A MECHANISTIC APPROACH FOR PREDICTING THE EFFECT OF VARIOUS FACTORS ON PARTITIONING BETWEEN FREE AND BOUND CHLORIDES IN CONCRETE

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by

Sayeed Munshi

PERMISSION TO USE

Head of the Department of Civil and Geological Engineering
University of Saskatchewan
Saskatoon, Saskatchewan
Canada S7N 5A9

ABSTRACT

The chloride-induced corrosion of reinforcing steel in concrete structures has become a widespread durability problem throughout the world. When concrete structures come in contact with chloride sources, the chloride ions will diffuse through the body of the concrete and ultimately reach the steel. Not all of the chloride ions which penetrate the concrete remain free in the pore solution. Some of the ions become bound to the hydration products in a chemical reaction to form calcium chloroaluminate hydrate (Friedel' salt). It is also well known that only the portion of the chloride ions that remains free is responsible for causing damage to the concrete structures by corroding steel rebar. Thus, the chloride binding capacity of the cementitious matrix plays a major role in controlling chlorides ingress and, consequently, the corrosion of steel reinforcement in concrete. The chloride binding capacity is affected by cement composition, environmental factors, and by the source of the chlorides ($CaCl_2$ vs. $NaCl$). To quantify the durability of new and existing structures, a clear understanding of the mechanisms of chloride penetration into the concrete cover is required.

Currently, most of the models available in the published literature for calculating free chloride ions in concrete use Fick’s law for chloride transport and chloride binding isotherms to account for bound chlorides. Binding isotherms are cement and environment specific. Thus, the existing models cannot be used for all types of cement and variable general environmental exposure conditions such as temperatures, pH levels, and chloride sources. A general mechanistic approach that can overcome those limitations is proposed in this thesis based on the concepts of ion-exchange theory for an accurate determination of chloride ingress in concrete under variable environmental conditions.

Some of the model input parameters, such as exchange capacity and the equilibrium constant for the exchange reaction, were not easy to determine directly from experiments and were determined through an inverse modeling procedure. Verification experiments were carried out by varying different environmental parameters and making comparisons with the simulated results using the corresponding parameters.

The experimental results showed that the proposed procedure is able to predict the amount of free chlorides in concrete, including predictions of chloride binding as a function of pH, temperature, chloride sources, and the presence of other ions such as carbonate. The proposed model was also used to clarify some unresolved issues such as the effect of chloride sources on binding and the effect of pH on the release of bound chlorides in the presence of carbonation.

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This thesis is dedicated with love to my parents,

Md Abu Taher Munshi

and

Ms Taslima Khatun.

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LIST OF SYMBOLS

AFm	Aluminium Ferrite Mono (one hydrated cement phase)
A	Cross sectional area of the sample slice (cm^2)
C	Concentration (mol/cm^3)
C_0	Chloride concentration at the exposed boundary (mol/L)
C_2	Ionic species 2 in the solution phase
C_b	Amount of bound chloride in *mg* Cl/ *g* of sample
C_e	Chloride concentration of the solution at equilibrium in (mol/L)
CEC	Cation Exchange Capacity
C_i	Initial chloride concentration of the external solution in (mol/L)
C_j	Bulk concentration of species *j* (mol/cm^3)
D_a	Apparent diffusion coefficient (cm^2/s)
D_{eff}	Effective diffusion coefficient (cm^2/s)
D_j	Diffusion coefficient of species *j* (cm^2/s)
F	Faraday’s constant (coul/eq)
I	Ionic strength (M)
$J(x)$	Unidirectional flux (mol/cm^{2}s)
K_i	Temperature-dependent equilibrium constant
l	Thickness of slice (cm)
M	The total number of aqueous master species
N	Number of species containing element *m*
R	Gas constant (cal.volt^{-1}.eq^{-1})
r_c	Carbonation ratio of hydrates
T	Absolute temperature (K)

t	Time (sec)
U	Electrical Potentials (V)
V	Artificial or forced velocity of ion (cm/s)
V	Volume of external solution in (ml)
W_d	The dry weights of the samples (g)
w_e	The evaporable water content (% g/g)
W_s	The saturated weight of the sample (g)
$x_{m,i}$	The stoichiometric coefficient of master species *m* in species *i*
z	Electrical charge of species
δC	Variation in concentration (mol/cm^3)
δE	Variation of potential (V)
δx	Variation in distance (cm)
Φ_{Mc}	Pitzer interaction parameter
C_1	Ionic species 1 in the solution phase
$\overline{C_2}$	Ionic species 2 in the solid phase
K_{ex}	Equilibrium constant for exchange reaction
a_i	The activity of species *i*
a_m	The activity of master species *m* forming species *i*
$Total_m$	The total concentration of element *m* in solution
$\Delta_r H^o$	The standard heat of reaction (Joules)
$\Delta_r S^o$	The change of entropies of reaction in standard state, (J/K)
γ_i	The activity co-efficient
m_i	The molality of ionic species *I* (mol/kg)
z_i	Charge of ionic species
a°	An adjustable parameter corresponding to the size of the ion

Ψ	Pitzer interaction parameter
C'	Chloride concentration in mol / L of pore solution

CHAPTER 1

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Introduction

1.1 Introduction

Concrete is the most widely used construction material in the world, not only due to its low cost, but also due to its high durability. However, in the last two decades, the instances of unsatisfactory durability of concrete structures have increased at an alarming rate. In addition, about 50% of the expenditures in the construction industry are spent on the repair, maintenance, and remediation of existing structures (Aitcin, 2006). The main cause of concrete deterioration is the corrosion of reinforcing steel inside the concrete. When steel reinforcement corrodes, the formation of rust leads to a loss of bonding between steel and concrete. The steel corrosion also causes a reduction in the effective cross-sectional area of the steel that leads to a reduction of steel strength. The volume of the rust product is higher than the volume of the uncorroded steel; this creates expansive pressure on the surrounding concrete that initiates tensile stresses in the concrete. After some time, the tensile stresses will reach a critical value and corrosion cracks start developing. With further production of rust, the crack widths will increase and eventually this will result in spalling, which exposes the reinforcing bars directly to the environment.

Reinforcing steel in concrete is initially surrounded by a highly alkaline (pH > 13) pore solution. At this pH, a thin protective layer of ferric oxide is formed on the surface of the steel. Disruption of the protective layer of ferric oxide takes place when the concentration of chloride ions in the vicinity of the reinforcing bars exceeds a critical threshold value. When the source of chlorides is the external environment, the chloride ions will diffuse through the body of the concrete and ultimately reach the reinforcing bars. Not all of the chloride ions that are in or that penetrate the concrete remain free in the pore solution. Some of the ions become bound to the hydration products through a chemical reaction to form calcium chloroaluminate hydrate (Friedel's salt) (Roberts, 1962; Mehta, 1977; Diamond, 1986; Taylor, 1990), while others get absorbed to the various hydrates of cement (Ramachandran, 1971; Ramachandran *et al.*, 1984; Blunc *et al.*, 1986). Thus, only a portion of the chloride ions remains free. It is the free chloride ions that are responsible for causing damage to the concrete structures by corroding reinforcing bars. The chloride binding capacity is affected both by cement composition and environmental factors. The binding of chloride ion is also affected by the associated cations of the chloride sources. For instance, in the case of $CaCl_2$, the binding of chloride ions is higher than in the case of $NaCl$ (Zibara, 2001).

Carbon dioxide, which diffuses as a dissolved substance in water or through the gaseous phase of concrete pores, reacts with different concrete phases, leading to carbonation. The carbonation reaction reduces the high pH of concrete to levels that could lead to corrosion even in the absence of chlorides. At the same time, the solubility of chloride compounds in cement (e.g., Friedel’s salt) will increase at lower pH values (Roberts, 1962). Therefore, they will release many chloride ions; thus, carbonation increases the amount of free chlorides in the concrete pore solution. The main product of carbonation, calcium carbonate, will precipitate on the surface of pores and so the pore size will be reduced. This will affect the porosity, permeability, and diffusivity in concrete.

A sound and reliable model for predicting the dynamic changes in the pore solution chemistry and mineral precipitation/dissolution due to chloride binding and carbonation in cement-based materials has been lacking. This has led to difficulties in predicting the effect of pore solution chemistry on the reinforcement corrosion inside the concrete and, consequently, in establishing a reliable evaluation of the subsequent durability risks. Fick's law is still the most widely used model for estimating the amount of free chlorides in concrete (Ababneh *et al.*, 2003; Cerny *et al.*, 2004; Jenson *et al.*, 1999; Nielson *et al.*, 2005). However, since Fick's law is only capable of representing physical diffusion with no chemical reactions between the diffusing ions and the solid matrix, it may not predict accurate results for the amount of free chlorides in the pore solution. The amount of bound chlorides has traditionally been addressed through use of experimentally determined binding isotherms. These isotherms are typically determined for the uncarbonated concrete and at a given temperature. Given their empirical nature, these approaches fail to address the effects of important parameters, such as temperature and pH variations, associated with variations in concrete mixes (use of cement, use of pozzolans, admixtures, etc.) as well as the in-service conditions. Although ion exchange has been mentioned in previous studies as probably the most important mechanism for chloride binding in concrete, no predictive model in the literature has actually tried to implement this mechanism into a mathematical model and investigate the quality of the predictions that could be achieved. It is precisely this gap that this research is trying to fill.

1.2 Objectives

This work focuses on chloride binding and the transport of chloride ions into concrete. The objectives of this research are as follows:

> The main objective of this research is to propose ion-exchange theory for estimating the amount of free and bound chlorides in concrete under different environmental conditions (e.g. variable temperature, pH, carbonation, etc.) inherently present under service conditions.

More specifically the objectives are:

1. To carry out tests to determine the anion exchange capacity and exchange coefficient for the exchange reactions between chloride ions and hydrated cement phases.

2. To carry out validation tests to determine if ion-exchange theory can be used for:
    - Predicting the effect of temperature on chloride binding isotherms.
    - Predicting the effect of the source of chlorides (NaCl vs. $CaCl_2$) on chloride binding isotherms.
    - Predicting the effect of concrete quality (w/c=0.5, w/c=0.6, w/c=0.7) on chloride ingress.

