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Time dependent diffusion in concrete—three laboratory studies

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Abstract

The rate of chloride diffusion into concrete decreases with time due to issues such as continued hydration and chloride binding. Data are presented from three projects where the specimens were continuously exposed to chloride solutions for periods ranging from 28 days to 3 years. Chloride profiles obtained from the specimens at various time intervals were used to calculate diffusion values using Crank's solution to Fick's second law. The time-dependant reduction coefficient, m, was determined using three methods, yielding different values. Since the reduction of calculated diffusion coefficients with time has great impact on service life predictions, and values are sensitive to the method used, it is imperative to also know how the diffusion and time-dependant reduction coefficients were obtained.

Keywords: Chloride; Long-term performance; Transport properties; Reduction coefficient

1. Introduction

It is well known that transport by diffusion in saturated concrete will occur in the presence of a chloride concentration gradient, created when at least one face is continuously exposed to water and salt [1]. Apparent diffusion coefficients for various concretes are often determined by fitting profiles of acid-soluble chloride concentration versus depth with Crank's solution (Eq. (1)) to Fick's Second Law of diffusion (Eq. (2)).

$$C(x,t) = C_{\mathrm{o}}\left(1 - \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right) \tag{1}$$

and

$$\frac{\partial c}{\partial t} = D_{\mathrm{a}}\frac{\partial^2 c}{\partial x^2} \tag{2}$$

where C_{o}—surface chloride concentration, C—the chloride concentration at depth, x, and time, t, and erf()—standard error function.

Both the surface concentration and diffusion coefficient can change with time. It is not correct to use the solution presented in Eq. (1) where either the surface concentration or the diffusion coefficient change with time. Other solutions of Fick's second law exist with varying surface concentration. The authors are not aware of any solutions to Fick's second law that combine a time-dependent surface concentration with a time-dependent diffusion coefficient. It must be remembered that these diffusion coefficients are determined for certain instances of age and chloride exposure periods. For example, the diffusion coefficient determined from profile grinding a concrete sample that had been ponded in salt solution for 28 days after achieving a maturity of 28 days will reflect the average concrete properties, in terms of transport by diffusion, over the period of immersion (i.e. over a 28 day period from 28 to 56 days of age). The chloride diffusion coefficient of a concrete is time dependent. It will typically decrease as time passes since the capillary pore system will be altered as hydration products continue to form [1]. As well, some chloride ions will become chemically or physically bound as they penetrate the pore system. Time dependent diffusion

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Table 1
Summary of mixture characteristics

Set #	Mix code	Cement (kg/m^3)	Silica fume (kg/m^3)	Slag (kg/m^3)	Fly ash (kg/m^3)	HRM (kg/m^3)	Total cementing materials content (kg/m^3)	Water (kg/m^3)	w/cm ratio
1	1A	380	–	–	–	–	380	152	0.40
1	1B	350	–	–	–	30	380	152	0.40
1	1C	334	–	–	–	46	380	152	0.40
1	1D	460	–	–	–	–	460	138	0.30
1	1E	423	–	–	–	37	460	138	0.30
1	1F	405	–	–	–	55	460	138	0.30
2	2A	442	18	–	–	–	460	137	0.30
2	2B	355	20	125	–	–	500	149	0.30
2	2C	327	18	115	–	–	460	137	0.30
2	2D	345	*	115	–	–	460	137	0.30
2	2E	308	37	115	–	–	460	137	0.30
3	3A	375	–	–	–	–	375	150	0.40
3	3B	345	30	–	–	–	375	150	0.40
3	3C	345	–	–	30	–	375	150	0.40
3	3D	345	–	–	45	–	390	135	0.35
3	3E	330	–	–	45	–	375	150	0.40
3	3F	345	–	–	45	–	390	120	0.31
3	3G	330	45	–	–	–	375	150	0.40
3	3H	345	–	–	60	–	405	135	0.33

*CSA Type 10SF Blended cement with ~8% silica fume.

through concrete has been observed to be an exponential function [2].

$$D(t) = D_{\mathrm{ref}}\left(\frac{t_{\mathrm{ref}}}{t}\right)^{m} \tag{3}$$

where $D(t)$—diffusion coefficient at time t; D_{ref}—diffusion coefficient at some reference time t_{ref}; m—constant (depending on mix proportions).

