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Communication

Relation between colourimetric chloride penetration depth and charge passed in migration tests of the type of standard ASTM C1202-91

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Abstract

The great interest in the knowledge of the amount of chlorides that have penetrated into concrete is due to the fact that corrosion of reinforcement in concrete initiates when chloride content in contact with rebars exceeds a threshold value. So, a number of methods to measure the diffusion coefficient of Cl^- in concrete have been developed; one of them, from the use of a colourimetric method, derived from its ease in practice. Some questions have been raised about this method, concerning the amount of chlorides at which the colour change takes place. In this article, comparison between total chloride profiles in migration experiments of the AASHTO type (ASTM C1202-91), and results from colourimetric test, as well as a relationship between colourimetric penetration depth and charge passed, are given.

Keywords: Colourimetric method; Chloride penetration; Migration tests; Concrete

The most common present practice to measure the chloride penetration depth in an immersion test is the measuring of the chloride profile. The fitting of this profile to the so-called error function equation [1] enables the calculation of a diffusion coefficient. Another practice that is easier and quicker to perform is the colourimetric method, based on spraying a solution of fluoresceine (1 g/L in a 70% solution of ethyl alcohol in water) and then spraying a silver nitrate aqueous solution (0.1 M $AgNO_3$) on the cross section perpendicular to the penetrated surface [2]. In the absence of chloride, the concrete becomes dark-coloured, while in presence of chlorides the colour obtained is pink. This method has been used also to calculate the diffusion coefficient from migration experiments [3].

The use of this colourimetric method poses some questions because the colourimetric front seems to correspond to free chlorides in solution, and there is no agreement concerning the limit at which the colour change takes place (0.15% and 0.01% free chlorides by weight of cement in work by Otsuki et al. [4] and work by Collepardi [5], respectively). In Otsuki et al. [4], the colour change has been found to be in the range of approximately 0.36–0.8% by weight of cement as total chloride concentration.

In this article, results are presented on chloride profiles obtained after a migration test following ASTM C1202-91 procedure, and by applying a modified procedure; results are compared to the penetration depths obtained by the colourimetric method. The comparison has enabled verification that the shape of the profiles are not a sharp front but are the opposite: they are some times very flat [6]. In addition, the mean chloride concentration at which the colour changes, is given.

1. Methods

The proportioning of concretes used for the trials are presented in Table 1. The tests were carried out following the standard ASTM C1202-91. This standard recommends the application of a voltage of 60 V across the specimens during a 6-h period and the measurement of the electrical charge passed. Triplicate specimens were tested. For comparative purposes, other tests using a modification of the standard (12 V over 30 h) were also performed in some of the specimens.

After switching off the electrical field, the specimens were split in two halves and the penetration of chlorides was measured over one of the halves by using the colourimetric method [2]. The other half was used to determine the chloride profile by analysing the total chloride concentration at different depths by acid extraction and subsequent titration.

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Table 1
Different concretes used in the study

	Label							
	A	B	C	D	E	F	H	J
Binder	OPC	OPC	BFSC	FA	SF	BFSC	BFSC	FA
w/c	0.4	0.7	0.7	0.7	0.4	0.4	0.7	0.4
Cement (kg/m^3)	380	380	380	380	380	380	380	380
Sand (kg/m^3)	872.4	739.9	739.9	739.9	872.4	872.4	739.9	872.4
Gravel (kg/m^3)	1115.5	946.6	946.6	946.6	1115.5	1115.5	946.6	1115.5
Curing (days)	28	28	28	28	28	28	7	28

OPC: Ordinary portland cement; BFSC: blast furnace slag cement; FA: fly ash; SF: silica fume.

2. Results

Results of chloride profiles for the three replicate specimens are given in Figs. 1 through 11. The depth at which colourimetric method presents the colour change have also been plotted in the figures (indicated as vertical lines), as well as the chloride concentration range (shown by two parallel lines) in which it takes place. These last values are given in Table 2. It can be noticed that the voltage applied influences the range of depth in which the colour change takes place (comparison of concretes A, B, and J). The reproducibility of the front among the three replicate specimens is in general not too bad and it can be good in highly impermeable concretes, as for concrete E. A final observation to be made is the fact that the shape of the profiles is not sharp or vertical, but rather they are flat [6,7] and extend to a long depth.

