Cement Concrete & Aggregates Australia

Chloride Resistance of Concrete

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Contents

1	INTRODU	<u>ICTION</u>
2	CHLORID	DE-INDUCED STEEL CORROSION
3	FACTORS	S AFFECTING CHLORIDE RESISTANCE
_	3.1	General
	3.2	Factors Relating to Concrete 5
	3.3	Factors Relating to the Structure
4		DE TRANSPORT
-	4.1	Transport Mechanisms
		4.1.1 Diffusion
		4.1.2 Capillary suction and absorption
		4.1.3 Permeability
		4.1.4 Migration
		4.1.5 Absorption and desorption11
		4.1.6 Mixed modes
	4.2	Electrochemical Properties 12
	4.3	Marine Exposures 12
	4.4	Relative Severity of Exposure Conditions
5	CHLORID	DE RESISTANCE TESTS
	5.1	Indirect Measures15
		5.1.1 Cement type and water-cement ratio15
		5.1.2 Compressive strength 17
	5.2	Direct Measures
		5.2.1 Chloride diffusion coefficients
		5.2.2 Absorption, sorptivity, ISAT and AVPV
		5.2.3 Coefficient of permeability26
		5.2.4 Rapid chloride permeability test
	5.3	Electrochemical Properties 29
6	COMPAR	ATIVE PERFORMANCE DATA
7	CHLORIC	DE RESISTANCE ENHANCING MEASURES
-	7.1	Sealers
	7.2	Corrosion Inhibitor
	7.3	Other Admixtures 32
8	CONCLU	SIONS
9	REFERE	NCES

1 INTRODUCTION

Corrosion of steel reinforcement in concrete is the most common problem affecting the durability of reinforced concrete structures. Chloride-induced corrosion is one of the main mechanisms of deterioration affecting the long-term performance of such structures¹.

Concrete provides physical and chemical protection to the reinforcing steel from penetrating chlorides which may cause steel depassivation leading to increased risk of steel corrosion. The chloride resistance depends on the permeability of the concrete and the thickness of cover to the reinforcement. The integrity of the concrete cover under service load, in terms of cracking and crack width, also influences the resistance to penetrating chlorides. Corrosion of steel reinforcement is an electrochemical process. Hence electrochemical properties of concrete, such as resistivity, are important inherent properties affecting the corrosion rate of reinforcing steel.

Metha² reconfirmed from a review of case studies that it is the permeability of concrete, rather than its chemistry, which is the key to overall durability. The causes of high permeability are not limited to poor concrete proportion but poor concreting practice, such as incomplete mixing, inadequate consolidation and curing after placement, insufficient cover to reinforcing steel, and badly constructed joints. In service, concrete may exhibit various forms of cracking for reasons such as settlement, premature loading, overloads, and repeated impact. To obtain long-term durability of concrete marine structures, the control of concrete cracking in service through proper mix proportioning and concreting practice is of as much importance as the control of concrete permeability.

This report discusses the various factors affecting chloride resistance of concrete, mechanisms of chloride transport, related test methods and performance specifications. It also assesses additional measures to enhance the chloride resistance of concrete.

2 CHLORIDE-INDUCED STEEL CORROSION

Steel reinforcement embedded in concrete is inherently protected against corrosion by passivation of the steel surface due to the high alkalinity of the concrete. When a sufficient amount of chlorides reaches the steel reinforcement it permeates the passivating layer and increases the risk of corrosion. The resistivity of concrete can also be reduced, affecting the corrosion rate of the steel.



For use in reinforced or prestressed concrete structures the chloride concentrations in cements, mixing water, aggregates, and admixtures are strictly controlled, and the maximum permissible concentrations are given in building standards. AS 1379 ³ restricts the acid-soluble chloride of fresh concrete to 0.8 kg/m³ of concrete.

In most cases, however, excessive amounts of chloride in concrete originate from external sources. The penetration of chlorides into the concrete occurs by various transport mechanisms depending on the exposure conditions. There are significant amounts of chlorides in seawater but chlorides are more limited in groundwater and soil. In many countries de-icing salts, used to combat the build-up of snow and ice on transport infrastructures, are the greatest source of chlorides.

In seawater, chlorides usually pose a greater threat to steel in concrete than sulfates do to concrete as calcium sulphoaluminate or ettringite (the expansive reaction product of sulfate and tricalcium aluminate in the cement) is more soluble in the presence of chloride and hence does not cause the disruptive expansion.

Portland cement reacts with sodium chloride to form chloroaluminates or *Friedel's* salt, thus immobilizing the *chloride* and reducing the *free chloride ions* available to depassivate the steel.

The results of a 34-year long-term exposure of plain and reinforced concrete beams in a tidal seawater exposure in Los Angeles Harbour in California in 1959 and 1961⁴, where freezing and thawing does not occur, found that all plain concrete mixtures (stored at approximately mean tide) display excellent resistance to seawater attack, regardless of cement composition, water-cement ratio, cement content, the use of SCM, and method of curing. However, severe cracking due to corrosion of embedded reinforcing steel developed in some beams stored above high tide, while only minor or no cracking developed in companion beams stored in seawater near mean tide level. The most severe corrosion-induced cracking occurred in concrete with the highest w/c of 0.49 and least cover of 25 mm. The relatively greater degree of steel corrosion in beams stored above high tide is attributed to the greater availability of oxygen at the reinforcing steel surface. Corrosion-related distress was found to be sensitive to concrete cover and water-cement ratio. Prestressed steel appeared to be no more vulnerable to galvanic corrosion than ordinary deformed reinforcing bars. The nickel and painted-on epoxy coatings appeared to provide little, if any, additional protection against corrosion.

3 FACTORS AFFECTING CHLORIDE RESISTANCE

3.1 General

In Australia, a large majority of structures are built either near the coast (where they are exposed to airborne chlorides) or in direct contact with seawater. The durability of reinforced and prestressed concrete structures is thus highly dependent on the resistance of concrete to chloride penetration. The physical resistance of concrete to chloride penetration is influenced by factors relating to the concrete itself, such as the porosity of concrete and interconnectivity of the pore system; and to factors relating to the concrete structure such as the stress conditions and the integrity of the cover.

The *total chlorides* content, being the combined free and bound chlorides, does not give a realistic indication of the risk of corrosion to the reinforcement. It does, however, give an assessment of the long-term risk to structures exposed to chlorides which are also prone to carbonation under certain exposure conditions. Carbonation results in lower pH, enabling the chlorocomplexes to release free chlorides.

3.2 Factors Relating to Concrete

External chlorides penetrate into the interconnecting pores in concrete as bulk liquid by convection, and chloride ions diffuse further into the saturated pore system. Diffusion is controlled by concentration gradients of the free chlorides; thus the capacity of the concrete to physically adsorb and to chemically react with chloride ions affects the free chloride ions concentration in the concrete.

The chloride resistance of concrete is thus highly dependent on the porosity of concrete in terms of pore size, pore distribution and interconnectivity of the pore system. The porosity of concrete is determined by:

- the type of cement and other mix constituents;
- concrete mix proportions;
- compaction and curing.

The type of cement influences both the porosity of the concrete and its reaction with chlorides. The porosity of concrete is highly dependent on the water-cement and aggregate-cement ratios whereas the type and amount of cement affect the pore size distribution and chemical binding capacity of the concrete. The influence of cement type and water-cement ratio on the chloride resistance of concrete, measured in terms of effective diffusion coefficient, is shown in **Figure 3.1**.



Figure 3.1 Effect of water-cement ratio and cement type on the chloride resistance of concrete (CSIRO⁶)



Depth from surface (mm)

Figure 3.2 Variation of porosity with depth of concrete slabs cured using different methods (Gowripalan *et al* ⁵)

The porosity or permeability of insitu concrete is highly dependent on the degrees of compaction and curing during placing and the early life of concrete respectively. Curing greatly affects the porosity of the concrete cover which protects the steel from chloride-induced corrosion. The effectiveness of various curing regimes on the porosity of concrete is illustrated in **Figure 3.2**.

It has been found that curing can improve the chloride resistance of concretes, measured in terms of water sorptivity, to different degrees depending on the type of cement. The effectiveness of early curing on sorptivity is shown in **Table 3.1**.