This equation accounts for the influence of time (i.e. concrete maturity) on diffusivity. The m coefficient in Eq. (3) is a constant. It is dependent on variables such as the type of cementitious materials used and the mixture proportions, and has been developed to account for the rate of reduction of diffusivity with time.

Values for m for different concretes have yet to be well established, although some values have been published [2–6]. Further research to properly quantify this parameter would help to improve the accuracy of service life predictions. Estimates of when a critical chloride concentration is reached at the depth of the steel reinforcement would be more accurate if the changes in diffusion properties of a concrete with time were better taken into account.

In the field, the period of chloride exposure is usually significantly greater than the age of the concrete prior to contact with salt solutions. Given that the change in diffusion with time is non-linear, the determination of the effective age during the exposure that correlates to the average diffusion coefficient determined for that period is not straightforward. This paper presents an analysis of apparent diffusion data obtained at the University of Toronto to determine m values using three methods for mixtures with varying water-to-cementitious-

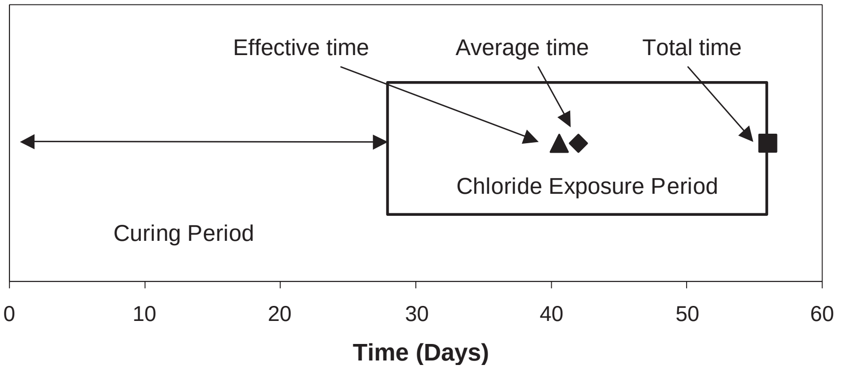

Fig. 1. Example of time used for calculation of m.

materials ratios and various supplementary cementing materials.

2. Bulk diffusion ponding test procedure

The apparent diffusion coefficient for each concrete mixture was determined using a Bulk Diffusion Test [7,8]; a similar procedure has recently been adopted as ASTM C1556-03. Each 50-mm thick, 100-mm diameter sample was epoxy coated on all sides except for the test face. The samples were then vacuum saturated with water as per ASTM C1202. They were sealed in plastic containers with the test face exposed to 1.0 mol/L NaCl solution at 23 °C, except in the case of the third series of mixtures, which were exposed to 165 g/L NaCl (approximately 2.8 mol/L) at 23 °C. Because the samples are initially saturated and then submerged in chloride solution, this test measures the chloride transport solely as a result of diffusion. The test does not, however, correct for chloride binding effects as total (acid-soluble) chloride contents are measured.

After removal from solution, the samples were profile ground on a milling machine using a 50 mm diameter diamond drill bit. Ten to twelve 0.5 mm thick layers were collected at different depths. The powdered samples were dried in an oven at 105 °C for 24 h. Subsequently, the samples were put through a nitric acid digestion process, and then filtered to remove excess solids, as explained in detail by McGrath [7]. Determination of the total chloride content at the different depths was determined using automatic potentiometric silver nitrate titration of the remaining liquid solutions. The resulting plot of chloride content versus depth was fit with Fick's Second Law of diffusion using Crank's solution (Eq. (1)) to determine the apparent diffusion coefficient, D_a, and surface concentration, C_o.

It should be further noted that the background chloride concentration, that is the chloride in the original mix ingredients, was subtracted from the total chloride concentrations determined at all depths. A commercially available, curve-fitting software program was used to determine C_o (surface concentration) and D_a (apparent diffusion coefficient) from the data using a non-linear, least-squares method, using Eq. (1). The best fit was determined by adjusting both of the unknowns to achieve the highest coefficient of determination, r^2.

