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Chloride diffusivity based on migration testing

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Abstract

The present article presents the results of an experimental investigation, where the chloride diffusivities from steady-state migration, non-steady-state migration, and electrical conductivity measurements were compared. A very good correlation between all these diffusivities were obtained, but the non-steady-state migration testing gave a chloride diffusivity that was about 10 times higher than from the steady-state migration and up to several times higher than that from the conductivity method. A good correlation was also observed between the initial electrical conductivity, the conductivity of NaCl saturated concrete, and the charge passed through the concrete. The correlation was further good between the electrical conductivity and the diffusivity obtained from both the steady-state and the non-steady-state migration method. For a given binder system and type of concrete, measurements of initial electrical conductivity appear to provide a good basis both for estimation of chloride diffusivity and for routine control of concrete quality. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Durability; Transport properties; Diffusion; Chlorides

1. Introduction

In recent years, migration testing has been widely used for accelerated testing of chloride diffusivity in concrete [1]. Both steady-state migration [2] and non-steady-state migration testing [3], as well as testing of electrical conductivity [4,5], are being used for evaluation of chloride diffusivity in concrete. Due to the complexity of the transport mechanisms involved, however, a theoretical correlation between the results obtained from the different test methods is still lacking. In the literature, experimental data for establishing such a correlation are also very limited.

In the present article, the results of an experimental investigation are presented, where steady-state and non-steady-state migration testing, as well as conductivity testing were carried out. Since the rapid chloride permeability method [6] is widely used in North America, this method was also included in the test program.

2. Experimental

2.1. Materials

Four different types of concrete with a water-to-binder ratio of 0.40, 0.50, and 0.60 were produced. The cement was an ordinary portland cement, and for one of the mixtures, a high quality silica fume was also used. The aggregate was of siliceous origin with a 16-mm maximum particle size, and the superplasticizer (SP) was a naphthalene-based admixture with a solid content of 42%. The composition of the concrete mixtures is shown in Table 1, and some characteristics of the concrete are shown in Table 2, from which it can be seen that the 28-day compressive strength varied from 39.7 to 74.3 MPa.

A number of $\phi\,100 \times 200$ mm concrete cylinders from each concrete mixture were produced and cured in water at room temperature for approximately 6 months. Then, the specimens were coated with a 5-mm thick epoxy resin and cut into 50-mm thick concrete slices before being subjected to a standardized water saturation procedure [6] and further testing.

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Table 1
Composition of concrete mixtures

		Mixture proportions (kg/m^3)						
						Aggregate		
Mix number	Water-to-binder ratio	Cement	Silica fume	SP	Water	0–8 mm	8–11 mm	8–16 mm
A	0.40	397	–	8.1	159	1047	418	418
B	0.50	380	–	2.6	190	1000	408	408
C	0.60	326	–	–	195	1002	423	423
SFB	0.50	342	38	3.8	190	950	408	408

2.2. Experimental

The steady-state migration testing was carried out according to NT Build 355 [7]. Initial conductivity was also measured on the basis of this method. In order to simulate more natural exposure conditions, natural seawater was also used in addition to the pure NaCl solution, the chloride concentration being the same (0.6 M). A voltage of 12.0 V was applied, and both electrical resistance and current were monitored throughout the test duration. The steady-state diffusivity (D_{ssm}) was calculated by the following formula [Eq. (1)]:

$$D_{\mathrm{ssm}} = \frac{RT}{zF\Delta E}\frac{VL}{Ac_{0\mathrm{A}}}\frac{\mathrm{d}c_{\mathrm{B}}}{\mathrm{d}t} \tag{1}$$

where D_{ssm} is the diffusion coefficient measured by steady-state migration (m^2/s), z is the absolute value of chloride ion valence ($z=1$), F is the Faraday constant ($F=96{,}480$ J/V mol), ΔE is the absolute value of potential difference across the specimen (V), R is the gas constant ($R=8.314$ J/K mol), T is the absolute temperature (K), L is the thickness of the specimen (m), t is the test duration (s), A is the area of the cross-section of the specimen (m^2), V is the volume of the down-stream cell (m^3), $c_{0\mathrm{A}}$ is the chloride concentration in the up-stream cell (M), and c_{B} is the chloride concentration in the down-stream cell (M).

For the non-steady-state diffusivity [3], the depth of chloride penetration was measured on the freshly exposed splitting surface after spraying with a 0.1 N AgNO$_3$ solution. The diffusivity was calculated on the basis of the average of 20 readings of the chloride penetration depth.

$$D_{\mathrm{nssm}} = \frac{RTL}{zF\Delta E}\frac{x_{\mathrm{d}}-\alpha\sqrt{x_{\mathrm{d}}}}{t} \tag{2}$$

where $\alpha = 2\sqrt{\frac{RTL}{zF\Delta E}}\cdot\mathrm{erf}^{-1}\left(1-\frac{2c_{\mathrm{d}}}{c_0}\right)$, D_{nssm} is the diffusion coefficient (m^2/s), z is the absolute value of chloride ion valence ($z=1$), F is the Faraday constant ($F=96{,}480$ J/V mol), ΔE is the absolute value of potential difference across the specimen (V), R is the gas constant ($R=8.314$ J/K mol), T is the absolute temperature (K), L is the thickness of the specimen (m), x_{d} is the penetration depth (m), t is the test duration (s), erf^{-1} is the inverse of error function, c_{d} is the minimum free chloride concentration in concrete detected by 0.1 N AgNO$_3$ solution ($c_{\mathrm{d}}=0.07$ M), and c_0 is the chloride concentration in the up-stream cell (M).