3. To use ion exchange theory for the following parametric studies. A comparison with data published in the literature will be made whenever possible.

- Effect of pH on chloride ion binding isotherms.
- Effect of carbonation on chloride ion binding isotherms.
- Effect of the source of chlorides (NaCl vs. $CaCl_2$) on chlorides ingress (profile through depth as a function of time).
- Effect of carbonation on chlorides ingress (profile through depth as a function of time).

1.3 Scope and Methodology

The scope of the work consists of an experimental program and numerical simulations. The experimental program is intended to determine some unknown parameters needed for the simulations and to provide data for verifying the simulated results. In the analytical study, an approach is developed for estimating the amount of free and bound chloride ions along their penetration path into concrete considering all major chemical interactions as well as to determine the effect of other factors, such as carbonation, associated cations, pH, and temperature, on chloride binding.

1.4 Organization of thesis

Work in the investigation began by reviewing the available related published literature to gain familiarity with the scope and methodologies of analysis and experimental programs. Existing papers on cement chemistry, the mechanism of chloride binding in cement paste, the determination of chloride isotherms and profile, the determination of concrete transport parameters, as well as the existing methods used to estimate the free chloride ions in concrete, are reviewed in Chapter 2.

Chapter 3 describes the proposed method for estimating free and bound chloride ions in concrete and determining the chloride profiles and the effects of various environmental factors. All of the chemical reactions and transport equations used in the proposed models are also discussed.

Most of the parameters required for the proposed approach were not available in the literature. To determine those required parameters and also to verify whether the proposed method gives realistic results, experiments were carried out. The complete experimental program is discussed in Chapter 4.

Chapter 5 presents the numerical simulations and experimental results. Procedures for estimating the unknown parameters needed for the simulations are described. Comparison of the simulated and experimental results is also shown in that chapter.

A summary of the findings of this investigation is presented in Chapter 6, from which conclusions are drawn and recommendations for future work are made.

CHAPTER 2

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Literature Review

2.1. Introduction

Chloride-induced corrosion is one of the major deterioration processes that occur in reinforced concrete structures. Research on chloride ions binding in concrete has been taking place for a long time. The chloride binding capacity of Ordinary Portland Cement (OPC) in the presence of admixed $CaCl_2$ salt was demonstrated as early as 1962 (Roberts, 1962). During the 1980s, a small number of researchers showed that chloride binding at room temperature takes place in the form of a chloro-complex called “Friedel’s salt”(Diamond, 1986; Page *et al.*, 1981). This chapter summarizes the background information relating to chloride ion binding in concrete by providing an overview of the various mechanisms that have been proposed to explain it together with the various factors that affect it. Different models used for determining chloride ion concentration profiles in concrete together with their advantages and limitations are briefly described here. The most important experimental procedures usually used for determining the diffusion coefficient of chloride ions into concrete as well as the various techniques commonly used for extracting the free and bound chlorides from the cement-based samples are also described in this chapter.

2.2. Chloride Binding

When chloride ions come in contact with the cement paste component, a portion of the available chloride ions gets bound both physically and chemically to the cement paste. These bound chloride ions do no take part in the corrosion of steel reinforcement and subsequent deterioration of concrete. The two types of chloride binding are described below.

2.2.1. Chemical Binding

Chemical binding is the result of chemical reactions between chloride ions and certain cement hydration products, leading to the binding of chloride ions. The main constituents of cement are $3CaO.SiO_2$ ($C_3S=$ tricalcium silicate), $2CaO.SiO_2$ ($C_2S=$ dicalcium silicate), and, in lesser amounts, $4CaO.Al_2O_3.Fe_2O_3$ (C_4AF = tetracalcium aluminoferrite), $3CaO.Al_2O_3$ (C_3A = tricalcium aluminate), and $CaSO_4.2H_2O$ (gypsum). It is believed that chloride ions are chemically bonded in the C_3A (TriCalcium Aluminate) phase of cement to form calcium chloroaluminate hydrate or Friedel’s salt ($3CaO.Al_2O_3.CaCl_2.10H_2O$) (Roberts, 1962; Mehta, 1977; Diamond, 1986; Taylor, 1992; Rasheeduzzafar, 1992; Nevile, 1995; Suryanvanshi *et al.*, 1996). Studies also found that the C_4AF (TetraCalcium Alumino Ferrite) phase has the ability to bind chloride ions, in a similar way to C_3A, by the formation of Friedel's salt $3CaO.Al_2O_3.CaCl_2.10H_2O$, or its iron analogue, $3CaO.Fe_2O_3.CaCl_2.10H_2O$, for both mixing chloride and external chloride penetrations (Roberts, 1962; Taylor, 1992; Rasheeduzzafar, 1992; Nevile, 1995; Suryanvanshi *et al.*, 1995; Csizmadia *et al.*, 2001).

Binding of chloride ions occurs for both admixed chloride as well as external chlorides (Diamond, 1986; Saito & Kawamura, 1992; Kouloumbi and Batis, 1994; Suryanvanshi *et al.*, 1995; Suryanvanshi & Swamy, 1996). In the case of admixed chlorides, chloride ions are bound into the unhydrated C_3A phase during the hydration process to form Friedel's salt (Roberts, 1962; Diamond, 1986; Taylor, 1990; Suryavanshi *et al.*, 1995). However, the presence of sulphate creates competition for the available C_3A. C_3A reacts preferentially with sulphates to form ettringite and, after the consumption of all the sulphates, the remaining C_3A reacts with chlorides to form Friedel's salt (Mehta, 1977; Enevoldsen, 1994).

In the case of external chlorides, a large amount of the C_3A phases has already hydrated. Migdley and Illstone (1984) found that only unhydrated C_3A reacts with penetrating chloride ions, but others suggested that hydrated C_3A phases react with chloride ions to form Friedel's salt (Nagataki *et al.*, 1993). Birnin-Yauri and Glasser (1998) mentioned that during the chloride penetration in concrete, chloride ions get bound in AFm phases and form Friedel's salt, which is more stable.

Ben-Yair (1974) explained that the chloride binding process is the direct chemical reaction between the C_3A phase and the $CaCl_2$. In the case of admixed chloride NaCl, he explained the chemical binding with the following reactions:

$$Ca(OH)_2+2NaCl=CaCl_2+2Na^-+2OH \text{ ……………………. } (2.1)$$

$$C_3A+CaCl_2+10H_2O=C_3A.CaCl_2.10H_2O \text{ …………………… } (2.2)$$

More recent studies suggested that the binding of chloride ions in cement paste to form Friedel's salt happens by an ion exchange mechanism (Suryavanshi *et al.*, 1996; Luo *et al.*, 2003). The hydration products of C_3A and C_4AF are the hydroxy AFm, which have a double-layered structure. The interlayer ions are hydroxyl ions that are exchanged by chloride ions present in the pore solution, and then the hydroxyl AFm converts to Friedel's salt. Figure 2.1 shows a schematic representation of the process of chloride ion binding according to the theory of ion exchange. Suryanvanshi *et al.* (1996) explained the phenomenon using the following reaction:

$$R^{+}\text{-}OH^{-} + Cl^{-} \rightarrow R^{+}\text{-}Cl^{-} + OH^{-} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2.3)}$$

where R is the principal layer of hydroxy AFm, $\left[Ca_2Al(OH)_6.2H_2O\right]^{+}$

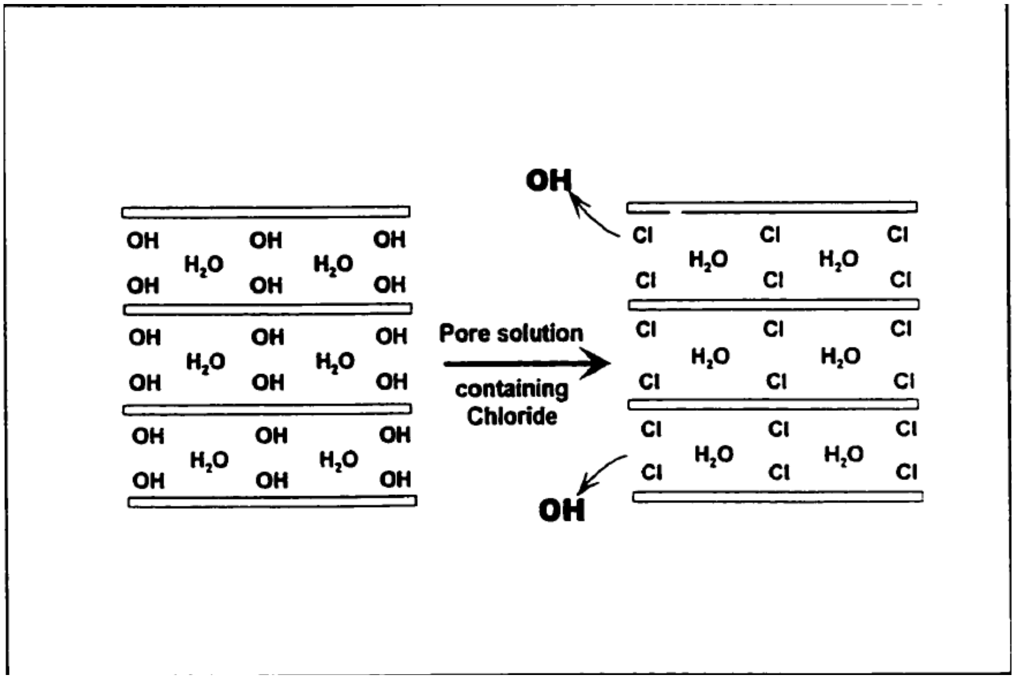

Figure 2.1: Schematic showing the ion exchange between the chloride ion and the hydroxyl ion residing in the interlayer spaces of a hydroxyl AFm phase (Glasser, 1999).

