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An overview and sensitivity study of a multimechanistic chloride transport model

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Abstract

Service life prediction models have been developed in order to ensure adequate durability of reinforced concrete structures in chloride environments. Many of the models currently available are overly simplistic, assuming chloride ingress occurs solely by diffusion and that boundary conditions and concrete properties (i.e., diffusivity) remain constant with time. This paper describes a recently developed model that considers multimechanistic transport, chemical binding, and the time-dependent nature of concrete properties. The results of a sensitivity analysis carried out on eight of the input parameters in the model are also reviewed. © 1999 Elsevier Science Ltd. All rights reserved.

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The penetration of chloride ions through concrete surfaces to steel reinforcement resulting in corrosion is an issue of primary concern for reinforced concrete projects, such as parking, bridge, and marine structures. In efforts to control this significant problem, numerous innovations in concrete technology have been made. One of these improvements includes the development of service life prediction models.

Service life prediction models are proving to be invaluable tools for several reasons. More and more, owners want to be assured of the design life of structures they intend to build. Several major tunnel and bridge projects in Europe, Asia, and North America have recently included specifications for chloride diffusion and permeability limits in order to achieve 100-year service lives [1]. It is widely known that high performance concretes can be designed using low water-to-cementitious materials ratio and water content, supplementary cementing materials, superplasticizers, and can be ensured with good curing and construction practices. However, implementing these criteria and/or increasing cover depth does not provide any quantification of the service life of a project unless mathematical models are applied [2]. Estimation of residual service life is also crucial when developing economical and efficient repair strategies for a deteriorated structure. Cores can be taken from existing structures to determine the depth of ion ingress; established chloride profiles, relating concentration with depth over time, can be used to make predictions of the remaining service life. This information can then be used to assess life cycle costs to design the most timely and cost effective maintenance plan [3].

Many of the models currently available assume that the transport of chlorides is dictated by diffusion alone. There are, however, several other mechanisms that influence the rate of chloride ingress in concrete surfaces and resulting concentrations at various depths, including sorptivity, permeation, wicking, and chloride binding [1], as shown in Fig. 1. Failure to consider these contributing factors can result in a poor estimation of a structure's useful life. Recognizing this fact, the model described here was developed to take account of most of the critical parameters that affect the rate of chloride penetration in concrete.

This paper serves as an introduction to this model by describing its capabilities, the theoretical background upon which it is based, and the limitations on its use. A sensitivity study carried out on eight of the input parameters in the model is also reviewed.

1. Description of the chloride transport model

The chloride transport model described here is a PC-based program that makes service life predictions for reinforced concrete projects where chloride-induced corrosion can compromise the durability of the structure. The model is capable of incorporating the following considerations into its calculations:

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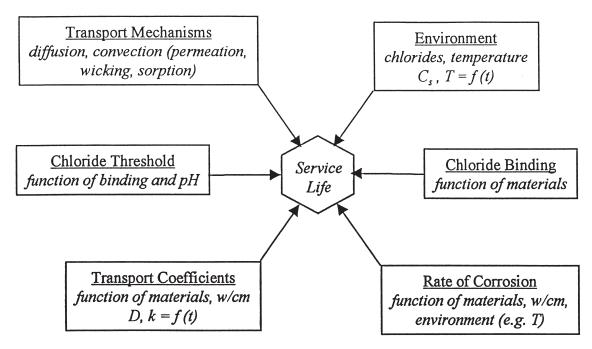


Fig. 1. Issues related to service life modelling.

- initial chloride profile due to sorption or prior history,
- initial diffusion value (D) for concrete,
- time-dependent reduction of D,
- · nonlinear chloride binding isotherms,
- superposition of a hydraulic head on an external salt water environment.
- varying surface concentration with time,
- monthly variations in temperature during a year, and
- chloride build up due to wicking (evaporation from inside face).