	RTA sorptivity (mm in 24 hours)				
Type of cement	1-day sealed 27-day air-cured	7-day sealed 21-day air-cured	7-day wet 21-day air-cured		
GP	14	17	5		
GB1	33	27	10		
GB2	40	28	1		
GB3	>50	35	0		

TABLE 3.1	Influence of curing	on sorptivity of	various Grade 50	concretes (Khatri et al 6)
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In the past, the durability property of concrete was specified by maximum water-cement ratio and minimum cement content. With the availability of a range of chemical admixtures and supplementary cementitious materials (SCM), it has become increasingly difficult to specify durability prescriptively. Performance-based specifications are becoming more common and are quantified by the use or adaptation of test methods that measure the principal chloride transport mechanism for specific exposure conditions.

3.3 Factors Relating to the Structure

Concrete structures in service are subjected to varying stress conditions resulting in both macro and microcracking. Flexural cracks are expected and are controlled by limiting the stress in the steel and/or spacing of reinforcement. Thermal cracking is controlled by limiting the differential temperature and restraint conditions during casting and in service⁷.

Research under the *Concrete in the Oceans* programme⁸ found that while macrocrack width may influence corrosion in the short term, the influence decreases with time and that in the long term the influence of crack width on corrosion is likely to be insignificant. There are two possible reasons for the reduced influence of crack width with time: unfavourable electrochemical process and healing of cracks. Research by Japan Port and Airport Research Institute⁹ revealed that narrow cracks (<0.5 mm) were healed during 15 years of exposure of specimens in a tidal pool created by using seawater directly from the sea irrespective of the cement types. It was noted that the deposits, found at the root of the crack, created a highly alkaline media and thereby stopped the corrosion reaction over the steel bars at the root of the crack. It has been reported¹⁰ that chloride concentration increases with crack width being more significant for crack width exceeding 0.5 mm. Cracks 0.3 mm or less in width undergo self-healing, especially in seawater when magnesium and carbonates combined with calcium hydroxide to form insoluble products of magnesium hydroxide (brucite) and calcium carbonate (aragonite) and subsequently fill the cracks.

Concrete under tension has been found to allow greater chloride penetration than the same concrete under compression¹¹. This was attributed to the microcrack at the aggregate-paste interface in the tension zone which expedites chloride diffusion. On the contrary, a reduction in the porosity of the concrete in the compression zone may impede chloride diffusion.

In practice, structural concrete with crack widths within a specified limit is considered to have the same chloride resistance as stress-free concrete. The effect of stress condition can be factored into the chloride resistance of structural concrete such as the diffusion coefficient used to model service life¹².

The integrity of the cover concrete depends on structural design, attention to detailing to control crack width and the compaction the concrete around the steel reinforcement. With such measures in place, the resistance of concrete to chloride penetration will largely depend on the quality of the concrete and to a lesser extent on the stress condition of the structural concrete.

4 CHLORIDE TRANSPORT

The transportation of chloride ions into concrete is a complicated process which involves diffusion, capillary suction, permeation and convective flow through the pore system and microcracking network, accompanied by physical adsorption and chemical binding¹³. With such a complex transportation process, it is necessary to understand individual transport mechanisms and the predominant transport process in order to pinpoint the appropriate method for quantifying the chloride resistance of concrete.

4.1 Transport Mechanisms

Individual transport mechanisms and the associated test methods are described in this section. There is usually more than one transport mechanism involved. Most performance-based specifications are based on the predominant transport mode applicable to the specific exposure condition.

 Table 4.1 summarises the primary chloride transport mechanisms applicable to structures in various exposure conditions.

Exposure	Example of structures	Primary chloride transport mechanism
Submerged	Substructures below low tide.	Diffusion.
	Basement exterior walls or transport tunnel liners below low tide. Liquid containing structures.	Permeation, diffusion and possibly Wick's action.
Tidal	Substructures and superstructures in the tidal zone.	Capillary absorption and diffusion.
Splash and spray	Superstructures about high tide in the open sea.	Capillary absorption and diffusion. (Also carbonation)
Coastal	Land based structures in coastal area or superstructures above high tide in river estuary or body of water in coastal area.	Capillary absorption. (Also carbonation)

TABLE 4.1 Primary	/ chloride transr	port mechanism	for various	exposures
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4.1.1 Diffusion

Diffusion is a transfer of mass of free molecules or ions in the pore solution resulting in a net flow from regions of higher concentration to regions of lower concentration of the diffusing substance. This mode of transport operates in fully saturated media such as fully submerged concrete structures. For porous material like concrete, the diffusion coefficient, D, is the material characteristic property describing the transfer of a given substance driven by concentration gradient.

In *steady-state* chloride diffusion, the effective driving force is the gradient of the free chloride ions in the pore solution; the diffusion coefficient is referred as D_{free} or D_f . D_f can be determined from the difference in concentration of chloride ions in the two cells separated by the concrete. This type of test is used only in research as it is extremely time consuming and thin sections of mortar or concrete are tested.

In the transient or *non-steady-state* diffusion process, the mass balance equation describes the change of concentration in a unit volume with time. This can be accounted for by Fick's second law of diffusion:

 $\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \qquad (1)$

An analytical solution to Equation 1 is given as:

$$C_{x} = C_{s} \left[1 - erf\left(\frac{x}{2\sqrt{Dt}}\right) \right] \qquad (2)$$

where C_x is the chloride concentration at distance x,

x is the distance from the exposed surface,

 C_s is the surface chloride concentration,

D is the chloride diffusion coefficient,

t is the exposure time, and

erf is the error function.

The diffusion coefficient, *D*, is determined from the best-fit curve represented by **Equation 2** for the measured chloride profile.

For concrete, the diffusing chloride may be partially immobilized due to chemical interaction or physical adsorption. Then the balance equation must be extended by a sink, s:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) - s$$

Immobilization of diffusing material is of considerable importance for the experimental determination of diffusion coefficients. As long as the binding capacity of the test specimen is not yet exhausted, the net flow of diffusing material appears to be low. Then, the diffusion coefficient is underestimated. In cases where the sink, *s*, is not taken into account an 'apparent' diffusion coefficient, $D_{apparent}$ or D_a , may be deducted from the acid-soluble chloride profile from the experiments, which then depends on time, *t*.

ASTM C 1556¹⁴ is a standard method for determining the apparent chloride diffusion coefficient of cementitious mixtures by bulk diffusion. Precision estimates are given for both apparent diffusion coefficient and surface chloride concentration. It refers to a precision data source from an interlaboratory study of NORDTEST NT Build 443¹⁵.

In a *non-steady-state* diffusion process, the gradient of the free chloride ions in the pore solution is the effective driving force; the diffusion coefficient derived from measured free chloride concentration profiles is the effective diffusion coefficient, $D_{effective}$ or D_e . The effective diffusion coefficients can also be derived from measured concentration profiles in existing structures and serve as a basis for estimates on the future progress of the chloride penetration.

4.1.2 Capillary suction and absorption

Capillary absorption is the transport of liquids due to surface tension acting in capillaries. It is influenced by the viscosity, density and surface tension of the liquid and the pore structure (radius, tortuosity and continuity of capillaries) and surface energy of the concrete. Chloride can therefore be transported in the liquid solution.

When concrete in not in permanent contact with a liquid such as in the tidal zone, a *non-steady state* transport of the liquid prevails. In this case, the amount of liquid absorbed at the surface of the concrete as well as the amount of liquid transported at any distance from the surface is a function of time.

For short-term contact of the concrete with a liquid, the velocity of the take-up is referred to as initial absorption rate, a, given by the mass of the liquid absorbed per unit area and a function of the contact time, *t*:

$$a = \frac{\Delta m}{A \times f(t^n)}$$

where $a = absorption rate (g/m^2 s^n)$

 Δm = take-up of liquid (g)

A = area in contact with water (m²)

 $f(t^n) = \text{time function}$

A time function = \sqrt{t} is usually valid but functions other than \sqrt{t} may also be valid.

In practice, *non-steady state* capillary absorption is the mode of transport measured as sorptivity or initial surface absorption test (ISAT). In Australia, a variation of sorptivity has been used. CSIRO measures the take-up of liquid per unit area as a depth. This technique has been adopted by the Roads & Traffic Authority of New South Wales¹⁶.

Capillary suction may also develop into a *steady-state* transport phenomenon if suitable boundary conditions are kept constant over time. A concrete member in contact with water on one side will take up the liquid by capillary suction. If the evaporation of the water at the opposite side is in equilibrium with the take-up of water, capillary suction transports the water over a certain section of the concrete member in a *steady-state* process.

