Testing and Specifying Chloride Resistance of Concrete

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Abstract A wide range of test methods has been used to measure the resistance of concrete to chloride penetration. Each method is purported to measure the property of concrete central to the chloride transport mechanism into concrete. They include water absorption, water permeability, chloride diffusion, chloride migration and electrochemical resistance. In this paper, an assessment of five commonly specified properties: namely the water-cement ratio, 28-day diffusion coefficient, sorptivity, volume of permeable voids, and ASTM C1202 rapid chloride permeability; was made in terms of its relation to the long-term chloride diffusion coefficient taking into consideration the precision of the test methods. The long-term chloride diffusion coefficient is derived from the chloride penetration profile into concrete after one-year immersion in sodium chloride solution. The results cover a range of concretes commonly used in Australia.

Design for Durability

Engineers design structures to satisfy both the functional and sustainable requirements. For reinforced concrete structures, the choice of concrete is particularly important for long-term performance of structures built in aggressive environments. Structures in coastal and marine environments are required to be corrosion resistant as chlorides, abundant in these environments, are particularly corrosive to structural steel and steel reinforcement. In reinforced concrete structures, the concrete cover provides the necessary protection against the penetrating chlorides. Structural design and detailing limit and control the distribution and width of cracking to limit access of chlorides to the steel reinforcement.

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The choice of concrete should be based on concrete with suitable fresh and hardened concrete properties: fresh concrete properties suitable for the geometry of structural members and the construction method used; hardened concrete properties and structural design which minimize crack width and provide good protection to the steel reinforcement throughout its service life.

In designing for durability against chloride-induced corrosion, the quality of concrete will affect both the initiation and propagation periods of the service life. Cao and Sirivivatnanon, 2001 presented a comprehensive service life model based on a chloride diffusion transport mechanism. The model takes into account the diffusivity decay, temperature and stress condition on the chloride diffusion coefficient. There has been considerable research bridging the knowledge gaps in terms of temperature effect Tang (1996), and the effect of crack width on corrosion (Lim, 2000 and Jang et al., 2011).

Khatri and Sirivivatnanon (2004) applied a simple statistical approach in defining a characteristic service life concept similar to the familiar characteristic strength. The FIB Model Code for service life design (2006) was based on probabilistic service life design with various approaches to define the end of service life. Sirivivatnanon et al (2007a) applied the concept of limit-state service-life design to better define the end of service life. The concept is currently being researched and is probably best the approach to service-life design by design engineers who apply limit-state to their structural design.

Chloride Transport Mechanisms

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 binding (Kropp and Hilsdorf, 1995). 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. Individual chloride transport mechanisms and the associated test methods have been described in CCAA Report on Chloride Resistance of Concrete (2009).

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 I*** summarizes the chloride transport mechanisms applicable to structures in various exposure conditions. It is generally accepted that the predominant chloride transport mechanism is that of diffusion. The strength of various test methods used in measuring the chloride resistance of concrete can therefore be assessed by its correlation to diffusion, and in particular, to the long-term diffusion coefficient.

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.

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. The 'apparent' diffusion coefficient, $D_{apparent}$ or D_a, may be deducted from the acid-soluble chloride profile from the experiments.

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 ingress of the chlorides.

Table I Chloride transport mechanisms into concrete under various exposures

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

Testing and Specifications

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.

Two comprehensive sets of research data along with other specific experimental outcomes are used to relate each concrete property to the long-term chloride diffusion coefficients. CSIRO (1998) examines a range of properties of concretes proportioned from one Type GP and three Type GB cements. The Type GB cements include 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, such as the mean compressive strength. 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 al (1996) 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 ASTM 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.

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. Water-cement ratio has therefore been used to specify 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 1***. They show great divergence ranging from 5 to 30 x 10^{-12} m^2/s

at high w/c of 0.6 to a narrow range of 1 to 4 x 10^{-12} m^2/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 resistant concrete, both the type of cement and maximum water-cement ratio must be specified.

