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Field indicator of chloride penetration depth

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Abstract

Chloride-induced corrosion of steel reinforcement is causing serious damage to many concrete structures. A number of methods to evaluate the chloride penetration into concrete have been developed. The most common practice in measuring the chloride profile is very time consuming. A simple colourimetric method of measuring the depth of chloride penetration into concrete by spraying a 0.1-N $AgNO_3$ solution is very attractive. But some questions have been raised about its sensitivity. In this article, the results from colourimetric tests and the corresponding quantity of chloride detected at the colour-change boundary, determined for more than 70 concrete samples, are given. The magnitude and variation of chloride concentrations are compared with those reported in the literature and evaluated in relation to typical chloride threshold values. In addition, a relationship between the colourimetric penetration depth and the charge passed during testing to ASTM C1202 is shown.

Keywords: Colourimetric method; Silver nitrate spray; Chloride penetration; Concrete

1. Background

Chloride-induced corrosion of steel reinforcement is known to be a major cause of concrete deterioration. It has been established [1,2] that the water-soluble and free chlorides play a significant role in the corrosion of steel in concrete. A simple method that can be used in field investigations to estimate the depth of penetration of soluble chlorides in concrete was always desirable.

An easy and quick practice of spraying 0.1 N silver nitrate aqueous solution on a cross-section of split concrete to determine a depth of chloride penetration became very attractive since Otsuki et al. [3] and Collepardi [4] published the results of their work. This practice is often called a colourimetric method because the spraying of 0.1 N $AgNO_3$ solution on a freshly broken concrete surface leads to the formation of white and black regions with well-distinguished boundaries. The white region is due to precipitation of AgCl, and hence, represents the area that contains chloride. The black region is assumed to correspond to the 'no chloride zone'. The white colourimetric front seems to correspond to free and water-soluble chlorides, and measuring the depth of the white front will give an idea of how far chloride has penetrated into concrete.

The sensitivity of this colourimetric method is still questionable as there is no consensus in the chloride ion concentration corresponding to the colour-change boundary. Otsuki et al. [3] found that although the total chloride content at the colourimetric front varied from approximately 0.4–0.5% for paste, 0.8% for mortar and 0.5% for concrete, the corresponding soluble chloride concentration was relatively constant and was in the order of 0.15% by weight of cement for the investigated pastes, mortar and concrete with different water/cement ratios. The exact accuracy of chloride ion concentrations detected was not discussed. The work by Collepardi [4] showed the limit of 0.01% free chloride content by weight of cement at the boundary.

Andrade et al. [5] tried to quantify the chloride ion concentration at the depth where the colour change took place using the chloride profiles obtained for the concrete which underwent the rapid chloride permeability test (RCPT) following the ASTM C1202 procedure. In this case, the total chloride content or acid-soluble chloride were analysed after the test and no water-soluble chloride content was measured. Andrade et al. [5] found that the value (with a 95% confidence rate) of total chloride concentration at which the change of colour took place for concrete made

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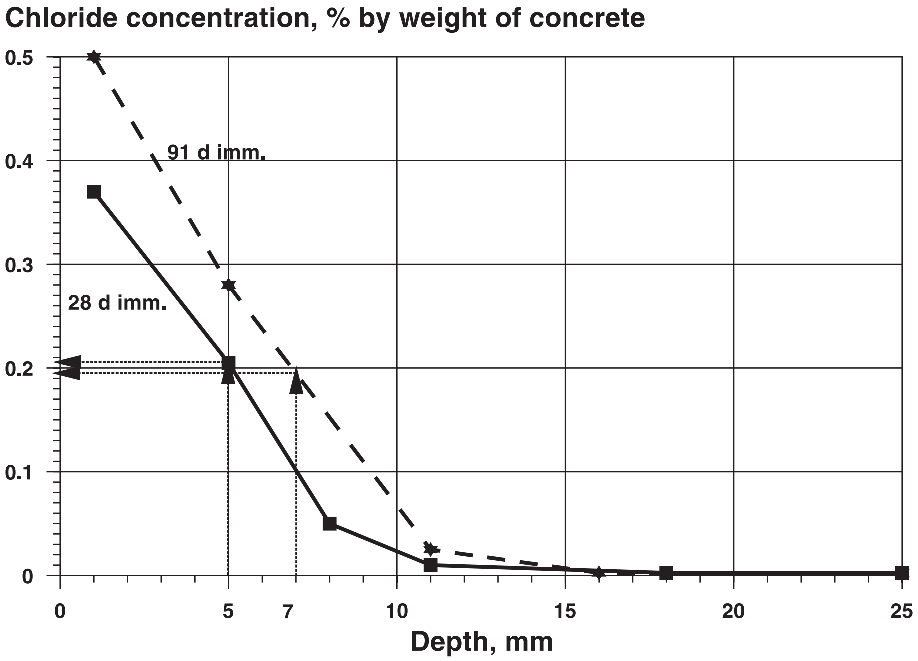

