

# Effect of Time-Dependent Chloride Profile and Temperature Variation on Chloride Diffusion in Concrete

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## ABSTRACT

Reinforcement corrosion due to chlorides diffusion is one of the main problems in reinforced concrete structures exposed to certain environments. The diffusion rate is function of chloride surface concentration, concrete temperature, humidity, composition and microstructure. The intruded chlorides are partially chemically bound by the concrete and it is the unbound or free chloride which upon exceeding a defined threshold initiates corrosion. The time to corrosion initiation depends on the above variables; therefore, it is important to model their spatial and temporal variations in a manner that will yield a realistic estimate of the actual initiation period. In this study, the chloride surface concentration and temperature temporal variations are approximated in several ways to gauge the sensitivity of the chloride diffusion kinetics to them. Temperature profiles with constant 6-hours, daily, monthly, seasonally and yearly variations are used to approximate the actual temperature variation recorded for Toronto, Canada in a typical year. The surface chloride concentration is assumed either constant or allowed to vary monthly according to the reported values for Toronto. It is discovered that due to the limited temperature range encountered even in cold regions like Toronto, the diffusion kinetics is not very sensitive to the temperature approximation method, but it is more sensitive to the way the surface chloride variation is approximated. For structures subjected to deicing salt applications, assuming constant seasonal temperature and monthly chloride variation in the analysis may yield a realistic estimate of the time to corrosion initiation and thus the prediction of the life-time of the structure.

**Keywords:** corrosion, chlorides diffusion, thermal effect, surface concentration, finite element modelling

## 1.0 INTRODUCTION

Reinforced concrete (RC) is the most popular construction material, but the deterioration of RC structures exposed to chlorides, which induce reinforcement corrosion and subsequent damage to concrete, is a serious and costly problem.

Chlorides enter concrete structures mainly through permeation of de-icing salts in cold regions or the ingress of sea salt along coastal area. The corrosion of the steel bars, termed steel reinforcement, begins when the chloride concentration at the level of reinforcement reaches a critical threshold. The kinetics of the chemical reactions, the rate of permeation of chlorides and the evolution of damage to the concrete microstructure are dependent on the prevailing hygrothermal conditions, which are in turn affected by the ambient conditions.

Any realistic modelling of chlorides diffusion must account for the effects of some key parameters influencing the kinetics and deleterious effects of chlorides diffusion in concrete. Generally, it is believed that the free chlorides diffusing through the concrete pore solution cause corrosion (Hirao, *et al.*, 2005). However, other studies indicate that bound chlorides can also contribute to the corrosion

process by being released or as bound compounds through electric influences (Glass & Buenfeld, 2000). Hence, it is important to model this phenomenon. Different mathematical models are proposed to describe the relationship between bound and free chlorides. Freundlich and Langmuir non-linear binding isotherms are the most popular as expressed by equation 1 and 2, respectively (Glass, *et al.*, 1997).

$$C_b = \alpha C_f^\beta \quad (1)$$

$$C_b = \frac{\alpha C_f}{1 + \beta C_f} \quad (2)$$

where,  $\alpha$  and  $\beta$  are coefficients determined experimentally,  $C_b$  and  $C_f$  are the bound and free chloride concentration, respectively.

Tests have shown the dependency of binding capacity on temperature and chlorides concentration (Zibara, 2001). This is often modeled using Arrhenius law (Saetta *et al.*, 1993)

$$D_2 = D_1 e^{\left(\frac{U}{R} \left(\frac{1}{T_0} - \frac{1}{T}\right)\right)} \quad (3)$$

where,  $D_1$  and  $D_2$  are the diffusion coefficients at reference temperature  $T_o$  and specified temperature  $T$ , respectively,  $U$  is the activation energy for chloride diffusion.  $R = 8.31$  J/mol.K is the universal gas constant and  $e$  is the base of natural logarithm. The energy  $U$  is function of the water/cement ( $w/c$ ) ratio (Saetta *et al.*, 1993) as well as temperature, but it varies between 29.6 to 45.8 kJ/mol. For a constant  $w/c$ , as indicated below, it can be expressed as function of temperature.

$$\frac{U}{R} = 4600 * \left[ \frac{30}{(T - 263)} \right]^{0.39} \quad (4)$$

where  $T$  is the concrete temperature ( $^{\circ}$ K).

