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Determination of chloride diffusion coefficient of concrete using open-circuit potential measurements

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Abstract

The rate of chloride ion ingress into concrete is of great importance for the performance of reinforced concrete structures exposed to chloride-contaminated environments. The service life of reinforced concrete structures subjected to such exposure conditions is closely related to the rate of chloride ion diffusion through the concrete. This paper presents the determination of the apparent chloride diffusion coefficient of concrete using open-circuit potential measurements. The chloride diffusion coefficients obtained are in the range of 6.4×10^{-8} to 12.4×10^{-8} cm^2/s for a simulated seawater tidal condition, which is quite consistent with those reported in the literature. This indicates that open-circuit potential measurements can be considered as an approximate but simple method of assessing the diffusivity of chloride through concrete. Limited with the testing conditions and the characteristics of concrete used, results indicated that the time necessary for corrosion initiation of concrete with a cover depth of 7 cm ranges from 3 to 6 years for the seawater exposure, whereas it is only 1.5 years for a 3% sodium chloride exposure.

Keywords: Concrete; Chloride; Diffusion; Corrosion; Corrosion initiation

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1. Introduction

Concrete has many enemies in service, but by far the most important one continues to be the destructive effect of corrosion of reinforcement embedded in concrete subjected to chloride-contaminated environments. Chloride ions are the primary agents that are able to destroy the natural passivity of reinforcement in alkaline concrete condition. The time required for chloride ions to diffuse through the concrete cover to the reinforcing steel in quantities large enough to break down the passivity of the reinforcing steel depends mainly on the permeability of concrete. Permeability may be a function of several mechanisms such as absorption, intrusion due to alternate wetting and drying and capillary suction or diffusion [1]. Among these mechanisms, diffusion is assumed to be the basic phenomenon for chloride ion ingress through concrete on the assumption that the concrete is generally moist. The extent of diffusion is closely related to the quality of concrete and its pore structure [2], to the cracks present in the surface of concrete [3], and to the thickness of the cover depth [4,5]. In addition, slower initiation of corrosion activity has been reported in cases when thicker concrete cover over the reinforcing steel is used since corrosion mechanism depends primarily on the availability of oxygen and chloride contents at the rebar surface, and on their diffusion rates through concrete [6].

With regard to durability, determination of chloride diffusivity of concrete to reliably predict service life of reinforced concrete structures subjected to chloride-bearing environments is essential. Chloride diffusivity is a complex phenomenon, as the movement of chloride ions through the concrete is slowed down by other ions present in the pore solution of concrete. Therefore, convenient determination of the chloride diffusion coefficients of concrete is rather difficult. Two different methods, such as long-term immersion tests and electrically accelerated chloride ingress tests, have recently been used to accomplish this purpose [7,8]. Long-term immersion tests require chloride extractions from different levels of concrete samples, and quantification of chloride contents by using this method is rather tedious and

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time-consuming. On the other hand, although they provide rapid information about the diffusion properties of concrete, electrically accelerated test procedures may not be reliable due to the possible adverse effects of the relatively high voltage imposed on the rebar in concrete [9].

This paper deals with the determination of the apparent chloride diffusion coefficient of concrete subjected to chloride-contaminated environments. Time to corrosion initiation profiles obtained using the associated chloride diffusion coefficients of concrete exposed to a synthetic seawater and a 3% sodium chloride solution are also presented.