Fig. 1. Example of water-soluble chloride profiles for concrete immersed in 3% NaCl solution for 28 and 91 days, showing how the chloride concentrations at the colour-change boundaries were derived.

with different types of binder was 1.13 ± 1.4% by cement weight or 0.18 ± 0.2% by concrete sample weight, with quite a high coefficient of variation of 62%.

Earlier work carried out at CSIRO by Sirivivatnanon and Khatri [6] on a limited number of concrete samples immersed in 3% NaCl solution and then sprayed with 0.1 N $AgNO_3$, revealed that the concentration of water-soluble chloride at the boundary varied from 0.84% to 1.69% by weight of the binder. The average detectable level was around 1.2% by weight of the binder. This level was almost 10 times higher than that found by Otsuki et al. [3], with a large range of possible variation shown by the coefficient of variation of 27%.

The scope of this work was to find the variability of the water-soluble chloride concentrations at the colour-change boundary and to evaluate the suitability of the silver nitrate colourimetric technique in a field application. The suitability is considered in relation to typical chloride threshold levels for steel-reinforced concrete structures.

For this purpose, the chloride profiles for 42 concretes made with different types of binder were determined after continuous immersion in 3% NaCl solution for 28 and 91

Table 1
Chloride concentrations at the colour-change boundary for concrete immersed in 3% NaCl for 28 and 91 days

Mix ID	Binder type	After 28-day immersion			After 91-day immersion		
		Depth detected (mm)	% Cl^- by weight of concrete	% Cl^- by weight of binder	Depth detected (mm)	% Cl^- by weight of concrete	% Cl^- by weight of binder
A1	GP	10	0.045	0.28	10	0.145	0.89
A2	10% FA	8	0.140	0.86	8	0.175	1.08
A3	20% FA	9	0.055	0.34	10	0.130	0.80
A4	30% FA	9	0.120	0.74	9	0.145	0.89
A4R	30% FA	10	0.085	0.52	–	–	–
A5	10% MS	7	0.195	1.19	8	0.145	0.89
A6	10% MS	5	0.205	1.26	7	0.195	1.20
A7	10% MS	6	0.115	0.71	7	0.165	1.01
A8	10% SF	6	0.115	0.71	8	0.170	1.05
A9	HS	5	0.130	0.79	5	0.205	1.25
A10	Triple blend	6	0.210	1.29	7	0.225	1.38
A11	Triple blend	6	0.175	1.07	7	0.230	1.41
A12	Triple blend	7	0.100	0.61	7	0.225	1.38

GP = general purpose cement, FA = fly ash, MS = microsilica, SF = silica fume, HS = high slag cement, triple blend = a mix of GP, microsilica and FA in different proportions.

days. Subsequently, the chloride penetration depth was examined using 0.1 N $AgNO_3$ indicator. The soluble chloride concentration at the colour-change boundary was found. Some concrete samples were tested for chloride profiles and chloride penetration depths with 0.1 N $AgNO_3$ indicator after being immersed in 3% NaCl solution for more than 4 years. The average concentration of water-soluble chloride at which the colour changed was calculated for more than 70 measurements. The level of chloride detected at the colour-change boundary was examined in relation to typical chloride threshold values for steel corrosion in concrete found in the literature. The chloride penetration depths determined by the 0.1 N $AgNO_3$ indicator were also compared to ASTM C1202 test results obtained for most concrete, to see if relationships exist between concrete rapid chloride permeability and the chloride penetration depicted by this colourimetric method.