Capillary absorption is an important mechanism with respect to the ingress of chlorides into concrete. Non-saturated concrete in contact with a salt solution will take up the salt solution by capillary forces; chlorides thus penetrate into the concrete much faster than by diffusion alone. Simultaneously, chlorides are transported by diffusion to increase the depth of penetration.

4.1.3 Permeability

Permeability is a measure of the flow of liquids or gases through a porous material caused by a pressure head. The permeability of concrete depends on the pore structures and the viscosity of the liquids or gases. This mode of transport is applicable for concrete structures in contact with liquid under a pressure head, such as in liquid-retaining structures. Dissolved chlorides and gases are therefore transported by convection with the permeating water into concrete.

Water permeability can be determined in two ways: steady-state and non-steady-state water permeability. A coefficient of permeability is a material characteristic which is obtained in saturated flow which occurs under a steady-state flow when a constant flow rate is established. It is expressed as the volume of water per unit area of surface per unit time, flowing through a concrete under a constant pressure head and at a constant temperature. Thus water permeability has a unit of m³/(m²·s) or m/s. The permeability of concrete varies between 10⁻¹⁶ and 10⁻¹⁰ m/s. In a saturated sample the water flow in the pores due to hydraulic pressure can be described by D'Arcy's law:

 $Q = K_w \Delta P A / I$

where Q = water flow (m³/s)

 K_w = coefficient of water permeability (m/s)

 ΔP = pressure difference (m) across the sample

A =surface area of sample (m²)

/ = thickness of sample (m)

The time to obtain steady-state flow depends on the pressure applied as well as the composition, size and degree of saturation of the sample. A period of 2 days to 2 weeks may be required for concrete with a water-cement ratio of 0.75 to 0.35 for vacuum-saturated samples under a 3.5-MPa pressure head. A coefficient of variation for repeatability of around 10% has been found for such test.

The CSIRO constant flow water permeability test¹⁷ is based on the steady-state saturated water flow through a 50-mm-thick concrete sample under a pressure gradient of 0.7 MPa. For concrete with very low water permeability less than 1.3×10^{-13} m/s, a non-steady-state water permeability is preferred by measuring the depth of water penetration under a constant pressure. The coefficients of water permeability determined by both methods have been found

to correlate well and a guide to the selection of the more suitable method was developed based on the 28-day compressive strength and the age of concrete at testing¹⁷. The guide is that the constant flow method is preferred if:

 $2.3 \times (T)^2 + 1.1 \times (F_c^{28})^2 \le 10,400$

Where T is the age of the concrete when tested (days), and

 F_c^{28} is the 28-day compressive strength in MPa

The DIN 1048 is one version of the penetration method which reports the water penetration depth as a simplified indicator of water permeability.

4.1.4 Migration

Migration is the transport of ions in electrolytes due to the action of an electrical field as the driving force. In an electrical field, positive ions will move preferentially to the negative electrode and negative ions to the positive one. Migration may generate a difference in concentration in a homogeneous solution or may provoke a species flux in the direction of concentration gradients. This mode of transport may occur accidentally when there is a stray current leakage, or intentionally in concrete rehabilitation techniques.

One popular technique which measures chloride ion migration or the electrical conductance of concrete is the AASHTO T277 or ASTM C1202¹⁸, developed by D Whiting. In these methods, a potential difference of 60 V(DC) is maintained across the ends of 51-mm-thick slices of a concrete cylinder, one of which is immersed in a sodium chloride solution, the other in a sodium hydroxide solution. The amount of electrical current passing through the concrete during a six-hour period is measured and the total charge passed, in coulombs, is used as an indicator of the resistance of the concrete to chloride ion penetration. ASTM C1202 provides precision in terms of single-operator and multi-laboratory precision.

The technique has also been used in combination with others to accelerate the transport of chloride ions such as in the CTH rapid method¹⁹.

4.1.5 Adsorption and desorption

Adsorption is a fixation of molecules on solid surfaces due to mass forces in mono- or multi-molecular layers. Desorption is liberation of adsorbed molecules from solid surfaces.

Adsorption of chlorides is controlled by the micropore structure and the characteristics of the hydrated products, and in particular the specific surface area and surface charge of the pore walls.

4.1.6 Mixed modes

The transport mechanism depends on the boundary conditions as well as on the moisture state and its distribution in the concrete element. Pure *permeation* of a chloride *solution* as well as pure *diffusion* of chloride *ions* will prevail only for a moisture-saturated concrete in which no capillary forces can be active. If dry or non-saturated concrete is exposed to a chloride solution, however, capillary absorption is the dominant mechanism. Nevertheless, small hydraulic pressure heads can support the ingress by permeation, and the diffusion of ions simultaneously carries the ions also into narrow pore spaces where no capillary flow any longer occurs. Except for concrete elements that are continuously submerged in seawater, these mixed modes of chloride transport obviously prevail in most cases for concrete structures in service.

The relative importance of various modes of chloride transportation has been evaluated by examination of the sensitivity of key parameters on the chloride concentration profile²⁰. A transport model based on diffusion, convection and chloride binding was used. It was found that the chloride penetration is sensitive only to the permeability coefficient for concrete at higher permeability of the order of 1.0×10^{-13} m/s (applicable to concrete with w/c of around 0.35) and at great cover depth, whereas for low permeability of the order of 2.0×10^{-16} m/s, the chloride ingress is virtually dependent only on the diffusion coefficient. The range of the diffusion coefficient used was $0.33-2.53 \times 10^{-12}$ m²/s. Other parameters considered include the diffusivity decay constant, temperature of exposure, critical chloride threshold, surface chloride concentration and depth of cover. It was found that the chloride ingress is extremely sensitive to the diffusion decay constant, temperature and depth of cover, and is linearly dependent on critical threshold.

4.2 Electrochemical Properties

Some of the electrochemical properties used in studying corrosion of steel reinforcement in concrete include resistivity and conductivity of concrete, and half-cell potential of reinforced concrete. The resistivity of concrete measures the resistance of concrete against the flow of electrical current and is highly dependent on the moisture condition and the ionic nature of the pore solution. Resistivity therefore reflects the chloride resistance of concrete. The resistivity of concrete increases with time due to continued hydration of cement, and will also decrease with ingressing chloride ions²¹. With macro corrosion, the resistivity of concrete will impact corrosion current and hence the rate of corrosion. Resistivity therefore affects the corrosion resistance rather than the chloride resistance of concrete.

4.3 Marine Exposures

Marine structures are exposed to chlorides from seawater in four exposure conditions:

- submerged zone
- tidal zone
- splash and spray, and
- coastal zone.

Submerged structures are subject to sustained direct contact with seawater. Chlorides penetrate into concrete mainly by *ion diffusion*, and to some extent *permeation* of the salt solutions. The concrete surface zones may form protective coatings with a low permeability due to ion exchange reactions with other compounds of seawater, resulting in films of $Mg(OH)_2$ and $CaCO_3$. Therefore, the penetration rate of chlorides into these structures is often considerably lower than estimated from laboratory experiments, where no protective films can be formed due to the test method chosen.

Structures in tidal or splash and spray zone are subject to cyclic exposure to seawater. Ingress of chlorides into the concrete is supported by *capillary absorption* of the seawater upon direct contact. Capillary absorption gains importance as the degree of drying between the individual wetting periods increases. The splash and spray zone is sometime referred to as the atmospheric zone²².

Coastal structures may be subject to considerable chloride concentration in the atmosphere, which may be deposited or washed out with rain at the surface of structures. Ingress of chlorides into the concrete is supported by *capillary absorption* of the seawater upon direct

contact, and chloride removal during wash out is possible through reverse diffusion. With long drying periods, carbonation of the concrete surface may lead to the release of the bound chlorides in the carbonated zone.

There are exposure conditions where concrete is in contact with seawater under significant hydrostatic pressure. In cases where the opposite face of a concrete element is subject to drying condition such as immersed transport tunnel or basements, Wick action needs to be considered²³.

 Table 4.1 summarises the primary chloride transport mechanisms applicable to structures in various exposure conditions.

A field study conducted by Veritec's Seawater Laboratory in Norway²⁴ on the effect of static and dynamic loads on corrosion behaviour of reinforced concrete structures in various exposures has found that for completely submerged concrete, diffusion of oxygen to the embedded steel is nearly totally restricted due to blocking of pores and the cracks by the formation of calcareous products on the concrete surface. No corrosion was found and the danger of localised attack on reinforcing steel, exposed in the bottom of a submerged crack with a surface width up to 1 mm was negligible. The corrosion conditions for concrete structures spanning through several environmental zones (multi-zone) differ from those found on a completely submerged structure due to a more ample oxygen supply. No significant effects of loading condition on the corrosion behaviour were found for both the submerged and multi-zone structures.