The program can generate various results with the information provided. The user can view the input parameter relationships graphically. If an experimental profile is provided, an average diffusion coefficient can be calculated since the model is capable of finding a curve of best-fit for the data entered. From this, it is also possible to produce a predicted chloride profile at a future time. Finally, the predicted time to initiation of corrosion can be determined by specifying the cover depth to the steel reinforcement and corrosion threshold concentration. It should be noted that although the chloride transport model presented in this paper does not account for the rate of corrosion, there are other models being developed at the University of Toronto that take this influence into consideration [4].

2. Theoretical background

The chloride transport model estimates life expectancy using finite difference analysis with coordinates time (s) and depth (mm). It incorporates several theoretical and analytical formulations to account for the different mechanisms involved in chloride ingress through concrete.

2.1. Transport equation

The transport of chlorides by diffusion and convection was modeled in the program using Eq. (1):

$$\frac{dC}{dt} = D \cdot \frac{d^2C}{dx^2} - \bar{v} \cdot \frac{dC}{dx} + \frac{\rho}{n} \cdot \frac{dS}{dt}$$
 (1)

where

C = "free" chloride in solution at depth x after time t,

S = "bound" chloride

D = diffusion coefficient

 ρ = concrete density

n = porosity

 \overline{v} = average linear velocity = $\frac{Q}{nA} = -\frac{k}{n} \cdot \frac{dh}{dx}$

Q =flow rate

A = cross-sectional area

k = hydraulic conductivity

h = hydraulic head

The left-hand side of this equation indicates the rate of change in chloride concentration with time. Three different mechanisms are represented by the three terms on the right-hand side of the equation. The first term, the diffusion term, comes from Fick's second law for one-dimensional, nonstationary flow in a semi-infinite medium. The second term describes the changes in chloride concentration due to convective flow and the third term takes account of chloride binding by the hydrates.

2.2. Diffusion

Transport by diffusion in saturated concrete occurs in the presence of a chloride concentration gradient, created when

at least one face is continuously exposed to water and salt. The program accounts for the rate of ion diffusion through concrete with the following relationship shown in Eq. (2):

$$D(t,T) = D_{\text{ref}} \cdot \left(\frac{t_{\text{ref}}}{t}\right)^m \cdot \exp\left[\frac{U}{R} \cdot \left(\frac{1}{T_{\text{ref}}} - \frac{1}{T}\right)\right]$$
 (2)

where

D(t,T) = diffusion coefficient at time t and temperature T

 D_{ref} = diffusion coefficient at some reference time t_{ref} and temperature T_{ref}

m =constant (depending on mix proportions)

U = activation energy of the diffusion process

R = gas constant

T = absolute temperature

This equation accounts for the influence of age and temperature on diffusivity and was developed from previously published studies. The form of the relationship is consistent with those proposed by Mangat and Molloy [5]. The constant *m* accounts for the decay of the diffusion coefficient with time. It is mainly dependent on the type of cement. Low values in the range of 0.2–0.3 are common for normal portland cement mixtures, while much higher values (0.5–0.7) could be attributed to the use of fly ash and slag at normal replacement levels [6].

2.3. Permeability

Permeability is the rate of fluid ingress driven by a pressure gradient [1]. It is generally known that the permeability coefficient varies with time, as a result of continued hydration of the cement paste, and with temperature, due to its influence on the viscosity and density of the penetrating fluid. Unfortunately, there is a definite lack of well-established relationships for this behaviour in the literature.

This chloride transport model accounts for time dependent permeability as shown in Eq. (3):

$$k(t,T) = \frac{k_{ref}}{Z} \cdot \left(\frac{t_{ref}}{t}\right)^n \tag{3}$$

where

k = permeability coefficient at time t and temperature T

 k_{ref} = permeability coefficient at some reference time t_{ref}

Z = viscosity temperature correction factor

n = porosity

Not all reinforced concrete structures are subject to pressure-driven flow of water; permeability can be ignored in the analysis by letting h, the hydraulic head, in the transport equation equal zero.