Table 2
Diffusion coefficients (10^{-12} m^2/s) for HRM concrete exposed to chloride at 28 days of age at 23 °C

Mix code	Mix design	Chloride exposure period (days)				
		28	90	140	365	1095
1A	0.40 w/cm—0% HRM	19.08	11.75	6.13	6.26	–
1B	0.40 w/cm—8% HRM	8.25	5.73	3.79	2.30	1.70
1C	0.40 w/cm—12% HRM	5.86	3.52	3.18	1.72	0.97
1D	0.30 w/cm—0% HRM	9.64	5.87	5.39	–	3.43
1E	0.30 w/cm—8% HRM	3.76	2.88	2.16	1.43	0.84
1F	0.30 w/cm—12% HRM	2.95	2.76	1.49	0.90	0.56

Table 3
Fitted surface concentration (percent by mass of concrete) for HRM concrete exposed to chloride at 28 days of age at 23 °C

Mix code	Mix design	Chloride exposure period (days)				
		28	90	140	365	1095
1A	0.40 w/cm—0% HRM	0.33	0.34	0.64	0.63	–
1B	0.40 w/cm—8% HRM	0.69	0.58	0.61	0.68	0.73
1C	0.40 w/cm—12% HRM	0.58	0.53	0.60	0.58	0.68
1D	0.30 w/cm—0% HRM	0.42	0.44	0.56	–	0.52
1E	0.30 w/cm—8% HRM	0.52	0.49	0.72	0.83	0.76
1F	0.30 w/cm—12% HRM	0.50	0.48	0.73	0.69	0.90

3. Materials, casting, and sample preparation

The data presented and analyzed in this paper are from three studies carried out at the University of Toronto. The first set of concrete mixtures was cast at w/cm of 0.30 and 0.40 with 0%, 8%, and 12% by mass replacement of cement by high reactivity metakaolin (HRM) [9–11]. Engelhard Corporation manufactured the HRM used in the project. The Portland cement used was Type I/II low-alkali produced by Lafarge North America (Woodstock plant).

The second set of concrete mixtures was cast at a w/cm of 0.30 [12]. Various replacement levels of silica fume and slag were tested. The silica fume was SKW undensified silica fume from Bécancour, Québec and the slag was from Lafarge in Hamilton, Ontario. Lafarge also manufactured the CSA Type 10SF blended silica fume cement present in one of the mixtures.

These two sets of concrete mixtures were cast, cured and prepared in the same manner. Three 75 mm deep×250 mm×350 mm slabs were cast from each mixture and were compacted on a vibrating table. All of the concrete was initially covered with wet burlap and plastic for 20 h. After demoulding, the slabs were cured for 5 days in lime water, and then stored at 23 °C and 50% RH. At 25 days of age, six 100 mm diameter cores were cored from the formed face of each slab with a diamond-topped core drill. All cores were saw-cut to 50 mm thickness. After sealing their sides, the samples were placed in a 50% RH, 23 °C environment until

Table 4
Summary of m values for HRM concretes (Set #1)

Mix code	Mix design	m_{total}	r^2	m_{ave}	r^2	m_{eff}	r^2
1A	0.40 w/cm—0% HRM	0.57	0.99	0.68	0.99	0.87	0.99
1B	0.40 w/cm—8% HRM	0.55	0.97	0.62	0.95	0.77	0.94
1C	0.40 w/cm—12% HRM	0.60	0.99	0.68	0.99	0.87	0.99
1D	0.30 w/cm—0% HRM	0.32	0.88	0.35	0.88	0.41	0.96
1E	0.30 w/cm—8% HRM	0.51	0.98	0.58	0.99	0.71	0.96
1F	0.30 w/cm—12% HRM	0.56	0.98	0.63	0.98	0.87	0.96

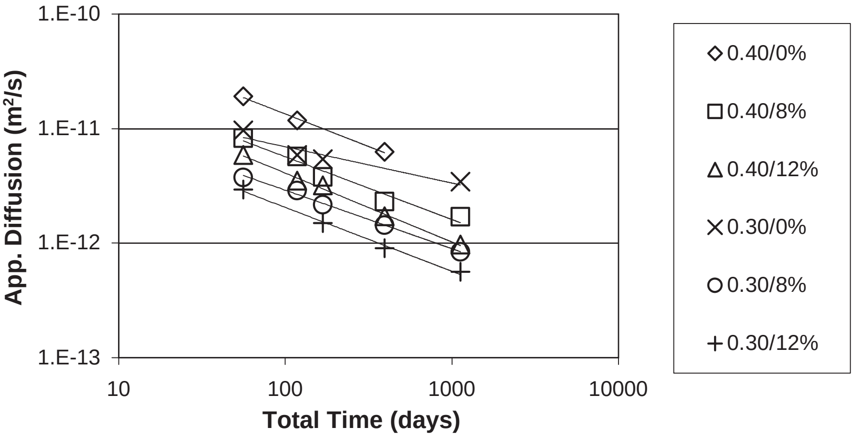

Fig. 2. Time-dependent diffusion coefficients (m_{total}) for HRM concretes.

the sample preparation and chloride exposure (in 1.0 mol/L NaCl) was initiated at approximately 28 days of age.