4.4 Relative Severity of Exposure Conditions

The severity of various exposures is reflected in specifications. Mehta² highlighted that, for example, both FIP and ACI 357R have similar recommendations of 50-mm cover thickness over principal reinforcing steel and 75-mm over prestressing tendons in submerged zone. In the splash zone and the atmospheric zone, which are subject to seawater spray, the recommended cover thickness is 65 mm for reinforcing steel and 90 mm for prestressing steel. Stirrups may have 13 mm less cover than the preceding recommended values.

The Australian Standard on Concrete Structures, AS 3600, has three exposure classifications: B2 – coastal (up to 1 km from coastline and usually referred to as atmospheric exposure), B2 – permanently submerged, and C – tidal or splash zones. A study²⁵ comparing chloride ingress into structural and fender prestressed concrete piles of Iluka Wharf, at the mouth of the Clarence River in northern New South Wales, revealed the tidal or splash zone to be the most severe followed by the fully submerged and atmospheric zone. The severity was determined by comparing the level of water-soluble chloride found at an depth of 65 mm from the surface after up to 25 years of exposure. The durability performance of Port Kembla Olympic Pool, with structural components situated in various marine environments, was investigated after over 60 years of exposure²⁶. The findings in terms of chloride profiles also supported the relative classification of exposure conditions in AS 3600 of B2 for atmospheric and submerged zones and C for tidal zone.

In contrast to the above, a Norwegian study of a 60-year-old reinforced concrete pier in Oslo harbour²⁷ found higher chloride concentrations in concrete pillars in the continuously submerged zone than in those in the tidal zone. However, it was noted that the locations just above and within the tidal zone the chloride penetration was measured on concrete cores drilled out through jackets of repaired pillars. Hence the concretes are different and exposed for less than 60 years.

5 CHLORIDE RESISTANCE TESTS

The chloride resistance of concrete is quantified in terms of its properties and the minimum thickness of the concrete cover protecting the reinforcement from the external environment. Concrete has traditionally been proportioned for structural strength capacity and for durability. For durability, concrete mixes are usually prescribed by the maximum water-cement ratio and/ or the minimum cement content. ACI 257R-84 (Reapproved 1997) Guide for the *Design and Construction of Fixed Offshore Concrete Structures*, for example, specified maximum w/c and corresponding nominal concrete cover for various marine exposures.

The advent of chemical admixtures and the use of supplementary cementitious materials (SCM) has provided great flexibility in the production of workable concrete with specific hardened concrete properties to suit each application. These technological developments mean that concrete can have very different properties at the same water-cement ratio depending on the type and amount of cement and chemical admixture. As an example, the relationships between 28-day compressive strength of concrete and water-cement ratio of two types of cement (GP and GB) are shown in **Figure 5.1**.





A range of concrete properties have been used as a measure of its resistance to chloride penetration. Each will be described and discussed in terms of its relevance to chloride transport mechanism, its adoption in specifications and testing precision, and its relationship to measured long-term chloride profile quantified as effective or apparent chloride diffusion coefficients. The long-term chloride profile is considered the best measure of the mixed modes of chloride transportation and in particular the chloride level at cover depth.

Long-term research data Two comprehensive sets of research data along with other specific experimental outcomes will be used to relate each concrete property to the long-term chloride diffusion coefficients. CSIRO⁶ examined a range of properties of concretes proportioned from one Type GP and three Type GB cements. Type GB cements comprised cement with either a 30% fly ash, a 65% ground granulated blast-furnace slag or a 10% silica fume content. All

the concretes were membrane-cured for 7 days and tested at 28 days, except compressive strength specimens which were moist cured for 28 days. A set of specimens were immersed in 3% sodium chloride solution and the effective chloride diffusions, $D_{e.28}$ and $D_{e.365}$, were obtained after a 28-day and one-year immersion period respectively. Sherman et al²⁸ also investigated a range of concrete properties and corresponding apparent chloride diffusion coefficients, $D_{a.365}$, after 365-day ponding conducted using AASHTO T259. Fifteen mixtures of concrete were proportioned from Type I cement with and without silica fume (at 5% and 7.5%) at w/c of 0.30, 0.40 and 0.46. The concretes were cured in a number of ways including water cured, wet burlap covered and heat cured.

5.1 Indirect Measures

5.1.1 Cement type and water-cement ratio

The porosity of concrete is highly sensitive to water-cement ratio. The connectivity of the pore system depends on the amount of original mixing–water filled space and the degree to which it has been filled with hydration products. Capillary pores are those voids remaining that were originally filled with mixing water: ie pores with diameters in the range of 3.2 to 3,000 nm²⁹. These capillary pores will cease to be connected at different times in the age of the concrete as a function of w/c and curing condition³⁰. If stored moist, these times are approximately:

w/c	0.4	0.5	0.6	0.7	>0.7
time	3 d	14 d	6 m	1 y	never

Water-cement ratio has therefore been used to specify for durability. However, various types of cements have been found to affect chloride resistance of concrete differently. The cement chemical composition affects both the porosity and chloride binding capacity of cement. The effective chloride diffusion coefficient, D_e , of concrete incorporating a Type GP and three Type GB cements, derived from concrete after one year immersion in 3% sodium chloride solution, are shown in **Figure 5.2**. They show great divergence ranging from 5 to 30 x 10^{-12} m²/s at high w/c of 0.6 to a narrow range of 1 to 4 x 10^{-12} m²/s at low w/c of 0.4. Similar findings are shown for concrete made from an ASTM Type I cement and a blend of ASTM Type I and silica fume. For high chloride resistance concrete, both the type of cement and maximum water-cement ratio must be specified.

The Roads and Traffic Authority of New South Wales (RTA) has used such prescriptive requirements in the B 80 specifications³¹. These are shown in **Table 5.1**.

	Curing period requirement (days)			Other requirements		
Exposure classification	SL cement	Blended cement containing BFS* and/or FA**	Blended cement containing AS***	Minimum cement content (kg/m ³)	Maximum w/c (by mass)	Min strength for durability, f _{c.min(d)} (MPa)
B2	7	14	7	370	0.46	40
С	N/A	14	7	420	0.40	50

TABLE 5.1 Wet curing and other requirements in RTA specifications

*blast furnace slag, **fly ash, ***amorphous silica



Figure 5.2 Effect of water-cement ratio and cement type on the chloride resistance of concrete (CSIRO⁶) (Sherman *et al.*²⁸)

5.1.2 Compressive strength

Both strength and transport characteristics are linked to the pore structure of the concrete. Concrete with low porosity usually has high strength and high resistance to the penetration of aggressive ions. It has been shown³², for example, that oxygen permeability (*K* in 10⁻¹⁶ m²) and the compressive strength of concrete ($f_{c.28}$ in MPa) made of different types of cement can be related. For a range of concretes manufactured from three Type GP cements, the water permeability (K_{28} tested at 28-day in 10⁻¹² m/s) and the mean 28-day compressive strength ($f_{c.28}$ in MPa) has shown excellent correlation, with correlation coefficient R exceeding 95% as shown in **Figure 5.3**. Increases in compressive strength reflect reduced porosity.



Mean 28-day compressive strength (MPa)

Figure 5.3 Influence of concrete strength on water permeability



Mean 28-day compressive strength, f_{c28} (MPa)

Figure 5.4 Influence of strength on medium-term chloride diffusion (CSIRO⁶) (Sherman et al.²⁸)

Australian Bridge Design Standard AS 5100.5 specifies compressive strength grade and corresponding nominal cover for concrete exposed to different environments including B2 and C ('permanently submerged' in sea water and 'in tidal or splash zones' respectively).

For a range of concrete manufactured from Type GP and three Type GB cements, and ASTM Type I cement and Type I and silica fume, the diffusion coefficient of concrete after 365-day exposure in 3% sodium chloride solution, D₃₆₅, have been found to correlate well with their corresponding mean 28-day compressive strength, as shown in **Figure 5.4**. However, the type of cement has been found to greatly influence these longer-term chloride diffusion coefficients, especially for medium to low strength grade C20 to C32 concrete. For higher strength C40 to C50 concrete commonly specified for concrete structures in aggressive environments, such differences diminish as shown in **Figure 5.4**.