2.4. Chloride binding

One way in which chlorides can be bound in the concrete matrix occurs when they chemically react with the hydration products of cement. Chloride ions are primarily bound chemically in a reaction with C₃A to form calcium chloroaluminate, which is often referred to as Friedel's salt [7]. Since only chlorides that are dissolved in the pore solution (free chlorides) are involved in the corrosion of the reinforcement, chloride binding will effectively reduce the amount of free chlorides available to initiate the deterioration process. The chloride-binding capacity of a concrete, that is the amount of chlorides that are complexed by the hydrated phases of the matrix, is modeled by the Langmuir isotherm, shown in Eq. (4):

$$S = \frac{\alpha \cdot C}{1 + \beta \cdot C} \tag{4}$$

where S is the amount of chloride bound, C is the free chloride in solution, and α and β are constants that are dependent on the concrete binder composition. The relationship between free and bound chlorides is unique for each cementitious system since its components, such as C_3A content, supplementary cementing materials, and pH of the pore solution influence its overall binding capacity. The effect of binding on the rate of chloride ingress has been dealt with in detail elsewhere [7].

2.5. Wicking

"Wick action is the transport of water (and any species it may contain) through a concrete element from a face in contact with water to a drying face" [8]. Structures in which this mechanism may influence chloride transport include basements, tunnel liners, roof slabs, and parking deck soffits.

The chloride transport model offers the user the option of including wick action in the service life prediction calculations. The program employs the partial differential equation [Eq. (5)] for water motion due to wicking formulated by Buenfeld et al. [8]:

$$\frac{dw}{dt} = \frac{d}{dx}D_w(w)\frac{dw}{dx} - \frac{S_p^2}{2x} \cdot \frac{dw}{dx}$$
 (5)

where

 D_w = water vapour diffusivity function

w =water content

x =depth from wet face

 $x_i = \text{depth from wet/dry interface}$

 $S_p = \text{sorptivity}$

Buenfeld et al. [8] also derived the following steady-state analytical solutions for the position of the wet/dry interface and the flow rate at equilibrium, respectively [Eqs. (6) and (7)]:

$$x_i = \frac{L}{1 - \frac{2D_w}{S_p^2} \cdot \ln \frac{\rho - w_x}{\rho - w_l}} \tag{6}$$

$$Q = \frac{\rho n}{L} \left(\frac{S_p^2}{2} - D_w \cdot \ln \frac{\rho - w_x}{\rho - w_l} \right)$$
 (7)

where

L = thickness of element/specimen

 ρ = density of liquid water

 $w_r = \text{concentration of saturated vapour}$

 w_l = concentration fo vapour at dry face

Q = flow of water from dry face

n = porosity

3. Assumptions and limitations

Certain assumptions generally must be made in the application of theoretical formulations to perform specific calculations. It is crucial, though, to understand how these assumptions affect the results obtained.

The following assumptions are implicit in the model from the theory on which it was based:

- the analysis is one-dimensional,
- the concrete is homogeneous and isotropic (no cracking),
- the concrete is fully saturated in the modeling region (except for case of drying front for wicking),
- the liquid carrying the chlorides is incompressible,
- diffusion coefficient is constant with depth,
- the concrete is under isothermal conditions, and
- there is an infinite supply of liquid to flow into the concrete.

While the program models the changing chloride concentration vs. depth profile over time, the concentration at the concrete surface and its change with time must be specified by the user. This defines the boundary condition at the surface. The other boundary, that is the bottom of the element, is defined as a zero chloride flow condition and the chloride profile at this point has a slope of zero.

The role of wicking and its influence on chloride transport has not been studied in-depth, and analytical and/or empirical relationships for this mechanism have yet to be well established. The model currently employs the solutions of Buenfeld et al. [8]. This work is limited by the fact that it assesses the position of the evaporation front without recognizing the influence of fluid flux due to hydrostatic effects. It also seems that published wicking solutions from Buenfeld et al. [8] result in a positive flow in the absence of a moisture gradient, the case where there is 100% relative humidity at the "dry side" of an element. The process of chloride wicking is the subject of ongoing research at the University of Toronto.

