Assessment of predictive characteristics for highly durable concrete mixes and test method analysis for determination of age factors

2019

Presented at Concrete 2019 Conference, Sydney

Authors

Jason Chandler, Project Manager, Boral Australia

David Hocking, Technical Manager – Concrete, Boral Australia

Christopher Jones, Technical Sales Manager, Boral Concrete

Farzad Moghaddam, Senior Materials Engineer, Boral Concrete

Tony Song, Senior Development Engineer, Boral Concrete

ASSESSMENT OF PREDICTIVE CHARACTERISTICS FOR HIGHLY DURABLE CONCRETE MIXES AND TEST METHOD ANALYSIS FOR DETERMINATION OF AGE FACTORS

Jason Chandler[1], David Hocking[2], Christopher Jones[3], Farzad Moghaddam[4] and Tony Song[5]
[1] Project Manager, Boral Concrete
[2] National Technical Manager – Concrete, Boral Concrete
[3] Technical Sales Manager, Boral Concrete
[4] Senior Materials Engineer, Boral Concrete
[5] Senior Development Engineer, Boral Concrete

Abstract: Some limitations exist within current test methodology for the assessment of chloride ingress in concrete. Conventional test methods are limited when testing concrete with high resistance to the impact of chlorides. This is because the test results can be skewed by a lack of sensitivity within the methods. Chloride diffusion coefficient (NT443) test method measures chloride concentration at varying depths. When a more durable concrete, or a concrete containing reasonable quantity of chloride binding slag cement is assessed, there are times when they do not pass more than a few millimetres into the concrete, skewing the result to read higher than what it actually is and adversely affects the accuracy of the mathematical models used to determine the chloride concentrate profile. A ten year investigation has commenced assessing different test methods at varying concrete maturity across a series of cement blends and investigating age factors for service life modelling. In this report, a comparison is made between various prescriptive and performance parameters and chloride diffusion coefficient. Age factors for various cement blends are derived based on interim data available.

1. Introduction

Assessing a concrete's durability is a process of initial investigation and modelling. Reliable long term field and laboratory data is very difficult to source, and assessment of durability must often rely on a combination of prescriptive mix design, infrequent or low sample data point test results and a concrete maturity or age factor to account for how the durability will change with time.

Prescriptive mixes such as those found in AS5100.5 and NSW RMS B80 Table B80.6 provide some guidance on designing durable concrete. They are however by their nature, limited to historical design methodology and may not take into account contemporary or innovative mix design practices. These prescriptive cementitious blends may not represent current best practice. The guidelines also rely strongly on w/c ratio, not taking into account the possibilities around different cement blends and the potential site difficulties of placing low w/c ratio and less workable concrete into structures.

Single data points of any testing method provide only a snapshot of performance at a discrete point in time. Previous characteristics, or future performance is not able to be determined. Also, in highly durable concrete, cured for a standard 28 or 56 days, the test method itself can include significant error. It is not uncommon for instance that NT443 chloride diffusion results can attempt to measure diffusion at a point where chlorides are representative of normal background levels of the concrete itself. It means, there has been no diffusion to that point in the time allowed by the testing, or it may be that for certain high slag cement blends, that the inherent chloride binding properties of the concrete does not result in diffusion at any greater depth. This makes understanding the effect of time and the age factor even more difficult when predicting service life modelling of a concrete structure.

Bamforth[1] suggested values for age factor in straight OPC, OPC + FA and OPC + GGBFS blends. The task of determining the age factor in more complex and differing blends is often taken to be a combination of these values. With improvements in concrete technology and the use of new materials, it is difficult to accurately assign the age factor to apply. In some cases the improved early age strength of these materials can give rise to the belief that the long term durability is affected. Without long term data to refer to, the use of innovative and better performing concretes may be unnecessarily disallowed.

Buenfeld and Newman[2] assessed that in determining chloride diffusion change with time, the rapid chloride penetration (RCP) method may be used as a proxy for the longer period durability test. Tennakoon, Shayan, Sanjayan and Xu[3] used this methodology in assessing a series of geopolymer materials by conducting a series of trials of concrete where long term (up to 500 days) tests of RCP were conducted. From these results a decay factor was calculated for different geopolymers.

This study aims to assess in a similar way different concrete mix designs by Rapid Chloride Penetration (ASTM C1202), Chloride Migration (NT492) and Chloride Diffusion (NT443) and calculate age factors through the decay rate with time of the test results.