The affinity between the negative ion exchanger and negative ions like Cl^- and hydroxide ion increases in the following order (Maslehuddin *et al.,* 1997):

$$SO_4^{-2} > Cl^- >> OH^- \text{ ……………………….. (2.4)}$$

According to this equation, Cl^- ions can easily replace OH^- ions in negative ion exchangers. They explained the ion exchange reaction for chloride binding in the following way:

$$R^+\text{-}OH^- + Na^+ + Cl^- \rightarrow R^+\text{-}Cl^- + Na^+ + OH^- \text{ ………………….. (2.5)}$$

This is similar to what was suggested by Suryanvanshi *et al.* (1996)

2.2.2. Physical Binding

Chloride ions can also physically adsorb onto the surface of Calcium Silicate Hydrate (C-S-H) which is the hydrated product of cement phase $3CaO.SiO_2$ (C_3S = tricalcium silicate) and $2CaO.SiO_2$ (C_2S = dicalcium silicate). This kind of chloride binding is known as the physical binding of chloride ions (Diamond, 1986; Tang and Nilsson, 1993). Physical adsorption is believed to be due to electrostatic or Van der Waals forces between charged particles. In this case, it is between the chloride ions and the surface of the C-S-H.

2.3. Factors Affecting Chloride Binding

The binding of chloride ions in cement paste depends on several factors. A large amount of published data has been gathered over the years regarding the factors affecting the binding of chloride ions in cement paste. The findings of the previous studies regarding these factors are briefly described below.

2.3.1. Cement Composition

It has been reported that both the C_3A and C_4AF phases of cement chemically bind chloride ions to form Friedel's salt. Hence, it is only natural that the amount of these phases in cement plays a significant role in chloride binding.

The amount of C_3A in cement has been shown to have a decisive significance on the binding of chloride ions in cement paste (Roberts, 1962; Rasheeduzzafar *et al.*, 1992; Sandberg & Larsen, 1995; Nagataki *et al.*, 1993). As mentioned in Zibara (2001), Holden *et al.* (1983) found that the concentration of free chloride ions in the pore solution of cement paste decreased as the C_3A content in cement increased. Rasheeduzzafar *et al.* (1991, 1992) found a similar trend when they tested four Portland cements with C_3A content ranging from 2% to 14% and with different levels of chloride addition (0.3, 0.6, 1.2, and 2.4 % Cl- by mass of concrete), as can be seen in Fig 2-2. To find the effect of C_4AF on chloride binding, Suryavanshi *et al.* (1995) studied chloride binding in sulphate resistant portland cement which has a higher percentage of C_4AF and a lower percentage of C_3A. Their results suggested that C_4AF reacted with chloride ions to form the chloro-complex $3CaO.Fe_2O_3.CaCl_2.10H_2O$, which has an identical crystalline structure to Friedel's salt.

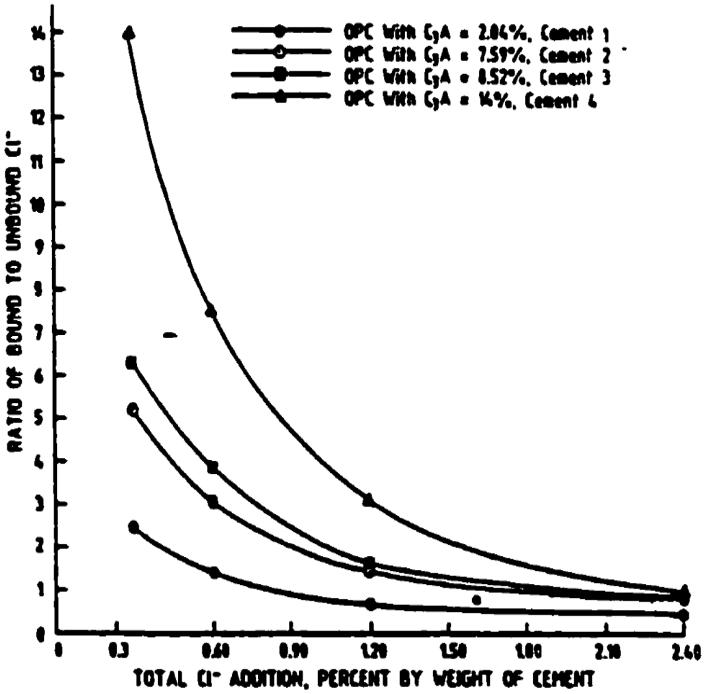

Figure 2.2: Effect of C_3A content on the binding of chloride ions in cement paste.

(Rasheeduzzafar *et al.*, 1991)

Some other studies also found that C_4AF binds chlorides, similarly to C_3A, by the formation of the iron analogue of Friedel's salt, $3CaO.Fe_2O_3.CaCl_2.10H_2O$, for both mixing chloride and external chlorides (Roberts, 1962; Taylor, 1992; Rasheeduzzafar, 1992; Nevile, 1995;Csizmadia *et al.*, 2001). Hence, higher amounts of C_3A and C_4AF in cement paste increase the number of binding sites for chloride ions, and as a result, more chloride ions can be bound in the cement paste.

2.3.2. Chloride ion Concentration

It is obvious from the literature that the chloride concentration in the pore solution plays a decisive role in the binding of chloride ions in cement. Almost every study in the literature suggested that chloride binding increases as the chloride concentration in the pore solution increases.

Some studies (Arya and Newman, 1990; Tuutti, 1982) suggested that the relationship between free and bound chloride is linear. Arya and Newman (1990) found that the chloride concentration in the mix water (for an internal source) or in the penetrating solution (for an external source) is one of the primary factors that influence the chloride binding and that the chloride binding is proportional to the initial concentration. Tuutti (1982) also found a linear relation between free and bound chloride ions and defined a factor, K_d, which is the ratio between free and bound chlorides per unit weight of cement. On the other hand, a number of other studies suggested that this relationship is non-linear. Tang and Nilsson (1993) proposed that the relationship between free and bound chloride follows Langmuir isotherms at low chloride concentrations (< 0.05 mol/l) and the Freundlich isotherm at higher concentrations. Sergi *et al.* (1992) found a non-linear relationship between free and bound chlorides that follows the Langmuir isotherm.

2.3.3. Temperature

The surrounding temperature of the pore solution is one of the factors that affect the binding of chloride ions in cement. Most of the results showed that there is a decrease in bound chlorides as temperature increases.

Roberts (1962) studied chloride binding at different temperatures (25°C, 50°C and 90°C) and found an increase in free chloride concentration in the pore solution as temperature increases. Maslehuddin *et al.* (1997) found in their experiments that the free chloride concentration in the specimens that contained sodium chloride increased with the exposure temperature. Kayyali and Haque (1988) reported that hot weather conditions around 30°C resulted in the release of the bound chloride ions into the pore solution. To investigate the effect of temperature on chloride binding in cement paste, Hussain and Rasheeduzzafar (1993) performed an experiment using three types of cement, varying the C_3A content with three different chloride levels, and used two different levels of temperatures: 20°C and 70°C. Their results showed that, for all three types of cement, there is an increase in free chlorides in the pore solution when the temperature increases. At a temperature of 70°C, the hydroxide ion concentration in the pore solution is reduced and the concentration of free chloride is increased by the decomposition of chloro-aluminates. The net effect of the two reactions is an decrease in the OH/Cl ratio of pore solution (Hussain and Rasheeduzzafar, 1993; Hussain *et al.* 1995).

Maslehuddin *et al.* (1997) found a significant decrease in the chloride binding of mortars when the curing temperature increased from 20°C to 40°C, 55°C, and 70°C. Siegwart (2003) found that, for a temperature increase of 20°C, the free chloride content is almost doubled.

There are also a very few studies that found that chloride binding increases as temperature increases. Arya *et al.* (1990) examined the binding of chloride ions in cement at different curing temperatures: 8°C, 20°C, and 38°C. Their results showed that there is an increase in bound chlorides as the curing temperature increases.

2.3.4. Water-Cement Ratio

Water cement ratio has a significant effect on chloride ions binding in the cement paste. Most of the published data suggest that the binding of chloride ions in cement paste increases as the water-cement ratio increases. The reason for that is related to the fact that the hydration of cement paste with higher water-cement ratios is higher compared to cement paste with lower water-cement ratios (Delagrave *et al.*, 1996). Hence, a cement paste with a higher water cement ratio has more binding sites available compared to a similar cement paste with a lower water-cement ratio. Delagrave *et al.* (1996) found in their study that the 0.25 water/binder ratio pastes clearly tended to bind significantly less chlorides than the 0.45 water/binder mixtures. While investigating chloride binding in concrete exposed to seawater, Mangat and Molloy (1995) also concluded that the amount of bound chlorides in concrete increases as the water-cement ratio increases.

Tang and Nilsson (1993) found that the water-cement ratio has some influence on the chloride binding isotherms of cement paste when the bound chloride is expressed using the unit weight of the sample; the amount of bound chloride increases as the water-cement ratio increases. However, when the bound chlorides are expressed using the unit weight of C-S-H gel, then water-cement ratio has no influence, which indicates that the amount of C-S-H gel increases as the water-cement ratio of the cement paste increases. Hence, they suggested that the observed difference is due to differences in their degrees of hydration at different water cement ratios.

There are also experiments that had opposite results. Sumranwanicha and Tangtermsirikula, (2004) showed that cement pastes with higher water to cement ratios bind less chloride than those with lower water to cement ratios.

2.3.5. Effect of pH

The binding of chloride ions in cement paste has been shown to depend on the hydroxide ion concentration or the pH of the pore solution. Tritthart (1989) found that more chloride ions are bound in the case of cement pastes with pore solutions having a lesser hydroxide ion concentration. He explained that both hydroxide and chloride ions compete for the same binding sites, and if the pore solution has less hydroxide ions, then more chloride ions are available to compete for the binding sites, which results in more binding of chloride ions. Hussain *et al.* (1995) found a similar trend when they added NaOH to cement paste that was treated with NaCl solutions and they found that there was a decrease in chloride binding with increased hydroxide concentration.

Tritthart (1989) studied the effect of pH on chloride binding for external chloride. He immersed cement paste in chloride solutions with different pH values and his results clearly showed that chloride binding increases as the pH of the chloride solution decreases. Sandberg (1999) also found that, as the hydroxide ion concentration drops, the chloride binding and the solubility of calcium hydroxide increases. In their investigation of the effect of seawater on concrete, Mangat and Molloy (1995) concluded that the bound chloride content of concrete decreases as the pH increases.

