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CHLORIDE DIFFUSION COEFFICIENT DETERMINATION FOR SPECIFICATIONS

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ABSTRACT: The chloride diffusion resistance of reinforced concrete can have a major influence on durability. A move to performance-based specifications is therefore to be encouraged in the case of highway structures, where the client expects a long trouble-free service life. The introduction to practice of service life modelling and performance-based specifications requires a parallel development in user-friendly test methods. This paper reports on experience with three techniques used to determine apparent chloride diffusion coefficients: long-term immersion tests with chloride analysis by Volhard titration, tests of medium duration with chloride analysis by an internal-calibration potentiometric method and short-term Nordtest rapid migration tests. Concrete compositions tested included Portland cement, pfa and ggbs mixes. It was found that medium and long-term tests were consistent, but care is needed with early age tests.

Keywords: Chloride ingress, Diffusion coefficients, Test methods.

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INTRODUCTION

Significant national funds are being invested on a worldwide basis in the construction of transport networks to handle the huge increase in traffic of the past few decades. The service life of reinforced concrete structures included in these networks, particularly those exposed to chloride environments, is a topic of major concern to many agencies such as highway authorities and managers of port facilities. It is well documented [1, 2] that chloride ingress can initiate corrosion of reinforcement and hence reduce the service life of reinforced concrete structures.

The chloride diffusion resistance of reinforced concrete has a major influence on the durability of highway structures exposed to de-icing salts. It is therefore important that this parameter be included where possible in the specification of concrete for structures with long service lives. Reliance on prescriptive durability parameters, such as water/cement ratio or cement content, is no longer the only option, given recent developments in service life modelling. However the development of service life models and performance-based specifications requires a parallel development in user-friendly test methods. Test methods that are slow to yield results are unlikely to find favour in performance-based specifications.

Figure 1 shows the range of variation possible in service life calculations if the threshold concentration or cover is changed, based on the above apparent diffusion coefficient and notional chloride surface concentration. However, if future practice leads to an increased use of de-icing salts in Ireland, service life models will be required to adapt to match the increased chloride level acting on the structure. Correspondingly, the diffusivity required for a 100 year design life can be determined, and as such, it is necessary that reliable methods are available for assessing chloride diffusivity in concrete.

MATERIALS AND METHODS

Materials

The mix composition and details of the concretes used in the experimental programme are given below in Table 1. The tests involve:

- long-term immersion tests with chloride analysis by Volhardt titration,
- medium-term ponding tests with chloride analysis by an internal-calibration potentiometric method
- short-term Nordtest rapid migration tests.

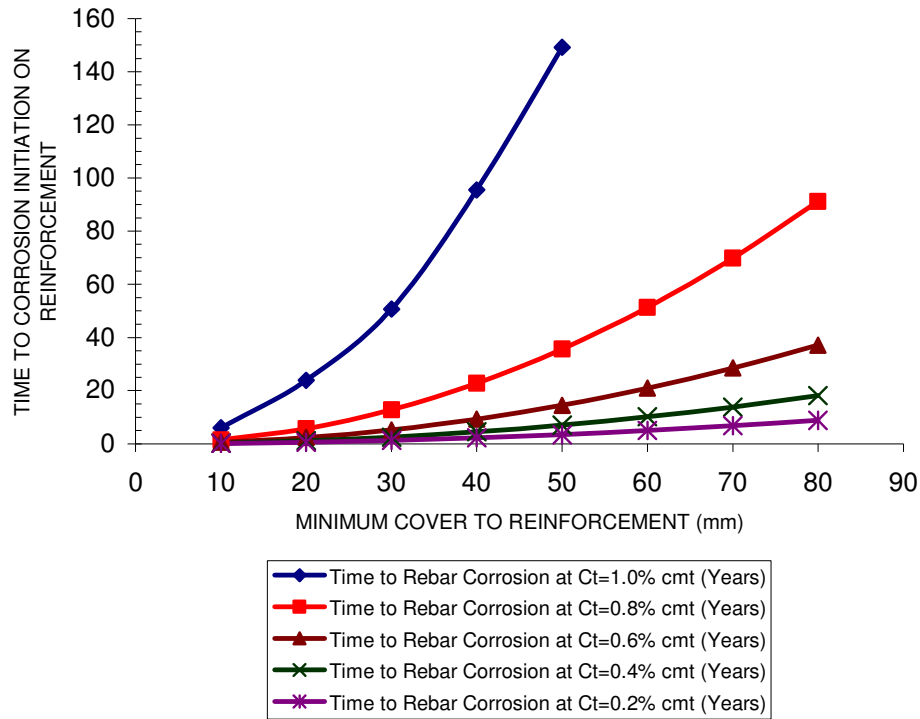


Figure 1. Graph showing the increase in service life prediction with increased risk of corrosion against cover to reinforcement for a notional surface concentration of 1.2% and apparent chloride diffusion coefficient of $6 \times 10^{-12} \text{ m}^2/\text{s}$

