presence of chloride ions alters the extent and nature of the chemical reaction so that less expansion is produced in concrete due to the sulfates in seawater.

As can be seen, the intensity of the sulfate attack is a complex question which is influenced by many factors. In practice, however, it is difficult to consider all the factors involved and in most cases, the severity of the attack is related mainly to the sulfate concentration and the means for combating it are specified accordingly.

### Factors Affecting Sulfate Resistance of Concrete

Sulfate attack on concrete will take place when the sulfate solution penetrates the concrete and chemically reacts with its constituents, mainly the cement matrix. Thus, factors affecting sulfate resistance of concrete are not only those influencing the chemical reaction with the cement matrix, but also those influencing the permeability and the overall quality of the concrete.

#### Cements

The relationship between sulfate resistance of portland cement and its tricalcium aluminate (C₃A) content is well established. Portland cement containing less than 5% C₃A has been classified as sulfate resisting cement and used as the specification criterion in many codes and standards for cement all over the world, including the Australian Standards until relatively recently.

### Table 1 Recommendations for Concrete Exposed to Sulfates

<table>
<thead>
<tr>
<th>Sulfate concentration, SO₄²⁻</th>
<th>Min cement content (kg/m³)</th>
<th>Min curing – equivalent moist curing (days)</th>
<th>Added protection needed?</th>
<th>Min concrete cover to reinforcement (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>in water (mg/L)</td>
<td>in soil (%)</td>
<td>Cement type</td>
<td>Max w-c ratio</td>
<td></td>
</tr>
<tr>
<td>&lt;400</td>
<td>&lt;0.4</td>
<td>GP, GB</td>
<td>0.55</td>
<td>300</td>
</tr>
<tr>
<td>400–600</td>
<td>0.4–0.6</td>
<td>GP, GB</td>
<td>0.5</td>
<td>330</td>
</tr>
<tr>
<td>600–3000</td>
<td>0.5–1.2</td>
<td>SR</td>
<td>0.55</td>
<td>300</td>
</tr>
<tr>
<td>3000–6000</td>
<td>1.2–2.0</td>
<td>SR</td>
<td>0.45</td>
<td>370</td>
</tr>
<tr>
<td>&gt;6000</td>
<td>&gt;2.0</td>
<td>SR</td>
<td>0.45</td>
<td>370</td>
</tr>
</tbody>
</table>
Studies have shown that cements potentially containing less calcium hydroxide on hydration perform well in sulfate exposure, e.g., certain portland/blast furnace slag cements and portland/fly ash cements. The effectiveness of these cements in enhancing the sulfate resistance of concrete has been the subject of extensive work and many explanations for the improvement have been offered. It was recognised that a limit on C3A content for these cements is neither appropriate nor applicable and that a reliable performance test method and associated criteria are required to characterise cements in terms of their performance. As part of the development of the Australian Standard AS 3972 as a performance-based specification for portland and blended cements, the cement industry, under the auspices of Standards Australia Committee BD/10, completed an extensive investigation which resulted in replacing the limit on C3A for sulfate resisting (Type SR) portland cement by a performance test and a performance limit suitable for Type SR cement, being either portland or blended cement.

A standard test method for measuring expansion of a standard mortar prism exposed to a standard sodium sulfate solution for an extended period of time has been established and is published as AS 2350.14. A maximum limit for expansion after 16 weeks of sulfate exposure is set at 900 microstrain for Type SR cement. This maximum limit takes into account not only the performance of the cement but also the precision of the test method. The precision of the test method is such that the difference between two test results for the expansion after 16 weeks of exposure to a standard sodium sulfate solution, obtained in two different but experienced laboratories under conditions of reproducibility, may be expected (probability of 95%) to be up to 300 microstrain. This maximum limit for expansion implies that it must not be exceeded by one or any result. For example, a sulfate resisting cement could have an average, or target, expansion at 16 weeks of 600 microstrain or less so that a single result obtained in a different laboratory may not exceed the maximum limit set in the Standard.

Caution should be exercised in interpreting the expansion results. The test method is inherently of lower precision than other performance tests, e.g., strength or drying shrinkage. Thus, for example, a cement producing an average expansion result of 500 microstrain may not be of a significantly better performance than another cement with an average expansion result of 600 microstrain.