Some other factors involved in chloride transport have not been studied extensively to date, and therefore have not yet been addressed in the model. These include accounting for chlorides present in concrete when they are physically bound or in a chemi-sorbed state [9], dispersion of the chloride front as it travels through the pores of the concrete cover, and inhomogeneities in concrete resulting in local variations of chloride penetration fronts [1]. The role of moisture in chloride transport is also neglected since it is assumed that the concrete is fully saturated.

It must also be noted that the service life prediction per-

formed by the program is based on estimating the time to initiate corrosion of the steel in a structure. Therefore, issues such as the corrosion rate of steel, conditional response of the structure, and the effect of cracks or other preferential pathways are beyond the scope of the model.

In all, the model provides useful information regarding the various roles of the different mechanisms and their interaction. However, the resulting data should not be taken as absolute, because of the associated limitations.

4. Sensitivity study

The objective of this study was to analyse the sensitivity of the predicted time to initiation of corrosion to changes in certain input variables, as determined by the University of Toronto Chloride Transport Model. It was performed by varying the parameter of interest over a valid range, relevant to field applications, while maintaining the other parameters at the specified base case values for comparative purposes.

4.1. Input parameters investigated

Since the program is capable of modeling several different transport mechanisms that can greatly influence the durability of a structure, there are many material and environmental properties that can be controlled in order to obtain a realistic service life estimate. The following seven of the allowable input parameters were investigated in this sensitivity study:

- m, constant dependent on mix proportions, which controls the rate of reduction of diffusivity,
- *T*, absolute temperature of exposure for structure,
- *C_{crit}*, threshold concentration or critical chloride level required to initiate corrosion of steel,
- D_{ref} , diffusion coefficient at some reference time t_{ref} and temperature T_{ref} ,
- k_{ref} , permeability coefficient at some reference time t_{ref} ,
- C_o, surface concentration, and
- · depth of cover.

4.2. Method of sensitivity analysis

The values used for the base case, along with the relevant range of investigation for each parameter, are summarized in Table 1. These values were chosen from various sources to best represent a range of realistic field exposures and properties of certain concrete mixtures.

The values to be inputted for those parameters that were not considered in the sensitivity analysis also had to be defined. The value for U, the activation energy of the diffusion process, from the diffusion coefficient equation was taken to be 35000 J/mol [10]. The viscosity temperature correction factor, Z, included in the permeability coefficient equation was set to 1.0. A porosity, n, of 8% was used. A hydraulic gradient, h, of 25 m/m was used when investigating the effects of pressure-driven flow; this is a high gradient as may be found in a tunnel lining with 10 m of water over a 400-mm thickness. An age of 28 days was specified as the

Table 1
Input parameters and range of sensitivity investigation

Input	Range of investigation*	
m	Varied from 0 to 0.7 by steps of 0.1	
T	Two cases considered [13]: northern North America (Charlottetown, PEI): 5°C; southern North America (Miam Florida): 24°C	
C_{crit}	Varied from 0.02 to 0.2% by weight of concrete [12] by steps of 0.03 (0.05% by weight of concrete)	
D_{ref}	Two cases considered [14]: high performance concrete (0.3 w/cm, 25% slag, 8% silica fume) $D_{ref} = 0.33 \cdot 10^{-12}$ m ² /s (23°C, 180 days); typical bridge deck concrete (0.4 w/cm, 25% slag) $D_{ref} = 2.53 \cdot 10^{-12}$ m ² /s (23°C, 120 days)	
k_{ref}	Two cases considered: high performance concrete (0.3 w/cm, 25% slag, 8% SF): $k_{ref} = 1.86 \cdot 10^{-16}$ m/s [15]; typical bridge deck (0.4 w/cm, 25% slag): $k_{ref} = 1.00 \cdot 10^{-13}$ m/s (pressure driven flow ignored in base case—hydraulic gradient , $h = 0$)	
C_o	Three typical cases considered [16]: bridge deck; 0–14.8 kg/m³ over 25 years ; parking structure; 0–17.8 kg/m³ over 15 years; severe marine environment; constant surface concentration of 17.8 kg/m³	
cover depth	Varied from 30 to 60 mm with 10-mm steps	

^{*} Base case values are shown in bold.

time at which concrete was first exposed to chlorides. Finally, to carry out the finite difference model, the number of blocks for analysis was set to 100 and the thickness of the element was set to 100 mm so that each element in the analysis was 1 mm thick.