2.3.6. Effect of Carbonation

The effect of carbonation on chloride binding is very important because chloride ions can penetrate into cement paste in the presence of carbonation. All the available research shows that bound chlorides get released in carbonated areas. Kayyali and Haque (1988) studied the influence of accelerated carbonation on the chloride binding of cement. Their results showed a significant increase of free chloride in the pore solution of carbonated samples compared to the non-carbonated samples. Suryavanshi and Swamy (1996) studied the role of atmospheric carbonation on the stability of Friedel's salt in a chloride contaminated concrete slab and they found that the higher the degree of carbonation, the lower the amount of Friedel's salt.

The process of releasing bound chlorides from Friedel's salt was not clearly explained in the previous research efforts. Carbonation occurs when carbon dioxide gas is dissolved in water to form a weak carbonic acid. As a result, there is a decrease in pH. Thus, some researchers suggested that the carbonation of Friedel's salt could be correlated with the pH of the liquid phase. In their study, Saeki *et al.* (2001) expressed the relation between liquid pH and carbonation ratio as follows:

$$\left.\begin{array}{ll} pH<7.5 & r_c=1 \\ 7.5<pH<9 & r_c=-0.4*pH+4 \\ 9<pH<11.5 & r_c=-0.16*pH+1.84 \\ pH>11.5 & r_c=0 \end{array}\right\} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.6)$$

where pH is the pH of the liquid phase and r_c is the carbonation ratio of hydrates.

However, the results of a more recent study by Ishida *et al.* (2005) contradict the relationship between the pH of the liquid phase and carbonation of Friedel's salt. In their experiment, they found that the rate of Friedel's salt decomposition is faster than the rate of hydroxide ion reduction due to carbonation. They also found that the decomposition of Friedel's salt already occurred even at high pH values of the solution. Hence, they concluded that the decomposition rate of Friedel's salt was not a function of pH alone.

2.3.7. Associated Cation

Studies in the published literature showed that the source of chloride ions has a significant influence on the amount of chloride ion binding in concrete (Arya *et al.*, 1990; Suryavanshi *et al.*, 1996; Kawamara *et al.*, 1988; Al-hussaini *et al.*, 1990; Trittihart, 1989). Most of the studies used NaCl and $CaCl_2$ as chloride ion sources since they are the most common chloride sources that normally come in contact with concrete structures. Their results showed that more chlorides are bound in concrete in the case of a $CaCl_2$ source compared to the NaCl source.

In their experimental investigation, Al-hussaini *et al.* (1990) found higher levels of free chloride in the case of a NaCl source, compared to the $CaCl_2$ source, at all chloride levels up to 2% by mass of cement. Delagrave *et al.* (1997) reported that the amount of bound chlorides is clearly enhanced for the samples immersed in a calcium chloride solution. The influence of the associated cation is particularly marked in the low chloride concentration range.

Arya *et al.* (1990) found that a greater proportion of chloride ions become bound when they originate from $CaC1_2$ rather than NaCl, both for external and internal chlorides. They explained that Friedel's salt is more rapidly formed in case of $CaCl_2$ than NaCl. According to Ben Yair (1974), $CaCl_2$ can directly react with aluminate phases to form Friedel's salt, whereas NaCl has to react with $Ca(OH)_2$ to form $CaCl_2$ before combining with aluminate phases to form Friedel's salt. This longer chain of reaction retards the chemical combination of chlorides for the case of NaCl. Pruckner and Gjorv (2004) describe the reactions of forming Friedel’s salt from $CaCl_2$ and NaCl as follows:

for $CaCl_2$:

$CaCl_2$+$3CaO.Al_2O_3.6H_2O(s)$+$4H_2O$®$3CaO.Al_2O_3.CaCl_2.10H_2O(s)$ ………… (2.7)

and for NaCl:

2NaCl(aq)+$3CaO.Al_2O_3.6H_2O(s)$+$Ca(OH)_2(s)$+$4H_2O$®$3CaO.Al_2O_3.CaCl_2.10H_2O(s)$ …… (2.8)

On the other hand, Suryavanshi *et al.* (1996) found that the pH of the pore solution with $CaCl_2$ additions is significantly lower compared to that with NaCl additions. Hence, they explained that, in case of $CaCl_2$, the lower availability of OH^- ions in pore solution offers less competition during chloride binding. Thus more chloride ions can get bound in the case of $CaCl_2$ compared to NaCl.

Although all the published data suggest the same trend, that more chlorides are bound when calcium chloride is used compared to sodium chloride, they all fall short of explaining the fundamental reason behind this behaviour and only speculations have been formulated so far.

2.4. Modeling of Chloride Binding

A number of methods for predicting the chloride ion concentration profiles in cement paste have been proposed by various researchers. The most common method has been the application of Fick’s second law. Knowing the apparent chloride diffusion coefficient, the chloride concentration profiles can be calculated and plotted for various exposure conditions (Wee *et al.*, 1997)

Tang and Nilsson (1992) developed a mathematical model to predict the chloride concentration profile of concrete structures by performing short-term diffusion tests on OPC paste under the action of a constant electrical field. Andrade and Sanjuan (1994) applied the Nernst-Planck and Nernst-Einstein equations to calculate the chloride ion diffusion coefficient in concrete from ionic migration experiments in which an electrical field was applied. Funahashi (1990) produced a grid pattern with time and concrete depth. Knowing the initial interior and boundary chloride ion concentrations, future chloride ion concentration profiles can be calculated at each grid point using a computerized finite difference method.

As mentioned in Geiker *et al.* (2007), predictive models, such as the DuraCrete model, Life-365, and the HETEK model, all make use of a combination of ingress models and experimentally based material parameters.

Siegwart *et al.* (2003) examined the relationship between free and bound chloride based on published data from eleven papers. They derived a polynomial binding expression in which the free chloride is a function of C_3A. They carried out least squares approximations for different types of polynomial functions (biquadric, bicubic, biquartic, and triquartic) and found that the biquadric function gives a best fit curve. They did not consider the phenomenon of chloride binding and their method was empirical and not analytical in nature.

The main limitation of these above-mentioned models is that they do not explicitly consider the mechanism of chloride ion binding in cement paste. Also, they do not consider the effects of other factors on chloride binding such as temperature, pH, water cement ratio, carbonation, and chloride sources.

2.5. Methods for Determining the Free Chloride in the Pore Solution

Different methods were used for extracting the pore solution and determining the free chloride concentration in the cement pore solution. The most widely used methods, together with their advantages and disadvantages, are described bellow

2.5.1. Extraction by Squeezing Under High Pressure

This method involves extracting the pore solution from cylindrical samples of concrete using a high-pressure device and analysing the extract. As mentioned by Arya and Newman (1990), this method was first reported by Longuet *et al.* in 1973. Barneyback and Diamond (1981) developed the pore solution extraction device that was used later by others (Maslehuddin *et al.*, 1997; Rasheeduzzafar *et al.*, 1991; Byfors *et al.*, 1986).

Figure 2.3 shows the pore press device developed by Barneyback and Diamond (1981). As the load is applied, the specimen fractures and then remoulds. Pore fluid extracted during this period collects in the drain ring scribed in the upper face of the lower platen. The fluid is drawn off by means of a syringe via a stainless steel fluid drain and a short length of plastic tubing. The extracted fluid can then be analysed by potentiometrically titrating.

Most researchers have reported that the pore press method gives accurate measurements for free chlorides. Arya and Newman (1990) reported that, irrespective of whether chlorides are introduced internally or externally, the fluid extracted through the pore pressure technique is representative of the fluid in the specimen. They also concluded that the chloride concentration of the expressed solution is the same as that in the pore fluid, regardless of the pressing procedure. According to Tritthart (1989), using the pore extraction method, comprehensive information can be obtained not only on chloride content, but also on the type and concentration of all substances dissolved in the pore water. The pore solution extraction method is known to be more accurate when used on cement paste as compared to concrete (Sandberg, 1999).

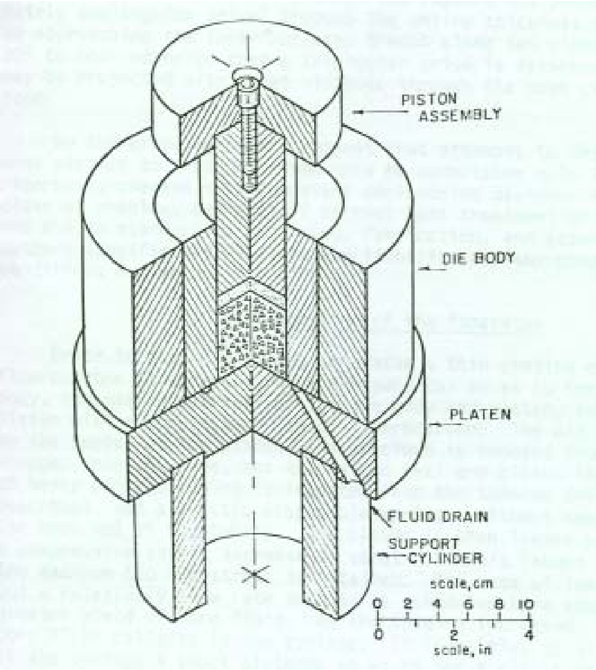

Figure 2.3: Isometric half-section of pore extraction device.

(Barneyback & Diamond, 1981)

However, although the pressing procedure is relatively straightforward, there are a number of practical difficulties associated with the pore press. Pore presses are not, currently, commercially available. The removal of cores from concrete structures is an expensive and often destructive operation. Furthermore, a proportion of the free chloride is leached during coring. The most notable difficulty is the evaporation of the free water. These difficulties will limit the use of this method as a routine part of investigative surveys of existing structures (Arya and Newman, 1990).