The third set of concretes studied involved different levels of ultra-fine fly ash (UFFA) or silica fume [13]. Three different groups of mixtures were investigated. The first group was cast with a cementitious materials content of 375 kg/m^3 and a water content of 150 kg/m^3, thereby yielding a water-cementitious materials ratio (w/cm) of 0.40. For these mixtures, the level of superplasticizer was adjusted to produce a slump in the range of 125 to 175 mm. A second series of three mixtures with UFFA was cast with a lower water content of 135 kg/m^3. The aim was to maintain the superplasticizer at a similar level to the control mixture at a water content of 150 kg/ m^3 and take advantage of the enhanced workability provided by UFFA by reducing the unit water content. The third group contained a single mixture with a water content of 120 kg/m^3 (mix 3F). The purpose of this mixture was to produce a mix with a similar superplasticizer content as that used in the mix with 8% silica fume and a water content of 150 kg/m^3 (i.e. mix 3B) and again maintain the target slump by reducing the water content.

Boral Material Technologies (BMT) supplied all the Portland cement, ultra-fine fly ash (UFFA), standard Class F fly ash (i.e. Sandow Generating Station) and superplasticizer for the third study. The UFFA is produced by classification of a typical ASTM Class F fly ash and is distributed by BMT under the trade name Micron3. Bulk chloride diffusion tests for these samples were initiated at 28 days. After curing for 28 days in the fog room at 23 °C, 100-mm diameter×50-mm-thick test specimens were cut, the curved surfaces and one flat face were sealed with epoxy and the specimens were then vacuum saturated. After saturation, specimens were immersed in a sodium chloride solution (165 g/L NaCl) in a sealed container at laboratory temperature (nominally 23 °C). The test method used on this set of samples follows the Nordtest ponding standard [8].

All three series of concretes used the same aggregates. The fine aggregate had a density of 2700 kg/m^3, an absorption of 1.4%, and a fineness modulus of 2.56. A crushed 10 mm limestone with a density of 2670 kg/m^3 and absorption of 1.67% was used as the coarse aggregate. All mixtures included an ASTM Type A water-reducer, a naphthalene sulfonate-based superplasticizer and an air-entraining agent.

A summary of the mixture proportions of the various concretes analyzed is presented in Table 1.

4. Determination of the reduction coefficient

The reduction coefficient is often determined using Eq. (3). The apparent diffusion values calculated using Eq. (1)

Table 5
Diffusion coefficients (10^{-12} m^2/s) for slag/silica fume concretes exposed to chloride at 28 days of age at 23 °C

Mix code	Mix design	Chloride exposure period (days)			
		28	90	365	1095
2A	0.30 w/cm—4% SF	4.78	3.75	1.58	0.84
2B	0.30 w/cm—4% SF, 25% Slag[a]	4.66	–	1.16	0.70
2C	0.30 w/cm—Type 10SF, 25% Slag	4.41	3.03	1.18	–
2D	0.30 w/cm—8% SF, 25% Slag	4.41	–	1.06	0.46
2E	0.30 w/cm—4% SF, 25% Slag[a]	–	3.02	1.29	0.85

[a] Mixture 2B and 2E contain 500 and 460 kg/m^3 total cementing materials respectively.

Table 6
Fitted surface concentration (percent by mass of concrete) for slag/silica fume concretes exposed to chloride at 28 days of age at 23 °C

Mix code	Mix design	Chloride exposure period (days)			
		28	90	365	1095
2A	0.30 w/cm—4% SF	0.37	0.36	0.47	0.96
2B	0.30 w/cm—4% SF, 25% Slag[a]	0.40	–	0.43	0.70
2C	0.30 w/cm—Type 10SF, 25% Slag	0.40	0.38	0.59	–
2D	0.30 w/cm—8% SF, 25% Slag	0.41	–	0.39	0.51
2E	0.30 w/cm—4% SF, 25% Slag[a]	–	0.46	0.77	0.77

[a] Mixture 2B and 2E contain 500 and 460 kg/m^3 total cementing materials respectively.