Chlorides diffusion can only occur in the presence of water in the capillary pores. The dependency of the diffusion coefficient on pore relative humidity can be written as (Saetta *et al.*, 1993)

$$D_2 = D_1 \left( 1 + \frac{(1-h)^4}{(1-h_c)^4} \right)^{-1} \quad (5)$$

where,  $D_1$  and  $D_2$  are the diffusion coefficients at saturated condition and humidity level  $h$ , respectively.  $h$  is the pore relative humidity in concrete, and  $h_c$  is the humidity where the value of diffusion coefficient drops halfway between its maximum and minimum values. The value of  $h_c$  can be determined experimentally.

Maturity of concrete leads to change in the microstructure of concrete and it reduces the rate. This phenomenon can be modelled (Maage, *et al.*, 1996) using

$$D_2 = D_1 \left( \frac{t_{ref}}{t} \right)^m \quad (6)$$

where,  $D_1$  and  $D_2$  are the diffusion coefficients at reference time  $t_{ref}$  and considered time  $t$ , respectively. The  $t_{ref}$  refers to the time when the diffusion coefficient is measured, and  $m$  is the age reduction factor. Quantity  $m$  can be calculated as shown below (Mangat & Molloy, 1994)

$$m = 2.5(w/c) - 0.6 \quad (7)$$

In this study, the chloride surface concentration and temperature temporal variations are approximated in several ways to gauge the sensitivity of the chloride diffusion kinetics to them. Temperature profiles with constant 6-hours, daily, monthly, seasonally and yearly variations are used to approximate the actual temperature variation recorded for Toronto, Canada in a typical year. The surface chloride concentration

is assumed either constant or allowed to vary monthly according to the reported values for Toronto. The dependency of the diffusion coefficient on temperature,  $w/c$  ratio and relative humidity will be modeled using equations 3 to 6. The main focus will be on the manner in which the concrete temperature and chloride temporal variation are approximated and the effect of the approximation on the chloride concentration profile through the concrete member thickness. The parametric analysis will first consider the effect of each parameter separately and then investigate their combined effect.

## 2.0 ANALYSIS METHOD

The equation governing both one dimensional chloride diffusion and heat conduction is (Zienkiewicz, 1977)

$$a \frac{\partial \phi}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial \phi}{\partial x} \right) \quad (8)$$

where, for heat conduction,  $a = \rho c$ ,  $\rho$ ,  $c$  and  $D = K_{xx}$  are the concrete density, specific heat capacity, and thermal conductivity, respectively. For chlorides diffusion,  $a = 1$  and  $D = D_a$  is the apparent diffusion coefficient. The coefficient  $D_a$  can be written as (Martin-Perez *et al.*, 2000).

$$D_a = \left( \frac{D_e}{1 + \frac{1}{w_e} \left( \frac{\partial C_b}{\partial C_f} \right)} \right) \quad (9)$$

where,  $w_e$  is the evaporable water content,  $D_e$  is the effective diffusion coefficient ignoring binding.

By introducing the effects of temperature, pore relative humidity, and maturity age on diffusion, equation 9 can be modified as.

$$D_a^* = D_a e^{\left( \frac{U}{R} \left( \frac{1}{T_o} - \frac{1}{T} \right) \right)} \left( 1 + \frac{(1-h)^4}{(1-h_c)^4} \right)^{-1} \left( \frac{t_{ref}}{t} \right)^m \quad (10)$$

In this study, equation 8 is solved by developing and validating a one-dimensional finite element program (Zienkiewicz, 1977).

One-way coupling is assumed between heat transfer and chloride diffusion process. In other words, temperature affects the diffusion rate but not vice versa. Hence, an incremental time-dependent analysis is performed where thermal analysis is

conducted first and the temperature value at the end of the previous time step is used to compute the temperature dependant value of moisture, chloride binding, and diffusion coefficient at the beginning of the new time step.