2. Theoretical background of chloride diffusion prediction

Chloride ion diffusion into the micropores of concrete can be modeled to predict chloride concentration at the reinforcing bar surface in concrete. Fick's second law of diffusion is frequently used for this purpose where chloride ion diffusion into concrete is from one direction only [10]. This enables prediction of the apparent chloride diffusion coefficient of concrete when the chloride concentration at any time is known as a function of depth.

$$\frac{\partial C}{\partial t} = D_{\mathrm{a}} \frac{\partial^2 C}{\partial x^2} \tag{1}$$

An analytical solution to Eq. (1), assuming that the flux of chlorides at any time is proportional to the chloride concentration gradient in the concrete of a semi-infinite medium, is as follows when reasonable assumptions are specified as proposed by Browne [11]:

$$C_x = C_{\mathrm{s}}\left[1 - \mathrm{erf}\left(\frac{x}{2\sqrt{D_{\mathrm{a}} t}}\right)\right] \tag{2}$$

where C_x is the chloride ion concentration at depth x after exposure time t for a surface chloride concentration of C_{s} at the concrete surface, D_{a} is the apparent chloride diffusion coefficient, and the expression erf is the Gaussian error function. The Gaussian error function can be defined by the expression given below:

$$\mathrm{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z \mathrm{e}^{-t^2} \mathrm{d}t \tag{3}$$

where $x/(2\sqrt{D_{\mathrm{a}} t})$ is replaced by the variable z. The erf(z) can be expanded as:

$$\begin{aligned} \mathrm{erf}(z) &= \frac{2}{\sqrt{\pi}}\left(z - \frac{z^3}{3} + \frac{1}{2!}\frac{z^5}{5} - \frac{1}{3!}\frac{z^7}{7} + \frac{1}{4!}\frac{z^9}{9} - \cdots\right) \\ &= \frac{2}{\sqrt{\pi}} z + \frac{2}{\sqrt{\pi}}\left(-\frac{z^3}{3} + \frac{1}{2!}\frac{z^5}{5} - \frac{1}{3!}\frac{z^7}{7} + \frac{1}{4!}\frac{z^9}{9} - \cdots\right) \\ &= \frac{2}{\sqrt{\pi}} z + \frac{2}{\sqrt{\pi}} \sum_{k=1}^{\infty} (-1)^k \frac{z^{(2k+1)}}{(2k+1)} \end{aligned} \tag{4}$$

At $z = 0$, erf(0) = 0; $z = \infty$, erf(∞) = 1.0, but when $z = 3$, erf(3) is already very close to 1.0. Therefore, erf(z) can be taken equal to 1.0 when $z \geq 3.0$ in the computation.

Corrosion does not commence unless the chloride content at the rebar surface in the concrete exceeds a critical value, known as the threshold chloride level. Many factors affect the threshold level including concrete mix proportions, environmental conditions, the type of cement, mineral additives, etc. [12,13]. Rebar corrosion sometimes occurs at a relatively low chloride content while sometimes being negligible at higher chloride contents. It has also been reported elsewhere [14] that a relatively lower chloride concentration may be sufficient to initiate rebar corrosion in concrete exposed in the splash zone of a marine environment than concrete in the submerged zone. Considering exposure conditions frequently encountered, several researchers have attempted to assess the threshold chloride content for uncracked normal-strength concrete and have reported that the threshold chloride content may vary from 0.2% to 0.5% by weight of cement [15]. ACI Building Code 318 [16] specifies a maximum water soluble chloride content in concrete exposed in chloride-bearing conditions to be 0.15% by weight of cement. Chlorides in concrete can be found in different forms. Some of the chlorides are chemically bound to cement paste to form calcium chloroaluminates and calcium chloroferrite, some are physically absorbed to the pore wall, and some are free chlorides dissolved in the pore solution [17]. In concrete, only chlorides dissolved in pore water cause the corrosion process, not those chemically bound in the cement phases.

3. Experimental investigation

3.1. Program layout

A concrete mixture with a maximum aggregate size of 12 mm and a slump of 80 mm was used. Relatively high water to cement ratio of 0.60 and a concrete cover of about 20 mm over the reinforcing steel in the concrete slabs were spec-

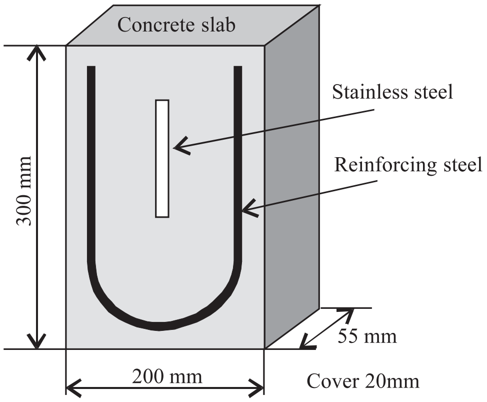

Fig.1. Sketch of concrete slab with embedded U-shaped rebar.