Since the concrete quality may vary to some extent from one test specimen to another, efforts were made to obtain the non-steady-state diffusivity on the basis of the same test specimen and the same experimental setup as that for the steady-state test method. This approach was based on the following understanding. Before the chloride ions pass through the concrete specimen, the chloride concentration profile in the concrete specimen and chloride front move gradually towards the down-stream side. Fig. 1(a) and (b) shows a critical stage of the chloride concentration profile and the chloride penetration front in a concrete specimen when the first chloride ions penetrate through the specimen ($t=t_1$). Fig. 1(c) shows the chloride concentration in the down-stream cell in the steady-state migration setup. Before the steady state is reached ($t<t_2$), the transition period from t_1 to t_2 is due to an uneven distribution of the chloride content in the specimen. When $t>t_2$, the chloride concentration in the specimen keeps constant and the profile is a straight line. The time for the first chloride ions to pass through the specimen corresponds to t_1, while t_0 is determined by the interception of the steady-state $c-t$ curve and the time axis as shown in Fig. 1(c). Theoretically, the non-steady-state diffusivity should be based on the average of the unevenly distributed chloride front (the dash line in Fig. 1(b) with penetration depth of x_{d}). When this average front

Table 2
Characteristics of the concrete

		Fresh concrete		Hardened concrete	
Mix number	Water-to-binder ratio	Slump (mm)	Air content (%)	28 days of compressive strength (MPa)	Total porosity (%)[a]
A	0.40	220	1.3	66.0	11.8
B	0.50	200	1.7	51.4	14.7
C	0.60	190	1.7	39.7	14.6
SFB	0.50	160	1.6	74.3	15.0

[a] Ref. [1].

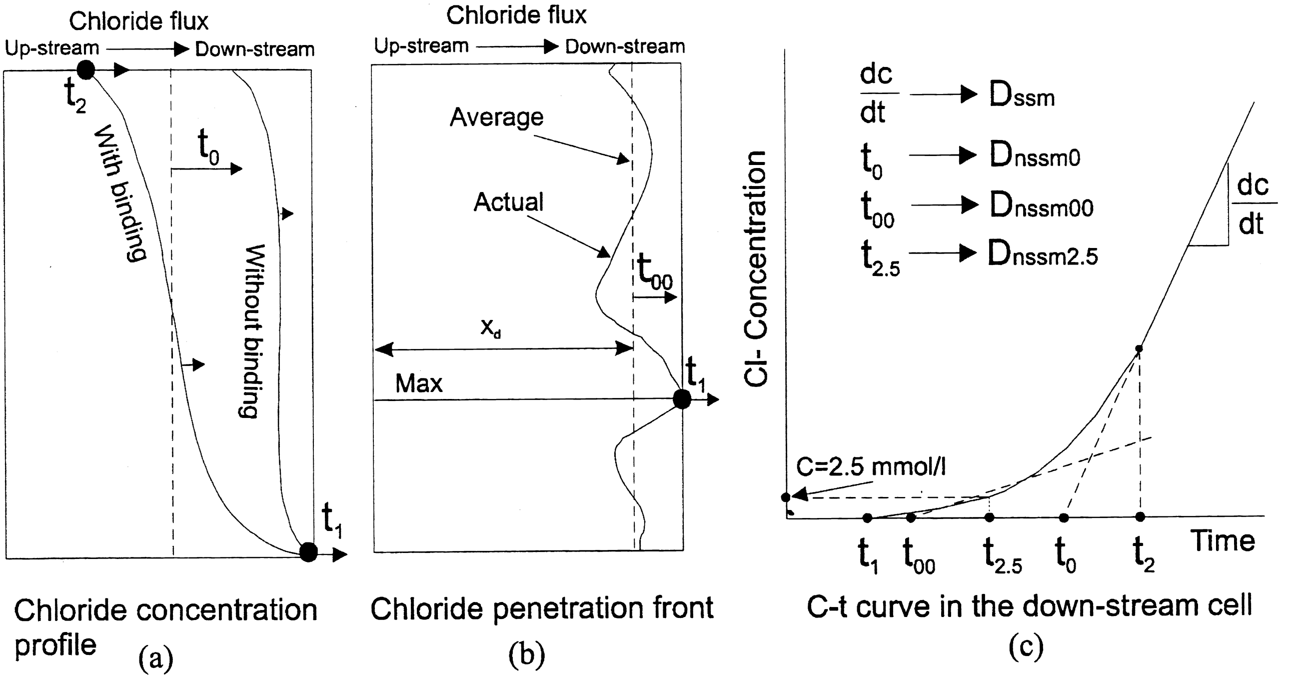

Fig. 1. A typical experimental observation of chloride penetration through a concrete specimen and determination of the time when the chlorides successively penetrate through the concrete specimen.

reaches the edge of the down-stream surface, the time is marked as t_{00}. Since it is not easy to determine t_{00}, however, a regression line based on the first several observations in the range of 1–5 mmol/l was used as a basis for the determination of t_{00}. This was assumed to correspond to the time when the average penetration depth was equal to that of the specimen thickness. In addition, the time $t_{2.5}$ corresponding to a chloride concentration of 2.5 mmol/l in the down-stream cell as suggested by Halamickova et al. [8] was also recorded.

Based on Eq. (2), the non-steady-state diffusivity was calculated, where D_{nssm}, D_{nssm0}, D_{nssm00}, and $D_{nssm2.5}$ are the diffusivities based on the standard procedure [3] from t_0, t_{00}, and $t_{2.5}$ with penetration depth equal to the thickness of the concrete specimen, respectively.

The advantage of using t_0, t_{00}, or $t_{2.5}$ is that the non-steady-state diffusivity and the steady-state diffusivity can be obtained from the same test specimen and the same experimental setup. While both t_0 and t_{00} are relatively easy to determine, the determination of $t_{2.5}$ is more difficult to determine since the chloride concentration is not continually monitored.