Pore solution extraction under pressure results in the release of some loosely bound chloride that, in turn, may result in an overestimation of the level of free chloride. Failure to take these loosely bound chlorides into account may result in errors when using the resulting binding relationship to model chloride transport. (Glass *et al.*, 1996)

2.5.2. Leaching Method

Leaching methods are based on mixing powdered samples with a solvent and measuring the amount of chloride passing into the solution. Water or ethanol is used as the solvent for this method (Tritthart, 1989). This is a standard method described in the ASTM standard C1218 with water as the solvent. Some researchers referred this technique as the "decantation method" (Haque and Kayyali, 1995). According to the ASTM standard C1218, specimens previously exposed to a chloride solution are crushed and sieved through an 850µm (No. 20) sieve. 10 g of the sieved powder and 50 mL of deionised water are mixed and stirred and then boiled for five minutes. The boiled sample is then sealed and stored for 24 hours. After 24 hours, the mixture is thoroughly stirred and decanted over a filter paper. The filtrate is then used for Cl^- determination using a potentiometer.

The amount of chloride ions released into the solution depends upon the method adopted, which involves factors like the fineness of the pulverized sample, the amount of water added, the temperature, the agitation method, and the time allowed (Arya *et al.*, 1987)

Arya *et al.* (1987) showed that ethanol is ineffective as a leaching solvent and grossly underestimates the free chloride content, whereas the leaching technique that used water as a solvent gave values comparable to those resulting from the pore press technique. Hence, they suggested that leaching techniques offer a more practical method of determining the free chloride content than the pore press.

However, Haque and Kayyali (1995) found that the chloride ion concentration determined from the leaching technique gave an overestimation of the chloride ions in the pore solution.

2.5.3. Quantitative X-ray Diffraction Analysis.

This method is the indirect method for determining the free chloride concentration in concrete. A method based on using quantitative X-ray diffraction analysis is used for determining the amount of bound chloride in the C_3A phase of cement paste. The total chloride content is determined by a standard method and then the amount of free chloride is calculated by deducting the bound chloride from the total chloride. The results showed reasonable agreement with corresponding pore press values. At this stage of development, the method overestimates free chloride content since no account is taken of binding due to C_2S, C_3S and C_4AF phases. However, quantitative X-ray diffraction analysis is an expensive technique and it is unlikely that its use would become commonplace for such a purpose (Arya and Newman, 1990)

2.6. Method for Determining the Total Chloride Content

2.6.1. Acid Soluble Extraction

To determine the total chloride content, the standard method mentioned in ASTM C 114-04 is to dissolve a cement or concrete sample in concentrated acid. The powdered sample is dispersed in water and nitric acid is added slowly to it. Then the mixture in the beaker is covered and heated rapidly until boiling. After that, it is filtered and the filtrated sample is analysed for chloride content by using potentiomentric titration. Al-Hussaini *et al.* (1990) noted that the determination of the total chloride content using acid soluble extraction might be inaccurate. While the quantity of chloride extracted increases with the nitric acid concentration and temperature, even aggressive conditions such as boiling nitric acid might result in less than 90% of the total chloride being determined (Dhir *et al.*, 1990).

Acid soluble extraction may underestimate the total chloride content of samples. Possible reasons for this include errors associated with the method as well as its failure to release all strongly bound chloride (Glass *et al.*, 1996).

2.7. Experimental Method for Determining the Chloride Diffusion in Concrete

In saturated concrete, chloride ions are penetrated by a pure diffusion technique where the difference in concentration is the driving force. In the case of pure diffusion, the penetration rate of chloride ions is usually calculated using experiments assuming steady-state or non-steady-state flow. In the case of steady-state flow (Goto and Roy, 1981; Page *et al.*, 1981) a "diffusion cell" made of two chambers separated by a cement paste sample was used. One chamber was filled with a chloride solution while the other had no chloride at all. The effective diffusion coefficient (D_{eff}) was calculated using Fick's first law:

$$-J(x) = D_{eff} \frac{dC(x)}{dx} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.9)$$

This method is time consuming and a constant concentration has to be maintained in the chamber containing the chloride solution and also in the chloride free chamber (Andrade, 1993).

In the case of non-steady-state flow conditions, concrete blocks are maintained in contact with a solution of constant chloride concentration and the chloride profile is measured as a function of time (Andrade, 1993). In this case, Fick's second law is used to calculate the apparent diffusion coefficient (D_a):

$$-J(x) = \frac{\partial C(x)}{\partial t} = D_a \frac{\partial^2 C(x)}{\partial x^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.10)$$

This type of test is also very time consuming and exhibits several uncertainties regarding the rigorous application of Fick's law. Figure 2.4 shows the diffusion cell used by Andrade and Sanjuan (1994).

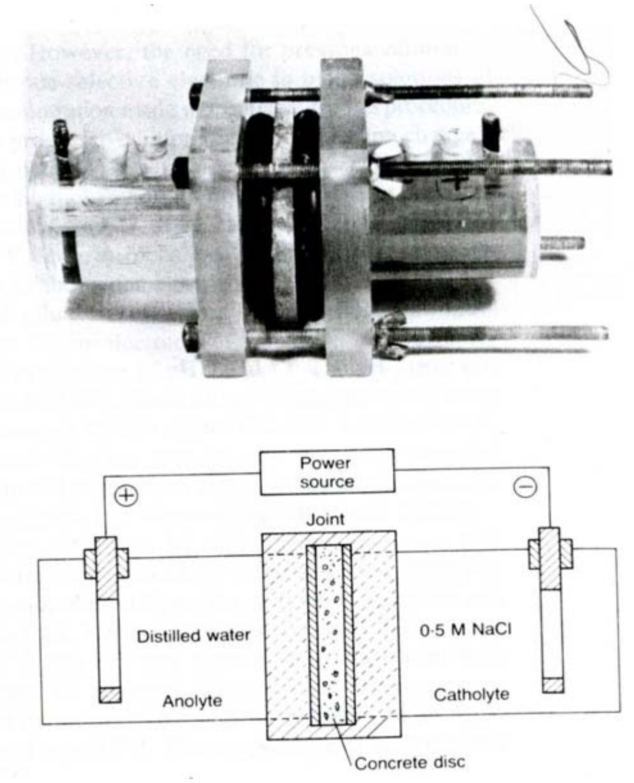

Figure 2.4: Cell used for diffusion experiment. (Andrade and Sanjuan, 1994)

Since the natural diffusion experiments are time consuming, attempts have been made to calculate the diffusion coefficient during shorter experiment. Some researchers determined the diffusion coefficient from resistivity measurements (Buenfield and Newman, 1984). Some others accelerated the rate of penetration by applying an electrical field (Goto and Roy, 1981; Li and Roy, 1986; Hansen *et al.*, 1990; Detwiler *et al.*, 1991).

The application of an external electrical field to force ionic transport through concrete was first used in the late seventies, but its theoretical basis has only recently begun to be studied (Andrade, 1993).

Currently, the most frequently used methods for the determination of salt diffusion coefficients in concrete use the experimental set-up designed for the so-called ‘‘Rapid Chloride Permeability Test’’ (sometimes called the ‘‘Migration Test’’), which was developed at the beginning of the 1980s in the USA (AASHTO, 1983). The experiment uses two cells separated by a plate specimen of the measured material. In measuring chloride diffusion, cell 1 normally contains a NaCl solution, and cell 2 is filled with a NaOH solution of the same molar concentration as that of the chloride source solution. Two meshes of electrodes are fitted, one on each side of the concrete specimen, in such a way that the electric field is applied primarily across the test specimen (Cerny *et al.*, 2004). After establishing steady-state conditions, the diffusion coefficient can be determined using the Nernst–Planck equation (Andrade, 1993):

$$-J_j(x) = D_j \frac{\partial C_j(x)}{\partial x} + \frac{z_j F}{RT} D_j C_j \frac{\partial E(x)}{\partial x} + C_j V(x) \quad \ldots\ldots\ldots\ldots\ldots\ldots (2.11)$$

Under saturation conditions, the forced velocity can be neglected because there is no head difference. By assuming a constant electrical field across the sample, the above equation can be simplified for the effective diffusion (Andrade, 1993) as:

$$D_{eff} = \frac{J.R.T.l}{z.F.C.\delta E} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.12)$$

in which all parameters are known and the chloride flux, J, can be calculated from the slope of the linear part of the downstream chloride plot against time, and l is the thickness of the sample disc.

Andrade (1993) mentioned some limitations of this method. In the case of oxidable electrodes, a dissolution of metals and oxides will be generated; for example, in the case of graphite electrodes, the dissolution process will be: $C \rightarrow CO + CO_2$. Again, if the voltage difference is too high, then there will be an evolution of chloride gas in the positive electrode through the reaction: $2Cl^- \rightarrow Cl_2 + 2e^-$. When the voltage is applied, not only chloride, but also other ions start moving and thus this test accounts for the total current, not that due to the chloride only. The high voltage drop causes heat formation, which in turn changes flow speed.

Truc *et al.* (2000) used the upstream flux to determine the chloride diffusion coefficient and reported that the value is equal to the diffusion coefficient from the downstream flux. McDonald and Northwood (1995) used stirrers in both cells to prevent chloride ion gradients building up at the cement paste disc-solution interfaces.

Another possibility for determining the salt diffusion coefficient is to use a mathematical analysis of measured salt profiles. A typical experiment for the determination of the salt profile in a concrete specimen was described by Baroghel-Bouny *et al.* (1997, as mentioned in Cerny, 2004). After curing the concrete samples in a wet condition, they were exposed to a chloride solution on one face to allow the chloride penetration in one dimension only. After a certain time, they were sliced near the surface for chloride analysis. Total and free chloride ion measured by potentiometric titration using a titrated silver nitrate solution and the chloride profiles were plotted. The diffusion coefficient was determined using the simple analytical solution of the parabolic problem with an error function:

$$C(x,t)=C_0\left[1-\operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right] \quad \text{………………………..} \; (2.13)$$

2.8. Summary

This chapter summarized the published studies related to chloride binding in concrete. To evaluate the lifespan of steel reinforced concrete structures, it is necessary to determine the free chloride profile in concrete exposed to different environmental conditions. This chapter briefly reviewed the currently available models for calculating the chloride ion profile in concrete along with their limitations. The previous sections also dealt with relevant topics such as the mechanism of chloride binding, the different factors affecting chloride binding, and the current methods to determine the free and total chloride concentrations, along with their advantages and disadvantages. The various methods used for determining the chloride diffusion coefficient were reviewed in this chapter. Examination of the published data revealed the following:

1. Very few existing models considered the binding of chloride ions in concrete in their calculation of the chloride profile. Moreover, those who considered the chloride binding were not able to predict the chloride binding under arbitrary environmental conditions.
2. There is no clear explanation available regarding the mechanism of releasing bound chlorides due to carbonation and also the role of pH in this process.
3. More chloride ions are bound if the chloride source is calcium chloride compared to sodium chloride. The published research does not provide a decisive explanation for what is causing this.