The sensitivity analysis was carried out by varying the parameter of interest over the valid range, while maintaining the other variables at their respective base case settings to generate values for time to initiation of corrosion. The sensitivity was also observed graphically; profiles were produced after 18250 time steps of analysis (50 years) for each case for the parameters m, T, C_o , D_{ref} , and k_{ref} . Relationships

for predicted service life vs. cover depth and critical concentration were also determined.

5. Results and discussion

The predicted service life for the specified base case was found to be 148 years. This represents the time for the chloride concentration to build to 0.05% by weight of concrete at a cover depth of 60 mm. This high life expectancy was anticipated based on the quality of the concrete specified (high performance concrete), as well as other conditions chosen for the base case.

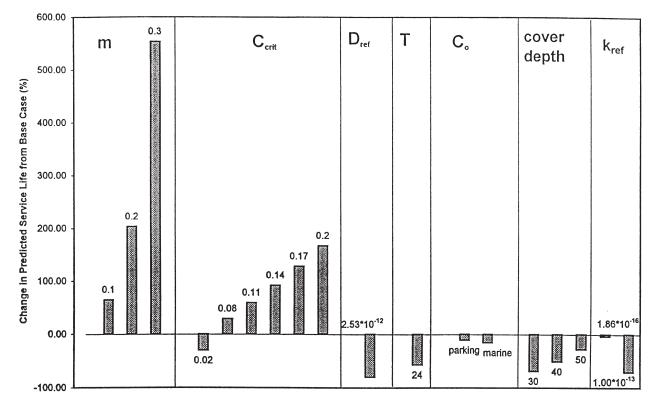


Fig. 2. Percent change in predicted service life. Comparison of sensitivity of different input parameters (Base case: m=0, Ccrit = 0.05%, Dref = 0.33 $*10^{-12} \text{m}^2/\text{s}_1$, T=5 C, Co = bridge, cvr = 60 mm, h=0.

Table 2 Variation in chloride concentration at level of reinforcement after 50 years

	Value used in analysis	[CL ⁻] at cover depth of 60 MM (% wt of concrete)
Parameter		
\overline{m}	0	0.0008
	0.1	0.0001
	0.2	0
	0.3	0
T(°C)	5	0.0008
	24	0.0261
D_{ref} (m ² /s)	$0.33 \cdot 10^{-12}$	0.0008
· ·	$2.53 \cdot 10^{-12}$	0.1496
k_{ref} (m/s)	h = 0	0.0008
,	$1.86 \cdot 10^{-16}$	0.0008
	$1.00 \cdot 10^{-12}$	0.1047
C_o	Bridge	0.0008
(% weight of concrete)	Parking	0.0014
	Marine	0.0026

The results for the sensitivity of the estimated service life to changes in certain input parameters are presented in Fig. 2. The information is reported in terms of the percent change in the service life assessment from the base case prediction.

Sensitivity can also be analysed in terms of the resulting chloride profiles at a certain point in time. Table 2 compares the sensitivity of chloride concentrations to changes in m, temperature, diffusion coefficient, permeability coefficient, and surface concentration after 50 years of exposure when the level of the reinforcement is 60 mm.

Several interesting observations can be made on the sensitivity of the predicted service life, as well as the chloride profiles after 50 years of exposure, by examining the effects of changes in each of the parameters investigated in this study. It should be noted that the results of this study are

somewhat dependent on the base case variables used, even though efforts were taken to represent realistic field conditions and material properties. Under different "base case" conditions, changes in the input parameters may affect the estimated life expectancy of a structure to varying degrees.