Based on the measurement of electrical conductivity, the diffusivity can be calculated on the basis of the following equation [4,5]:

$$\frac{\sigma}{\sigma_0} = \frac{D}{D_0} \tag{3}$$

where σ and D are the conductivity and the chloride diffusivity of the concrete, while σ_0 and D_0 are the conductivity and the chloride diffusivity of the concrete pore solution, respectively. If the conductivity and the diffusivity for the pore solution are known, the chloride diffusivity of the concrete can be obtained by a conductivity measurement. Since σ_0 and D_0 are not easy to determine, however, it was assumed in the present study that after the steady state had been reached, the concrete pore solution in the specimen would be roughly similar to the solution in the up-stream cell. Then, the chloride diffusivity could be estimated by Eq. (3). The conductivity was calculated from electrical resistance measured under 1-K frequency.

The rapid chloride permeability test [6] was carried out with the modification that instead of 60 V, 12 V was applied across the test specimen. Also, electrical current was measured every 4 h during a period of 30 h. Thus, the charge passed through the specimen was the total charge accumulating during a test period of 30 h.

3. Results and discussion

3.1. Chloride migration and steady-state diffusivity

For all test series, the chloride concentration both in the up-stream and the down-stream cells as well as the electrical resistance were measured throughout the test duration, some typical results of which are shown in Figs. 2 and 3. In the up-stream cell, the chloride concentration rapidly decreased during the non-steady-state period, but then gradually leveled out at about 0.3 M for all test series. The speed of chloride concentration drop was mainly

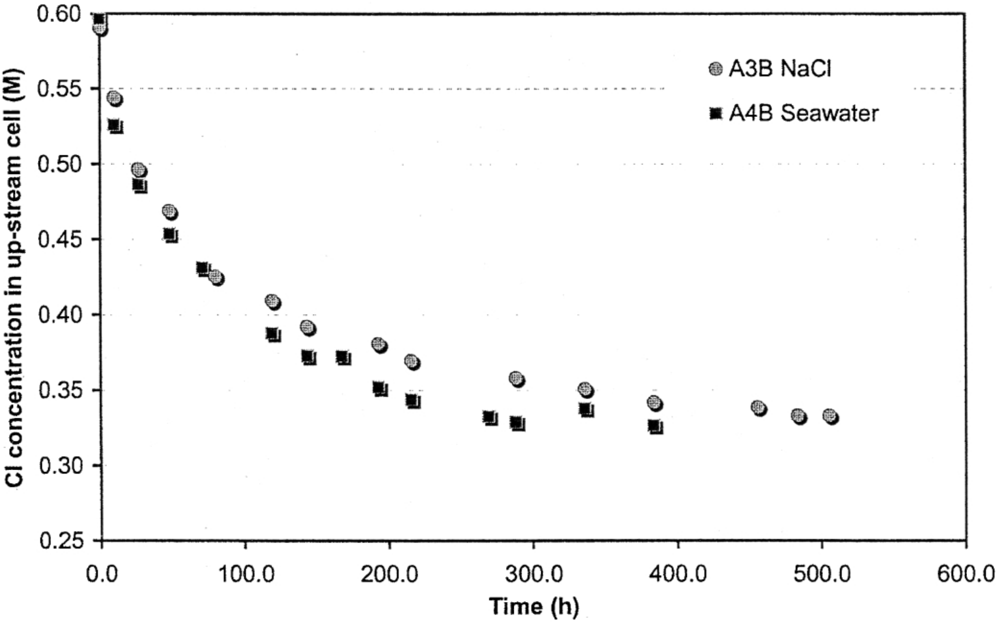

Fig. 2. Chloride concentration in the up-stream cell for two typical specimens during migration testing.

determined by the concrete quality and the type of salt solution in the up-stream cell. Based on 500 chloride measurements from 24 test series, it was observed that the chloride concentration was reduced faster from the seawater than from the NaCl solution. In the down-stream cell, a steady-state migration was mostly obtained after a concentration of 0.015–0.020 mol/l had been reached (0.004–0.005 mol of chloride ions had passed through the concrete specimen). Then, a linear *c–t* curve was obtained. By renewing the chloride solution in the up-stream cell, the slope of the *c–t* curve was not much affected. For all test series, the slope of the *c–t* curve was much higher from seawater than from the NaCl solution. This confirms that the type of chloride source solution is very important for the chloride diffusivity measurements [9].

During the migration process, both electrical conductivity and current changed continually. For all test series, the conductivity was first reduced during the non-steady-state period, but then leveled out in the transitional period