All of the materials used for the concretes are sourced in Ireland. The first subset of concrete samples for the long-term tests had a composition of normal Portland cement (NPC) and limestone aggregate. The control concrete had a cement content of 360 kg/m^3 , with pulverised fuel ash (pfa) subsequently included at replacement levels of 15%, 30% and 40%. The pfa used was a fine grade pfa with 12.5% retained on a 45-micron sieve. The second subset of concrete samples had a similar composition to the first set, but with a coarser grade of pfa used. The first subset is denoted with a superscript ^{‘1’}, the second with ^{‘2’}.

The concrete samples used in the short and medium term tests involved the use of an NPC binder, with replacement levels of pfa of up to 30%, and ground granulated blast furnace slag (ggbs) with replacement levels of up to 50%.

Methods

Three separate methods are used to determine diffusion coefficients. These methods are described by test duration and are discussed below.

Table 1 . Mix Designs

LONG TERM TEST SAMPLES				SHORT AND MEDIUM TERM TEST SAMPLES				
Mix Code	Cement content (kg/m ³)	pfa content (kg/m ³)	Total binder content (kg/m ³)	Mix Code	Cement content (kg/m ³)	pfa Content (kg/m ³)	ggbs Content (kg/m ³)	Total binder content (kg/m ³)
NL 0	360	0	360	320-0	320	0	0	320
NL 15¹	330	58	388	320-30s	225	0	95	350
NL 30¹	285	121	406	320-50s	160	0	160	320
NL 40¹	260	173	433	320-15p	305	55	0	360
				320-30p	285	120	0	405
NL 0	360	0	360	400-0	400	0	0	400
NL 15²	330	58	388	400-30s	280	0	120	400
NL 30²	285	121	406	400-50s	200	0	200	400
NL 40²	260	173	433	400-15p	380	65	0	445
				400-30p	355	150	0	505

Long-term testing: immersion

The long-term testing programme involved immersing concrete samples in a saturated sodium chloride solution. The samples used were of dimensions 0.28 x 0.28 x 0.075 m and the concentration of the sodium chloride solution was calculated to be 5.6 M. In such conditions it was considered that diffusion would be the dominant chloride transport mechanism. Samples were removed periodically and chloride content was determined using the method of Volhard titration [4,5]. This method involves extracting a concrete dust sample that is first dissolved in a solution of nitric acid. The solution is filtered into a clean conical glass flask through fast hardened ashless paper. A measured excess of 0.1 mol L⁻¹ silver nitrate solution is added into the sample, followed by 2-3 ml of nonyl alcohol and 1 ml of saturated ammonium ferri-sulphate solution is then added. This is titrated using ammonium thiocyanate until the first permanent red/orange colour is achieved. The chloride content of the sample is determined using Equation 1 below.

$$J = \left[V_5 - \left\{ \frac{(V_6 \ m)}{0.1} \right\} \right] x \frac{0.3545}{M_c} x \frac{100}{C_1} \quad (1)$$

where;

M_c = the mass of sample used (in grams)

V_5 = the volume of 0.1 mol L⁻¹ silver nitrate solution added (in ml)

V_6 = the volume of ammonium thiocyanate solution used (in ml)

m = the molarity of the ammonium thiocyanate solution used (mol L⁻¹)

C_1 = the binder content of the sample used (in %)

This procedure was continued for a period of 18 months. Chloride concentrations are plotted over depth, and from the resultant profile an apparent chloride diffusion coefficient is determined.