2. Mix designs and methodology

2.1 Mix Designs

Seven different cementitious blends were selected and mix designs developed in compliance with the prescriptive cementitious content and W/C ratio of AS5100.5-Table 4.4.1(A) for exposure classification C2. Binary blends were in compliance with AS5100.5-Table 4.4.1(B) and ternary and quaternary blends were developed to best comply with the author's perceived intent of the Standard. Cementitious content was set at 470kg and W/C at 0.36. Two of these mixes were also trialed at higher W/C ratio, denoted by "HW/C". Proprietary cementitious product ZEP® was used in some mixes. ZEP® is a ground granulated slag compliant with AS3582.2. Aggregates were kept constant except for minor adjustments in sand for yield purposes and the high range water reducer adjusted to target slump. Lastly, a mix was developed containing nil GP cement and 100% ZEP®.

Table 1. Concrete mix designs

Mix Identifier	Mix 1	Mix 2	Mix 3	Mix 3-HW/C	Mix 4	Mix 4-HW/C	Mix 5	Mix 6	Mix 7	Mix 8 Nil GP
GP Cement (kg)	470	235	235	235	140	140	140	350	235	0
GGBFS (kg)	0	0	235	235	95	95	70	0	115	0
ZEP® (kg)	0	235	0	0	235	235	190	0	0	465
Fly ash (kg)	0	0	0	0	0	0	70	115	115	0
20mm Agg. (kg)	600	600	600	600	600	600	600	600	600	590
10mm Agg. (kg)	350	350	350	350	350	350	350	350	350	350
Man Sand (kg)	420	420	420	410	420	370	400	400	390	400
Fine Sand (kg)	420	420	420	410	420	370	400	400	390	400
Set Retarder (ml)	100	100	100	100	100	100	100	100	100	100
HRWR (ml)	460	720	320	190	730	80	610	290	200	1280
HRWR-SR (ml)	360	360	360	360	360	360	360	360	360	360
Slump (mm)	200	210	195	220	200	210	200	220	200	190
Water (L)	170	170	170	180	170	206	170	170	168	198
Air content (%)	2.4	1.8	2.0	1.6	1.8	1.8	2.0	2.0	2.6	1.6
Fresh concrete density (kg/m^3)	2430	2430	2420	2410	2430	2370	2400	2380	2370	2400
W/C Ratio	0.36	0.36	0.36	0.39	0.36	0.44	0.36	0.36	0.36	0.43

All mix weights in kg/m^3 SSD except admixtures at ml/100kg cementitious.

2.2 Methodology

Trial mixes were prepared in accordance with AS1012.2. In each case an attempt was made to achieve a target slump of 200mm. Specimens were cast to measure:

- Compressive strength at 7, 28, 56, 180, 365. 730, 1825 and 3650 days
- Apparent volume of permeable voids (AVPV) at 7 and 28 days curing
- Sorptivity with C exposure and 14 days curing
- Rapid chloride penetration (RCP) at 7, 28, 56, 180, 365. 730, 1825 and 3650 days
- Chloride migration coefficient (CMC) at 7, 28, 56, 180, 365. 730, 1825 and 3650 days
- Chloride diffusion coefficient (CDC) after 56 days curing with soaking in salt solution for 35, 70, 105, 175, 350, 735, 1820 and 3640 days. Additional tests were done on concrete cured for less time prior to exposure to salt solution. Curing ages of 7 and 28 days were tested with 35 days in salt solution.

To assess the effectiveness of concrete properties in determining durability of concrete, 56 day standard cured with 35 day salt water soaking, CDC results were considered the measure of durability and compared with the other measured properties at that age. The exception being the AVPV testing which is compared to 28 day cured test results.

Age factor calculations were made for each of the chloride ingress test methods up to the availability of data. As of the writing of this paper some tests out to 1 year have been completed and an interim position taken based on available results. The final testing program is designed for 10 years and it is expected that with time a more definitive comparison between methods and mixes will be available.

It is noted that mix 8, the nil GP mix exhibited significantly extended set times, and as such some of the early results may be misrepresentative.

3. Results and Discussion

3.1 Cementitious blend and W/C Ratio

CDC results of concrete mixes at 56 day curing are presented in Table 2. Mix 1 was as expected the worst performing mix but is included as a control mix only. The results of other mixes notionally complying with AS5100.5 range from 9.85×10^{-13} m^2/s for mix 5 (Ternary GP/GGBFS/ZEP®) up to 2.29×10^{-12} m^2/s for mix 6 (Binary GP/FA). The differential suggests that cementitious blend plays a significant part in producing concrete resistant to chloride ingress.