5.2 Direct Measures

5.2.1 Chloride diffusion coefficients

It is generally recognised that diffusion is the principal chloride transport mechanism from the external environment into concrete. This is especially true in dense concrete where pore water or vapour is well maintained in the concrete except for a few millimetres at the surface. Chloride diffusion coefficient. D, is a measure of the resistance of concrete to chloride diffusion. The 'diffusion coefficient' and 'concrete cover' combine to provide a measure of the resistance of concrete to chloride ingress. They also enable the prediction of service life and hence are the most direct means of specifying chloride penetration resistance.

The diffusion coefficient can be determined from a non-steady-state or a steady-state of chloride test using Fick's second and Fick's first law respectively. Due to time constraints and specimen configuration, it is more common for the chloride diffusion coefficient of concrete to be determined from a non-steady-state test.

In non-steady-state chloride diffusion, the diffusion coefficient derived from the total or acid-soluble chloride profile, which accounts for both the free and bound chloride, is the apparent diffusion coefficient, D_a . The diffusion coefficient derived from the free or water-soluble chloride profile is the effective diffusion coefficient, D_e . Both D_a and D_e are highly dependent on the exposure period with an order of reduction found from a 28-day exposure to tens of years of exposure as shown in **Figure 5.5**. The curing period and age of the concrete at the commencement of exposure to chloride also influences the resultant diffusion coefficient but to a lesser extent than exposure period as shown in **Table 5.2**. In this case, the diffusion coefficients are of the same order. In durability specifications in term of chloride diffusion coefficient, both the age of concrete and exposure period must be clearly specified.

Outing partial prior	Diffusion coefficient after 28-day exposure, $\mathbf{D}_{e.28}$ (10 ⁻¹² m ² /s)			
to exposure (days)	Concrete 1	Concrete 2	Concrete 3	
28	3.17	3.50	3.17	
56	2.25	1.21	1.22	

TABLE 5.2 Influence of curing and age of concrete on D_{e} (Cao *et al* ³³ 1993)



Figure 5.5 Dependence of non-steady-state chloride diffusion coefficient on exposure period (Vallini and Aldred ³⁴)





Figure 5.6 Short-term exposure diffusion coefficient $D_{e.28}$ as indicator for longer-term diffusion coefficient, $D_{e.365}$ (CSIRO⁶)

The chloride diffusion coefficient, determined from a steady-state chloride diffusion, is the effective chloride diffusion coefficient and is considered to be the asymptote of the corresponding non-steady-state effective chloride diffusion coefficient, D_e, derived from an indefinite exposure period.

In Australia, the first major project where concrete was specified for durability by diffusion coefficient was the West Tuna and Bream B concrete gravity-base offshore structures in 1993. The apparent chloride diffusion coefficient of the 56-day cured concrete after 28-day immersion in substituted ocean water was $0.8 \times 10^{-12} \text{ m}^2/\text{s}$.

The apparent diffusion coefficient results of two properly conducted tests, according to ASTM C1566, should not differ by more than 39.8% of the mean value.

Diffusion coefficients from a short-term exposure period (say 28 days, $D_{e.28}$) are the more practical specification used for major infrastructure projects when there is sufficient leadtime for the appropriate concrete mix design to be developed and tested prior to commencement of construction. Such diffusion coefficients are reasonably good indicator of the longer-term chloride resistance, $D_{e.365}$, as shown in **Figure 5.6** for a set of one Type GP and three Type GB cement concretes. The correlation coefficient, R, of 74% indicates that short-term diffusion coefficients are not necessarily a very good indicator of longer-term chloride resistance. The results also show a reduction of diffusion coefficients with exposure period, with the value of $D_{e.28}$ being about a third of $D_{e.365}$.

5.2.2 Absorption, sorptivity, ISAT and AVPV

A number of absorption-related properties are used to indicate the porosity and durability potential of concrete. Absorption, initial surface absorption (ISAT), sorptivity and apparent volume of permeable void (AVPV) are each fundamentally a measure of capillary absorption or absorption rate of concrete.

Absorption is a measure of multi-dimensional capillary absorption of water into concrete. The amount of water absorption of a concrete depends on the porosity and its interconnectivity, the moisture condition or degrees of internal drying and the temperature of the water. AS 1012.21. BS 1881: Part 122 and ASTM C642 are the respective Australian, British and American Standard test methods for water absorption determination.

Absorption has been used as a measure for durability in concrete products such as pipes and blocks. It has not been commonly used to measure the chloride resistance of concrete, possibly because it is not a good indicator of chloride diffusion coefficient as shown in **Figure 5.7**.





Sorptivity is a measure of one-dimensional capillary absorption rate as a function of time and provides a good indication of the pore structure and its connectivity of the near-surface concrete. There are two methods of measuring sorptivity. The first (RTA T362) measures the depth of penetrating water front into the concrete and the second (ASTM C1585-04) measures the depth of water penetration indirectly through the weight gain in the concrete. The sorptivity is calculated from the slope of the curve of the depth of water penetration with time in mm/hour^{1/2} or the weight gain against time and converted into mm/min^{1/2} or mm/s^{1/2} for the respective methods.

The Roads and Traffic Authority of New South Wales (RTA) has used sorptivity¹⁶ as an alternative performance-based specification (Provision A) in RTA B 80 specifications ³¹. The RTA sorptivity for exposure classes B2 and C **Table 5.3** is measured over a soaking period of 24 hours, hence RTA sorptivity of 1 mm is equivalent to 0.026 mm/min^{1/2}, and RTA sorptivity of 3.8 mm is equivalent to 0.1 mm/min^{1/2}.

Exposure	osure Minimum cement water/cement ratio sification content (kg/m ³) (by mass)	Maximum	Maximum sorptivity penetration depth (mm)		
classification		Portland cement	Blended cement		
B2	370	0.46	17	20	
С	420	0.40	N/A	8	

TABLE 5.3 Durability	requirements for	concrete (Prov	vision A) in RTA	B80 ³¹
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Sorptivity has been found to be a good performance indicator of chloride resistance of concrete. In **Figure 5.8**, the relationship between sorptivity and medium-term effective chloride diffusion coefficients of a range of concretes (one Type GP and three Type GB) is shown to have reasonably good correlation (R = 76%). Lower sorptivity indicates better chloride resistance.

For Class C exposure, a maximum sorptivity limit of 8 mm or 0.21 mm/min^{1/2} is specified for blended cement. It can be observed from **Figure 5.8** that such low sorptivity would indicate a concrete with a very low diffusion coefficient. Such low sorptivity has been found to be difficult to measure and no precision statement is available for the RTA sorptivity.





The sorptivity of matured concrete (tested at 19 years old) has also been found to give a good indication of the long-term chloride resistance of a range of concretes exposed in the splash zone in Port Fremantle in Western Australia ³⁴. The concrete mixes were proportioned from a range of cements including Type GP cement, Type GB cement with 30–65% GGBS and Type GB cement with 10% silica fume, all at nominal water-cement ratio of 0.4. A good correlation coefficient R of 85% is found as shown in **Figure 5.9**. The sorptivity is measured using a method similar to ASTM C1585.

ASTM C1585 states that the repeatability coefficient of variation is found to be 6.0% in preliminary measurements for the absorption for a single laboratory and single operator.

It should be noted that the non-steady-state apparent diffusion coefficient, $D_{a.19yr}$ is about an order of magnitude below the non-steady-state effective diffusion coefficient, $D_{e.365}$, and the sorptivity of the matured concrete is correspondently an order of magnitude below the sorptivity of the 28-day-old concrete. These are good examples of the reduction of diffusion coefficient with exposure time, and the limitation of specifying diffusion coefficient from short-term exposure tests.

The initial surface absorption test (ISAT) is a British Standard method used to measure the water absorption of a concrete surface³⁵. The ISAT is reported to be sensitive to small changes in concrete mix constituents, strength grade and curing. The test is particularly useful for field measurement of insitu concrete surface absorption as the equipment is portable and is inexpensive. However, the surface absorption, like all permeation properties, is very sensitive to the moisture condition of the concrete and hence conditioning of the surface prior to testing is important. In principle, ISAC measures the sorptivity of concrete. However, the geometry of the opening of the cap and its contact with concrete surface mean that the complex two-dimensional absorption measured needs to be analytically converted into the standard one-dimensional sorptivity. In addition, it cannot be used to estimate the porosity of the concrete³⁶.