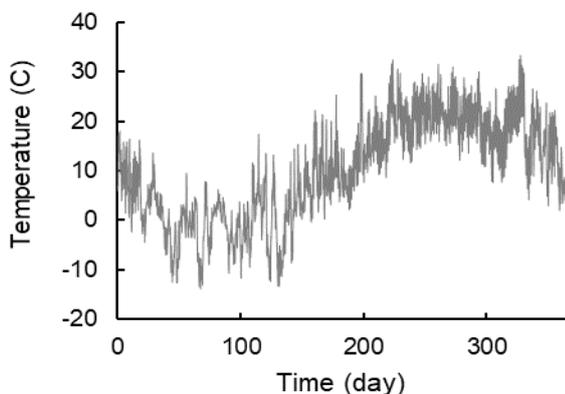
When binding is included, the problem becomes non-linear in which strictly speaking an iterative method needs to be applied to find the precise solution. However, diffusion in concrete is slow by nature, thus for small time increments the free chloride concentrations at the end of the previous time step can be used in conjunction with the selected isotherm to estimate  $\frac{\partial C_b}{\partial C_f}$ .

### 3.0 MODELED DIFFUSION SCENARIO

A finite element program is developed by the authors, using the MATLAB platform, to solve equation 8, which governs time-dependent heat and mass transfer. The program is validated by comparing its results with available numerical and experimental data in the literature.

The modelled specimen is assumed to be part of a 200-mm thick concrete bridge deck slab having a one square meter surface area normal to the diffusion direction. In Canada, currently the minimum concrete cover for bridge deck slab is specified as  $70 \pm 20$  mm ("CSA S6-14," 2014). However, for bridges built between 1970~1990, the minimum cover was specified as 50 mm. Thus, here the depths of interest for chloride concentration are 50 and 70 mm from the slab surface.

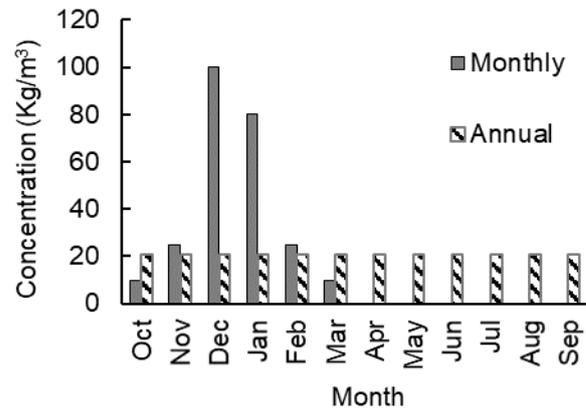
The typical annual temperature variation for Toronto, Canada is shown in Fig. 1 (*Environment Canada, 2017*).



**Fig. 1.** Hourly annual temperature for Toronto, Ontario, Canada

The typical monthly applied salt surface concentration, as reported by the City of Toronto, (*Salt Management Plan, 2004*) is illustrated in Fig. 2. The figure also shows the equivalent computed

average annual salt surface concentration that is used in the current analysis. For the purpose of this investigation, the authors have estimated the surface salt concentration from the actual amounts of rock salt usage. Note, however, the purpose of the current study is to investigate the effect of the numerical idealization of the actual salt and temperature temporal profiles on chloride diffusion in the concrete rather than the exact amount of salt used. If the diffusion coefficient is assumed to be independent of salt concentration, then the conclusions of the study will not be limited by the actual magnitude of the surface salt concentration.



**Fig. 2.** Annual salt concentration for Toronto, Ontario, Canada

The average annual relative humidity for the city of Toronto is reported as 75% (*Environment Canada, 2017*). BSB (*Brunauer et al. 1969*) adsorption isotherm is used to relate the pore relative humidity to the evaporable water content as follows

$$w_e = \frac{Ck_m V_m h}{(1-k_m h)[1+(C-1)k_m h]} \tag{11}$$

where,  $w_e$  is the evaporable water content expressed in terms of water per grams of cementitious material,  $V_m$  is the monolayer capacity,  $C$  and  $k_m$  are two parameters of the model. More information regarding the experimental parameters are provided by *Xi et al. (1994)*.