Table 7
Summary of m values for slag/silica fume concretes (Set #2)

Mix code	Mix design	m_{total}	r^2	m_{ave}	r^2	m_{eff}	r^2
2A	0.30 w/cm—4% SF	0.60	0.99	0.69	0.99	0.88	0.99
2B	0.30 w/cm—4% SF, 25% Slag[a]	0.64	0.99	0.74	0.98	0.96	0.98
2C	0.30 w/cm—Type 10SF, 25% Slag	0.69	0.99	0.83	0.99	1.11	0.99
2D	0.30 w/cm—8% SF, 25% Slag	0.75	0.99	0.87	1.00	1.19	1.00
2E	0.30 w/cm—4% SF, 25% Slag[a]	0.57	0.98	0.62	0.97	0.77	0.96

[a] Mixture 2B and 2E contain 500 and 460 kg/m^3 total cementing materials respectively.

Table 8
Diffusion Coefficients (10^{-12} m^2/s) for UFFA and SF concretes exposed to chloride at 28 days of age at 23 °C

Mix code	Mix design	Chloride exposure period (days)		
		40	90	365
3A	0.40 w/cm—100% OPC	13.30	10.30	5.61
3B	0.40 w/cm—8% SF	3.68	3.30	1.33
3C	0.40 w/cm—8% UFFA	5.33	3.77	1.59
3D	0.35 w/cm—12% UFFA	3.77	2.73	1.00
3E	0.40 w/cm—12% UFFA	4.86	2.79	1.22
3F	0.31 w/cm—12% UFFA	3.50	2.02	1.26
3G	0.40 w/cm—12% SF	2.59	1.88	1.09
3H	0.33 w/cm—16% UFFA	2.89	2.20	1.39

are plotted with time on a log–log scale. Linear regression analysis of the data is used to determine m. Published values [2–4] of m typically use the maturity achieved at the end of the exposure period as the time basis. Mangat and Molloy [2] and Bamforth [3] used specimens continuously exposed to chlorides. Tang and Nilsson [4] used a short-term test (several hours to several days in duration) at varying maturities. Other researchers [14] have investigated the change in the diffusion coefficient due to maturity effects only. In these cases, virgin (non-chloride contaminated) samples of the mature concrete are exposed to chlorides for a constant short period of time (i.e. 35 days) at various ages. It was found that the ratio of the time-dependant reduction coefficient for continuous exposure to that found by exposing mature concrete for short times is approximately 0.64 [14]. In this paper, specimens were exposed to chlorides continuously. The use of achieved maturity as time will be given the designation m_{total} in this paper.

Determination of the diffusion coefficient reduction presents problems. The diffusion coefficient for each exposure period in fact lies somewhere in between the instantaneous values one would find if the specimen were tested at the beginning of the exposure period and at the end. The equation often used to determine the apparent diffusion coefficient (Eq. (1)) assumes that the diffusion coefficient remains constant with this time. As the concrete matures, hydration decreases the ability of ions to penetrate. Therefore, during the exposure period, the diffusion coefficient is changing. As noted above, previously published literature used the calculated apparent diffusion coefficient and the time at the end of the exposure period to calculate m. Using Eq. (1) is inaccurate; using the time-dependent solution is more appropriate (D in Eq. (1), being replaced by the function in Eq. (3)). The difficulty with this approach is that D_{ref} and m cannot be solved independently using one profile.

Rather than determining m by linear regression of a log D vs. log time plot, Thomas and Bamforth [6] used a multi-mechanistic finite-difference model developed at the University of Toronto [15]. Experimental chloride diffusion profiles at six ages (ranging from 6 months to 8 years) were examined. The model used the average surface concentration found for all ages of each concrete mixture. An initial diffusion coefficient (at 28 days) and a reduction coefficient (m) were determined by minimizing the sum of the squares of the errors for all ages.

An intuitive approach to the diffusion coefficient changing during the exposure period would be to use Eq. (1), but to plot the average age while exposed to the