Table 1
Composition of seawater used in the testing program

Ion	ASTM seawater concentration, mg/l	Synthetic seawater concentration, mg/l
CL^{-}	19,500	17,500
Mg^{2+}	1,329	1,020
SO$_4^{2-}$	7,634	4,020

ified. To have a concrete mixture that could be easily consolidated with external vibration, nearly equal volumes of sand and coarse aggregate were used. The cement used was ASTM Type I with a content of 300 kg/m^3.

Each concrete slab, measuring 55 × 200 × 300 mm, contained a U-shaped rebar. Concrete slab thickness and width was adjusted to have a cover of 20 ± 1 mm between the rebar, and the sides and face of the slabs. The U-shaped rebar was 15-mm nominal diameter deformed type and was bent around a 127-mm-diameter mandrel. For the electrochemical corrosion rate measurements, a 100-mm-long stainless steel rod was placed in the center of each slab as a counter electrode. Wires were attached to the counter electrode and to the rebar to provide the necessary connections to the measuring devices (see Fig. 1). The connections were patched with an epoxy compound. Twelve concrete slabs were cast for the program. They were moist cured for 14 days at 20 ± 2 °C at a relative humidity of not less than 95% before being placed in the accelerated testing chamber. Following the curing period, eight concrete slabs were exposed in the synthetic seawater and the remaining four slabs in the 3% sodium chloride solution.

3.2. Exposure conditions

The tidal zone of marine structures and bridge decks are subjected to frequent applications of corrosion-inducing solutions that were simulated in an accelerated manner in the laboratory. To simulate marine environment synthetic seawater, a modified version of ASTM D 1141 [18] was used and its composition is given in Table 1. To simulate deicing salts application; a 3% sodium chloride solution was used.

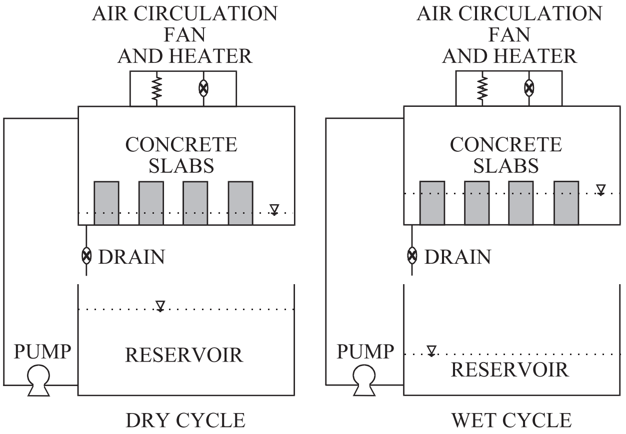

Fig. 2. Schematic illustration of the MESS.

Table 2
Chloride contents of concrete slabs exposed in the synthetic seawater

Depth from exposed surface, mm	Cl (mg)/ concrete (kg)	Cl (%) by weight of concrete	Cl (%) by weight of cement	Cl content (kg/m^3)
5	1398	0.140	1.03	3.08
10	668	0.067	0.49	1.47
15	436	0.044	0.32	0.97
20	401	0.040	0.29	0.88

The marine environment simulated setup (MESS) consisted of two chambers as sketched in Fig. 2. One of the chambers was used for the marine condition and the other for the deicing salt application. Each chamber has two fiberglass–wooden tanks, a pump, heaters, and blowers. The tanks were connected so that the upper tank was a container for the concrete slabs while the bottom one was a reservoir for water during the dry cycle. The wet–dry cycling was electronically controlled by a computer. A 2-h wet cycle followed by a 4-h dry cycle was adopted to give four complete cycles within a 24-h period as opposed to two tidal cycles in a natural marine environment. This was done to accelerate the corrosion activity. The wet portion of the cycle was operated at 32 ± 2 °C and the dry portion of the cycle was at a temperature of 68 ± 2 °C. Concrete slabs were placed vertically in the upper tanks of the MESS and the water level adjusted so that in the dry cycle one third of each slab was immersed and in the wet cycle two thirds was submerged.