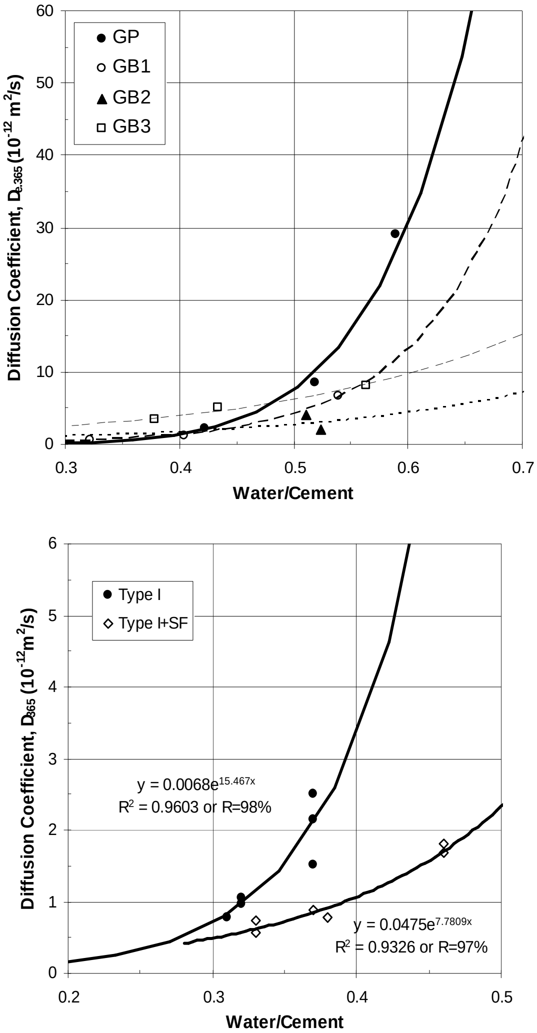

Figure 1 Effect of water-cement ratio and cement type on the chloride resistance of concrete (CSIRO, 1998) (Sherman et al 1996)

The Roads and Traffic Authority of New South Wales (RTA, 2008) has used such prescriptive requirements in the B 80 specifications. These are shown in ***Table II***.

Table II Wet Curing and other requirements in RTA specifications

Exposure classification	**Curing period requirement (days)**			**Other requirements**		
	SL cement	**Blended cement containing BFS* and/or FA****	**Blended cement containing AS*****	**Minimum cement content (kg/m3)**	**Maximum w/c (by mass)**	**Min strength for durability, fc.min(d) (MPa)**
B2	7	14	7	370	0.46	40
C	N/A	14	7	420	0.40	50

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

Chloride diffusion coefficients

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.
The curing period and age of the concrete at the commencement of exposure to chloride also influence the resultant diffusion coefficient but to a lesser extent than exposure period as shown in ***Table III***. In this case, the diffusion coefficients are of the same order. In durability specifications, both the age of concrete and exposure period must be clearly specified.

Table III Influence of curing and age of concrete on D_a (CSIRO,1993)

Curing period prior to exposure (days)	**Apparent Diffusion Coefficient after 28-day exposure, Da.28 (10-12 m2/s)**		
	Concrete 1	**Concrete 2**	**Concrete 3**
28	3.17	3.50	3.17
56	2.25	1.21	1.22

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 lead time for the appropriate concrete mix design to be developed and tested prior to commencement of construction. Such diffusion coefficients are a reasonably good indicator of the longer-term chloride resistance, $D_{e.365}$, as shown in ***Figure 2*** for a set of one Type GP and three Type GB cement concretes. However, the correlation coefficient, R, of 74% indicates that short-term diffusion coefficients are not necessarily the best 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 $D_{e.365}$.

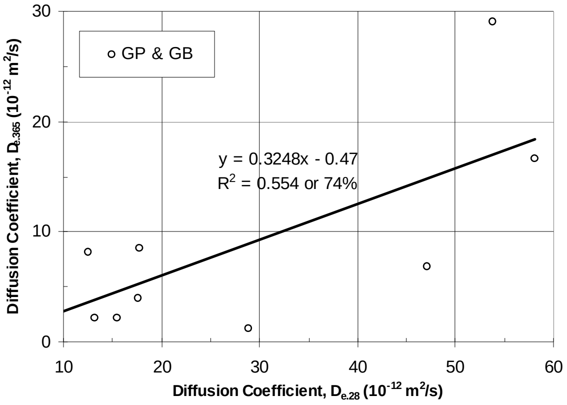

Figure 2 Short-term exposure diffusion coefficient De.28 as indicator for longer-term diffusion coefficient, De.365 (CSIRO, 1998)

According to ASTM C1566, the repeatability and reproducibility coefficient of variation of the apparent diffusion coefficient are 14.2% and 20.2% respectively. Hence the results of two properly conducted tests by the same operator should not differ by more than 39.8%. The results of two properly conducted tests in different laboratories should not differ by more than 56.6%.