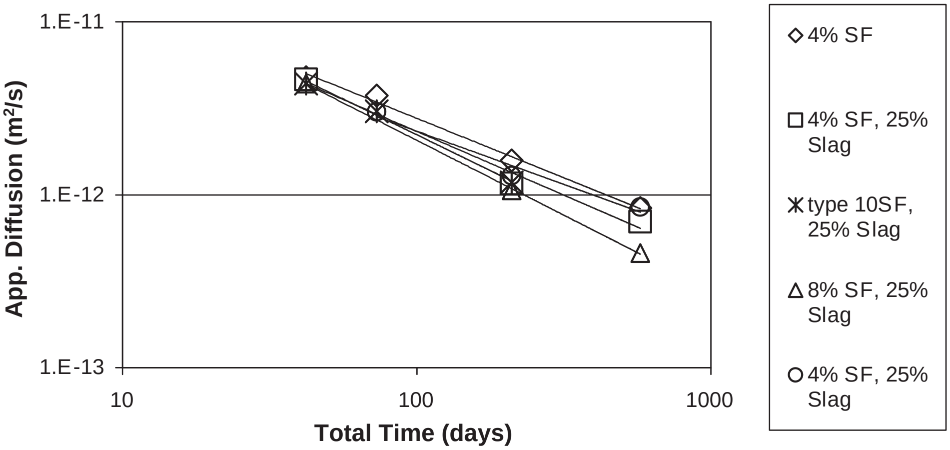

Fig. 3. Time-dependent diffusion coefficients (m_{total}) for slag/silica fume concretes.

Table 9
Summary of m values for UFFA and SF concretes (Set #3)

Mix code	Mix design	m_{exp}	r^2	m_{total}	r^2	m_{eff}	r^2
3A	0.40 w/cm OPC	0.49	0.99	0.58	1.00	0.73	1.00
3B	0.40 w/cm—8% SF	0.61	0.93	0.72	0.97	0.94	0.96
3C	0.40 w/cm—8% UFFA	0.69	0.99	0.82	1.00	1.11	1.00
3D	0.35 w/cm—12% UFFA	0.77	0.98	0.91	0.99	1.28	1.00
3E	0.40 w/cm—12% UFFA	0.77	1.00	0.91	0.98	1.28	0.99
3F	0.31 w/cm—12% UFFA	0.55	0.96	0.64	0.92	0.82	0.92
3G	0.40 w/cm—12% SF	0.49	1.00	0.57	0.96	0.71	0.99
3H	0.33 w/cm—16% UFFA	0.41	1.00	0.48	0.99	0.59	0.99

chloride solution as the time basis. (A specimen exposed for a 28-day period from 28 to 56 days would yield an average age of 42 days). This method is reported as m_{ave} in Tables 4, 7 and 9.

Stanish and Thomas [5] recognized that the diffusion values determined give an average diffusion value over the time period of chloride exposure. Their calculated effective age corresponds to an instantaneous diffusion value that is equivalent to the diffusion value determined experimentally. The effective time, the method used to determine m_{eff}, takes into account both maturity and exposure time.

The time-dependent reduction coefficient, m, is calculated in this paper by three methods using the exponential function proposed by Mangat and Molloy [2]. The three methods discussed use differing techniques to represent time, generating different m values. The time used as the basis to calculate m for each method for a specific exposure period is shown schematically in Fig. 1.

5. Results and discussion

The time-dependant reduction coefficient, m, was calculated for the three data sets using three methods. The apparent diffusion was calculated using Eq. (1) for all three methods. They differ in the value used as the time basis. The first method, m_{total}, uses concrete maturity versus the calculated apparent diffusion coefficient. The second method, m_{ave}, uses average age during the exposure period versus the calculated apparent diffusion coefficient. The third method, m_{eff}, uses the method of Stanish and Thomas [5].

Table 2 presents the diffusion values determined for the HRM concretes studied by Hooton, Gruber and Boddy [10,11]. Table 3 gives the fitted surface concentration. It can be seen that for some of the concrete mixtures that the surface concentration is fairly stable; in others there is an unexplained sharp increase between 90 and 140 days of chloride exposure. Table 4 gives the three reduction coefficients determined using each of the three methods. Good exponential fits were found in all cases with r^2 values ranging from 0.88 to 0.99. Fig. 2 presents the data for the time-dependent diffusion coefficients based on total time, or m_{total} values.

The m_{total} coefficients determined seem high compared to other reported values using maturity as the time axis such as those from Bamforth [3] (PC: m=0.27), and Tang and Nilsson [4] (PC with w/cm of 0.70: m=0.25; PC with w/cm of 0.32: m=0.31). However, the values determined for m_{ave} and m_{total} of the 0.30 w/cm, 0% HRM mixture are similar to these values. Some general trends were found for all calculation methods. The reduction coefficient increases with increasing replacement levels of HRM. For the same level of HRM, the reduction coefficient increases with increasing water to cementing materials ratio, but the initial diffusion coefficient is lower.