The pore relative humidity  $h$  is assumed equal to the air relative humidity for the months where salt is not applied while during the salt application months, the pore relative humidity is assumed to be 100% due to the occurrence of rain and snow in these months.

For chloride binding, the Freundlich isotherm is used. A regression analysis by *Dousti and Shekarchi (2015)*, considering different temperatures, concentrations, and cementitious materials, resulted in the following values of  $\alpha$  and  $\beta$  for use in the Freundlich isotherm:

$$\alpha = a_1T^2 + b_1T + c_1 \tag{12}$$

$$\beta = a_2T^2 + b_2T + c_2 \tag{13}$$

where, T is the temperature (°C), a<sub>1</sub>, a<sub>2</sub>, b<sub>1</sub>, b<sub>2</sub>, c<sub>1</sub>, and c<sub>2</sub> are coefficients determined based on the concrete binder composition. For modeling binding, these equations were applied in the current study.

### 3.1 Finite Element Idealization

The through thickness finite element discretization consists of linear one-dimensional elements. The mesh consists of uniform 7.5 mm long elements and the time step is taken as 6 hours throughout the analysis period. This discretization is applied to both the heat transfer and the diffusion analysis.

An additional node was added on the surface and was used to apply the chloride surface concentration. The concrete first node starts at 1 mm from the surface. This is needed when the varied surface concentration is applied because dropping the chloride concentration at the concrete first node will lead to diffusion from inside towards the free surface which does not occur in real-life.

The concrete used in the analysis is assumed to be made with Ordinary Portland Cement (OPC) and its properties are summarised in Table 1.

**Table 1.** Concrete properties adopted for OPC

Property	Value	Unit
Heat capacity	1.932 x 10 <sup>6</sup>	J/m <sup>3</sup> .°C
Convective heat coefficient	0.07	W/m <sup>2</sup> .°C
Thermal conductivity	1.4	W/m.°C
w/c <sup>(1)</sup>	0.3	--
Binder content	450	kg/m <sup>3</sup>
First exposure time	120	Days
Effective Diffusion coefficient at 120 days	1 x 10 <sup>-12</sup>	m <sup>2</sup> /s
Initial chloride concentration	0	kg/m <sup>3</sup> solution
α <sup>(2)</sup>	5.4 ~ 6.4*	--
β <sup>(3)</sup>	0.36 ~ 0.45*	--
w <sub>e</sub> <sup>(4)</sup>	0.05 ~ 0.10*	m <sup>3</sup> /m <sup>3</sup> of concrete
h <sub>c</sub> <sup>(5)</sup>	0.75	--

\* values are function of temperature

(1) water to cement ratio

(2) binding parameter, calculated using equation 12

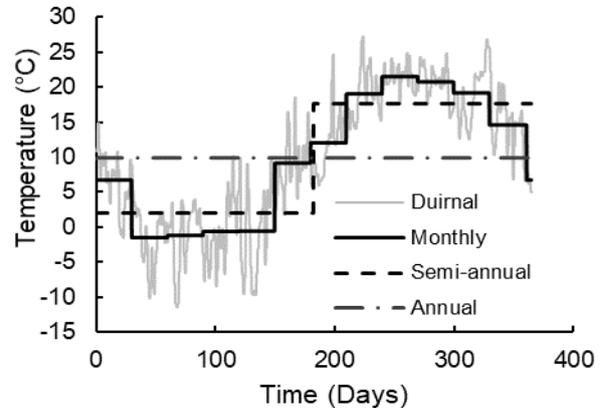
(3) binding parameter, calculated using equation 13

(4) evaporable water content, calculated using equation 11

(5) humidity level at which the value of diffusion coefficient drops halfway between its maximum and minimum values. Adopted from (Martin-Pérez, 1999)

All the properties in Table 1, except the binding model, were adopted from (Martin-Pérez, 1999) The binding model used in the current investigation is given by equation 12 and 13 and is based on the work of (Dousti and Shekarchi, 2015).