Sorptivity and AVPV A

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

Sorptivity

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^{½} or the weight gain against time and converted into mm/min^{½} or mm/s^{½} for the respective methods. The Roads and Traffic Authority of New South Wales (RTA) has used sorptivity as an alternative performance-based specification (Provision A) in RTA B 80 specifications.

The RTA sorptivity for exposure classes B2 and C as shown in ***Table IV*** is measured over a soaking period of 24 hours, hence RTA sorptivity of 1 mm is equivalent to 0.026 mm/min^{½}, and RTA sorptivity of 3.8 mm is equivalent to 0.1 mm/min^{½}.

Table IV Durability Requirements for Concrete (Provision A) in RTA B80

Exposure classification	**Minimum cement content (kg/m3)**	**Maximum water/cement (by mass)**	**Maximum sorptivity penetration depth (mm)**	
			Portland cement	**Blended cement**
B2	370	0.46	17	20
C	420	0.40	N/A	8

Sorptivity has been found to be a reasonable performance indicator of chloride resistance of concrete. In ***Figure 3***, the relationship between sorptivity and longer-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.

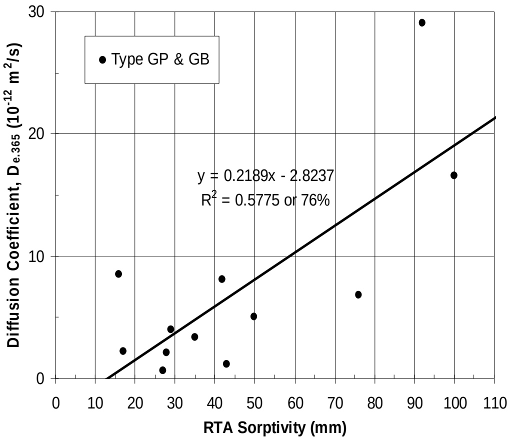

Figure 3 Influence of RTA sorptivity on longer-term effective chloride diffusion (CSIRO, 1998)

For Class C exposure, a maximum sorptivity limit of 8 mm or 0.21 mm/min^{½} is specified for blended cement. It can be observed from ***Figure 3*** 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.

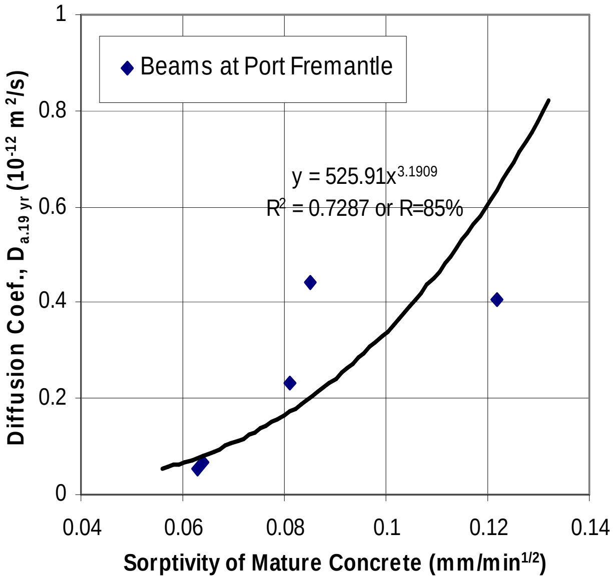

Figure 4 Sorptivity of 19-year-old concretes and apparent chloride diffusion coefficient, Da, after 19-year exposure in splash zone in Port Fremantle (Vallini and Aldred, 2003)

The sorptivity of matured concrete (tested at 19 years old) has also been found to give a reasonable indication of the long-term chloride resistance of a range of concretes exposed in the splash zone in Port Fremantle in Western Australia (Vallini and Aldred, 2003). 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 4***. The sorptivity is measured using a method similar to ASTM C1585.