3.3. Quantification of chloride content

To determine whether the threshold value necessary for active corrosion has been reached, it is common to analyze for chloride contents in concrete at the level of the rebar. In the study, only water-soluble chloride contents were determined since they are assumed to be responsible for corrosion process. The procedure followed for sampling was in accordance with ASTM C 1218 [19]. Powder samples of concrete were taken by successive drillings with a rotary impact drill. Multiple adjacent drillings were made along the reinforcing bar imprint in concrete slabs that were broken open for visual examination, and the powder was mixed to improve statistical accuracy. Drilling was also carried out to the depths of 5, 10, 15, and 25 mm of the concrete slab to obtain representative chloride profiles. A simplified method as prescribed elsewhere [20] was used in determining water-soluble chlorides and the associated data are given in Table 2 for a concrete of 2200 kg/m^3 unit weight.

4. Results and discussion

4.1. Determination of the time to depassivation

A certain depression in the open-circuit potential of rebar in concrete is a good indication of either the depassivation

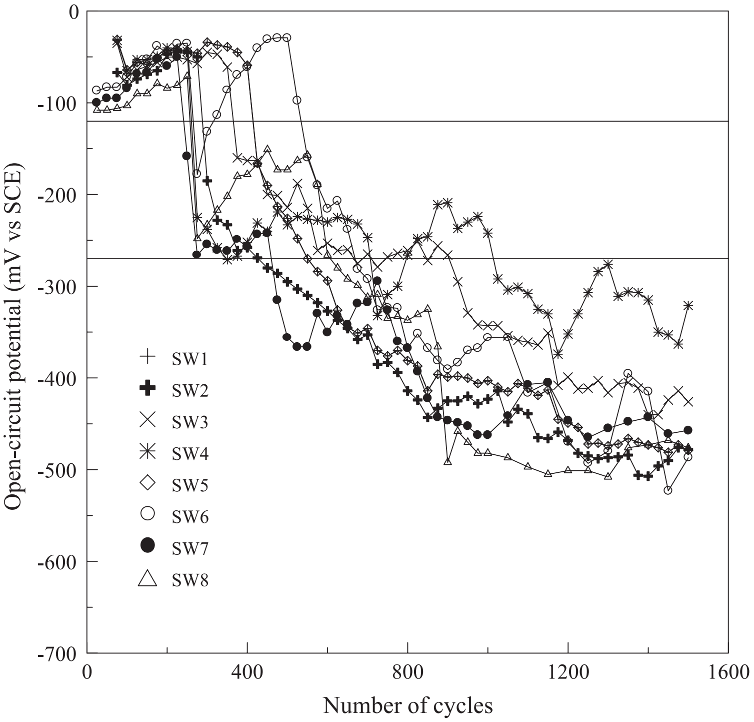

Fig. 3. Open-circuit potential measurements in the synthetic seawater exposure.

or a transition to the active corrosion initiation. The value of the transition potential measured depends on the reference electrode used. According to the guidelines involved in the measurement of open-circuit potentials of the steel embedded in concrete given in ASTM C 876 [21], the probability of corrosion initiation is greater than 90% when open-circuit potentials are more negative than − 350 mV relative to the copper–copper sulfate electrode (CSE) and − 270 mV relative to the saturated calomel electrode (SCE). The shift to active potential is associated with the so-called "thresh-