With reference to Fig. 3 in the analysis, the actual temperature variation is approximated by assuming constant average temperature over different lengths of time, viz. 6 hrs (quarter-diurnal), 12 hrs (semi-diurnal), 24 hrs (diurnal), monthly, seasonally, semi-annually, and annually. The air temperature is applied as convection boundary condition.



**Fig. 3.** Temperature of concrete at 100 mm depth from the surface averaged over different durations

The salt surface concentration is assumed to either vary monthly, per the data provided by the City of Toronto, or assumed constant throughout the year as shown in Fig. 2. The constant value is computed by averaging the actual annual amount of salt applied mainly in the winter over the entire year, which yields an average surface concentration of 20.8 kg/m<sup>3</sup>. In practice, where actual annual variation is not known, it is not uncommon to use an average value as a first approximation.

### 3.2 Finite Element Verification

Verification of the current finite element (FE) model was performed by comparing the results for a specific case analysed by (Martin-Pérez, 1999). The input data are given in Table 2, which are the same as those used by Martin-Pérez. The binder is assumed to be 60% OPC and 40% slag and fly ash.

The free chloride profiles obtained from the current analysis are shown in Fig. 4 and are identical to the ones reported by Martin-Pérez in kg/m<sup>3</sup> of pore solution.

## 4.0 ANALYSIS RESULTS

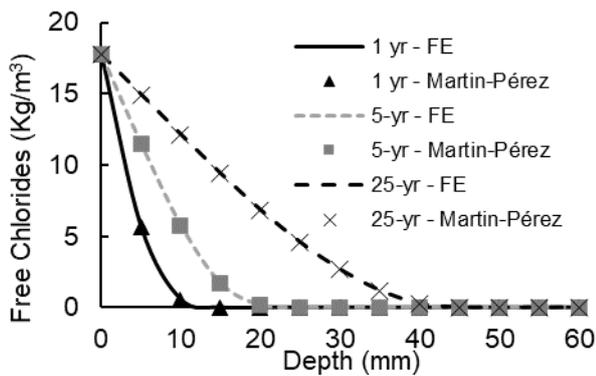
### 4.1 Temperature Temporal Variation Effect

To investigate the effect of temperature temporal variation approximation on chloride profile, a fixed surface chloride concentration of 20.8 kg/m<sup>3</sup> is assumed, and the temperature is assumed to vary as approximated in Fig. 3. The resulting slab chloride profile after fifty years is shown in Fig. 5.

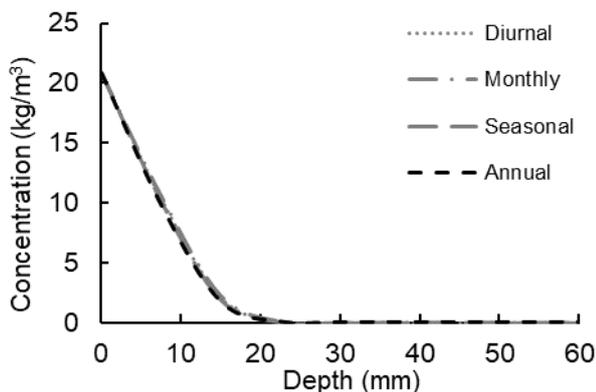
**Table 2.** Concrete properties (Martin-Pérez, 1999) used for the current finite element model validation.