Mix 3 (GP/GGBFS) with a higher W/C has a higher – but still very good – chloride diffusion coefficient at 56 days curing when compared to its companion mix, however with Mix 4 (Ternary GP/GGBFS/ZEP®) the relationship is reversed. Further, Mix 4 at W/C of 0.44 has a chloride diffusion coefficient value less than mixes 3 and 6, both of which are prescribed durable concrete designs and deemed appropriate for C2 exposure in accordance to AS5100.5 requirements.

The results indicate that cementitious blend is a more certain way of ensuring low chloride diffusion than W/C ratio up to a value of 0.44. Alternate blends should be considered as a means of reducing diffusion coefficients.

Table 2. W/C Ratio and CDC

	Mix 1	**Mix 2**	**Mix 3**	**Mix 3-HW/C**	**Mix 4**	**Mix 4-HW/C**	**Mix 5**	**Mix 6**	**Mix 7**	**Mix 8 Nil GP**
W/C Ratio	0.36	0.36	0.36	0.39	0.36	0.44	0.36	0.36	0.36	0.43
CDC @56 Day Curing ($\times 10^{-12}$ m^2/s)	5.63	0.998	1.33	1.91	1.15	1.00	0.985	2.29	1.07	1.40

3.2 Compressive strength

Compressive strength does not enable accurate prediction of concrete resistance to chlorides as shown in Table 3. In Figure 1, it may be claimed that increasing strength increases a concrete chloride diffusion coefficient. This is obviously not true but highlights that cement blend is by far a more accurate predictor.

Table 3. Compressive strength and CDC

	Mix 1	**Mix 2**	**Mix 3**	**Mix 3-HW/C**	**Mix 4**	**Mix 4-HW/C**	**Mix 5**	**Mix 6**	**Mix 7**	**Mix 8 Nil GP**
Compressive Strength @ 56 days (MPa)	91.0	69.5	90.8	91.8	63.8	52.0	64.8	75.5	80.8	49.8
CDC @56 Day Curing ($\times 10^{-12}$ m^2/s)	5.63	0.998	1.33	1.91	1.15	1.00	0.985	2.29	1.07	1.40

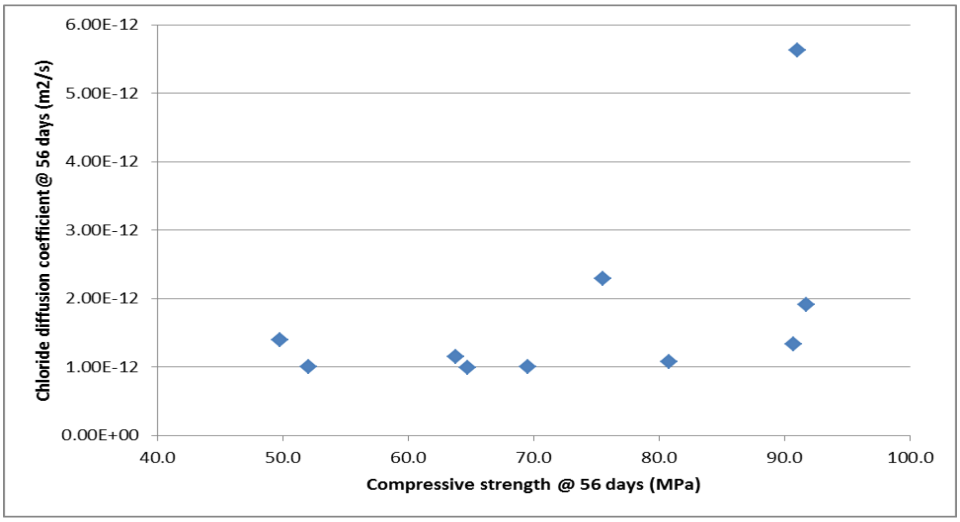


Figure 1. CDC at 56 days curing vs Compressive strength at same age

3.3 Apparent volume of permeable voids

The lowest result of AVPV was also the 2nd lowest chloride diffusion coefficient at the same age. Further correlation is not as strong. This is highlighted by the control, GP only mix, recording the 3rd lowest AVPV result as shown in Table 4 and Figure 2.