Therefore, the purpose of this research is to develop an approach which can be used for calculating the chloride profile in concrete, considering all relevant chemical interactions between chloride ions and the cement phases exposed to general environmental conditions, and also to find the proper and detailed solution of some unresolved matters in the literature such as the relationship of pH to the carbonation of Friedel's salt and the reason behind the effect of chloride sources on chloride binding.

CHAPTER 3

……

Modeling for Chloride Binding

3.1 Introduction

A number of methods to predict the chloride ion concentration profiles in cement paste have been proposed by various researchers (Tang and Nilsson, 1992; Sanjuan, 1994; Funahashi, 1990). The most common method used in the published research is the application of Fick's second law for chloride diffusion. For chloride binding, different chloride binding isotherms, such as the Langmuir isotherm or the Freundlich isotherm, have been used. Chloride binding isotherms describe the relationship between free and bound (or total) chlorides in concrete at a given temperature. They are unique to each cementious system since they are influenced by different factors, such as the type of cement, pH of solution, presence of carbonation, etc. Thus, the models used in the literature can be used for only one exposure condition and only for one specific type of cement, while in reality, the chloride attack in concrete structures occurs because of exposure to different elements, such as sea water, de-icing salt, and chloride-laden soil, or in industries such as food industries (osterias, etc.). Hence, there is a need for one approach that does not depend only on the chloride binding isotherm and that takes into account the detailed mechanisms of chloride binding along with the factors that influence chloride binding.

This chapter describes the theory of chloride binding in hydrated cement paste along with the component of the proposed reactive transport model.

3.2 Concrete Chemistry

Chloride binding takes place in the cement paste component of concrete. Thus, it is necessary to understand the chemistry of the cement paste to understand chloride binding in concrete. Cement paste is the product of hydration reactions of the constituents of cement. The main constituents of cement are $3CaO.SiO_2$ (C_3S = tricalcium silicate), $2CaO.SiO_2$ (C_2S = dicalcium silicate), and, in lesser amounts, $4CaO.Al_2O_3.Fe_2O_3$ (C_4AF = calcium aluminoferrite), $3CaO.Al_2O_3$ (C_3A = tricalcium aluminate) and $CaSO_4.2H_2O$ (gypsum). When cement is exposed to water, a series of reactions called "hydration reactions" occur between the cement constituents and water. Both calcium silicates (C_3S and C_2S) combine with water to form gel-like calcium silicate hydrates (C-S-H) and calcium hydroxide (CH) (Papadakis *et al.*, 1991).

$$2\left(3\mathrm{CaO.SiO_2}\right) + 6\mathrm{H_2O} \rightarrow \underset{\text{(C-S-H-gel)}}{3\mathrm{CaO.2SiO_2.3H_2O}} + 3\mathrm{Ca}\left(\mathrm{OH}\right)_2 \quad \text{.............. (3.1)}$$

$$2\left(2\mathrm{CaO.SiO_2}\right) + 4\mathrm{H_2O} \rightarrow \underset{\text{(C-S-H-gel)}}{3\mathrm{CaO.2SiO_2.3H_2O}} + \mathrm{Ca}\left(\mathrm{OH}\right)_2 \quad \text{.............................. (3.2)}$$

A portion of the $Ca(OH)_2$ is consumed during the hydration of the other constituents of Portland cement, C_4AF and C_3A. In the presence of gypsum, which is added to control "flash set", these hydration reactions are (Papadakis *et al.*, 1991):

$$4\,\mathrm{CaO.Al_2O_3.Fe_2O_3} + 2\mathrm{Ca(OH)_2} + 2\left(\mathrm{CaSO_4.2H_2O}\right) + 18\mathrm{H_2O} \rightarrow 6\,\mathrm{CaO.Al_2O_3.Fe_2O_3.2CaSO_4.24H_2O} \quad \text{...(3.3)}$$

$$3CaO.Al_2O_3 + \left(CaSO_4.2H_2O\right) + 10H_2O \rightarrow 3CaO.Al_2O_3.CaSO_4.12H_2O \text{ ....}(3.4)$$

When practically all gypsum has been consumed, the hydration reactions of C_4AF and C_3A produce AFm phases (Papadakis *et al.*, 1991):

$$4CaO.Al_2O_3.Fe_2O_3{+}4Ca(OH)_2 \rightarrow 6CaO.Al_2O_3.Fe_2O_3.2Ca(OH)_2.24H_2O \text{ ....}(3.5)$$

$$3CaO.Al_2O_3{+}Ca(OH)_2{+}12H_2O \rightarrow 3CaO.Al_2O_3.Ca(OH)_2.12H_2O \text{ ....}(3.6)$$

The AFm phases are anionic clay minerals that have positively charged main layers (fig.3.1). Anions incorporated between the layers balance the charge on the main layers. Water molecules are also incorporated into the interlayer. These phases crystallize as thin pseudo-hexagonal plates, composed of distorted portlandite-like octahedral layers, in which one third of the Ca^{2+}sites are occupied by Al^{3+} or Fe^{3+}. The substitution of Al^{3+} or Fe^{3+} for Ca^{2+} generates the net positive charge in the octahedral layers, and this substitution always occurs in a stoichiometric 2:1 ratio (Suryanvanshi *et al.*, 1996). In addition to anions, the inter-layer contains water molecules, and its water content varies with the type of anion. The inter layer anion can be easily exchanged.

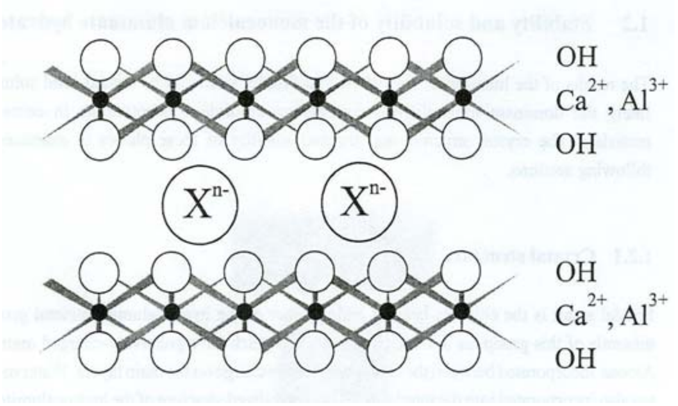

Figure 3.1: Schematic showing the ion exchange between the chloride ion and the hydroxyl ion (Glasser, 1999).

3.3 Chloride Binding

Chloride binding involves the processes through which chloride ions in the pore solution of concrete are fixed to different extents on certain cement hydrates. The term “bound chlorides” applies to any chloride ions that are not able to move freely in the pore solution of concrete. Chloride binding processes are generally classified into two categories: chemical binding and physical binding.

3.3.1 Chemical Binding

Chemical binding is the result of chemical reactions between chloride ions and certain cement hydration products, leading to the binding of chloride ions. The final product of the chemical binding of chloride ions is Friedel’s salt ($3CaO.Al_2O_3.CaCl_2.10H_2O$), which is another AFm phase, and its composition is $[Ca_2Al(OH)_6.2H_2O]^+.Cl^-$. In the case of admixed chlorides, the chloride ions are bound in the interlayer of the principal layers, $[Ca_2Al(OH)_6.2H_2O]^+$, of the AFm structures to balance the charges during the hydration process to form Friedel’s salt. However, if gypsum is present, it creates competition for available interlayer anions between chloride and sulphate ions. Sulphate ions being preferable to chloride ions, ettringite usually forms first, then Friedel’s salt will form after all the sulphate is consumed (Enevoldsen *et al.*, 1994).

In the case of external chloride ions that penetrate into hardened cement paste, the situation is different since most of the interlayer sites are already occupied by other anions like sulphate, carbonate, and hydroxide. In that case, chloride ions are bonded by ion exchange reactions to form Friedel’s salt. The ion exchange mechanism suggested in this study describes chloride binding as a replacement of hydroxide ions present in the interlayers of a hydroxy AFm phase by chloride ions present in the pore solution. This ion exchange mechanism leads to the formation of Friedel's salt, as expressed in the following reaction (Suryanvanshi *et al.*, 1996):

$$R^{+}\text{-}OH^{-} + Cl^{-} \rightarrow R^{+}\text{-}Cl^{-} + OH^{-} \text{ ....(3.7)}$$

where R is the principal layer of hydroxy AFm, $\left[Ca_2Al\left(OH\right)_6.2H_2O\right]^{+}$.

The complete exchange of ions does not always occur. Some compounds containing partly exchanged OH^{-} are often present, such as in $3CaO.Al_2O_3.nCa\left(OH\right)_2.(1\text{-}n)CaCl_2.xH_2O$. But for simplicity, we considered here that complete exchange occurs.

The equilibrium constant for the exchange reaction is given by:

$$K_{Cl/OH} = \frac{\{R\text{-}Cl\}\ \{OH^{-}\}}{\{R\text{-}OH\}\ \{Cl^{-}\}} \text{ ....(3.8)}$$

Brackes in the equation denote activities.

3.3.2 Physical Binding

Physical binding is the result of the physical adsorption of chlorides on the surface of the CSH-gels. Physical adsorption is due to electrostatic or Van der Waals forces between charged particles. In this case, the force is between the chloride ions and the surface of the C-S-H. The surface of the hydrated cement is negatively charged (Chatterji and Kawarmura, 1992), but due to the adsorption of cations (Ca^{2+}, Na^{+}) in the alkaline pore solution and the formation of a stern layer (Laidler and Meiser, 1995), the surface appears to be positively charged. This leads to the formation of an electrical, diffuse, double layer and the adsorption of negatively charged chloride ions takes place in the diffuse double layer to satisfy the electro neutrality. The adsorption capacity in the double layer depends on the surface area of the C-S-H, on the potential, and on the plane between the adsorbed cations and the diffuse double layer. The physical binding has been neglected in the current model.