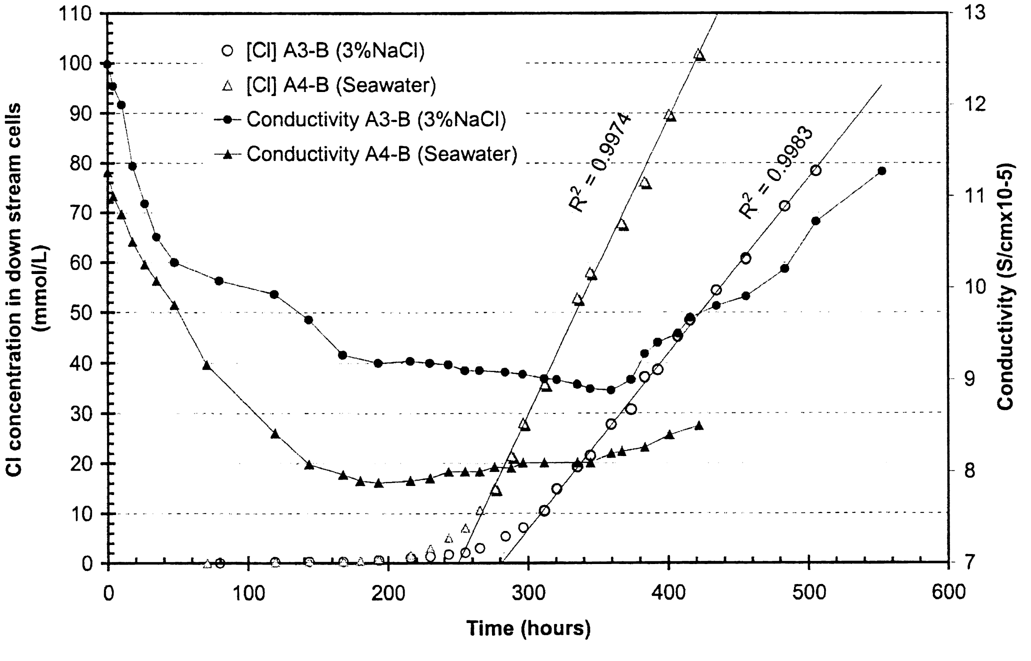

Fig. 3. Chloride concentration in the down-stream cell and electrical conductivity of two typical specimens during migration testing.

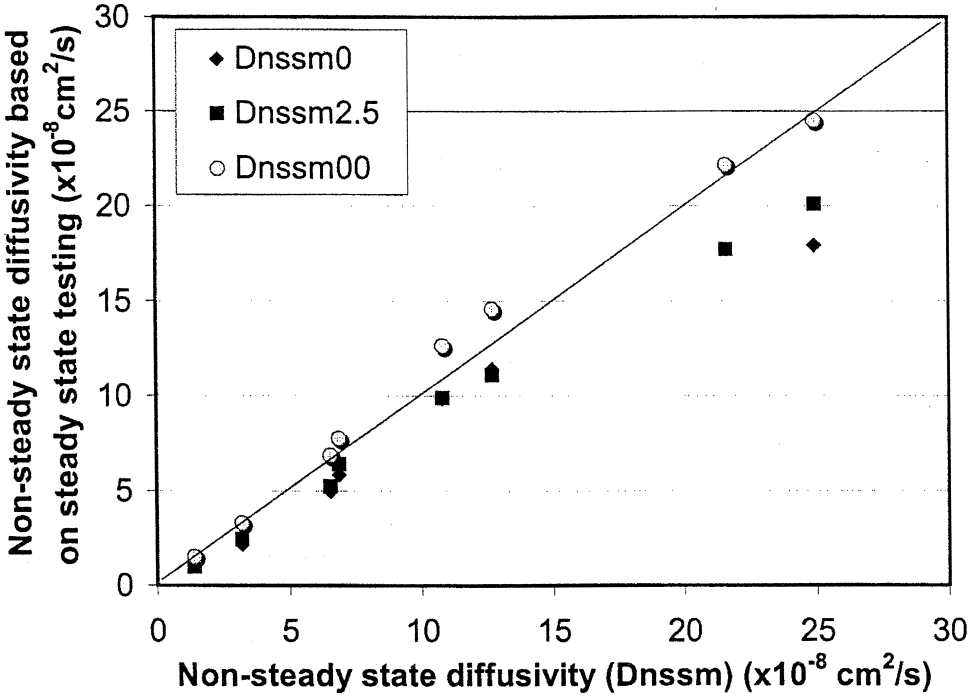

Fig. 4. Comparison of non-steady-state diffusivity measured on the basis of the standard method and the steady-state migration procedure.

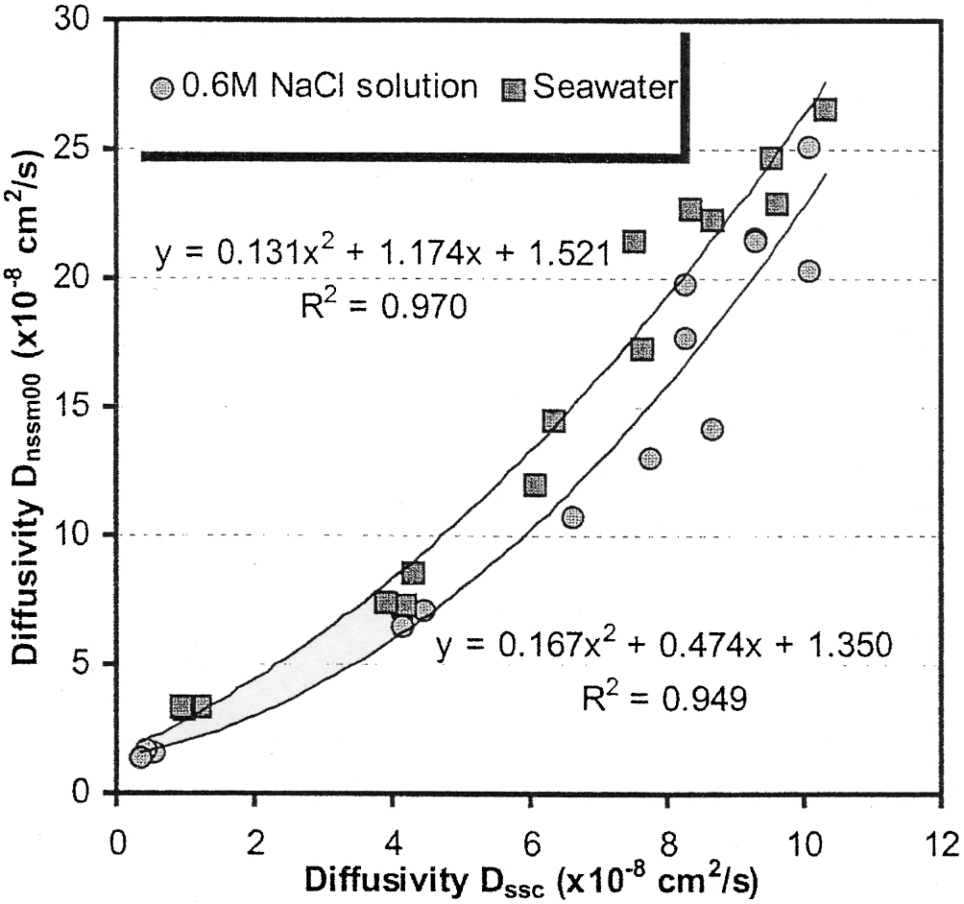

Fig. 5. Correlation between diffusivity from non-steady-state migration (D_{nssm}) and conductivity measurements (D_{ssc}).