2. Work details and experimental procedures

Among the 42 concretes used in this investigation, 24 were with known mixture proportions. Most of the binder systems used were a general purpose (GP) cement or GP with fly ash, silica fume or a high proportion of blast furnace slag.

At the age of 28 days, concrete cylinders 100 mm $\emptyset \times 200$ mm were sawn into 50-mm-thick samples. One sample was used for rapid chloride permeability testing according to ASTM C1202. The rest of the samples were epoxy coated leaving only one sawn surface free of coating, and were fully immersed in 3% NaCl solution for a specified period. After being taken out of solution, concrete samples were drilled in 2 mm steps with 20 mm $\emptyset$ drill-bits and the collected concrete powder was analysed for water-soluble chloride using an ion chromatography technique, and the chloride profiles were obtained. The drilled samples were then split in half, sprayed with 0.1 N $AgNO_3$ aqueous solution and the depth of the white front was measured to the nearest millimetre. The concentrations of water-soluble chloride at the colour-change boundaries were derived from the concrete chloride profiles. Fig. 1 gives an example of how chloride concentrations at the colour front depths of 5 and 7 mm were obtained from the chloride profiles for the same concrete being immersed for 28 and 91 days in 3% NaCl solution.

Table 2
Colourimetric depths and chloride concentrations at the colour-change boundary for concrete after immersion in 3% NaCl for more than 4 years

Mix ID	Binder type	Depth detected (mm)	% Cl^- by weight of concrete	% Cl^- by weight of binder
B1	GP	>50	0.100[a]	0.93
B2	GP	>50	0.095[a]	0.60
B3	GP	17	0.115	0.62
B4	30% FA	18	0.150	1.21
B5	30% FA	16	0.150	0.95
B6	30% FA	15	0.150	0.75
B7	7% SF	26	0.065	0.49
B8	7% SF	15	0.115	0.79
B9	HS	17	0.120	0.96
B10	HS	20	0.120	0.74
B11	HS	18	0.085	0.42

[a] B1 and B2 concrete samples were fully saturated by chlorides so the black–white boundary was not detected. The minimum chloride concentrations found in these samples are taken as the minimum chloride content detectable by the $AgNO_3$ indicator.

Table 3
Chloride concentrations at the colour-change boundary for concrete with unknown mixture proportions

Sample ID	After 28-day immersion		After 91-day immersion	
	Depth detected (mm)	% Cl^- by weight of concrete	Depth detected (mm)	% Cl^- by weight of concrete
C1	13	0.055	15	0.090
C2	9	0.080	11	0.080
C3	7	0.200	8	0.155
C4	11	0.030	12	0.110
C5	7	0.080	8	0.140
C6	6	0.085	7	0.180
C7	9	0.060	9	0.110
C8	8	0.065	10	0.085
C9	13	0.020	13	0.110
C10	8	0.125	10	0.130
C11	6	0.115	8	0.115
C12	8	0.105	9	0.085
C13	7	0.130	7	0.150
C14	10	0.070	11	0.100
C15	8	0.090	10	0.070
C16	8	0.080	8	0.120
C17	9	0.030	12	0.060
C18	8	0.090	9	0.115
C19	6	0.140	8	0.145

3. Results

For concrete with known mixture proportions, the colourimetric penetration depths detected with 0.1 N $AgNO_3$ indicator, and the concentration of soluble chloride corresponded to these depths derived from the concrete chloride profiles, are given in Tables 1 and 2. Table 1 shows the

Table 4
Rapid chloride penetration test (ASTM C1202) results

Sample ID	ASTM C1202 at 28 days (coulombs)	Sample ID	ASTM C1202 at 28 days (coulombs)	Sample ID	ASTM C1202 at 28 days (coulombs)
A2	2645	A12	1620	C10	1035
A3	2975	C1	2535	C11	510
A4	2580	C2	1400	C12	1075
A5	1465	C3	885	C13	560
A6	1280	C4	2305	C14	2230
A7	1310	C5	1435	C15	1405
A8	870	C6	825	C16	640
A9	590	C7	1015	C17	1475
A10	1405	C8	580	C18	1215
A11	1565	C9	1760	C19	495

results after 28 and 91 days immersion in 3% NaCl, and the results of long-term immersion are given in Table 2.