The second set [12] of diffusion coefficients is shown in Table 5. The fitted surface concentration at each time is shown in Table 6. Again, some of the concrete mixtures have stable chloride surface concentrations; others do not. The m values for the concretes with various replacement levels of silica fume and slag are presented in Table 7. Fig. 3

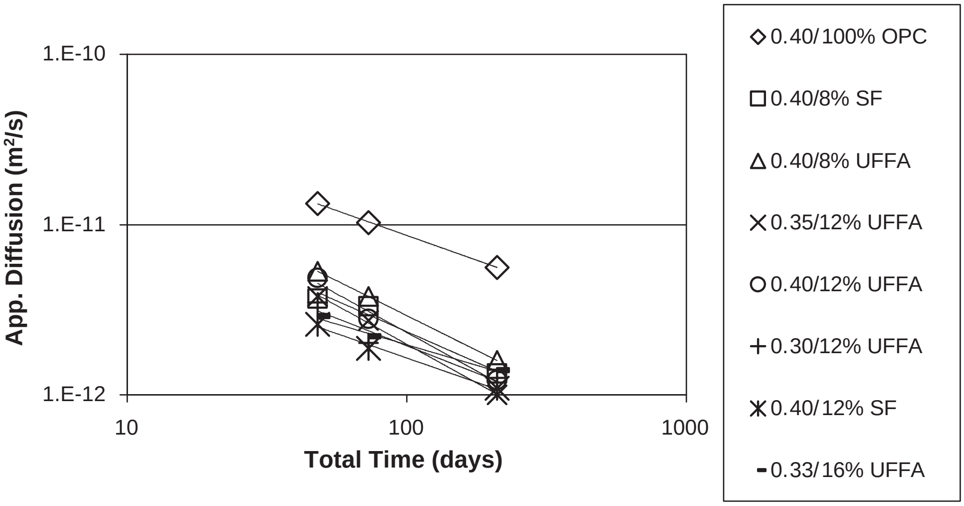

Fig. 4. Time dependant diffusion coefficients (m_{total}) for UFFA and SF concretes.

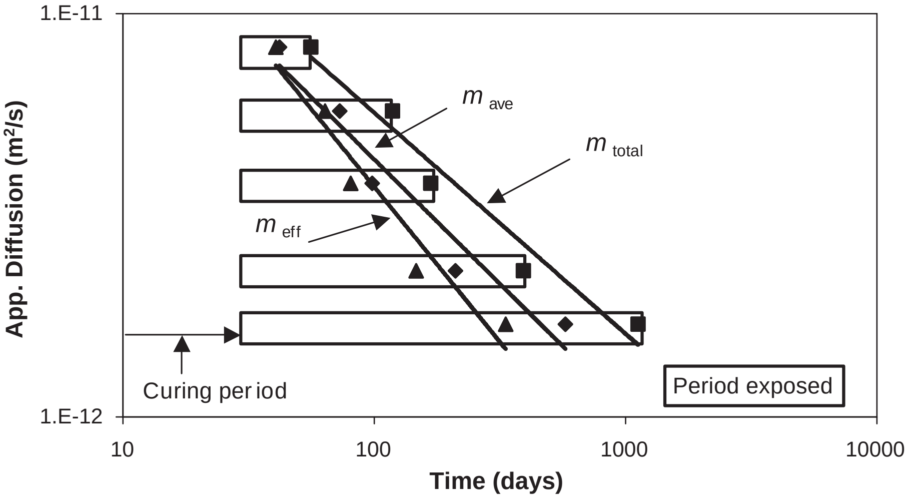

Fig. 5. Comparison of reduction coefficients (Mixture 1B–0.40 w/cm–8%HRM).

presents the results for the time dependent diffusion coefficients based on total time, or m_{total} values. The initial diffusion coefficients (28 day values in Table 5) are equal, but the secondary hydration effect in concrete containing blast furnace slag leads to a greater reduction in diffusion with time. The determined reduction coefficients (m_{total}) are similar to 0.62 for a combined data set of blast-furnace slag concrete found by Bamforth [3] and 0.63 for 0.32 w/cm, 6% silica fume given by Tang and Nilsson [4].