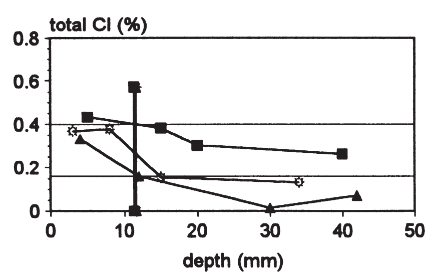

Fig. 1. Colour change for concrete A (12 V applied over 30 h).

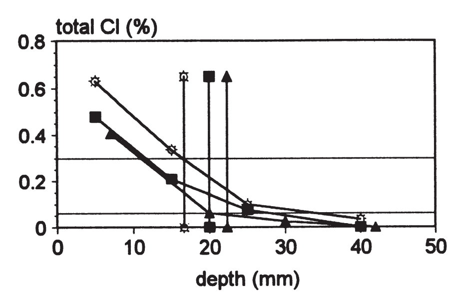

Fig. 4. Colour change for concrete A (60 V applied over 6 h).

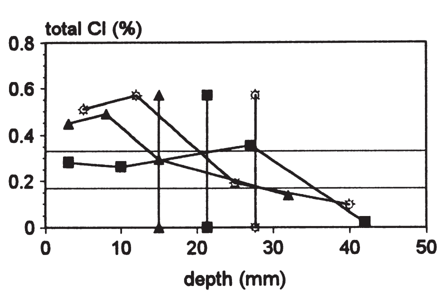

Fig. 2. Colour change for concrete B (12 V applied over 30 h).

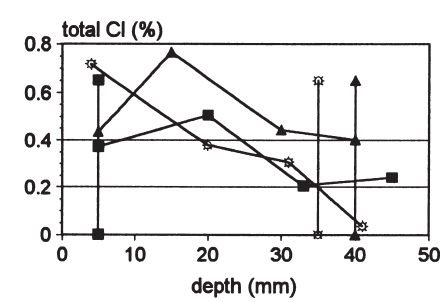

Fig. 5. Colour change for concrete B (60 V applied over 6 h).

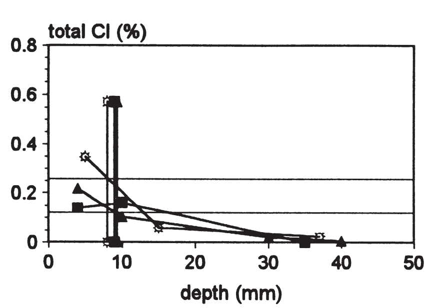

Fig. 3. Colour change for concrete J (12 V applied over 30 h).

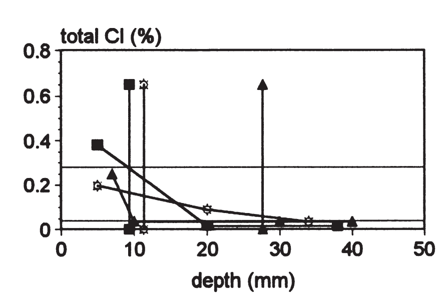

Fig. 6. Colour change for concrete C (60 V applied over 6 h).

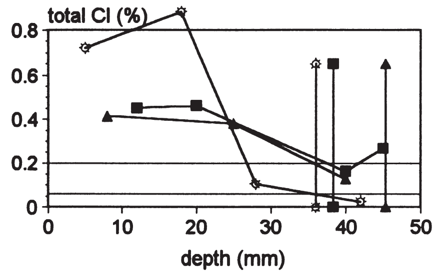

Fig. 7. Colour change for concrete D (60 V applied over 6 h).

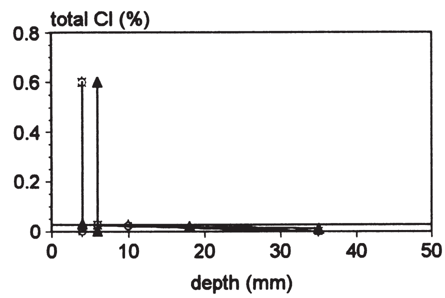

Fig. 8. Colour change for concrete E (60 V applied over 6 h).