The results on chloride concentration at the colour-change boundary for 19 concrete samples with unknown mixture proportions are presented in Table 3. In this case, the chloride concentration by the weight of binder was not known.

Results from the RCPT (ASTM C1202) are shown in Table 4.

4. Discussion

4.1. Percentage of chloride at the colour-change boundary

As can be seen from Tables 1–3, the amount of water-soluble chloride at the colour-change boundaries detected by silver nitrate varies from 0.28% to 1.41% by weight of the binder, and from 0.02% to 0.23% by weight of concrete. The average concentrations and statistical parameters regarding the water-soluble chloride found are presented in Table 5.

The average level of soluble chloride detected is around 0.9% by weight of the binder, with quite a high coefficient of variation of 33%. For the average level of 0.12% by weight of concrete, the coefficient of variation is even higher at 40%.

High variations of water-soluble chloride found at the colour-change boundary can be related to the method used to obtain the concrete powder at different depths for the chloride analysis. In our case, concrete was drilled with 20 mm ∅ drill-bits, which produced approximately 3 g of concrete dust from each 2 mm drilled step. This amount may not be totally representative of the whole concrete sample, especially if it contains a large percentage of aggregates and if there was an aggregate in the centre of the drilling path. In order to get better representative concrete samples at the certain depths for chloride analysis, an accurate profile grinding method suggested by McGrath and Hooton [7] may be used. This method allows the collection of concrete dust from the grinding path made with a wide grinding diamond bit (e.g. 50 mm ∅), which cross-travel along the concrete specimen surface with rotation. It is noted in the work of Otsuki et al. [3] that the concrete specimens prepared for the examination of chloride content were approximately 10 mm thick. This allows a greater sample and presumably a more average sample to be used for chloride analysis.

Table 5
Average chloride concentrations found at the colour-change boundary and statistical parameters

Chloride concentration	Min.	Max.	Average	Standard deviation	Coefficient of variation (%)	Number of observations
% by weight of concrete	0.02	0.23	**0.12**	0.05	40	74
% by weight of binder	0.28	1.41	**0.90**	0.30	33	36

In this work, the average detected level of 0.12% by weight of concrete and 0.9% by weight of binder revealed for water-soluble chloride supports the earlier findings by Sirivivatnanon and Khatri [6]. It is believed that it is also in agreement with findings by Andrade et al. [5], which showed the range of total chloride content found at the colour-change boundary to be 1.13 ± 1.4% by weight of cement or 0.18 ± 0.2% by weight of concrete. The relationship between free and total chlorides is unique for each cementitious system and exposure conditions, but being the part of total chlorides, the concentrations of water-soluble chlorides are always lower than the total. It was reported by the U.S. Transportation Research Board [8] that the water-soluble chloride portion could be 75–80% of the total chloride present in concrete.

4.2. Typical chloride threshold levels and chloride concentrations found at the colour-change boundary

The Building Research Establishment [9] has proposed a classification for assessing the risk of corrosion in terms of acid-soluble (or total) chloride contents by weight of cement: low, less than 0.4%; medium, 0.4–1.0%; and high, greater than 1%. A European state-of-the-art report [10] concludes that there is no consensus on the permissible levels of chloride, but indicates that corrosion will probably occur when the chloride ion concentration reaches 0.35–1.0% by weight based on the cement content. Locke [11] recommends that when the chloride level of bridge decks reaches 0.3%, the concrete must be removed to below the rebar level or the deck must be completely replaced.