5.1. Sensitivity to m

A comparison of chloride profiles resulting from different values of m is presented in Fig. 3. It was found that the predicted service life was extremely sensitive to small changes in the parameter m. This was to be expected as this parameter is an exponent in the diffusion equation. Overall, as the value of m was increased, the time to initiation of corrosion increased, and subsequently the chloride concentration at the level of reinforcement decreased (Fig. 2 and Table 2). Unfortunately, values for m for different concretes have yet to be well established, although values in the range of 0.6–0.7 (or higher) may be expected with moderate levels of fly ash or slag [11]. Research to properly quantify this parameter could greatly improve the accuracy of service life predictions.

5.2. Sensitivity to T

The chloride profiles obtained after 50 years at the two different exposure temperatures are shown in Fig. 4. As temperature increases, it was found that the rate of chloride ingress is accelerated. This effectively increases the chloride concentration at the reinforcing steel and reduces the predicted service life (Fig. 2 and Table 2). Therefore, for structures built where the exposure temperature is quite warm, it may be worthwhile economically to take action, such as the use of better quality concrete, to slow chloride ingress in order to increase the life expectancy of a project.

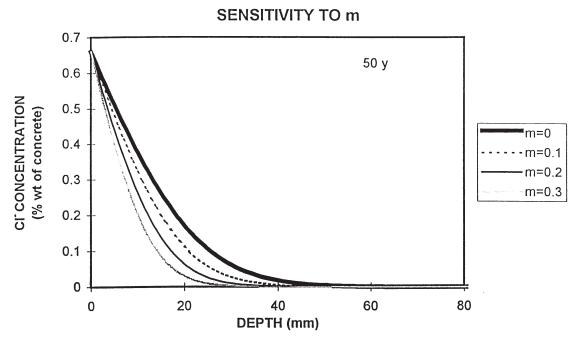


Fig. 3. Predicted chloride profiles with different *m* values.

SENSITIVITY TO TEMPERATURE

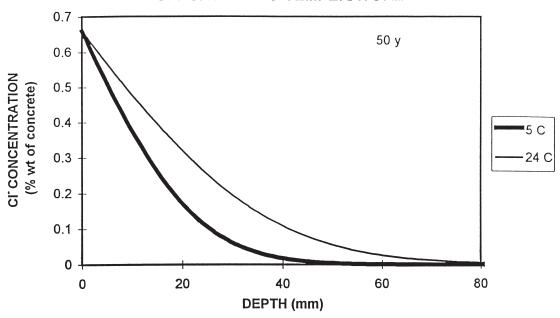


Fig. 4. Predicted chloride profiles with different T values.

5.3. Sensitivity to C_{crit}

There exists a large variation in reported values for the chloride concentration at the reinforcing steel required to initiate corrosion under specific conditions [12]; it is undeniably difficult to choose an appropriate value to incorporate into service life prediction models to obtain a reasonable estimate of the life expectancy of a structure. The study showed that this is critical, since the estimated life expectancies found for threshold concentrations ranging from 0.02 to 0.2% by weight of concrete differed by almost 300 years

(Fig. 2). It was found that the predicted service life increased almost linearly with increase in the critical concentration value used, as can be seen in Fig. 5. It should be noted that the sensitivity to the parameter C_{crit} would be expected to increase as the surface concentration decreases (i.e., as C_{crit}/C_o approaches unity).