It should be pointed out that the use of Type SR cement alone will not guarantee the production of sulfate resisting concrete. As outlined in this article, other factors are involved and should be considered as their effect may outweigh the effect of cement on the sulfate resistance of concrete.

Cement content Cement content of concrete significantly affects its sulfate resistance, regardless of the composition of the cement as is evident from Figures 1 and 2.
The data presented in these figures represent a range of portland and blended cements. The rate of deterioration decreases with increase in cement content, even in concretes made of ordinary portland cement. In other words, to produce sulfate resisting concrete, the use of sulfate resisting cement should be combined with the use of a minimum cement content. This conclusion is reflected in recommendations to produce sulfate resisting concrete (5).

Table 1.

**Water-cement ratio** Low permeability of the concrete is a significant factor influencing its resistance to sulfate attack. Given good quality materials, satisfactory proportioning and good concrete practice, the permeability of the concrete is a direct function of its water-cement ratio and the curing time. In other words, all other factors being equal, sulfate resistance of concrete increases with decreases in its water-cement ratio. This effect of water-cement ratio is shown in Figure 3 which is based on data obtained from exposure tests (6).
Admixtures  There are many types of admixtures available for incorporation in concrete to enhance certain properties, or to achieve economy, or both. Generally, the effect of admixtures on concrete properties depends not only on their formulation and their interaction with the cement, but also on the variations or adjustments they bring about in the proportions of the concrete mix. Thus, admixtures that effect reduction in water-cement ratio and/or increased workability can enhance the sulfate resistance of concrete, provided they are not used to reduce its cement content.

It is well established that admixtures containing calcium chloride adversely affect the sulfate resistance of concrete(7).

Construction practice  Concrete placing, compaction and curing are important factors in producing low-permeability concrete. Adding further water on site during placing of concrete to restore slump or to aid with the final finishing will impair the sulfate resistance of concrete. Adequate compaction and proper curing are required to produce dense concrete with discontinuous capillaries (low permeability).

Finishing of the concrete to provide a dense smooth surface, free of holes and defects can enhance the concrete resistance to sulfate.

Design and detailing  Properly designed and detailed structures and elements should provide for adequate reinforcement, correctly located to minimise cracking. Detailing to minimise ponding and/or areas of turbulence is important in reducing the intensity of the sulfate attack, thus enhancing the sulfate resistance of the concrete.

Sulfate Resisting Concrete

From the previous discussion it may be said that sulfate resistance of concrete can be significantly improved by producing dense impermeable concrete made of sulfate resisting cement, of low water-cement ratio, with sufficient cement content, which is properly placed, compacted and cured.

Various authorities have classified aggressiveness into a number of categories of increasing severity(5,8). Considering this classification and the types of cement currently available, Table 1 gives recommendations for concrete exposed to five classes of sulfates of increasing severity.

In using this table, a number of points should be borne in mind:

- In view of the many factors affecting the intensity of sulfate attack and the many factors influencing the sulfate resistance of concrete, as discussed earlier, these classifications and recommendations should be regarded as guidelines and must be examined in relation to the particular conditions met in practice.
The presence of acidic conditions as in the case of sulfuric acid, may require additional measures to be taken such as the provision of membranes and protective barriers, depending on concentration and temperature of the aggressive solution. Also, magnesium sulfate is more aggressive than sodium sulfate. In the presence of high amounts of magnesium ions (>1000 mg/l) additional measures may need to be taken(5).

As mentioned earlier, Type SR cement can be portland or blended cement complying with the performance requirements of AS 3972. Blended cements may contain fly ash or slag or silica fume or a combination of these.

Conclusion
The importance of the many influences on the sulfate resistance of concrete cannot be too highly emphasised. Whilst the influence of the cement type is important, obviously it is not the only influence. Indeed, in most situations other factors will have an equal if not over-riding influence. It is the mix design of concrete; reduced water content, increased cement content, proper placing, adequate consolidation and effective curing that will produce sulfate resisting concrete.

References
2 AS 3972 Portland and Blended Cements Standards Australia, 1997.
5 Sulfate and Acid Resistance of Concrete in the Ground Building Research Establishment BRE Digest 363, January 1996.
6 Verbeck, G Field and Laboratory Studies of the Sulfate Resistance of Concrete Performance of Concrete, ed. E G Swenson, National Research Council of Canada and the American Concrete Institute, 1967.