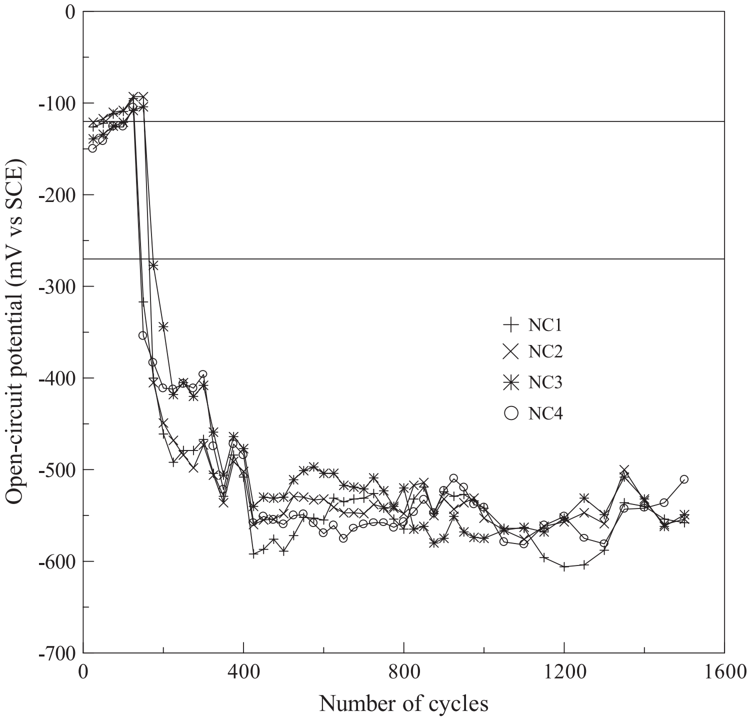

Fig. 4. Open-circuit potential measurements in 3% sodium chloride exposure.

old chloride content.” The time necessary for chloride ions to diffuse through concrete to reach the rebar surface to initiate corrosion process is known as the depassivation time, t_p.

Figs. 3 and 4 illustrate the variation of open-circuit potential for the rebar in the concrete slabs exposed in the synthetic seawater and in the 3% sodium chloride, respectively. The times associated with corrosion activation for each bar in the concrete slab corresponding to an open-circuit potential shift lower than − 270 mV relative to SCE are given in Table 3. Considering that four complete cycles are performed each day in the MESS, the corresponding average time necessary for depassivation is 44 days for the 3% sodium chloride and 142 days for the synthetic seawater, which is relatively short particularly for the sodium chloride exposure. The reason for this might be attributed to the clogging effect of brucite [$Mg(OH)_2$], the well-known reaction of magnesium sulfate of seawater and cement phases [22].

4.2. Determination of the apparent chloride diffusion coefficients

In calculating the values of C_s and C_x, the data tabulated in Table 2 are utilized to obtain the chloride profile as illustrated in Fig. 5. The graph shows the chloride content of concrete for the slabs exposed in the synthetic seawater. A polynomial fit with a high correlation was applied to chloride data to determine C_s and C_x. Based on the relationship; the values of C_s and C_x are 5.275 and 0.835 kg/m^3 of concrete, respectively. C_s is the surface chloride concentration corresponding to zero cover depth ($x = 0$), and C_x is the chloride concentration at the rebar surface ($x = 20$ mm) at the testing time, which is considered to be the threshold chloride concentration necessary for depassivation of the rebar. The threshold content is quite consistent with those reported elsewhere [14].