According to ASTM C1585, the repeatability coefficient of variation is 6.0%. Hence the results of two properly conducted tests by the same operator should not differ by more than 17.0%.

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.

Volume of permeable voids

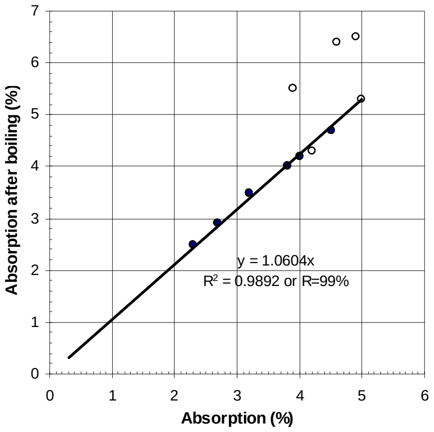

Figure 5 Effect of boiling on absorption (Sherman et al 1996)

Absorption is a method of determining the water absorption after immersion in water at room temperature, or after immersion and boiling in water. The 'volume of permeable voids (VPV)' is the 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***. 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, i.e., solid and voids. The AVPV has been used by VicRoads to classify concrete durability as shown in ***Table V.***

Table V VicRoads Classification for Concrete Durability based on the VPV

Durability classification indicator	Vibrated cylinders (VPV %)	Rodded cylinders (VPV %)	Cores (VPV %)
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

The chloride resistance of concrete has been found to improve with the reduction in VPV as shown in *Figure 6*. The resistance based on longer-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 (1996) found no correlation (R=12%) between VPV and medium-term apparent chloride diffusion coefficients, $D_{a.365}$. as shown in ***Figure 6***. From the two sets of slightly different data, there appears to be a significant change of chloride resistance around the critical VPV level of 12–13%.

There is no precision statement for VPV in ASTM C642 and AS 1012.21. Test results compiled by Walpole (2009) of two concrete samples tested by nine laboratories showed the repeatability and reproducibility coefficient of variation of 1.8% and 6.5% respectively. Hence the results of two properly conducted tests by the same operator should not differ by more than 5.1%. The results of two properly conducted tests in different laboratories should not differ by more than 18.4%.

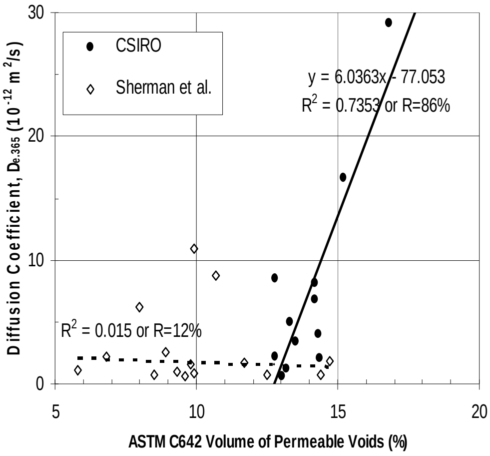

Figure 6 ASTM VPV28 & De.365 (CSIRO, 1998) and ASTM VPV42 & Da.365 (Sherman et al 1996)

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 C1202-05.

Table VI Chloride Ion Penetrability Based on Charge Passed (Whiting, 1981)

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

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 proposed as reproduced in ***Table VI***.

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 repeatability and reproducibility coefficient of variation of are 12.3% and 18.0% respectively. Hence the results of two properly conducted tests by the same operator should not differ by more than 34.8%. The results of two properly conducted tests in different laboratories should not differ by more than 50.9%.

The RCPT charge passed has been found to be a reasonable indicator of the chloride resistance of concrete. The charge passed measured at 28 days or 42 days, $RCPT_{28}$ or $RCPT_{42}$, correlates well with the longer-term apparent or effective chloride diffusion coefficients, $D_{a.365}$ or $D_{e.365}$, as shown in *Figure 7*. 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 $RCPT_{42}$ Data (≤1000 coulombs) are combined with $RCPT_{28}$ to show the combined relationship for the full range of charge passed shown in ***Figure 7***.