5.4. Sensitivity to D_{ref}

With all other parameters being equivalent, it was found that the use of high performance concrete causes a signifi-

PREDICTED SERVICE LIFE VS. CRITICAL CONCENTRATION

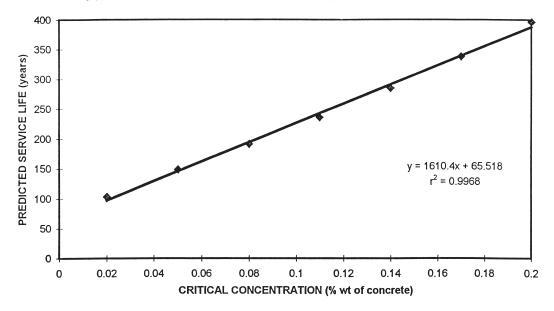


Fig. 5. Relationship between predicted service life and critical chloride concentration.

cant increase in life expectancy (Fig. 6). Consequently, the addition of silica fume to a concrete mixture as a method of lowering the resulting initial diffusion coefficient is an effective method to increase the service life of a structure. It is also interesting to note that under environmental conditions similar to those examined in this study it would be expected that typical bridge deck concrete (i.e., 0.4 water-to-cementitious materials ratio, 25% slag) would require periodic repair and maintenance since the design life of bridges is usually on the order of 50 years.

By comparison, after 50 years of exposure an increase in the diffusion coefficient by a factor of 10 increased the resulting chloride concentration at the depth of the reinforcement by about a factor of 180 (Table 2). These results emphasize the need for good laboratory testing to obtain good characterization of the diffusion properties of a concrete in order to predict the service life with any degree of confidence.

5.6. Sensitivity to k_{ref}

When pressure-driven fluid movement was considered for the high performance concrete case (i.e., $k_{ref} = 1.86 \cdot 10^{-16}$ m/s), there was an almost negligible change in the predicted life expectancy, even with a significant head of 25 m/m. This is not unanticipated since high performance concrete generally has very low permeability, as reflected by the value used, thereby limiting the increased fluid flow. This point is supported further by examining Fig. 7. The 50 year chloride profiles for the cases where permeability effects (h = 0) are ignored and for very low permeability concrete are virtually identical. Thus, when analysing concretes with very low permeability and low diffusion, the life expectancy can still be estimated well if the effects of pressure-driven flow are ignored. This is not the case for higher

permeability concretes. Fig. 5 shows if concrete has a higher permeability coefficient, fluid flow under a pressure head has a great influence on the rate of chloride ingress.

It can also be concluded that the service life estimation is sensitive to the choice of permeability coefficient used in the analysis by comparing the service lives predicted with the two different permeability coefficients when maintaining the same diffusion coefficient. After 50 years, the permeability increase from 1.86×10^{-16} to 1.00×10^{-13} m/s raised the resulting chloride concentration at the depth of the reinforcement by about a factor of 130.

5.7. Sensitivity to C_o

The estimated service life was found not to be extremely sensitive to changes in surface concentration, (Fig. 2). This can also be observed from the chloride profiles presented in Fig. 8. Changing surface concentration from typical bridge deck conditions to that for severe marine environments in the splash/ tidal zone only resulted in a 16% decrease in predicted service life, which is small in comparison to the effects noted with changes in other input parameters. Also, considering the bilinear surface concentration of the parking garage rather than marine conditions with the same long-term constant surface concentration of 0.79% by weight of concrete resulted in a 7-year difference in predicted service life. Again, this is a small difference in the scope of the sensitivity of the other parameters in the study; however, 7 years can make a large difference when evaluating repair strategies and life cycle cost analyses to determine the most economic course of action.

5.8. Sensitivity to cover depth

It is evident from this study that construction defects resulting in less than the specified depth of cover can have

SENSITIVITY TO DIFFUSION COEFFICIENT

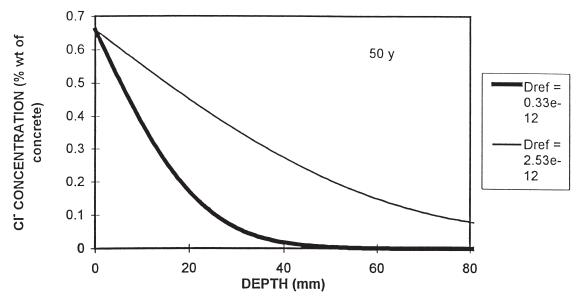


Fig. 6. Predicted chloride profiles with different D_{ref} values.