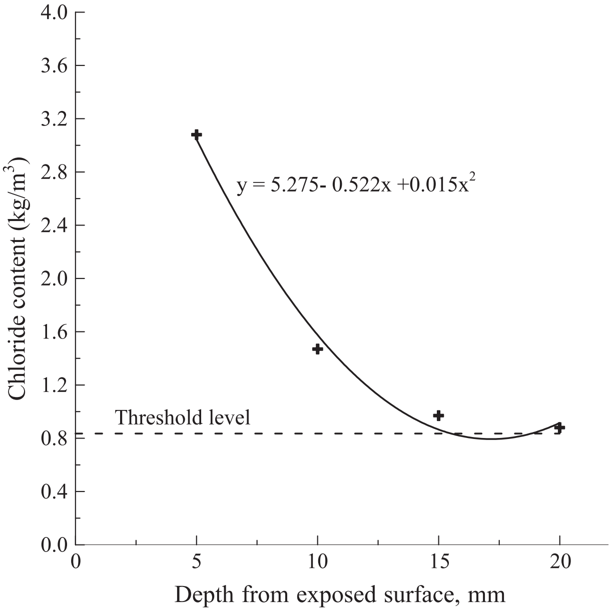

Fig. 5. Chloride concentration profile of concrete slab.

Knowing the values of C_s and C_x, Eq. (4) was initially utilized to calculate the error function for different z values using a microcomputer program. Subsequently, corresponding values were fed into Eq. (2) to determine the apparent chloride diffusion coefficient of concrete. In the equation, t corresponds to the depassivation time t_p, which was obtained previously for each rebar (see Table 3), and x stands for the cover depth.

Table 3
Time to corrosion initiation obtained using measured open-circuit potentials

Synthetic seawater		3% NaCl solution	
Rebar	t_p (days)	Rebar	t_p (days)
SW1	144	NC1	42
SW2	113	NC2	46
SW3	169	NC3	46
SW4	181	NC4	42
SW5	94		
SW6	163		
SW7	119		
SW8	156		

The apparent chloride diffusion coefficients obtained are in the range of 6.4×10^{-8} to 12.4×10^{-8} cm^2/s for concrete exposed in the seawater. Therefore, the average chloride diffusion coefficient is 8.2×10^{-8} cm^2/s, corresponding to an average exposure period of 142 days. This is quite consistent with chloride diffusion coefficients of the same concrete grade subjected to similar exposure conditions reported elsewhere [23]. The difference may be attributed to the different characteristics of concrete and to the testing conditions. Chloride ion diffusion in concrete

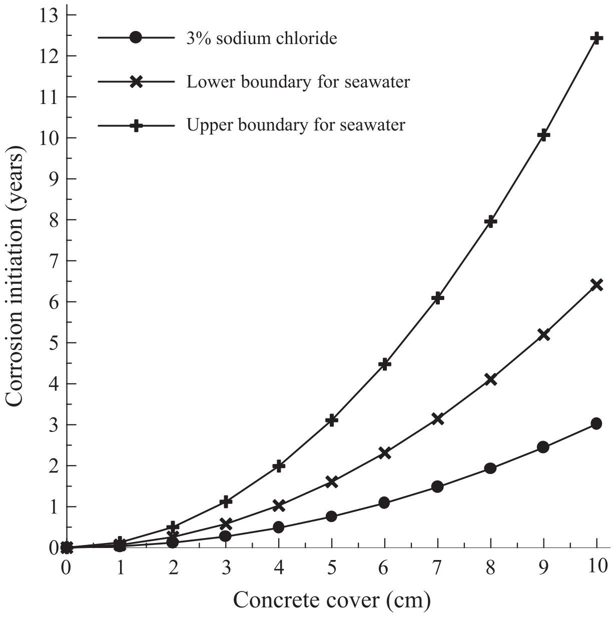

Fig. 6. Effect of exposure condition on corrosion initiation.