A tentative classification for concrete durability based on ISAT has been proposed as shown in **Table 5.4**. Experimental evaluation of ISAT-10, the ISAT measurement taken at 10 minutes, showed that localised material differences within the same concrete can cause variations of ISAT-10 up to $\pm 24\%$ whereas various curing regimes can produce ISAT-10 values of $\pm 63\%$ about a mean value of the same concrete³⁷.

Durability classification ranking	ISAT-10 (ml/m²/sec X 10 ⁻²)
1	<50
2	51–70
3	71–90
4	91–110
5	>110

TABLE 5.4 Tentative classification for concrete durability based on ISAT³⁷

The relationship between ISAT-10 and coefficient of chloride diffusion has been evaluated and is reproduced in **Figure 5.10**³⁷. ISAT-10 is an excellent indicator of chloride resistance of concrete quantified in terms of the effective diffusion coefficient. The relationship between ISAT and diffusion found in **Figure 5.10** is very similar to that between sorptivity and longer term effective diffusion coefficients shown in **Figure 5.9**.





Volume of permeable void is a method of determining the water absorption after immersion in water at room temperature, after immersion and boiling, and the 'volume of permeable voids (VPV)' or volume of water absorption after a period in boiling water of a hardened concrete sample. The high temperature affects both the viscosity and the mobility of the water molecules which may enable the greater displacement of pore system within the hardened concrete. This is shown in the relationship between absorption and the absorption after boiling in **Figure 5.11**. Boiling resulted in a 6% increase in absorption with the exception of a few outlying points. The ASTM C642 method measures the volume of permeable voids (VPV) as a percentage of the volume of the solid. The Australian Standard AS 1012.21 test method has been adapted from the ASTM method. It measures the apparent volume of permeable voids (AVPV) as a percentage of the volume of the bulk materials, ie solid and voids. The AVPV has been used by VicRoads to classify concrete durability as shown in **Table 5.5**.



Figure 5.11 Effect of boiling on absorption (Sherman et al.²⁸)

Durability classification indicator	Vibrated cylinders (AVPV %)	Rodded cylinders (AVPV %)	Cores (AVPV %)
1 Excellent	<11	<12	<14
2 Good	11–13	12–14	14–16
3 Normal	13–14	14–15	16–17
4 Marginal	14–16	15–17	17–19
5 Bad	>16	>17	>19

TABLE 5.5 VicRoads classification for concrete durability based on the AVPV

The chloride resistance of concrete has been found to improve with the reduction in VPV as shown in **Figure 5.12**. The resistance based on medium-term effective chloride diffusion coefficients, $D_{e.365}$, has been found to correlate well with the VPV with a correlation coefficient of 86% for VPV exceeding about 13%. At lower VPV in the range of 6–14%, Sherman *et al.* ²⁹ found no correlation (R=12%) between VPV and medium-term apparent chloride diffusion coefficients, $D_{a.365}$. as shown in **Figure 5.12**. From the two sets of slightly different data, there appears to be a change of chloride resistance around the critical VPV level of 12–13%.

Earlier research by Whiting³⁸ examined the relationship between VPV and the chloride content from 2 to 40 mm below the concrete surface as percentage by weight of concrete, after a

short-term 90-day AASHTO T259-80 ponding test in 3% sodium chloride solution. The results indicate improvement in chloride resistance with reducing VPV shown in **Figure 5.13**. It also supports the critical range of VPV of around 12%.

There is no precision statement for VPV in ASTM and AS standards. It is therefore extremely difficult in practice to set narrow compliance limits.





Figure 5.12 Relationships between ASTM VPV₂₈ and D_{e.365} (CSIRO⁶) and ASTM VPV₄₂ and D_{a.365} (Sherman *et al.*²⁸)



Figure 5.13 Influence of ASTM VPV on chloride resistance (Whiting ³⁸)

5.2.3 Coefficient of permeability

The term 'permeability' has been used to describe the ease with which a fluid moves through concrete and in general to describe its durability. Strictly this mode of transport is applicable only to concrete structures in direct contact with a liquid under a pressure head such as occurs in liquid-retaining structures. Dissolved chlorides and gases are therefore transported by convection with the permeating water into concrete.

The coefficient of water permeability, K₂₈, of concrete tested at 28 days has been found to correlate well with the compressive strength of concrete as shown in **Figure 5.5**. There is, however, limited information on the relationship between water or air permeability and chloride resistance. Earlier research³⁸ has examined the relationship between hydraulic and air permeability (m²) and chloride from 2 to 40 mm below the concrete surface after 90-day AASHTO T259-80 ponding test in 3% sodium chloride solution. **Figure 5.14** shows improvements in the chloride resistance of concrete with reduction in both hydraulic and air permeability. However, the air permeability is found to be a more sensitive indicator of chloride resistance than the hydraulic permeability.



Figure 5.14 Hydraulic permeability as an indicator of chloride resistance (Whiting ³⁸)

The DIN 1048 Part 5 is one version of the penetration method which reports the water penetration depth as a simplified indicator of water permeability. There is no precision statement available for water permeability coefficient nor for DIN 1048 test.

Oxygen or air permeability A prototype surface air flow (SAF) device for the estimation of concrete permeability has been developed ³⁹. The method measures the rate of air flow through a vacuum plate placed on a concrete surface under a vacuum of approximately 25 inches of mercury (16.6 kPa absolute pressure). The effective depth of measurement is approximately 12 mm below the surface. The method has been found to correlate well with chloride diffusion constants derived from 90-day ponding tests, as well as with true air permeabilities measured using a pulse decay technique on concretes with a variety of water-cement ratios as well as admixtures such as latex and silica fume.

5.2.4 Rapid chloride permeability test

The rapid chloride permeability test (RCPT) was first developed as a rapid means of assessing permeability of concrete to chloride ions. It was adopted as a standard test method for rapid determination of the chloride permeability of concrete by the American Association of State Highway and Transport Officials as AASHTO T277 in 1989 and subsequently as ASTM C1202¹⁸.

The technique basically measures chloride ion migration or the electrical conductance of concrete. In this method, a potential difference of 60 v DC is maintained across the ends of 51-mm-thick slices of a concrete cylinder, one of which is immersed in a sodium chloride solution, the other in a sodium hydroxide solution. The amount of electrical current passing through the concrete during a six-hour period is measured and the total charge passed, in coulombs, is used as an indicator of the resistance of the concrete to chloride ion penetration. A table classifying concrete resistance to chloride ion penetrability has been proposed⁴⁰ as reproduced in **Table 5.6**.

Whiting⁴⁰ examined the relationship between the rapid chloride permeability tested at 90 days, RCPT_{90} , and chloride penetration determined from the depth of 2 to 40 mm concrete surface after 90-day ponding test in 3% sodium chloride solution, $\text{Cl}_{(2-40\text{mm}).90}$. A very good correlation was found between the charge passed and the amount of penetrating chloride as shown in **Figure 5.15**.

Charge passed	Chloride ion penetrability
>4,000	High
2,000–4,000	Moderate
1,000–2,000	Low
100–1,000	Very Low
<100	Negligible

	TABLE 5.6 Chloride ion	penetrability based	on charge passed	(Whiting ⁴⁰)
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In Australia, the RCPT was first used in the early 1990s to specify highly durable concrete for the sea wall at Sydney Airport Parallel Runway project at the 1000-coulomb limit. According to ASTM C1202, the results of two properly conducted tests in different laboratories on the same material should not differ by more than 51%. The average of three test results in two different laboratories should not differ by more than 42%.



Figure 5.15 ASTM C1202 as indicator of chloride resistance (Whiting⁴⁰)



ASTM C1012 charge passed (coulomb)

Figure 5.16 RCPT_{28} versus $\text{D}_{e.365}$ and RCPT_{42} versus $\text{D}_{a.365}$

The RCPT charge passed has been found to be a good indicator of the chloride resistance of concrete^{17, 28}. The charge passed measured at 28 days or 42 days, RCPT₂₈ or RCPT₄₂, correlates well with the medium-term apparent or effective chloride diffusion coefficients, $D_{a.365}$ or $D_{e.365}$, as shown in **Figure 5.16**. The increase in the age of testing from 28 to 42 days is not expected to affect the charge passed by concrete with 'low' and 'very low' chloride penetrability and hence RCPT₄₂ Data (≤1000 coulombs) are combined with RCPT₂₈ to show the combined relationship for the full range of charge passed shown in **Figure 5.16**.