SENSITIVITY TO PERMEABILITY COEFFICIENT

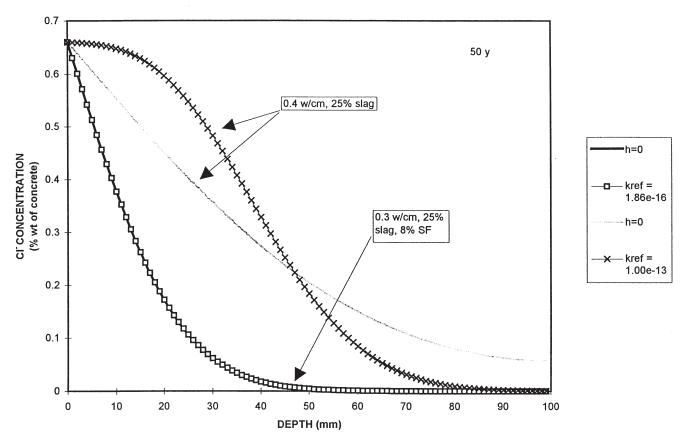


Fig. 7. Predicted chloride profiles with/without permeability effects for two concretes.

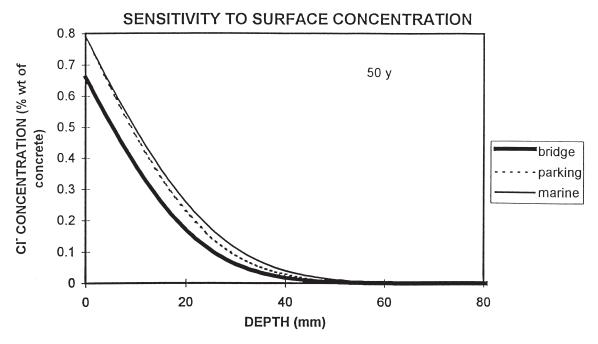


Fig. 8. Predicted chloride profiles with different C_o values.

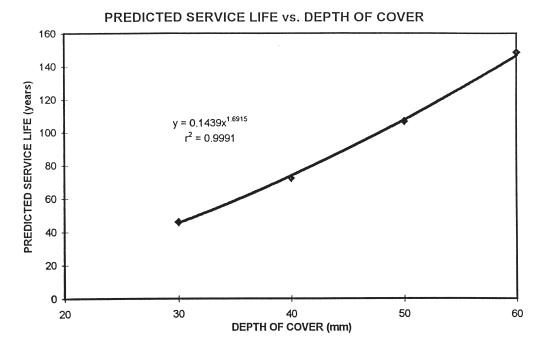


Fig. 9. Relationship between predicted service life and cover depth.

pronounced negative effects on the service life of a structure (Fig. 2). Fig. 9 presents the relationship found between predicted service life and different cover depths, with other parameters in the base case kept constant. This emphasizes the need to obtain uniform nominal cover depths in practice. "Typically, even with good quality control inspection, depths of cover will vary by ± 10 mm" [1]. Since the cover depth can expectedly be reduced at certain locations in a reinforced concrete project, it may be advisable to investigate this likelihood when performing service life predictions and to compensate for it.

6. Summary and conclusions

The results of the sensitivity analysis performed with this chloride transport model show that changes in all of the parameters in this study have some effect on the resulting predicted service life. Overall, the data emphasize the fact that the life expectancy of a structure can be drastically underor overestimated if efforts are not made to realistically represent the material and environmental properties involved in the situation that is modelled. The study also validates the importance of not basing service life prediction calculations on the diffusion process alone.

In all, the model discussed here is easy to use and very versatile. The various analysis tools incorporated into the program allow for it to be used for numerous applications, such as service life prediction, comparison of estimated chloride profiles at different time frames, or evaluation of the relative significance of altering certain mix proportions in the efforts to obtain an economic yet durable structure.

Most importantly, its use was extremely conducive to gaining a better understanding of the roles and interdependencies of the various mechanisms involved in the rate of chloride ingress through concrete.

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