Table 4. AVPV and CDC

	Mix 1	**Mix 2**	**Mix 3**	**Mix 3-HW/C**	**Mix 4**	**Mix 4-HW/C**	**Mix 5**	**Mix 6**	**Mix 7**	**Mix 8 Nil GP**
AVPV @ 28 days (%)	9.9	11.3	9.8	12.5	10.2	14.9	8.6	12.6	11.0	15.6
CDC @28 Day Curing ($x10^{-12}$ m^2/s)	6.68	1.05	1.87	2.28	1.39	1.11	1.08	4.36	1.97	2.00

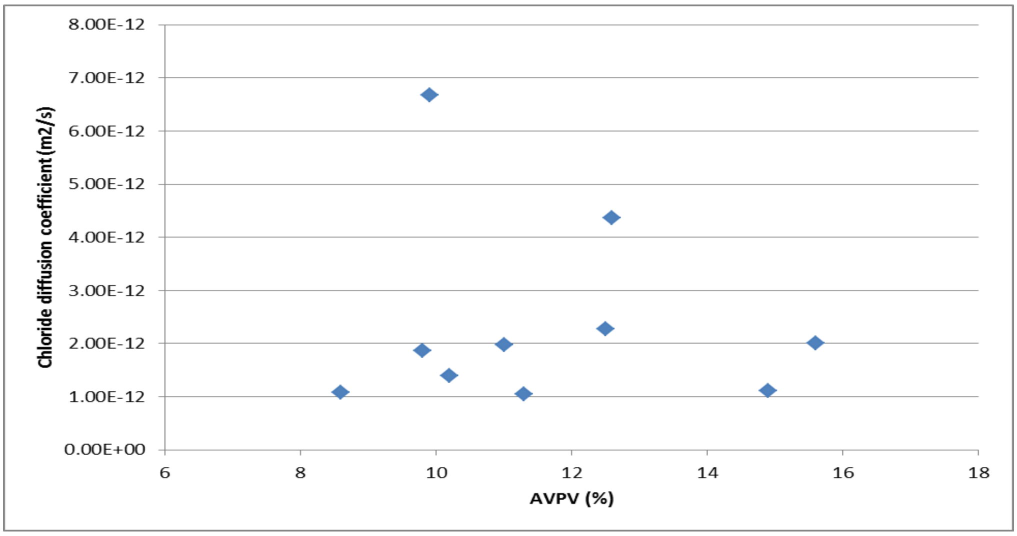


Figure 2. CDC at 28 days curing vs AVPV at same age

3.4 Sorptivity

Sorptivity is generally used as a measure of curing hence does not necessarily differentiate between concretes.

Table 5 – Sorptivity of concrete

	Mix 1	Mix 2	Mix 3	Mix 3-HW/C	Mix 4	Mix 4-HW/C	Mix 5	Mix 6	Mix 7	Mix 8 Nil GP
Sorptivity @ 14 days curing C exposure (mm)	2.7	2.9	2.6	2.5	3.5	1.9	2.4	3.2	2.3	3.9

Given that sorptivity of 8mm is considered acceptable for this exposure classification in NSW RMS B80 specification, all the results fall well under this value and would be considered acceptable (Table 5). The consistency of results for differing chloride diffusion performance suggests that this test method is not suitable as an indicator of durable concrete.

3.5 Rapid chloride penetration

Rapid chloride penetration test method ASTM C1202 is a much faster test than chloride diffusion and thus is suitable for quick assessment of a concrete mix. ASTM C1202 notes values below 1000 coulomb are considered to have very low chloride permeability. All durable mixes trialled, notwithstanding the Mix 1 control mix, achieved less than 1000 coulomb at 56 days (Table 6).

Table 6 - RCP and CDC

	Mix 1	Mix 2	Mix 3	Mix 3-HW/C	Mix 4	Mix 4-HW/C	Mix 5	Mix 6	Mix 7	Mix 8 Nil GP
RCP ASTM C1202 at 56d (coulomb)	3258	361	629	630	236	279	180	878	373	288
CDC @56 Day Curing ($x10^{-12}$ m^2/s)	5.63	0.998	1.33	1.91	1.15	1.00	0.985	2.29	1.07	1.40

A comparison between the two test methods at the same age suggests good correlation between chloride penetration and diffusion. The calculated straight line r-squared value is above 0.97 as seen in Figure 3.