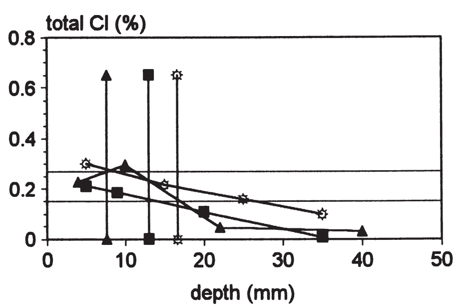

Fig. 9. Colour change for concrete F (60 V applied over 6 h).

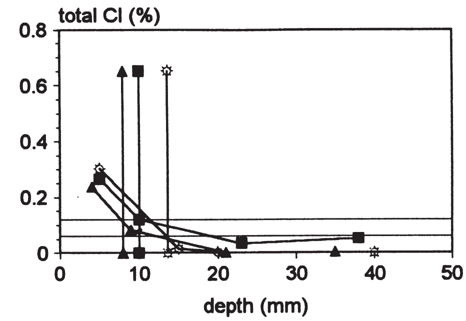

Fig. 10. Colour change for concrete H (60 V applied over 6 h).

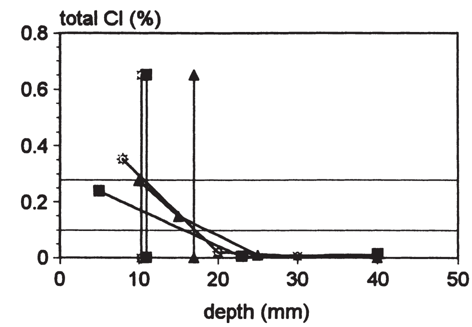

Fig. 11. Colour change for concrete J (60 V applied over 6 h).

3. Discussion

When making the comparison between chloride profiles for the different specimens, the fact that the profiles were of the total chloride content, while the colourimetric front detects free chlorides, must be considered. Unfortunately, no free chlorides were analysed after the test.

Regarding the total chloride content, the statistical parameters are presented in Table 3, where it can be seen that the value (with a 95% confidence rate) at which the colour changes for every concrete is 0.18 ± 0.2% by sample weight (1.13 ± 1.4% by cement weight). This value has to be considered as an average because the individual values can differ in an amount indicated by the variation coefficient (with an average value of 0.623). In Otsuki et al. [4], the colour change was found to be in the range of approximately 0.36–0.8% by weight of cement as total chloride concentration.

Concerning the voltage applied, it can be deduced that, in spite of the scatter, the average value of chloride concentration at which the change of colour takes place is independent of the voltage applied for a settled concrete (Fig. 12). However, the corresponding penetration depths (colour change) are different, as can be seen in Fig. 13. This indicates that the colour change depth depends on the amount of charge that effectively has passed through each specimen during the test.

A linear relationship [$Q(C/\text{cm}^2) = 3.56 + 2.54 \times \text{mm}$ (colour change); $r = 0.924$] between charge passed and depth at which colour change takes place is found. The scatter increases as concrete becomes more permeable. This means that the front depth depends on the charge density passed and not on the applied potential and, in consequence, it can be deduced that the charge density, Q, is itself a very good indication of the resistance to chloride penetration. Even more, when analysing the scatter between results corresponding to the three replicate specimens, it is clear than the dispersions corresponding to charge data are considerably smaller than those of colourimetric results, as can be seen in Fig. 14. It can be also deduced that the colourimetric method does not reproduce a sharp front but, rather, appears at a certain amount of free chloride content that shows a quite high scatter. From experimental data it can be observed that with the exception of concrete E, in general, the chloride content seems to be higher as the concrete is more dense (compare concretes D, J, and C and concretes F and H in Table 3). This is attributed to the fact that the chlorides determined are total chloride content and not the free chlorides. In this way, in more dense concretes, since migration of chlorides is slower than in more permeable concretes,

Table 2
Cl^- concentration (% vs. total sample) range in which the colour change takes place