Medium-term testing: ponding

For the medium-term tests, ponding was used as a method of accelerating chloride ingress into the concrete samples. The specimens used were of the same dimensions as those above, but with a recess cast into the surface to allow the sodium chloride solution to pond. The chloride solution used was again 5.6 M. The samples were ponded for 1 year, after which chloride concentrations were measured. The method used was that of internal calibration, as developed by Clemena & Apusen [6]. This alternative potentiometric method involves the cold digestion of concrete samples that are subsequently spiked twice with a relatively small and precisely measured amount of standard NaCl solution. The chloride content is calculated for each sample from the potential readings before and after the spiking by an equation derived from the Nernst equation. Clemena and Apusen have shown the method to be much faster than standard methods and with negligible loss in accuracy. Again, an apparent diffusion coefficient is determined from the chloride profile.

Short-term testing: rapid migration

The short-term test method used was the Nordtest rapid migration test [7]. This testing programme involved casting cylindrical specimens, which were cut and tested after 28 days. The test involves driving chloride ions through a preconditioned concrete section of diameter 100 mm and depth 50 mm under the action of an electric field. The catholyte used is a 10% sodium chloride solution, the anolyte 0.3 M sodium hydroxide. A voltage, typically of the order of 30 V is applied for 24 hours, after which the concrete sample is removed and split. The degree of chloride ingress is determined by spraying the broken surface with a 0.1 M silver nitrate solution. The silver will react with the chloride present, forming a visible precipitate that can be subsequently measured with a slide calliper. Resultant from this a non-steady-state migration coefficient can be determined. Tang & Nilsson [8] have subsequently determined how an effective diffusion coefficient can be determined, being a function of test duration, applied voltage and penetration depth.

DISCUSSION

Using the test methods described above, diffusion coefficients were determined.

Immersion Tests

Using the method of Volhard titrations apparent diffusion coefficients were assessed up to a period of 18 months. From Fig. 2 below, it can be seen that at least 6 months are required for diffusion coefficients begin to stabilise. It can be seen that the diffusion coefficients are quite consistent and after 18 months range from $0.78 \text{ m}^2/\text{s}$ to $1.89 \times 10^{-12} \text{ m}^2/\text{s}$. From 12 months onwards, the lowest diffusion coefficients correspond to increased pfa contents, indicating the increased time required for the beneficial effects of using pfa to be realised.

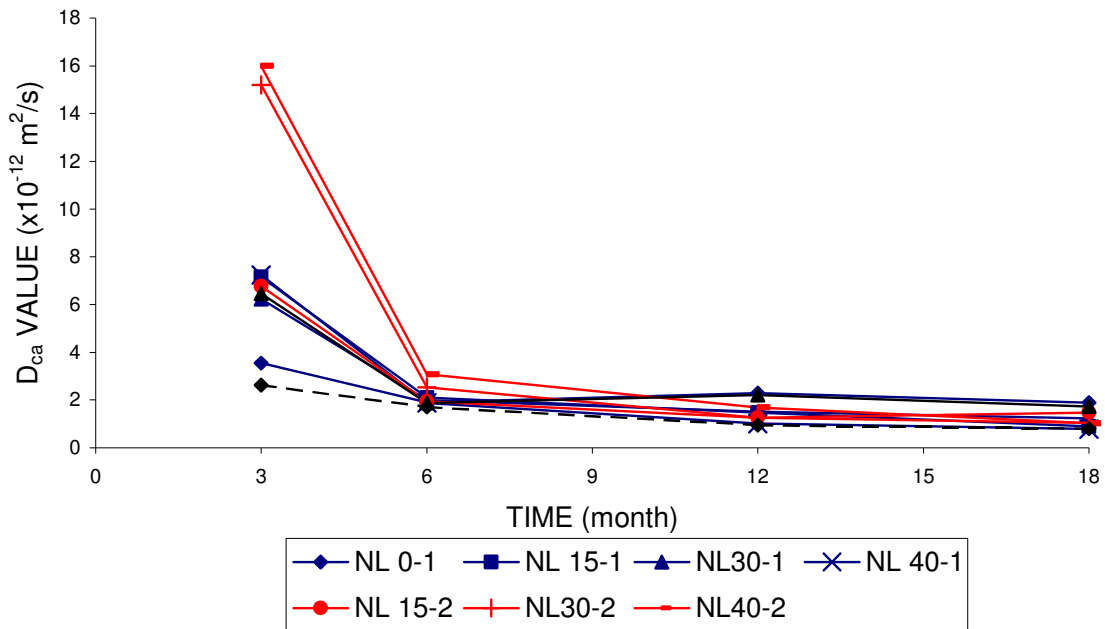


Fig. 2. Variation in apparent chloride diffusion coefficient with time – immersion tests

Ponding Tests

Results from the medium term testing were determined after 1 year and are listed below in Table 2. The output from the test was an apparent diffusion coefficient, denoted D_{ca} . From the results it can be seen that regardless of the cement content, the highest diffusion coefficient corresponds to the concrete with a 100% NPC binder. The beneficial effect of

the addition of ggbs and pfa is clear, with significant decreases recorded in apparent diffusion coefficient.