It was mentioned previously that the relationship between water-soluble and total chlorides is unique for each cementitious system. If the water-soluble chlorides are taken as 80% of total chlorides (but it could be as little as 30%), the level of water-soluble chloride of 0.28–1.41% by weight of binder found at the colour-change boundary during this investigation would lie within or beyond the chloride limitation ranges suggested for reinforced concrete in the abovementioned sources. Therefore, the white area detected by spraying of freshly split concrete surface with 0.1 N $AgNO_3$ aqueous solution can be considered as an area at risk for steel reinforcement.

4.3. Feasibility of using silver nitrate as a field indicator

Judgement about the feasibility of using silver nitrate as a field indicator for chloride penetration depth has to be made considering its strengths and weaknesses. The strength of this method is its simplicity and practicality for use in the field. The weakness is in its inconsistency of chloride concentrations at the colour-change boundary and its large range of possible variations shown by high coefficients of variation. Nevertheless, the authors believe that if 0.1 N $AgNO_3$ is used in a field investigation and the white–black boundary is detected, the white area can be judged as an

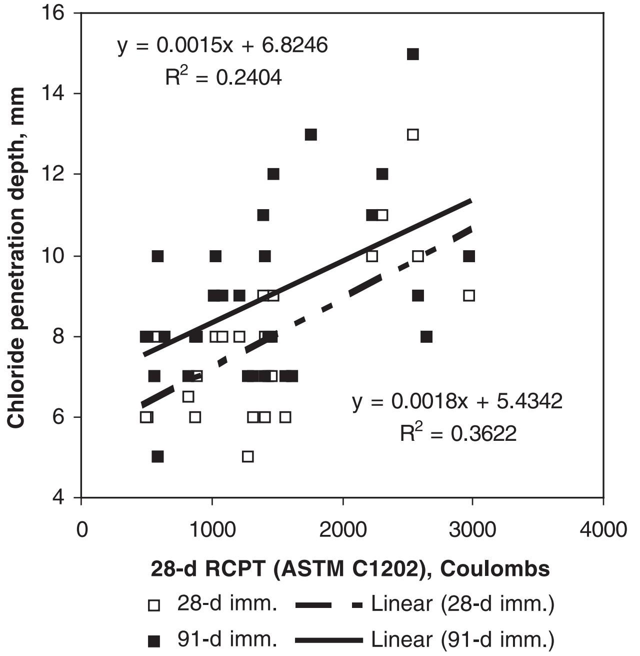

Fig. 2. Correlation between the chloride front depth and 28-day ASTM C1202 test results.

area at risk for steel reinforcement corrosion. More sensitive and more complicated methods can then be used to assess and clarify the risk.

4.4. Depth of penetration and RCPT (ASTM C1202) results

The relationships between the charge passed for different types of concrete during the RCPT, and the chloride penetration depth determined by 0.1 N $AgNO_3$ indicator for concrete after immersion in 3% NaCl for 28 and 91 days, are shown in Fig. 2. Although the correlations are very poor, it is clear that concretes of better quality, as indicated by low charge passed, show lower chloride penetration during immersion in 3% NaCl. The penetration depth increases with length of exposure, as would be expected, and it was possible to depict this depth increase using 0.1 N $AgNO_3$ indicator.

5. Conclusions

From this investigation, the following conclusions may be drawn:

1. A high variability of detected water-soluble chloride concentrations on the colour-change boundary was observed after spraying concrete with 0.1 N $AgNO_3$ indicator.
2. The average level of soluble chloride detected at the colour-change boundaries has been found to be 0.9% by weight of binder or 0.12% by weight of concrete, with high coefficients of variation of 33% and 40%, respectively.
3. The level of chloride from 0.28% to 1.41% by weight of binder found in this investigation for concrete with different binders, which can be detected by the silver nitrate indicator, lies within or beyond the chloride limitation ranges or chloride threshold levels suggested in the literature for reinforced concrete structures. Therefore, the white area detected by spraying 0.1 N $AgNO_3$ aqueous solution on a freshly split concrete surface can be judged as an area at risk for steel reinforcement corrosion.
4. Concretes of better quality, as indicated by low charge passed, show lower chloride penetration after different periods of immersion, and the penetration depth increases with the length of exposure, as would be expected.

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