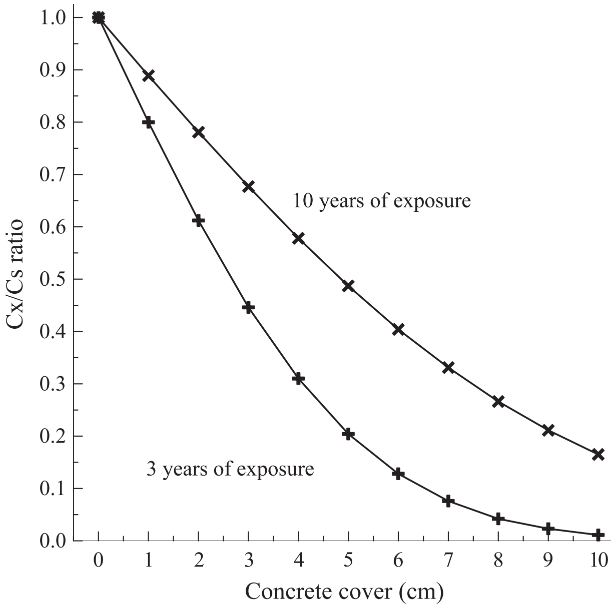

Fig. 7. Variation of C_x/C_s with respect to exposure time in seawater.

occurs if the concrete is saturated; however, alternate wetting and drying can lead to the buildup of high contents of chlorides as is the case in a tidal zone [24].

Fig. 6 shows the corrosion initiation profiles for a tidal exposure of the seawater and a 3% sodium chloride solution. To observe the interval in corrosion initiation in the seawater in relation with cover depth, the upper and the lower boundaries were determined using the associated diffusion coefficients. To obtain corrosion initiation profile for the 3% sodium chloride, the same surface chloride concentration C_s and the same threshold chloride concentration for depassivation C_x obtained for the seawater exposure were used in calculating the diffusion coefficient corresponding to the 3% sodium chloride since the same concrete mixture was used for both exposures. For a cover depth of 7 cm, it is seen that the time necessary for corrosion initiation ranges from 3 to 6 years for the seawater exposure, whereas it is only 1.5 years for a 3% sodium chloride exposure. It is obvious that concrete produced with portland cement only and with a cover depth of 20 mm is not likely to provide a reliable protection against chloride ingress even for concrete exposed in a marine tidal zone. To prolong the time, use of mineral additives such as fly ash and silica fume in concrete along with portland cement is of vital importance as they limit the penetration of chloride ion into concrete substantially [13]. Surely, using concrete with water to cement ratios as low as possible is equally, or more, important, in producing a less permeable concrete against chloride ingress.

4.3. Generation of C_x/C_s profiles

Fig. 7 shows the variation of C_x/C_s ratio with respect to cover depth of concrete exposed in the synthetic seawater. Such profiles provide quite useful information for the prediction of chloride content at the rebar surface in any given exposure time since the surface chloride content is, more or less, known, as the surface chloride content does not change drastically with time. The profiles were generated by using Fick's second law of diffusion for the average chloride diffusion coefficient of 8.2×10^{-8} cm^2/s. Regarding the profiles obtained, to avoid corrosion that provided with a cover depth of 5 cm for an exposure period of 3 years in the synthetic seawater exposure, a concrete cover of at least 9 cm is required for an exposure period of 10 years in the same exposure.

5. Conclusions

Based on the findings obtained from the foregoing investigation, the following main conclusions could be produced:

1. Based on the potential measurements, the time necessary for corrosion initiation in a 3% sodium chloride is 44 days only and is 142 days in the synthetic seawater exposure.
2. The apparent chloride diffusion coefficients obtained are in the range of 6.4×10^{-8} to 12.4×10^{-8} cm^2/s. The average chloride diffusion coefficient, corresponding to an average exposure period of 142 days in the synthetic seawater, is 8.2×10^{-8} cm^2/s.
3. For a concrete cover of 7 cm, it is observed that the time necessary for corrosion initiation ranges from 3 to 6 years for the synthetic seawater exposure; however, it is only 1.5 years for a 3% sodium chloride exposure.
4. To avoid corrosion that provided with a cover depth of 5 cm for 3 years in the synthetic seawater, a concrete cover of at least 9 cm is required for an exposure period of 10 years in the same exposure.
5. Overall, open-circuit potential measurements can be considered as an approximate but simple method of assessing the diffusivity of chloride through concrete.

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