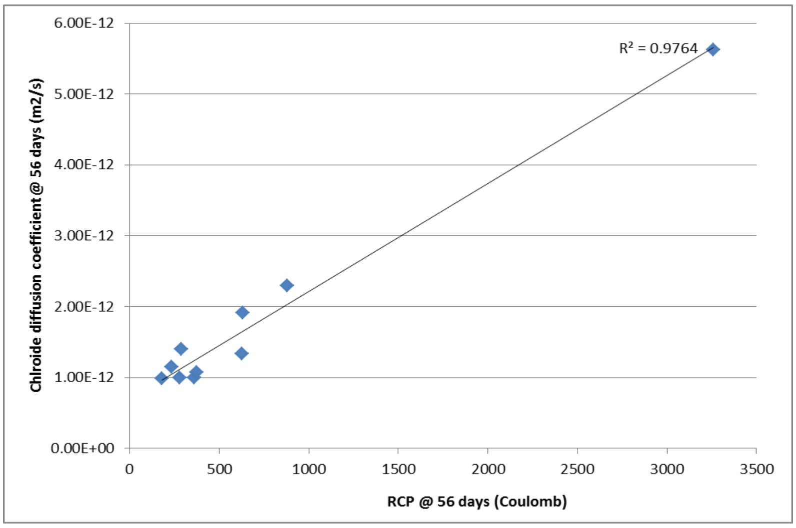


Figure 3. CDC at 56 days curing vs RCP at same age

The decay factor over time of each mix is calculated from charts of each mix. Mixes 6, 7 and 8 are based on values to 6 months. All others are based on 12 month data. Figure 4 shows examples of the charts for mixes 2 and 3 with best fit lines included to calculate the age factor being the absolute value of the power of x determined by the best fit lines. Other charts are excluded for brevity however the values are included in Table 7.

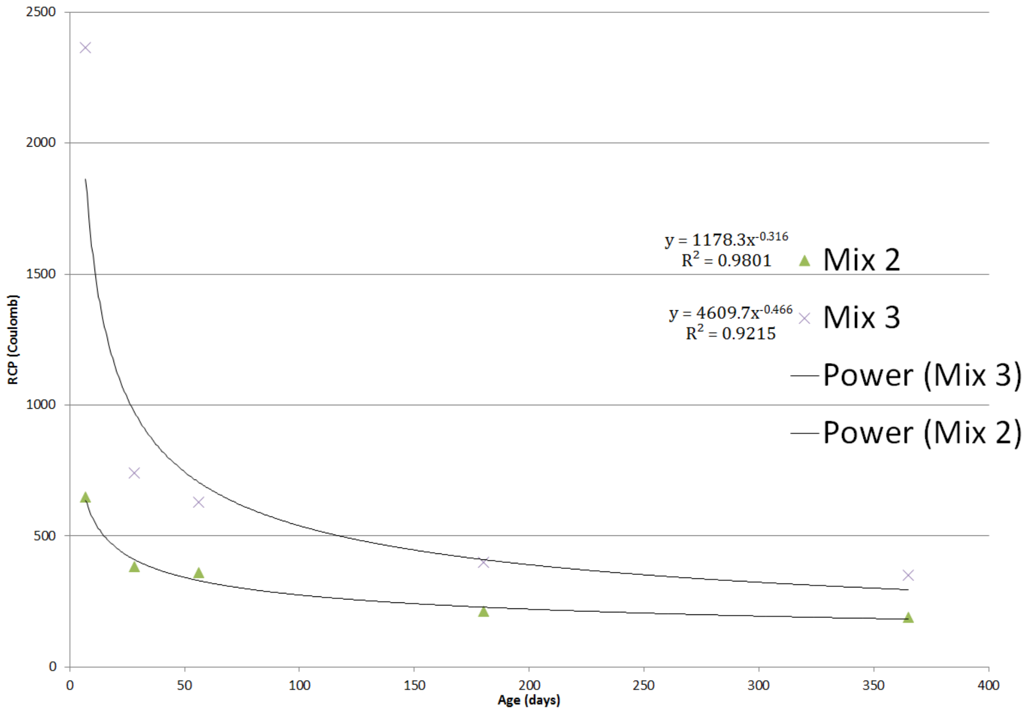


Figure 4. Changes in RCP with time for equivalent GGBFS and ZEP® mixes

Table 7. RCP results with time and RCP age factor

Age (days)	**Mix 1**	**Mix 2**	**Mix 3**	**Mix 3-HW/C**	**Mix 4**	**Mix 4-HW/C**	**Mix 5**	**Mix 6**	**Mix 7**	**Mix 8 Nil GP**
7	6741	648	2364	2504	463	567	519	7823	4631	2574
28	4129	382	740	927	293	369	257	2792	811	482
56	3258	361	629	630	236	279	180	878	373	288
180	1936	213	401	449	152	232	119	269	210	200
365	1904	189	352	405	130	185	101	Not available	Not available	Not available
RCP Age Factor	0.34	0.32	0.47	0.46	0.33	0.28	0.42	1.06	0.97	0.80

It is notable that the regression value for Mix 3 is lower and visually, the data points appear to level out more rapidly than the best fit trendline indicating that with more later age data the age factor is likely to decrease.