Concrete with RCPT charge passed below 2000 coulombs shows consistently good chloride resistance with $D_{a.365}$ below 3 x 10⁻¹² m²/s whereas concretes in the 2000- to 3000-coulomb range exhibit highly variable chloride resistance.

Sherman et al.²⁸ found that the correlations between RCPT and long-term chloride diffusion, the surface chloride concentration, and the time-to-corrosion to be highly variable and that it requires individual correlation between the test and every concrete mixture. The widely used 1000-coulomb cut-off limit was claimed to be arbitrary and misleading for many concretes, due to the widely different chloride permeability observed for concretes both meeting and failing such a coulomb limit-based specification. The use of heat curing was found in the same study, for example, to increase the coulomb values of concrete without increasing its actual chloride permeability.

5.3 **Electrochemical Properties**

Electrical resistivity of concrete is one of the most significant parameters controlling the rate of active corrosion of the embedded steel reinforcement. Insitu measurement of concrete resistivity can be made by using four equi-spaced electrodes with surface contacts. An alternating current, I, is passed via the concrete through the outer pair of contacts, and the resulting voltage, V, between the inner contacts is measured. For a semi-infinite homogeneous material, the resistivity is given by:

 $\rho = 2\pi a (V/I)$

where a is the contact spacing. A commercial instrument is available. However, results obtained from insitu measurement have been found to be highly variable. Recent investigation⁴¹ has revealed field measured electrical resistivity to vary with electrode spacing, concrete cover and the presence of embedded steel. Measurement should be taken with electrode spacing of less than 30 mm and as far away as possible from embedded steel.

The resistivity can be measured using the Wenner Bridge four-electrode method⁴². However, it is essential for the electrodes to be cast into the concrete to ensure good electrical contact. Such a method is therefore more commonly used in corrosion research and provides more consistent and repeatable measurements.

In a 5-year research on chloride-induced corrosion of steel in a range of concretes exposed to simulate tidal exposure, it was found⁴³ that concrete with high resistivity resulted in a substantially longer time before a probable active corrosion state. High resistivity concrete is defined as concrete with 28-day resistivity of greater than 4000 ohm cm or a 56-day resistivity of greater than 5000 ohm cm. The cover to reinforcement required is:

For low resistivity concrete
$$C = \left(\frac{2822}{S^{1.28}}\right) \times \sqrt{2}$$

For high resistivity concrete

$$= \left(\frac{2822}{S^{1.28}}\right) \times \sqrt{t}$$

 $C = \left(\frac{226,537}{S^{2.61}}\right) \times \sqrt{t}$

where C = cover to reinforcement (mm)

S = mean 28-day compressive strength (MPa)

t = time taken to reach a probable active corrosion (years).

COMPARATIVE PERFORMANCE DATA 6

The suitability of each property as a performance-based indicator for chloride resistance of concrete is considered from the precision of the test method, its relationship with medium-term chloride diffusion resistance, D_{e.365}, evaluated as the correlation coefficient, R (determined from least square method), for the corresponding range of measureable values. These are shown in Table 6.1.

TABLE 6.1 Precision and correlation of each property with chloride resistance

	D _{e.28} (10 ⁻¹² m ² /s)	f ₂₈ (MPa)	Sorptivity ₂₈ (mm/s ^{1/2})	ISAT-10 (10 ⁻² ml/ m²/s)	VPV ₂₈ (%)	RCPT ₂₈ (coulomb)	K (m/s)
Precision from relev	ant standards	s or othe	r sources				
Sources of precision	<i>ASTM</i> C1566	<i>ASTM</i> C39	<i>ASTM</i> C1585	Dhir <i>et al.</i>	ASTM C642	<i>ASTM</i> C1202	DIN 1048
Reportable to	0.001	0.1	0.1x10 ⁻⁴	NA ⁽¹⁾	NA	NA	NA
Repeatability CV	14%	3%	6%	±24%	NA	12.3%	NA
Reproducibility	20%	5% ⁽²⁾	NA	NA	NA	18%	NA
	(0)		

Correlation to $\mathbf{D}_{e,365}$ of a GP and three GB cement concretes (CSIRO)

Range of value correlation coef, <i>R</i>	10–60 74%	20–60 58% ⁽³⁾	15–100mm 76%	_	6–13, 13–18 12%, 86% ⁽⁴⁾	2–5 x10 ³ 76%	-
Critical range to one order change in D _{e.365} 1 to10 m ² /s	28	37	41 mm	_	1.5	1270	_
Increment used in classifications	_	10th MPa	RTA B80 12 mm	20	VicRoads 1–2%	C1202 1000	_

Correlation to other chloride resistance indicators, %

Sherman D _{a.365}	_	_	_	_	12 ⁽⁴⁾	89	_
Dhir D _{e.steady}	_	_	_	99(5)	_	_	_
Whiting Cl _{2-40 mm.90}	_	_	_	_	99	97	78

(1) Not available

(2) For 150-mm-diameter cylinders

(3) Better correlation R of 94% for Type GP cement and 80% for Type GB cements

(4) Correlation R of 86% and 12% are applicable to VPV range of 13–18% and 5–14% respectively

(5) Correlation to steady-state diffusion coefficient, D_{e.steady}

With the exception of compressive strength, sorptivity, VPV and RCPT correlate reasonably well with the medium-term chloride diffusion coefficient, $D_{e.365}$, with better than 75% correlation and around 74% between short-term $D_{e.28}$ and $D_{e.365}$. The correlation improves in all properties for high chloride resistance concretes. Compressive strength shows a poor correlation coefficient of 58% to the medium-term chloride diffusion coefficient unless the type of cement is also considered (94% for Type GP cement and 80% for Type GB cements). Hence strength and cement type are the most suitable parameters for a semi-prescriptive specification. For the ISAT and coefficient of water permeability, *K*, their relationships with other measures of chloride resistance are also determined and shown in **Table 6.1**. Very good correlation was found for ISAT and chloride in the 2- to 40-mm cover zone. The VPV, however, shows no correlation with the medium-term chloride diffusion coefficient in the VPV range of 6–13 %, the range specified by VicRoads for 'good' and 'excellent' concrete (vibrated).

In setting the performance limits for each chloride resistance property, the sensitivity of each property should be evaluated in terms of the 'critical range' and the corresponding repeatability of the test. The critical range chosen for comparison in **Table 6.1** is the range of each property required to detect a change of one order of magnitude in $D_{e.365}$ from 1.0 to10.0 x10⁻¹² m²/s.

7 CHLORIDE RESISTANCE ENHANCING MEASURES

This section examines the alternative methods used to improve the chloride resistance of concrete, viz surface treatments and the use of integral admixtures and corrosion inhibitors in concrete.

7.1 Sealers

Damp-proofing is a process of treating a concrete surface to reduce absorption. Dampproofing by the use of sealers is considered more economical than waterproofing. There are two categories of sealing materials: coatings and penetrating sealers. Surface coatings can be clear or coloured. Penetrating sealers can be either inert pore-plugging materials or chemically reactive products. Sealers are useful on surfaces exposed to cyclic wetting and drying but are not recommended in continually submerged situations.

A survey revealed that highway agencies in the United States and Canada were very interested in sealers but use remained limited. Linseed oil has been used although a number of agencies no longer use it because of its poor long-term performance. Highway agencies are more often using materials such as silanes and siloxanes. Preliminary experimental work carried out under the SHRP program⁴⁴ indicated that penetrating sealers could have a significant effect on the surface electrical properties of concrete, with electrical resistance in the near-surface layers of concrete staying higher after wetting than in untreated concretes. Additionally, regaining of insulation characteristics after removal of surface water was more rapid for sealed than for unsealed specimens.

Two test procedures have been developed to evaluate the effectiveness of sealers. The first 'surface resistance test' with a criterion of 200 k-ohms after 4 minutes of testing was selected for differentiating between effective and ineffective sealers. The second 'absorption method', a modified European procedure (RILEM II.4) indicated that column drops of less than 10 mm in 4 minutes are generally associated with effective sealers, while drops over 20 mm in 4 minutes are associated with ineffective sealers. Field trials in the states of Vermont, California and Minnesota showed good agreement between the test methods and the expected performance of the sealers in structures.

A recommended practice for the use of sealers is outlined in ACI 345.1R *Routine Maintenance* of *Concrete Bridge Members*.