Property	Value	Unit
Heat capacity	$1.932 \times 10^6$	J/m <sup>3</sup> .°C
Convective heat coefficient	0.07	W/m <sup>2</sup> .°C
Thermal conductivity	1.4	W/m.°C
w/c	0.3	--
Binder content	450	kg/m <sup>3</sup>
First exposure time	120	Days
Effective Diffusion coefficient at 120 days	$1 \times 10^{-12}$	m <sup>2</sup> /s
Surface chloride concentration	17.73	kg/m <sup>3</sup> solution
Initial chloride concentration	0	kg/m <sup>3</sup> solution
$\alpha$	1.05**	--
$\beta$	0.36**	--
$w_e$	0.08**	m <sup>3</sup> / m <sup>3</sup> of concrete
$h_c$	0.75	--

\*\* values are fixed and independent of temperature



**Fig. 4.** Free chloride's profile at different exposure durations using Martin-Pérez's parameters



**Fig. 5.** Free chloride's profile at 50-year using fixed surface concentration of 20.8 kg/m<sup>3</sup>

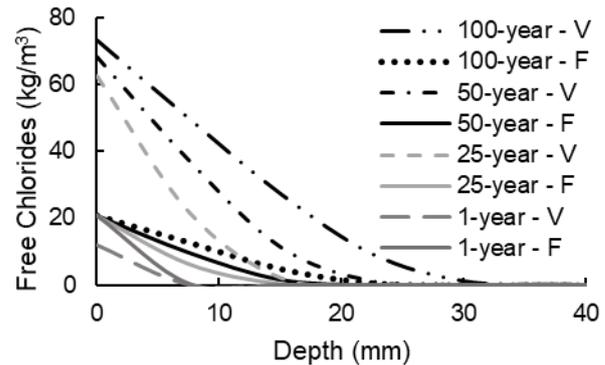
It is clear from Fig. 5 that the temperature temporal variation approximation has negligible effect on the chloride concentration profile through the slab.

It is worth mentioning that assuming heat transfer by conduction and convection may not be adequate in

every situation because transfer by radiation may play an important role.

#### 4.2 Chloride Surface Concentration Effect

Assuming constant annual temperature of 9.9 °C and either a fixed (F) chloride surface concentration throughout the analysis period or monthly variable (V) concentration as shown in Fig. 2, the diffusion analysis was performed for twenty-five, fifty, and hundred years. Figure 6 shows the computed free chloride concentration profiles through the slab thickness.

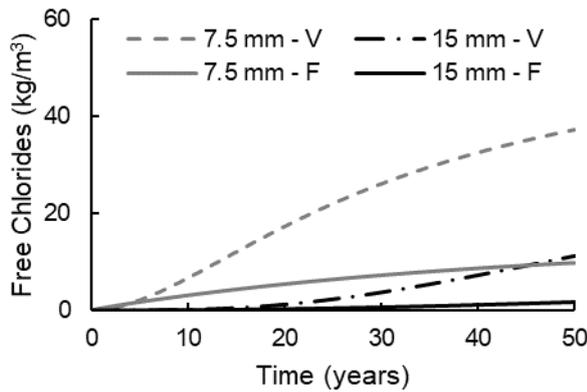


**Fig. 6.** Free chlorides profile after exposure to fixed (F) or variable (V) surface chloride concentration at constant temperature of 9.9°C

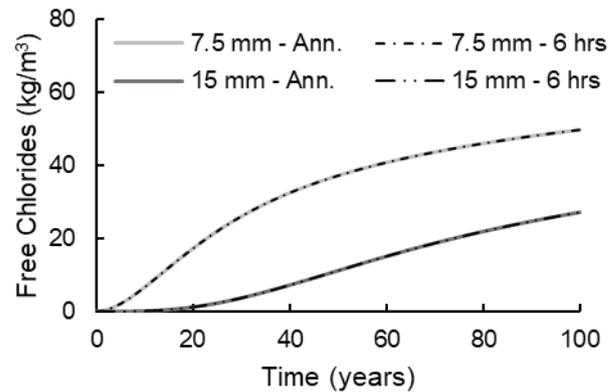
It can be concluded from the latter figure that up to 5 years a fixed surface chloride profile leads to approximately the same penetration depth as given by the variable surface chloride, thereafter, the fixed surface chloride profile underestimates the depth of penetration. The difference between the results of the two approximations becomes particularly obvious after ten years of exposure.