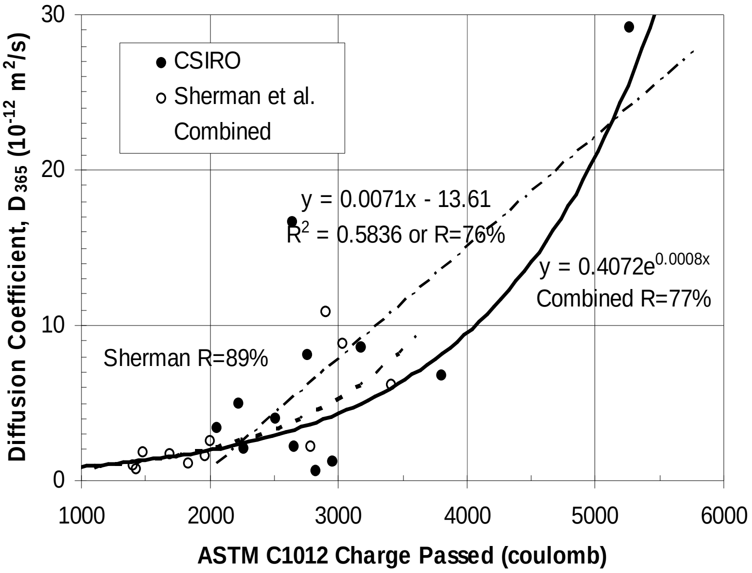

Figure 7 RCPT$_{28}$ versus D$_{e.365}$ and RCPT$_{42}$ versus D$_{a.365}$

Concrete with RCPT charge passed below 2000 coulombs shows consistently good chloride resistance with D$_{a.365}$ below 3x10^{-12} m^2/s. whereas concretes in the 2000- to 3000-coulomb range exhibit highly variable chloride resistance.

Sherman et al (1996) found that the correlations between RCPT and longer-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.

Comparative Performance Data

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 the longer-term chloride diffusion resistance, $D_{e.365}$, evaluated as the correlation coefficient, R for the corresponding range of measured values. These are shown in ***Table VII.***

Table VII Precision and correlation of each property with chloride resistance

	$D_{e.28}$ (10^{-12} m^2/s)	**Sorptivity$_{28}$ ($mm/s^{½}$)**	**VPV$_{28}$ (%)**	**RCPT$_{28}$ (Coulomb)**
	Precision from relevant standards or other sources			
Sources of Precision	**ASTM C1566**	**ASTM C1585**	**ASTM C642**	**ASTM C1202**
Reportable to	0.001	$0.1x10^{-4}$	0.1	NA
Repeatability CV	14%	6%	1.8%$^{(2)}$	12.3%
Reproducibility	20%	NA$^{(1)}$	6.5%$^{(2)}$	18%
	Correlation to $D_{e.365}$ of a GP & 3 GB cement concretes (CSIRO, 1998)			
Range of value	10–60	15–100mm	6–13, 13–18	2–5 $x10^3$
Correlation coef, R	74%	76%	12%. 86%$^{(3)}$	76%
Critical range: one order change in $D_{e.365}$ from 1 to10 m^2/s	28	41 mm	1.5	1270
Increment used in classifications		RTA B80 12 mm	VicRoads 1–2%	C1202 1000 coulomb

(1) Not available

(2) Analysis of proficiency test data compiled by Walpole (2009).

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

With the exception of water-cement ratio which is binder dependent, short-term diffusion coefficient $D_{e.28}$, sorptivity, VPV and RCPT correlate reasonably well with the longer-term chloride diffusion coefficient $D_{e.365}$. The VPV, however, shows no correlation with the longer-term chloride diffusion coefficient in the range of 6–13 % and further work may be required to support this. In setting the performance limits for each chloride resistance property, the sensitivity of each property should be considered in terms of the 'critical range' and the precision of the test. The critical range chosen for comparison in ***Table VII*** 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 $x10^{-12}$ m^2/s.

Conclusion

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 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.

For performance-based specifications, capillary absorption properties (sorptivity and VPV) and migration property (RCPT) have all been found to be as good an indicator of longer-term chloride resistance as the short-term chloride diffusion coefficient. Critical comparative performance data are given in Section 4. It was found that there are limits to the effective range of sorptivity (15–100 mm), VPV (13–17%), and RCPT (1000-5000 coulombs) that are sensitive to chloride resistance.

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