between t_1 and t_2 (Fig. 3). Later on, the conductivity started to increase again, following the same pattern as the current passing through the test specimen. A similar observation was made by Buenfeld and Newman [10], who studied natural diffusion from exposure to seawater. Andrade and Sanjuan [11], however, observed that the electrical current increased before the steady state of migration was reached.

During the migration testing, the following factors may affect the conductivity:

1. The chemical composition of the pore solution in the specimens will change due to the penetration of chlorides. A replacement of OH^- by Cl^- ions may cause a reduced conductivity.

2. After the chloride ions have penetrated the concrete specimens, a part of them will be bound to the hydration products. This may block some of the very fine pores or reduce the pore size, and hence cause a reduced conductivity.

3. In seawater, an interaction between the seawater and the concrete may occur, where precipitation of $CaCO_3$ and $Mg(OH)_2$ may block some of the smallest pores in a surface layer of the concrete. This may also cause a decreased conductivity.

4. Transportation of ions such as OH^- and Ca^{2+} may destroy the balance between the pore solution and the hydration products, which may lead to a decomposition of $Ca(OH)_2$ and the C-S-H gel. This may give an increased conductivity.

Based on the present observations, however, it appears that the factors that reduce the conductivity are dominant in the early stage of the migration process, while at a later stage, the leaching effect may cause an increased conductivity.

It should be pointed out that the conductivity of the silica fume concrete (SFB) became relatively stable after the steady state was achieved, which indicate that the SFB has a higher resistance against leaching compared to that of the ordinary portland cement concrete. Thus, if a concrete is susceptible to leaching, the duration of a steady-state migration testing should be limited in order to obtain a reliable diffusivity.

3.2. Non-steady-state migration diffusivity

In order to measure the non-steady-state diffusivity without splitting the test specimen as described in the standard method, several breakthrough times for the chloride front were applied. A comparison of the non-steady-state diffusivity (D_{nssm}) based on the standard method [3] and the diffusivity obtained on the basis of different breakthrough times are demonstrated in Fig. 4, from which it can be seen that the diffusivity on the basis of t_{00} is very close to that

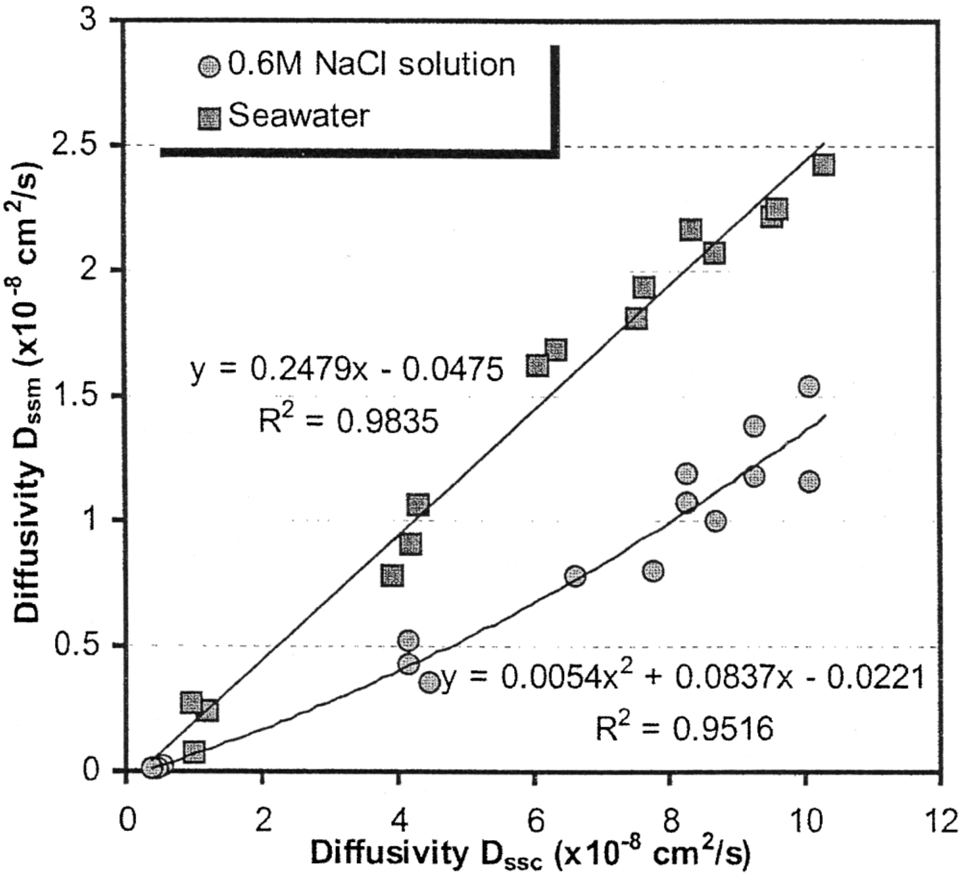

Fig. 6. Correlation between diffusivity from steady-state migration (D_{ssm}) and conductivity measurements (D_{ssc}).