	Label							
	A	B	C	D	E	F	H	J
12 V	0.16/0.4	0.17/0.33	—	—	—	—	—	0.12/0.26
60 V	0.06/0.3	0.2/0.40	0.04/0.28	0.06/0.2	0.026/0.03	0.15/0.27	0.06/0.12	0.1/0.28

Table 3
Average concentration of change of colour (% total sample) and statistical parameters for each type of concrete, voltage applied, and global parameters

	12 V			60 V							
	A	B	J	A	B	C	D	E	F	H	J
Average	0.273	0.260	0.176	0.166	0.323	0.156	0.106	0.028	0.206	0.086	0.180
Std. dev.	0.120	0.081	0.073	0.122	0.107	0.120	0.08	0.002	0.06	0.03	0.091
Var. coef.	0.441	0.314	0.417	0.733	0.333	0.766	0.757	0.071	0.291	0.352	0.509
Average		0.236					0.157				
Std. dev.		0.093					0.111				
Var. coef.		0.394					0.710				
Average						0.178					
Std. dev.						0.111					
Var. coef.						0.623					

Std. dev., standard deviation; Var. coef., variation of coefficient.

chlorides have more time to be able to bind in some extent. Providing that colourimetric front detects only free chlorides, total chloride concentration would be higher for more dense concretes.

On the other hand, a final consideration for practical purposes is to notice that during a 60-V migration test, the colour change is produced in the first 5 mm (corresponding to about 15 C/cm^2 passed) when the concrete is highly resistant to chlorides. It appears around 10 mm (around 30 C/cm^2) in simply good concretes, and beyond 10 mm for the most permeable concretes.

Although chloride profiling gives a complete picture of the chloride resistance of the concrete, it results in a much more time-consuming and expensive technique.

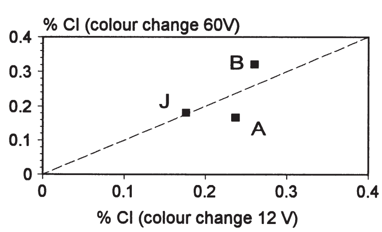

Fig. 12. Comparison between different applied voltages.

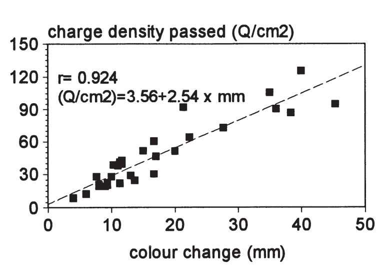

Fig. 13. Charge density passed (Q/cm^2) vs. depth at which the colour change takes place.

4. Conclusions

The main conclusions that can be drawn are:

- In present experimentation, the range of total chloride concentration (%) at which the change of colour takes place for every concrete has been found to be 0.18 ± 0.2 by sample weight or 1.13 ± 1.4 by cement weight (95% confidence) of total chloride content.
- The reproducibility of the front among the three replicate specimens is, in general, better for dense con-

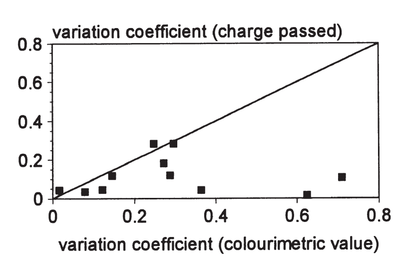

Fig. 14. Comparison between scatter of charge and depth of the colourimetric front.

cretes, and it is much better when smaller voltage values are applied. In general, the total chloride content at which colourimetric front is detected seems to be higher as the concrete is more dense.

- The average value of total chloride concentration at which the change of colour takes place for each concrete is independent of the voltage applied.
- The front depth depends on the electrical charge density passed Q(C/cm^2), existing in a linear relationship between it and the depth at which colour change takes place: [Q(C/cm^2) (passed) $= 3.56 + 2.54 \times$ mm (colour change)] being the dispersions corresponding to charge data smaller than those of colourimetric results.
- Very dense concretes enable the chloride colourimetric front to penetrate <5 mm in a 60 V, 6 h test. Good concretes present approximately 10 mm of penetration depth and permeable concretes enable deeper penetrations.

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