Age factors calculated for mixes 6, 7 and 8 are much higher than the others which may be a function of the lack of 365 day data, inaccurate measurements in immature concrete at 7 days or in the case of mix 8, the mix had only set 2 days prior to the 7 day test (Table 7). It is notable that the 2 mixes with same cement blends but differing W/C ratios have both displayed reasonable consistency in age factor calculation.

3.6 Chloride migration

The chloride migration coefficient obtained through the NT492 test method takes longer than RCP results but still represents a more rapid testing method than chloride diffusion as shown in Table 8.

Table 8. Chloride migration and diffusion coefficients

	Mix 1	Mix 2	Mix 3	Mix 3-HW/C	Mix 4	Mix 4-HW/C	Mix 5	Mix 6	Mix 7	Mix 8 Nil GP
CMC @ 56 days Curing ($x10^{-12}$ m^2/s)	8.71	1.51	2.75	2.92	1.16	1.53	0.925	4.24	2.10	1.55
CDC @56 Day Curing ($x10^{-12}$ m^2/s)	5.63	0.998	1.33	1.91	1.15	1.00	0.985	2.29	1.07	1.40

As with RCP, the chloride migration coefficient shows some correlation with the diffusion coefficient with an r-squared value of over 0.95.

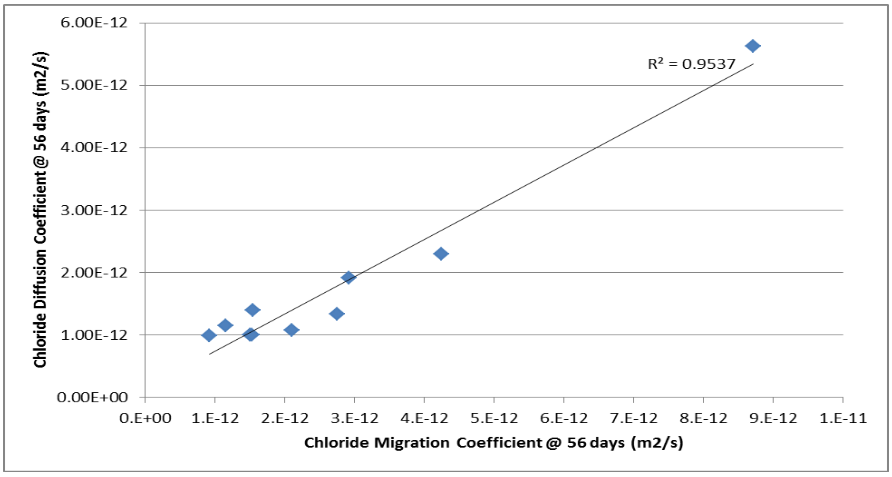


Figure 5. CDC at 56 days curing vs CMC at same age

From Table 9, the decay factor over time for each mix is calculated from exponential charts for each mix. As with RCP, mixes 6, 7 and 8 are based on 6 month data, the other mixes are assessed on 12 months duration.

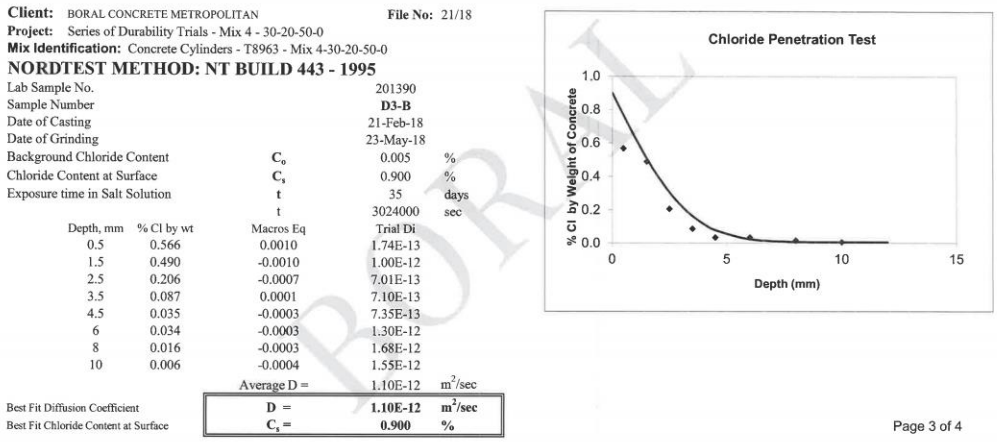
Table 9. CMC results ($x10^{-12}$ m^2/s) with time and CMC age factor