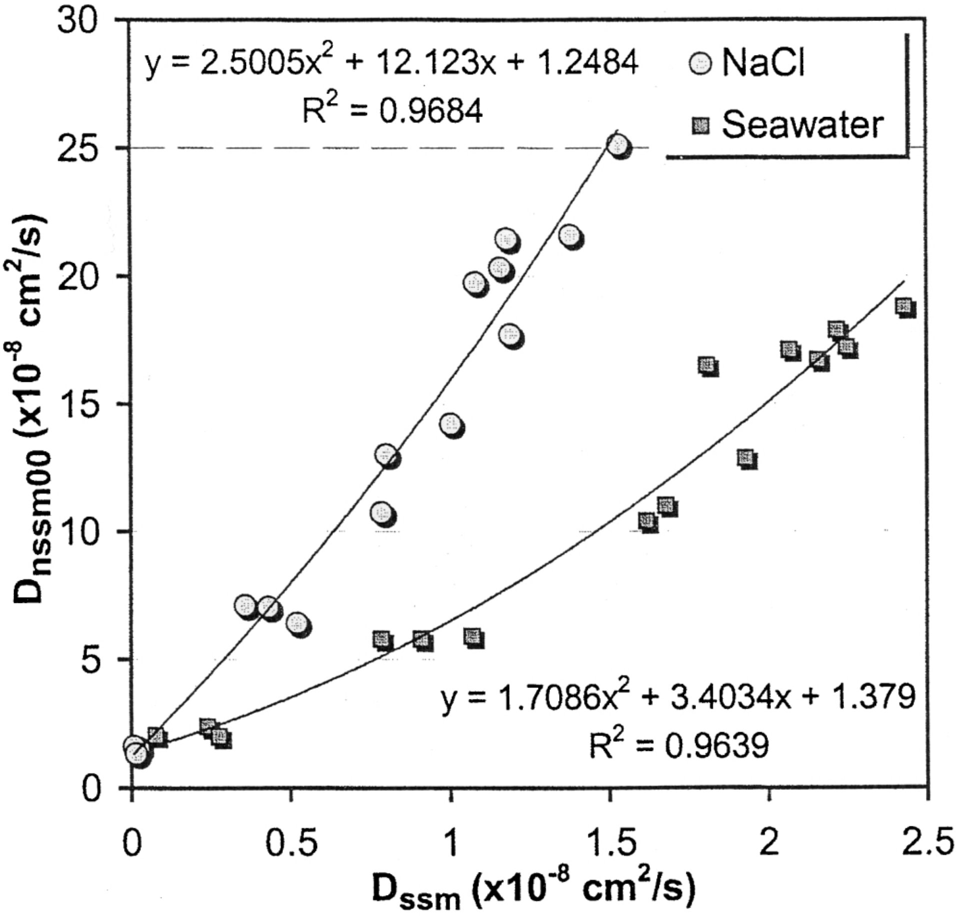

Fig. 7. Correlation between diffusivity obtained from steady-state migration (D_{ssm}) and non-steady-state migration (D_{nssm}).

obtained by the standard procedure. By using t_0 or $t_{2.5}$, the diffusivity is also quite close but slightly lower than that obtained from the standard procedure. It appears, therefore, that t_{00} can be used for non-steady-state migration testing. From a practical point of view, however, t_0 and $t_{2.5}$ may also be applicable. Thus, based on the same experimental setup,

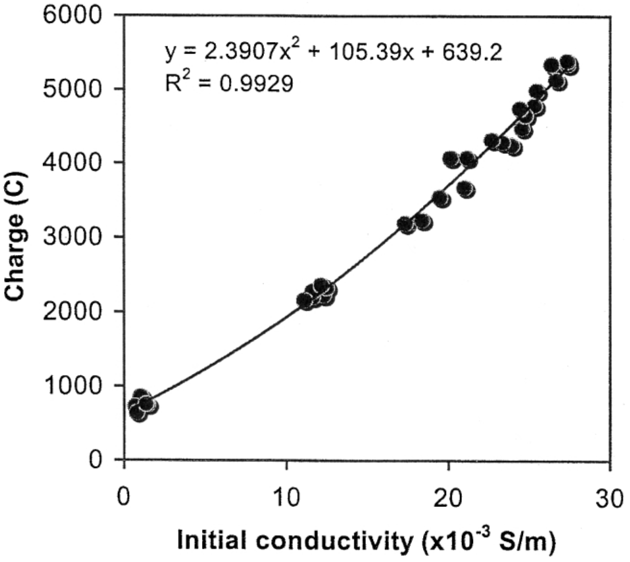

Fig. 8. Correlation between initial conductivity and charge passed through the specimen.

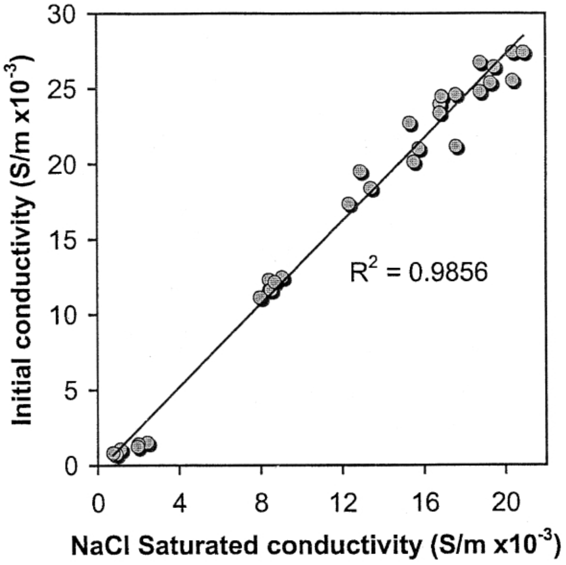

Fig. 9. Correlation between initial conductivity and conductivity of NaCl-saturated concrete.