The above difference between the results of the two approximations is further highlighted by the free chloride concentration variation with time of exposure at depths of 7.5 mm and 15 mm. It is evident that the assumption of a fixed surface concentration dramatically underestimates the chloride concentration, relative to the values predicted assuming variable surface concentration. Note, the point of this analysis is comparison of the relative values of the concentration rather than their absolute values.

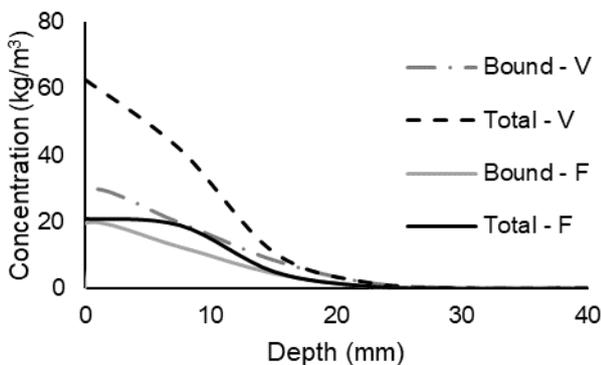
Assuming either variable or fixed surface chloride concentration, Fig. 8 shows the total and bound chloride concentration profiles through the thickness of the slab after 50 years. Once again, the two approximations lead to dramatically different results, and the assumption of a fixed concentration underestimates the expected chloride concentration within the slab.



**Fig. 7.** Comparison of free chloride concentration at 7.5 mm and 15 mm from the slab surface based on assumed fixed versus variable surface chloride concentration and constant temperature of 9.9°C



**Fig. 9.** Free chloride concentration at two concrete depths for temporally variable surface chloride concentration under 6-hourly constant or annually constant temperature exposure



**Fig. 8.** Bound and total chloride concentration profiles at 50-year for assumed fixed and variable surface chloride concentrations under constant temperature of 9.9°C

It can be inferred from Fig. 8 that at shallow depths, the concrete can bind almost all the chlorides in the case of fixed annual surface concentration. On the other hand, for variable concentration, a much lower percentage of chlorides is bound, consequently, the free chloride concentration remains high.

### 4.3 Combined Effects of Surface Concentration and Temperature Variations

Analyses were performed assuming 6-hourly constant or annually constant concrete surface temperature variation, but monthly variable chloride surface concentration. The results of the analyses are depicted in Fig. 9, which shows the temporal variation of chloride concentration at 7.5 mm and 15 mm from the concrete surface.

As found earlier, the temperature approximation method has practically no effect on the chloride concentration at these depths. As the depths are arbitrarily chosen, the overall conclusion of the analysis is that the assumption of a constant average annual temperature is adequate for computing the chloride concentration profile within a concrete member.

## 5.0 CONCLUSIONS

The effects of the approximation method used to represent the actual temporal variation of concrete surface temperature and chloride concentration on chloride concentration profile in a 200 mm thick concrete slab were investigated. The temperature was assumed constant 6-hourly, daily, monthly, seasonally or annually while the chloride surface concentration was assumed constant annually or monthly. The actual annual temperature and surface salt concentrations variations used in the analysis were obtained from data provided by the Canadian environment ministry, and the City of Toronto, respectively. Considering the concrete properties, temperature and humidity conditions, the surface salt concentration profile and the method of analysis used in this study, the following conclusions are reached:

- (1) Despite the actual variable temperature that a concrete member may be exposed to during the year, when modelling chlorides diffusion, the assumption of a constant annual average temperature seems adequate for determining the chloride concentration profile through the member thickness.
- (2) To obtain a relatively accurate estimate of the chloride concentration profile through the member thickness, the surface chloride temporal variation must be accurately represented in the diffusion analysis. Use of an average annual surface concentration may grossly underestimate the chloride concentration within the member.
- (3) In the current study, the chlorides surface concentration was assumed to be constant either monthly or annually, but further analysis is needed to determine how other temporal variations, e.g. weekly variation, of this parameter will affect the chloride diffusion kinetics.

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