Age (days)	Mix 1	Mix 2	Mix 3	Mix 3-HW/C	Mix 4	Mix 4-HW/C	Mix 5	Mix 6	Mix 7	Mix 8 Nil GP
7	18.4	2.96	7.67	8.07	2.10	3.12	2.73	25.7	15.6	7.12
28	10.6	2.03	3.01	4.01	1.42	2.01	1.19	8.63	4.21	2.41
56	8.71	1.51	2.75	2.92	1.16	1.53	0.925	4.24	2.10	1.55
180	6.58	1.11	2.38	2.00	0.739	1.11	0.749	1.54	1.04	0.654
365	5.31	0.821	1.21	1.50	0.643	0.904	0.675	Not available	Not available	Not available
CMC Age Factor	0.31	0.32	0.41	0.42	0.31	0.31	0.34	0.87	0.85	0.73

Again, the age factor for mixes 6, 7 and 8 are higher, possibly for the same reasons as the RCP testing. As with RCP age factors, those calculated using same cement blends at differing W/C ratios are very similar to each other.

3.7 Chloride diffusion

Chloride diffusion coefficient test method NT443 is the longest of the test methods in terms of time to complete. It has also been noted in Boral's internal trial program that highly durable concrete can sometimes be disadvantaged by the test method as chlorides do not always reach the required depths for measurements to be made. This leads to a situation whereby the background chloride content is measured, or slag cement chemical binds the chlorides, and sensitivity to testing errors are introduced to the diffusion rate calculations. The test method itself requires 6 layers from the concrete cylinder such that in each the chloride content is greater than ci+0.03 where ci is the background chloride content. An example is shown in Figure 6 where chlorides have only diffused (or been bound) to between 3.5 and 4.5mm in sufficient quantities to be measured but this does not allow enough layers for measuring.


Client: BORAL CONCRETE METROPOLITAN File No: 21/18
Project: Series of Durability Trials - Mix 4 - 30-20-50-0
Mix Identification: Concrete Cylinders - T8963 - Mix 4-30-20-50-0
NORDTEST METHOD: NT BUILD 443 - 1995

Lab Sample No.		201390	
Sample Number		D3-B	
Date of Casting		21-Feb-18	
Date of Grinding		23-May-18	
Background Chloride Content	C_o	0.005	%
Chloride Content at Surface	C_s	0.900	%
Exposure time in Salt Solution	t	35	days
	t	3024000	sec

Depth, mm	% Cl by wt	Macros Eq	Trial Di
0.5	0.566	0.0010	1.74E-13
1.5	0.490	-0.0010	1.00E-12
2.5	0.206	-0.0007	7.01E-13
3.5	0.087	0.0001	7.10E-13
4.5	0.035	-0.0003	7.35E-13
6	0.034	-0.0003	1.30E-12
8	0.016	-0.0003	1.68E-12
10	0.006	-0.0004	1.55E-12
		Average D =	1.10E-12 m^2/sec

Best Fit Diffusion Coefficient D = 1.10E-12 m^2/sec
Best Fit Chloride Content at Surface C_s = 0.900 %

Figure 6. Example of highly durable concrete with abnormally high diffusion coefficients at lower depths due to errors associated with little or no chlorides actually diffusing to those depths.

By limiting the curing time it may be possible to assess concrete before it becomes too impervious to chlorides. This however may disadvantage the maturing of the hydration products with higher supplementary cementitious mixes, particularly those high in slag cement.

Table 10. CDC (x10^{-12} m^2/s) at different curing ages (35 days immersion)

Age (days)	Mix 1	Mix 2	Mix 3	Mix 3-HW/C	Mix 4	Mix 4-HW/C	Mix 5	Mix 6	Mix 7	Mix 8 Nil GP
7	7.43	1.36	3.74	2.53	1.65	1.51	1.42	6.91	3.47	4.17
28	6.68	1.05	1.87	2.28	1.39	1.11	1.08	4.36	1.97	2.00
56	5.63	0.998	1.33	1.91	1.15	1.00	0.985	2.29	1.07	1.40
7-56 day %	132%	136%	281%	132%	143%	151%	144%	302%	324%	298%
28-56 day %	119%	105%	141%	119%	121%	111%	110%	190%	184%	143%

For this set of data it does not appear that there is a predictable relationship between the different curing ages. Alternatively, longer immersion time increases the quantity of chlorides reaching the lower depths and therefore the accuracy of the measurements. From this it would be expected that decay calculations would become more accurate.