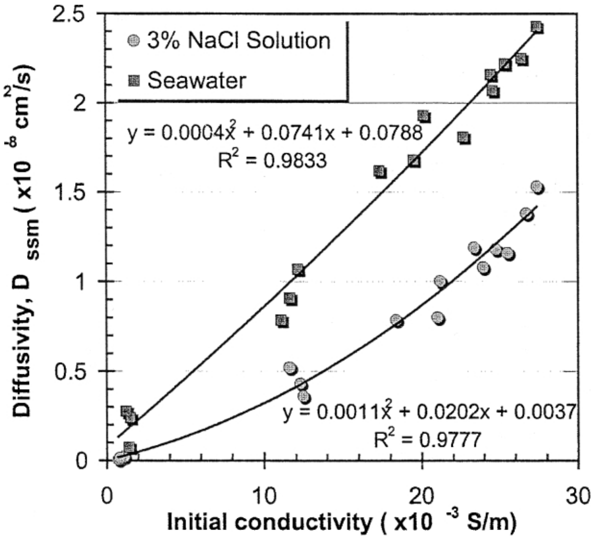

Fig. 10. Correlation between initial conductivity and chloride diffusivity from steady-state migration testing.

both the non-steady and the steady-state migration testing of chloride diffusivity could be carried out on the same test specimens. This provided a good basis for comparison of these two test methods.

3.3. Electrical conductivity

As discussed above, the conductivity became stable in the early stage of the steady-state migration testing. Then, it was assumed that the pore solution in the concrete was roughly equal to the NaCl solution in the up-stream cell, where the chloride concentration was about 0.32–0.30 M in all test series. Therefore, as a first-order approximation, a diffusivity denoted D_{ssc} was calculated by Eq. (3), using a chloride diffusivity of $D_0 = 1.48 \times 10^{-5}$ cm²/s [12] and a conductivity of $\sigma_0 = 30 \times 10^{-3}$ S/cm [13] for a 0.3-M NaCl solution.

3.4. Comparison of the different test methods

A correlation between the diffusivities obtained from the three different test methods is shown in Figs. 5–7. As can be seen, the diffusivities obtained from the steady-state migration, the non-steady-state migration, and the conductivity test method are well correlated, with values of the diffusivity in the following order:

$$D_{\mathrm{nssm}} > D_{\mathrm{ssc}} > D_{\mathrm{ssm}}$$

The non-steady-state migration method gave the highest chloride diffusivity (D_{nssm}) being about 10 times higher than the diffusivity from the steady-state migration and up to several times higher than that from the conductivity method. It should be noted that the value of D_{ssc} can be questioned by the assumptions made. However, a certain correlation between D_{ssc} and migration diffusivities (D_{nssm} and D_{ssm}) may still exist.

As can be seen from Fig. 8, there is also a very good correlation between the charge passed during 30 h and the initial conductivity of the specimens. This is in accordance with other observations [11,14,15]. A good correlation was also obtained when the initial conductivity was plotted against the conductivity of the NaCl-saturated concrete, i.e., the conductivity when steady-state migration was achieved (Fig. 9). In spite of different pore solutions in the portland cement concrete and the SFB, the conductivity of the NaCl saturated concrete was predictable based on the initial conductivity. These results also indicate that the initial conductivity, the chloride saturated conductivity, and the charge passed during 30 h can be used for estimation of chloride diffusivity and for evaluation of the concrete quality.

It was not surprising that a good correlation between the initial conductivity and the chloride diffusivity both from steady-state and non-steady-state migration testing could be observed (Figs. 10 and 11). This also indicates that the chloride migration diffusivity is predictable from a simple measurement of the initial conductivity. It should be noted, however, that the present correlations are based on a very limited number of test results. In order to provide a broader basis for evaluation, therefore, more test results were collected from available literature [16,17]. These results were all based on steady-state migration testing of portland cement and SFB with a binder-to-aggregate ratio and a water-to-binder ratio varying from 0.18 to 0.26, and from 0.34 to 0.60, respectively. As a result, Fig. 12 also demonstrates a good correlation between the initial conductivity and the steady-state migration diffusivity, which again indicates that the chloride migration diffusivity can be estimated with a reasonable accuracy from conductivity measurements. As can be seen from Fig. 13, a good correlation between steady-state and non-steady-state migration diffusivity was also observed.

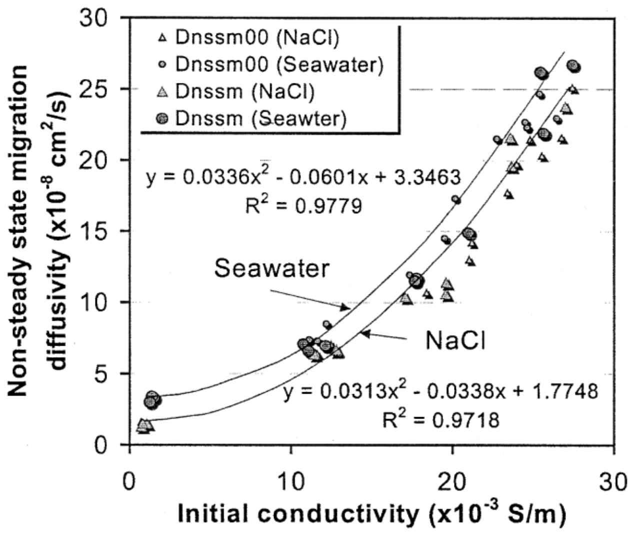

Fig. 11. Correlation between initial conductivity and chloride diffusivity from non-steady-state migration testing.