Table 2. Results of medium term ponding tests

MEDIUM TERM TESTS: PONDING					
Sample ID	400-0	400-30s	400-50s	400-15p	400-30p
D_{ca} ($\times 10^{-12}$ m ² /s)	6.39	5.12	2.70	1.36	2.01
Sample ID	320-0	320-30s	320-50s	320-15p	320-30p
D_{ca} ($\times 10^{-12}$ m ² /s)	12.67	2.89	1.65	2.9	2.03

Migration Tests

The results from the rapid migration tests are shown in Table 3. Using the method of Tang and Nilsson [8] an effective diffusion coefficient was calculated and is denoted D_{eff} . The most striking aspect of the results recorded is the poor performance of the concretes incorporating pfa. It is considered that this was due to the increased time required for pfa concretes to fully hydrate. The rapid migration tests were carried out after 28 days, which appears to have been insufficient for the pfa concretes. Conversely, no such problems are evident for the concretes incorporating ggbs, although it is possible that these concretes may improve further given more time.

Table 3: Results of short term migration tests

SHORT TERM TESTS: MIGRATION					
Sample ID	400-0	400-30s	400-50s	400-15p	400-30p
D_{eff} ($\times 10^{-12}$ m ² /s)	9.91	5.05	2.96	10.87	16.92
Sample ID	320-0	320-30s	320-50s	320-15p	320-30p
D_{eff} ($\times 10^{-12}$ m ² /s)	26.02	7.26	3.47	23.14	17.85

Comparison of Methods

Due to care taken to ensure that diffusion was the dominant transport process in the long-term immersion tests, a high degree of confidence can be taken in the diffusion coefficients produced. The apparent diffusion coefficients produced from the medium term ponding tests are generally in good agreement with these. With the exception of the 320-0 series, all of the ponding results lie within the range $1.3 - 6.3 \times 10^{-12}$ m²/s. This is a slightly wider band than that seen with the immersion tests, but is nonetheless quite

satisfactory. The results from the migration tests show quite a large amount of variability, ranging from $2.96 - 26.02 \times 10^{-12} \text{ m}^2/\text{s}$. It is likely though that the extending the concrete age will promote further hydration and reduce this variability.

CONCLUSIONS

From the results seen in the above testing programmes, it appears that medium-term ponding tests agree quite well with immersion tests, and as such would appear suitable for service-life prediction. Short-term tests, such as the rapid migration test appear to have potential for use, but sufficient time must be given for full hydration to occur. Care must also be taken in relating apparent and effective diffusion coefficients.

REFERENCES

1. RICHARDSON, M G, Fundamentals of Durable Reinforced Concrete. Spon Press/Taylor & Francis. New York. 2002. 272pp.
2. NEVILLE, A M, Properties of Concrete. Longman. London. 1995. 844pp.
3. CONCRETE SOCIETY. The Use of GGBS and PFA in Concrete. Technical Report No. 40. 1992. 142pp.
4. NORDTEST, NT Build 208: Concrete, Hardened: Chloride Content by Volhard Titration. Nordtest. 1996.
5. BRITISH STANDARDS INSTITUTION, BS 1881: Part 124. Testing Concrete: Methods for Analysis of Hardened Concrete. BSI. London. 1988.
6. CLEMENA, G G AND APUSEN, C M. An alternative potentiometric method for determining chloride content in concrete samples from reinforced-concrete bridges. Final Report VTRC 02-R18. June 2002. Virginia Transportation Research Council.
7. NORDTEST, NT Build 492: Concrete, Mortar and Cement-Based Repair Materials: Chloride Migration Coefficient from Non-Steady-State Migration Experiments. Nordtest. 1999.
8. TANG, L AND NILLSON, L, Rapid determination of the chloride diffusivity in concrete by applying an electric field. ACI Materials Journal. Vol. 89. No. 1. 1992. pp 49-53.