3.4 Description of the Proposed Reactive Transport Model

The model consists of two main parts: one is the reaction, which deals with chemical reactions such as speciation and ion exchange, and the other deals with the transport. In our case we only considered the diffusion process for the transport of chloride ions as shown in figure 3.2.

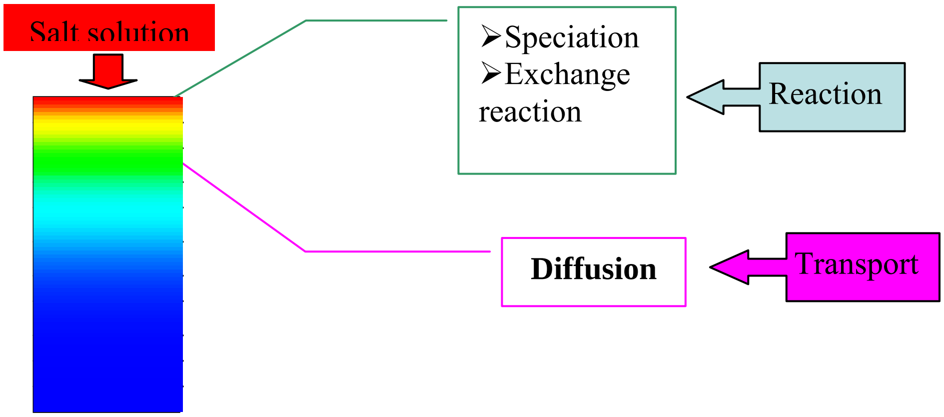

Figure 3.2. Schematic diagram of diffusion-reaction model

3.4.1 Equation for Reaction Modeling

The main equations used to determine the amount of unknown species are the mass action equation and mass balance equation.

The mass action reaction is as follows (Zhu and Anderson, 2002):

$$K_i = a_i \prod_m^M a_m^{-x_{m,i}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.7)$$

The mass balance equation for the component represented by master species m is:

$$Total_m = a_m + \sum_j^N a_{m,j} x_{m,j} \qquad \text{..............................} \ (3.8)$$

The dependence of the equilibrium constant (K) on temperature is modeled by the following equation:

$$\ln K = \frac{-\Delta_r H^o}{RT} + \frac{-\Delta_r S^o}{R} \qquad \text{..................................} \ (3.9)$$

where:

$\Delta_r H^o$ is the standard heat of reaction,

$\Delta_r S^o$ is the change of entropies of reaction in standard state, and

R is the gas constant.

The relationship between the activity (a_i) and concentration (m_i) of a species is given by:
$a_i = \gamma_i \times m_i$

The activity coefficient can be calculated using different equations for different ranges of concentrations. The concentrations and charges of ions in a solution are expressed by means of its ionic strength, defined as (Zhu and Anderson, 2002):

$$I = \frac{1}{2} \sum_i m_i z_i^2 \ \text{...} \ (3.10)$$

When $I < 0.1$, the activity coefficient can be determined using the Debye-Huckel equation (zhu and Anderson, 2002):

$$\log \gamma_i = -A z_i^2 \frac{\sqrt{I}}{1 + B a^\circ \sqrt{I}} \ \text{..} \ (3.11)$$

The Davies Equation is used for ionic strengths of up to $I = 0.5$:

$$\log \gamma_i = \frac{-Az_i^{\,2}\sqrt{I}}{1 + a^\circ \sqrt{I}} + 0.2Az_i^{\,2}I \text{ ....(3.12)}$$

For higher ionic strengths, the Pitzer method is used. The Pitzer method is valid for ionic strengths I< that are higher than 0.5. The Pitzer model equations for logarithms of activity coefficients of cations (M), anions (X), and neutral species (N) are given below for a solution containing an indefinite number of both neutral and ionic solutes. In each case, the summations of terms arising from the presence of individual salts, neutral species, and their mixtures are indicated.

For cations:

$$\begin{aligned}
\ln \gamma_M &= z_M^2 F + \sum_a m_a (2B_{Ma} + ZC_{Ma}) && \text{(i)} \geq \text{salt} \\
&\quad + |z_M| \sum_c \sum_a m_c m_a C_{ca} && \\
&\quad + \sum_c m_c \left(2\Phi_{Mc} + \sum_a m_a \Psi_{Mca} \right) && \text{(ii)} \geq 2 \text{ cations} \\
&\quad + \sum_a \sum_{<a'} m_a m_{a'} \Psi_{Maa'} && \text{(iii)} \geq 2 \text{ anions} \\
&\quad + 2\sum_n m_n \lambda_{Mn} + 3\sum_n m_n^2 \mu_{Mnn} && \text{(iv)} \geq 1 \text{ neutral} \\
&\quad + 6\sum_n \sum_{<n'} m_n m_{n'} \mu_{Mnn'} && \text{(v)} \geq 2 \text{ neutrals} \\
&\quad + 6\sum_n \sum_a m_n m_a \zeta_{Mna} && \text{(vi)} \geq 1 \text{ anion}, \geq 1 \text{ neutral} \\
&\quad + 6\sum_n \sum_c m_n m_c \eta_{Mnc} && \text{(vii)} \geq 2 \text{ cations}, \geq 1 \text{ neutral}
\end{aligned}$$

For anions:

$$\begin{aligned}
\ln \gamma_X &= z_X^2 F + \sum_c m_c (2B_{cX} + ZC_{cX}) && \text{(i)} \geq \text{salt} \\
&\quad + |z_X| \sum_c \sum_a m_c m_a C_{ca} &&
\end{aligned}$$

$$
\begin{aligned}
&+\sum_{a} m_a \left(2\Phi_{Xa} + \sum_{c} m_c \Psi_{cXa} \right) && \text{(ii)} \geq 2 \text{ anions} \\
&+\sum_{c}\sum_{<c'} m_c m_{c'} \Psi_{cc'X} && \text{(iii)} \geq 2 \text{ cations} \\
&+2\sum_{n} m_n \lambda_{Xn} + 3\sum_{n} m_n^2 \mu_{Xnn} && \text{(iv)} \geq 1 \text{ neutral} \\
&+6\sum_{n}\sum_{<n'} m_n m_{n'} \mu_{Xnn'} && \text{(v)} \geq 2 \text{ neutrals} \\
&+6\sum_{n}\sum_{c} m_n m_c \zeta_{ncX} && \text{(vi)} \geq 1 \text{ cation, } \geq 1 \text{ neutral} \\
&+6\sum_{n}\sum_{a} m_n m_a \eta_{Xna} && \text{(vii)} \geq 2 \text{ anions, } \geq 1 \text{ neutral}
\end{aligned}
$$

Where:

B, C, and Z are Pitzer Functions and

Φ is a function that contains parameters for interactions between ions of like sign and an unsymmetrical mixing term.

The parameters Ψ account for interactions between one ion of one sign and two dissimilar ions of opposite signs.

3.4.2 Ion exchange reaction

In the proposed approach, the mechanism of chloride binding in hydrated cement paste phases is assumed to occur through ion exchange. When solid substances come in contact with an aqueous solution, they show a marked tendency to lose certain components while retaining others. When this occurs, the components that are lost are replaced with similar species from the solution, but the basic structure of the original material is preserved. When the species lost or gained is ionic, the phenomenon is called ion exchange (Garrels and Christ, 1965).

The ion exchange reaction involves the process of exchanging an equivalent amount of ions from a binding site with more selective ions in the solution. The selectivity depends on the affinity of the ion to the binding sites. Ion exchange reactions are reversible processes. The equation of the ion exchange reaction can be written as:

$$\mathrm{mC_1^n+n\overline{C_2} \leftrightarrow m\overline{C_1}+nC_2^m} \quad \text{..........................(3.13)}$$

where:

n is the valence for ion 1,

m is the valence for ion 2,

C_1 is concentration of ionic species 1 in the solution phase,

$\overline{C_1}$ is concentration of ionic species 1 in the solid phase,

C_2 is concentration of ionic species 2 in the solution phase, and

$\overline{C_2}$ is concentration of ionic species 2 in the solid phase.

The thermodynamic equilibrium coefficient (K_{ex}) for ion exchange reactions expressed in the above equation, according to the law of mass action, can be written as:

$$K_{ex} = \frac{\left[\overline{C_1}\right]^m \left[C_2\right]^n}{\left[C_1\right]^m \left[\overline{C_2}\right]^n} \text{..(3.14)}$$

where the bracketed terms are the thermodynamic concentrations or activities.

Assuming that the total concentrations in both the solution and solid phases are constant, we can write the following relations:

$$nC_1 + mC_2 = C_0 \text{...............(3.15)}$$

$$n\overline{C_1} + m\overline{C_2} = \overline{C_0} \text{...............(3.16)}$$

where C_0 is the total solution concentration of ions 1 and 2, and $\overline{C_0}$ is the total solid concentration of ions 1 and 2 sorbed on the porous medium, measured as the ion exchange capacity. Using these two equations, we can rewrite the equation for the equilibrium constant in terms of only one ion as:

$$K_{ex} = \frac{\left[\overline{C}\right]^m \left[\left(C_0 - nC\right)/m\right]^n}{\left[C\right]^m \left[\left(\overline{C_0} - n\overline{C}\right)/m\right]^n} \text{.............................}(3.17)$$

Following the above equation, we can determine the relation of free ions and bound ions by knowing the exchange capacity and the equilibrium constant.

3.4.3 Equation for Transport Modeling

The core of the transport model is the balance equation of the extensive quantity of the ions in the pore solution, also referred to as the diffusion-reaction equation, and can be written as (Zhu and Anderson, 2002):

$$\frac{\partial \phi c_i}{\partial t} = D\frac{\partial^2 c_i}{\partial x^2} - v\frac{\partial C_i}{\partial x} + \sum_{k=1}^{n} R_i \text{ ....} (3.18)$$

in which c_i denotes the concentration (mass per unit volume) of the i^{th} species, R_i represents the source (or sink) term (i.e. the change in mass (due to chemical reactions) of the i^{th} species per unit volume of solution), D denotes the coefficient of molecular diffusion in concrete, and ϕ denotes the porosity. In the above equation, the mass of species are increased or eliminated in the source term by a number of mechanisms. These mechanisms may include homogenous reactions (chemical reactions within the aqueous phase itself) and heterogeneous reactions (reactions between the aqueous phase and solid phase, e.g., ion exchange and adsorption, precipitation/dissolution, etc.).