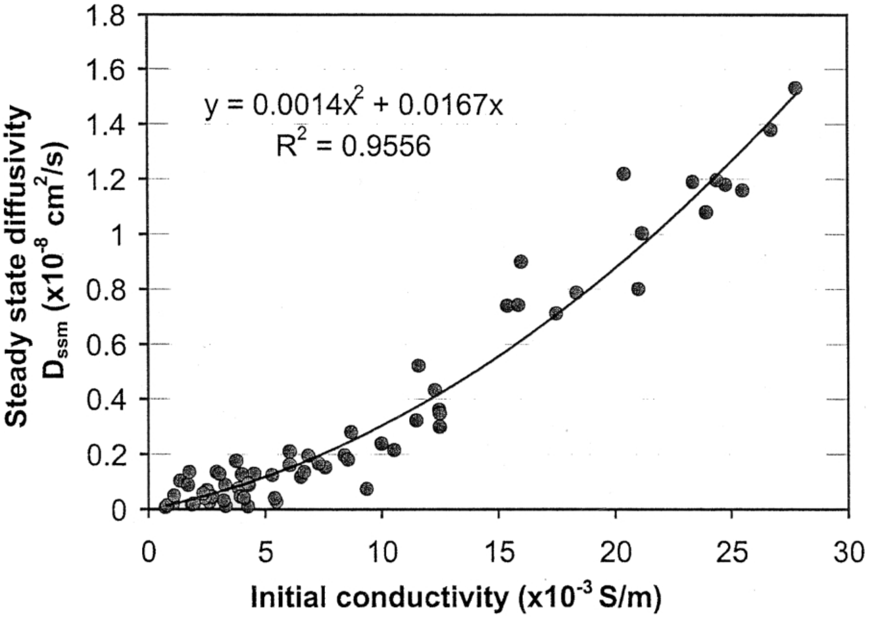

Fig. 12. Correlation between initial conductivity and steady-state chloride diffusivity.

It should be noted, that the above correlations are only based on a portland cement and silica fume type of binder system. Other types of binder system may give other correlations. For a given binder system and type of concrete, however, measurements of initial electrical conductivity appear to provide a good basis both for estimation of chloride diffusivity and for routine control of concrete quality. At present, it still appears to be difficult to establish a good theoretical basis for correlating the steady-state and the non-steady-state migration diffusivity, and the basis for estimating the diffusivity based on conductivity measurements does also appear to be quite superficial. However, the results from the present study may be used as a basis for estimating diffusivity values obtained from the different test methods.

4. Conclusions

Based on the results obtained from the present experimental investigation, the following conclusions appear to be warranted:

1. The chloride diffusivities obtained from steady-state migration (D_{ssm}), non-steady-state migration (D_{nssm}), and

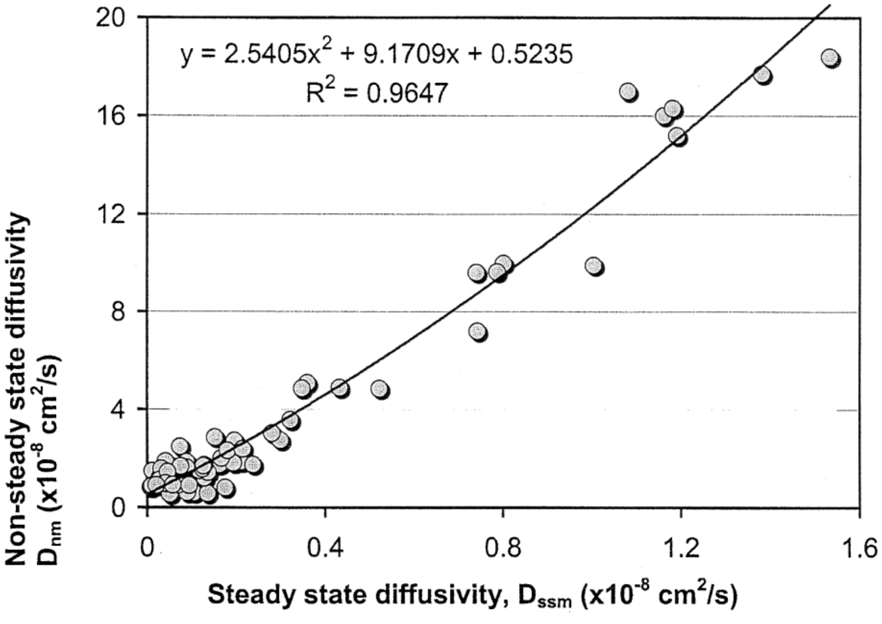

Fig. 13. Correlation between non-steady-state and steady-state chloride diffusivity.

electrical conductivity measurements (D_{ssc}) were well correlated with values of the diffusivity in the following order:

$$D_{\mathrm{nssm}} > D_{\mathrm{ssc}} > D_{\mathrm{ssm}}$$

The non-steady-state migration testing gave a chloride diffusivity that was about 10 times higher than from the steady-state migration and up to several times higher than that from the conductivity method. The value of D_{ssc} may vary due to different measurements and assumptions.

2. A good correlation was observed between the initial electrical conductivity, the conductivity of NaCl saturated concrete and the charge passed through the concrete. The correlation was also good between the conductivity and the diffusivity obtained from both the steady-state and the non-steady-state migration method.

3. An approach to the testing was established, where all the above test parameters could be compared on the basis of the same test specimens and the same experimental setup.

4. For a given binder system and type of concrete, measurements of initial electrical conductivity appear to provide a good basis both for estimation of chloride diffusivity and for routine control of concrete quality.

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