7.2 Corrosion Inhibitor

Corrosion inhibitors are admixtures incorporated into fresh concrete. ACI 222.3R *Design and Construction Practices to Mitigate Corrosion of Reinforcement in Concrete Structures* defines them as chemical substances that decrease the corrosion rate when present at a suitable concentration, without significantly change the concentration of any other corrosion agent. These admixtures act on the steel surface, either electrochemically (anodic, cathodic, mixedinhibitor) or chemically (chemical barrier) to inhibit chloride-induced corrosion above the chloride-corrosion threshold level. Commercial systems include an inorganic admixture containing calcium nitrite and several organic admixtures containing: alkanolamines; amines and esters; alkanolamines and amines and their salts with organic/inorganic acids; alkanolamines, ethanolamine and phosphate. Combined organic/inorganic concrete admixture containing amine derivatives and sodium nitrite are also available. There are also surface applied coatings which incorporate a corrosion inhibitor.

Laboratory evaluation and field performance Independent investigations⁴⁵ on the effectiveness and harmlessness of calcium nitrite as a corrosion inhibitor in cracked and uncracked concrete have found that calcium nitrite does not affect the chloride diffusion coefficient of concrete. The threshold value for the corrosion inducing chloride content to a depth of 20 mm is at least doubled in comparison to the untreated concrete. The initial results suggest that calcium nitrite could be effective under simulated severe exposure conditions even for 'poor' concrete (w/c = 0.5). Results after 400 days of exposure showed that calcium nitrite was harmless for the 'poor' concrete in the region of cracks. On the contrary, for the good quality concrete (w/c = 0.38), calcium nitrite seems to be effective even in the region of cracks with a width of 0.30 mm.

The effectiveness of a number of corrosion inhibiting systems were evaluated in field exposure of concrete barrier walls of the Vachon bridge located North of Montreal by the National Research Council (NRC) of Canada. The bridge is subject to the simultaneous effects of de-icing salt contamination, freeze-thaw and wet-dry cycles. The commercial systems investigated include an inorganic admixture containing calcium nitrite and several organic admixtures. The concrete is reported to have a water-cement ratio of 0.36, a CSA Type 10 cement content of 450 kg/m³, an air content of 6.5%, a slump of 80 mm, and an average 28-day compressive strength of 45 MPa. After 10 years exposure between 1996 and 2006 with measurements of half-cell potential, corrosion rate (Gecor 6 measuring polarisation resistance) and concrete resistivity, as well as coring and determination of chloride contents at various depths, it was concluded⁴⁶ that the inorganic admixture system gave consistently good performance, with a reduced risk of corrosion, followed by other organic concrete admixtures in comparison to the control system.

7.3 Other Admixtures

Apart from water reducers and high-range water reducers (superplasticisers) used to produce better chloride resistance concrete through the reduction of water-cement ratio, a range of admixtures are used to provide a physical barrier to reduce the rate of penetration of corrosive agents into the concrete. Bitumen, silicates and water-based organic admixtures consisting of fatty acids, such as oleic acid; stearic acid; salts of calcium oleate; and esters, such as butyloleate, are typically used in these types of admixtures. There are limited long-term studies evaluating the effectiveness of such admixtures.

The potential benefit of the use of an hydrophobic admixture on the chloride resistance of concrete has been studied in a long-term field exposure experiment at Port Fremantle in Western Australia. The mix proportions and long-term diffusion coefficients of mixes with and without the admixture have been reported³⁴.

It appears that the addition of this particular admixture resulted in an adjustment of water content resulting in GP cement concrete and possibly 65% GGBS concrete with higher watercement ratios than corresponding concrete without the admixture. However, for concrete with the same cement content, the admixture has resulted in substantial improvement in chloride resistance observed in terms of the diffusion coefficients after 6-year exposure in a splash zone. The improved chloride resistance remained moderate after 19-year exposure, with D_a around three times that of concrete with 10% silica fume.

8 CONCLUSIONS

Concrete provides physical and chemical protection to the reinforcing steel against penetrating chlorides which may cause steel depassivation, leading to increased risk of steel corrosion. The chloride resistance of concrete depends on the permeability properties of the concrete and the cover thickness to the reinforcement. The integrity of the concrete cover under service load, in terms of cracking and crack width, also influences the resistance to penetrating chlorides.

The resistance of the concrete depends largely on the porosity and interconnectivity of the pore system in the concrete, and to a lesser extent on the chemical binding capacity of the cement. The chloride resistance of concrete thus depends on the mix constituents, mix proportions, the degree of compaction and curing given to the fresh and hardened concrete.

A range of concrete properties has been used to measure the chloride resistance of the concrete. As diffusion and capillary absorption are the primary chloride transport mechanisms into most concrete structures exposed to chlorides, the relevant concrete property is thus quantified in terms of its relationship to a 365-day chloride profile or a 90-day penetrating chloride in the 2- to 40-mm cover region. The chloride diffusion coefficient, derived from the chloride profile after long-term exposure, is considered one of the best indicators of chloride resistance.

A number of parameters and corresponding test methods have been examined and, where appropriate, were related to various chloride transport mechanisms as follows:

Diffusion	Chloride diffusion coefficient, D _{e.28} (10 ⁻¹² m ² /s)
Capillary absorption	Absorption (%) Sorptivity (mm/min ^{1/2}), Initial Surface Absorption Test, <i>ISAT</i> (10 ⁻² ml/m ² /s)
	Volume of Permeable Voids, $VPV(\%)$ Compressive strength, f_{28} (MPa), an indirect measure of porosity
Permeability	Water Permeability Coefficients, K (m/s)
Migration	Rapid Chloride Permeability Test, RCPT (Coulomb)
All transport	Water-cement ratio, w/c.

The use of prescriptive specifications of cement type and w/c has been found to be extremely effective in specifying chloride resistance. The effect of the type of cement on chloride resistance of concrete is quite evident for concrete at higher w/c, but such distinctions diminish for concrete at low w/c below about 0.45 (0.35 for concrete with silica fume). There is, however, no acceptable method of testing w/c of hardened concrete; control of w/c can be only conducted at the batch plant.

A semi-prescriptive specification of cement type and compressive strength has also been found to be extremely effective in specifying chloride resistance. Like w/c, the distinction in chloride resistance between different cements diminishes as compressive strength increases beyond 40 MPa. This represents the most practical approach to specification and quality control using compressive strength grade and characteristic-strength-compliance criterion.

For performance-based specifications, capillary absorption properties (sorptivity, ISAT and VPV) and migration property (RCPT) have all been found to be as good as indicators of longer-term chloride resistance as the short-term chloride diffusion coefficient. Critical comparative performance data are given in Section 6. It was found that there are limits to the effective range of sorptivity (15–100 mm) and VPV (13–17%) that are sensitive to chloride resistance. There are no published precision data for these tests and narrow performance classes can be set only with known precision data. The water permeability has also been found to be a good indicator of only the short-term chloride resistance, hence its use should be limited to liquid-retaining structures.

The resistivity of concrete has been found to be a good indicator of chloride resistance in laboratory-based measurement. The variability of insitu resistivity measurement and the lack of correlation data with longer-term diffusion coefficient have so far prevented its use in chloride resistance specifications.

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CCAA OFFICES

SYDNEY OFFICE:

Level 6, 504 Pacific Highway St Leonards NSW Australia 2065 **POSTAL ADDRESS:** Locked Bag 2010 St Leonards NSW 1590 **TELEPHONE:** (61 2) 9437 9711 **FACSIMILE:** (61 2) 9437 9470

BRISBANE OFFICE:

Level 14, IBM Building 348 Edward Street Brisbane QLD 4000 **TELEPHONE:** (61 7) 3831 3288 **FACSIMILE:** (61 7) 3839 6005

MELBOURNE OFFICE:

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PERTH OFFICE:

45 Ventnor Avenue West Perth WA 6005 TELEPHONE: (61 8) 9389 4452 FACSIMILE: (61 8) 9389 4451

ADELAIDE OFFICE:

PO Box 229 Fullarton SA 5063 **TELEPHONE:** (61 8) 8274 3758

PREMIXED CONCRETE AND EXTRACTIVE INDUSTRIES OFFICE PO Box 243 Henley Beach SA 5022 **TELEPHONE:** (61 8) 8243 2505 **FACSIMILE:** (61 8) 8125 5822

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WEBSITE: www.ccaa.com.au

EMAIL: info@ccaa.com.au

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