Table 11. CDC (x10^{-12} m^2/s) results with time (56 days curing)

Immersion time (days)	Mix 1	Mix 2	Mix 3	Mix 3-HW/C	Mix 4	Mix 4-HW/C	Mix 5	Mix 6	Mix 7	Mix 8 Nil GP
35	5.63	0.998	1.33	1.91	1.15	1.00	0.985	2.29	1.07	1.40
70	4.76	0.904	1.04	1.29	0.952	0.923	0873	1.57	0.994	1.05
105	4.02	0.686	0.929	1.08	0.745	0.818	0.649	1.31	0.682	0.884
175	3.21	0.503	0.756	Not available	0.437	0466	0.381	Not available	Not available	Not available

Table 12. Age factors for each test method

Test Method	Mix 1	Mix 2	Mix 3	Mix 3-HW/C	Mix 4	Mix 4-HW/C	Mix 5	Mix 6	Mix 7	Mix 8 Nil GP
ASTM C1202	0.34	0.32	0.47	0.46	0.33	0.28	0.42	1.06	0.97	0.80
NT492	0.31	0.32	0.41	0.42	0.31	0.31	0.34	0.87	0.85	0.73

Age factors are determined and presented in Table 13 which are based on the values provided in tables 11 and 12. Given mixes 6, 7 and 8 are currently awaiting 1 year data for both RCP and chloride migration and all resulted in abnormal age factors, no assessment of age factor will be presented in this paper. Equally no assessment of CDC data will be presented at this stage due to insufficient data. Future test results and published information will allow for such discussion. At this stage age factors for cementitious blends in mixes 1, 2, 3, 4, and 5 are considered based on the RCP and CMC results only.

Table 13. Derived age factors for specific cementitious blends

Cementitious blend	Mix ID	Age factor
100% GP	Mix 1	0.32
50% GP / 50% ZEP®	Mix 2	0.32
50%GP / 50% GGBFS	Mix 3	0.44
30% GP / 20% GGBFS / 50% ZEP®	Mix 4	0.31
30% GP / 15% GGBFS / 40% ZEP® / 15% FA	Mix 5	0.38

4. Conclusions

- In differentiating highly durable concretes the most significant influence on low chloride diffusion is cementitious blend. W/C ratio has a lesser impact at levels less than 0.44.
- There are alternative cementitious blends to those prescribed in AS5100.5 or RMS 3211/B80 which produce concretes highly resistant to chloride ingress, even at higher W/C ratios
- Compressive strength, AVPV and sorptivity are less definitive of whether concrete will have good resistance to chloride ingress.
- RCP and CMC results at 28 days curing are good predictors of chloride diffusion.
- RCP and CMC results show similar rates of decay with time that allow the estimation of age factors for service life modelling of structures.
- Chloride diffusion coefficient results with extended immersion times provide more accurate diffusion coefficients, However the rates of decay in the first 6 months for the most durable concrete are skewed by the somewhat inaccurate measuring of earlier ages. It is expected this will correct with more data.
- Mixes 5, 7, 4 and 2 had the lowest chloride penetrations, chloride diffusion and migration coefficients. These mixes also comprised the higher proportion of GGBFS slag cement content, which also chemically binds the chlorides.
- Mixes containing ZEP® outperformed all other mixes at early age in each of the chloride durability tests and have thus far continued to outperform other comparable mixes. By restricting early chloride ingress while concrete is still theoretically curing to maturity there may be long term benefits.

5. Acknowledgements

The authors gratefully acknowledge the support of Boral Concrete and approval to publish this article. The opinions expressed are entirely those of the authors and not necessarily the policies and practices of the organizations they represent

6. References

1. Bamforth, P.B. “Spreadsheet model for reinforced corrosion in structures exposed to chlorides”, 1998
2. Tennakoon, C. , Shayan, A. , Sanjayan, J.G. & Xu, A. “Chloride ingress and steel corrosion in slag and flyash blended geopolymer concrete”, 2017
3. Buenfeld, N.R & Newman, J.B. “Examination of three methods for studying ion diffusion in cement pastes, mortars and concrete”, 1987