The third set of concretes, involving ultra-fine fly ash and silica fume, were tested for long-term diffusion and the results for their time-dependent diffusion properties are shown in Tables 8 and 9 and Fig. 4. As the data were obtained from a previous project, fitted surface concentrations were not available. Again, the m_{total} value obtained for the 0.40 w/cm, 100% PC mixture seems high compared to other reported values [3]. However, m_{total} values in the range of 0.6–0.7 (or higher) with moderate levels of silica fume, fly ash or slag seem typical of published values [2,3,6]. The effect of pozzolans can be seen by the lower initial diffusion coefficient. There are few, if any, published values of the time-dependant reduction coefficient using the average age method, m_{ave}, or the effective age method, m_{eff}. The majority of published data [2,3] uses the maturity of the specimen at the end of the exposure period as the time used to calculate the reduction coefficient (m_{total} in this paper). Yet, the diffusion coefficient determined for a particular exposure period does not correspond to the time at the end of the period but to some time bounded by the initial exposure time and termination of the exposure interval. The values reported in this paper using the total time method, m_{total}, are higher than those in the literature for the ordinary Portland cement mixtures but similar for those using pozzolans. The time-dependant reduction coefficients tend to be lower for ordinary Portland cement mixtures than for those using pozzolans regardless of the calculation method employed.

The calculated time-dependant reduction coefficient is highly dependent on the time value used: total, average, or effective time. The three methods discussed use differing approaches to represent time, yielding different m values. The total time method yields the lowest m value, while the effective time approach of Stanish and Thomas [5] yields the highest. The cause can be seen in Fig. 5; the apparent diffusion values are those given in Table 2 for mixture 1B, but the time plotted for each method changes the slope of the relationship. The differences in the predicted time-to-corrosion using these values of m can be seen in Table 10. Time-to-corrosion was determined using a service life prediction software package available free-of-charge over the Internet [16]. The results presented in this paper represent continuous chloride exposure for up to three years. Since the predicted service life is highly dependant on the value of m, longer-term exposure tests should be carried out to validate the reduction coefficient. Thomas and Bamforth [6] present data for specimens up to eight years of age.

Table 10
Service life implications of m (Mixture 1B)

	m_{total}	m_{ave}	m_{eff}
Time of initial D (days)	56	42	40.6
m	0.55	0.62	0.77
Time to corrosion (years)	27	41	99

$D_{\text{initial}}=8.25\times10^{-12}$ m/s;
Surface concentration, Cs=1.0% mass chlorides/mass concrete;
Depth of reinforcing=50 mm;
Critical chloride threshold, C_x=0.05% mass chlorides/mass concrete.

6. Conclusions

Data from three projects, for specimens continuously exposed to chloride solutions, were used to calculate diffusion values using Crank's solution to Fick's second law at various times. The effects of various pozzolans and water to cementing materials ratios are clearly seen in the chloride diffusion values presented. Initial chloride diffusion values (using 28 or 40 days of exposure from an early age) are higher in concrete mixtures at the higher (although commonly used) water to cement ratio of 0.40 without the addition of pozzolans. The chloride diffusion coefficient reduces more dramatically in concrete mixtures containing pozzolans showing their long-term hydration properties.

The time-dependent reduction coefficient, *m*, is calculated in this paper by three methods using the exponential function proposed by Mangat and Molloy [2]. The three methods discussed use differing techniques to represent time, generating different *m* values. The total time method yields the lowest *m* value, while the effective time approach of Stanish and Thomas [5] yields the highest. The reduction coefficient determined by one method can be transformed to one of the other methods if one knows the age at initial exposure and the period of exposure for each specimen.

Service life modeling is becoming a common tool for performance-based specifications of concrete structures [17]. The determination of diffusion coefficients and their time-dependant behavior clearly has an effect on the estimated time-to-corrosion. Currently, several experimental techniques exist to determine the chloride diffusion coefficient yielding different numerical values. To compound modeling difficulties, it is often difficult to determine the method used to establish the time-dependant reduction of the diffusion coefficient used in modeling software. The three methods used in this paper to calculate the reduction coefficient demonstrate that there is a significant difference in the time-to-corrosion depending on the method employed to calculate *m*. Reliance on a model's values for *m* may yield either overly conservative or unconservative estimates of service life. Since the reduction of diffusion with time has such a great impact on service life predictions, it is imperative to know how the chloride diffusion and reduction coefficients were obtained when making use of them and to move towards a standard method for their determination. General logic might suggest that Stanish and Thomas' weighted average time method may be best from a time standpoint, but it also is the least conservative for service life estimation. There is no long-term confirmation that one method is superior to another.

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