3.5 Software package selection

The successful prediction of the amount of free chlorides, bound chlorides, carbonation front, and their synergistic effects in porous media in general, and concrete in particular, requires the development or usage of a reactive transport computer code with the following attributes:

- the ability to handle transport by pure diffusion (most common mechanism under saturated conditions in concrete),
- the ability to handle high ionic strengths (typically seawater values and higher), and
- the ability to handle anion exchange for at least Cl^- and CO_3^{2-}.

Fortunately, a software package with all the above attributes already exists and was used in this study. PHAST, a computer program for simulating ground-water flow, solute transport, and multicomponent geochemical reactions, developed by David L. Parkhurst *et al.* 1980 at USGS, has been selected (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phast/abstract.html).

PHAST can be considered to be a member of the PhreeQC-based reactive transport models in which the flow and transport calculations are handled by a modified version of the code HST3D (http://wwwbrr.cr.usgs.gov/projects/GW_Solute/hst/index.shtml), which is restricted to constant fluid density and constant temperature, while the geochemical reactions are simulated with the geochemical model PHREEQC (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/index.html).

3.6 Validation tests for the software package

Although PHAST is a robust software package that has undergone extensive testing by the developers and users around the globe, it was still important to check whether it has the ability to predict some simple problems for which an analytic solution is known. This could be very useful in developing confidence in the predictions when dealing with more complicated problems.

Given the above required attributes, the following numerical tests were carried out.

- Transport by pure diffusion under constant boundary concentration.
- Estimation of the exchangeable cations in dune sand in equilibrium with dunewater (example from Appelo and Postma).
- Estimation of the exchanger composition using the Rothmund-Kornfeld equation for Brucedale subsoil (example from Appelo and Postma).

a) Transport by pure diffusion (Dirichlet boundary condition)

One mol/L of chloride solution was allowed to diffuse through a column with a diffusion coefficient of 1×10^{-12} m^2/s. This one dimensional simulation was run in PHAST and the result was compared with the analytical solution as predicted by Fick's second Law. The PHAST input files for these simulations are provided in Appendix A.

Figure 3.3 clearly shows that PHAST can predict exactly the same answer for the chloride distribution through depth as the analytical solution for all the times considered (5, 10, and 15 years).

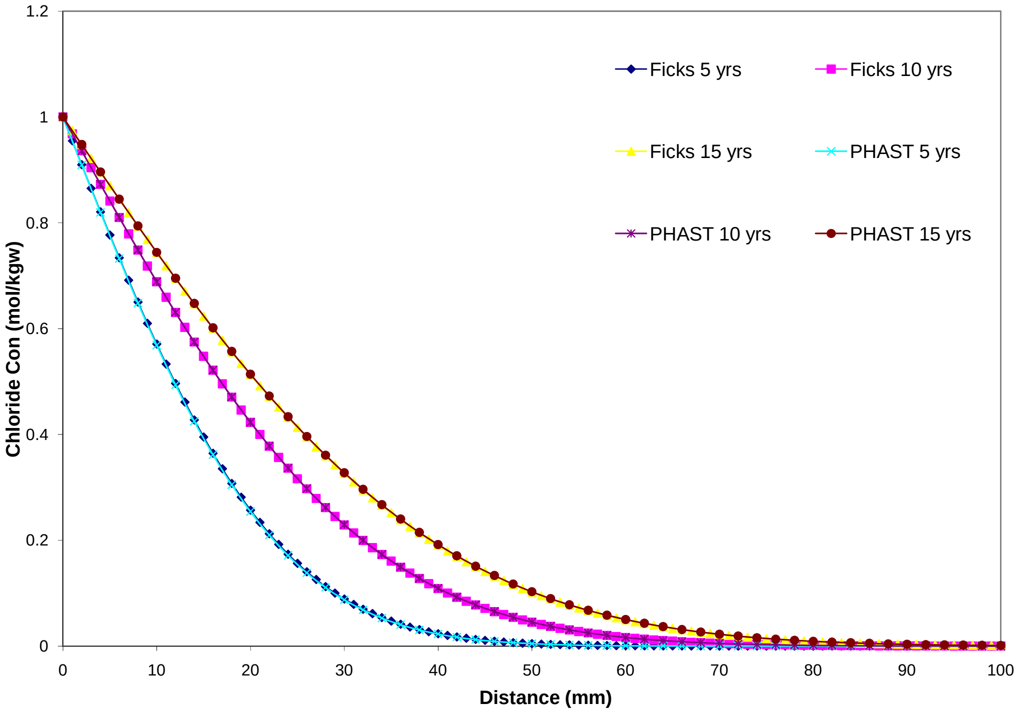

Figure 3.3: Comparison of PHAST simulation results with Fick's Law for chlorides ingress in 1D column by pure diffusion.

b) Estimation of the exchangeable cations in dune sand (Appelo and Postma, 2005)

This simulation involves calculating the exchangeable cations in dune sand with a CEC of 10 meq/kg (60 meq/L), in equilibrium with dunewater, Na^+ = 1.1, Mg^{2+} = 0.48, Ca^{2+} = 1.9 mmol/L. The equivalent fractions of Ca, Mg, and Na were calculated with PHREEQC and compared with the hand calculation done by Appelo and Postma (2005). The input and output files for this simulation are attached in Appendix A. Table 3.1 shows that PHREEQC results are in very good agreement with the analytical solution.

Table 3.1: Comparison of PhreeQC simulation results with analytical solution for cation exchange for dune sand.

Species	**Equivalent fraction by PHREEQC**	**Equivalent fraction by Hand Calculations**
CaX2	0.854	0.853
MgX2	0.136	0.138
NaX	0.00929	0.00932

c) Estimation of the exchanger composition using the Rothmund-Kornfeld equation for Brucedale subsoil (Appelo and Potema, 2005)

The exchange species CaX_2 is defined as:

$$0.618Ca^{+2} + 2KX = CaX_2 + 1.236K^+$$

Initially, the simulation was started with 100 mmol of K^+ in the presence of 417 mmol of KX exchanger. Then, Ca^{2+} was added while K^+ was removed and the K/Ca isotherm was plotted. The isotherm was compared with the observed data taken from Bloom and Mansell (2001) as shown in Figure 3.4. Figure 3.4 shows that the isotherm from PHREEQC results is in very good agreement with the experimental data obtained by Bloom and Mansell.

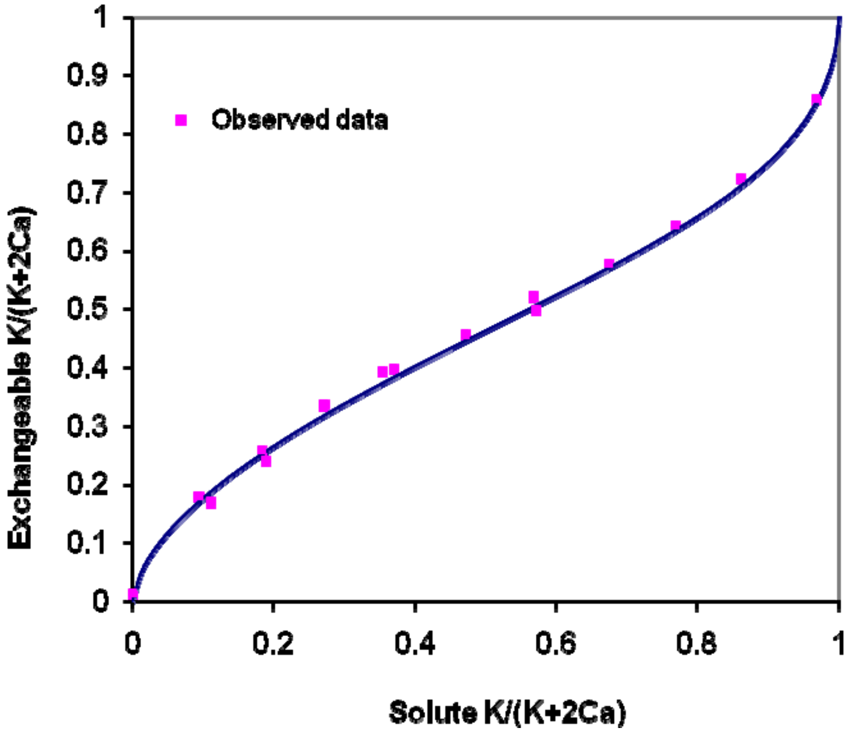

Figure 3.4: The K/Ca isotherm simulated by PHREEQC compared with observed data

Thus, it is apparent that the software package, PHAST, can produce very good results that are in agreement with numerical results and also experimental results aivailable in published literature.

CHAPTER 4

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Experimental Programme

In this study, a new approach is proposed that can calculate the amount of free chloride ions in concrete, considering the detailed mechanisms of chloride binding. The chloride ions are bound in cement paste through an ion exchange mechanism involving the exchange of hydroxide ions in the hydrated cement phases by chloride ions from the pore solution. To calculate the amount of free chloride ions, it is necessary we have to know the exchange capacity of the hydrated cement paste and the equilibrium constants for the ion exchange reactions, which are not available in the literature. The exchange capacity and equilibrium constants were determined through an inverse process, running simulations for chloride isotherms using the model and comparing the simulated curve with the experimental data. It is also necessary to know some transport parameters, such as porosity and the diffusion coefficient for chloride ions in concrete, for the simulation. The experimental data for chloride isotherms, as well as the diffusion coefficients, are available in the published studies, but these values are different for different types of cement samples and also depend on various factors. Hence, to determine the unavailable parameters required for the model and to verify it, all the experiments were carried out on samples for which all the properties are known. Thus, the experimental program is divided into two major parts.

- Part 1 is focused on the calibration of the model by determining parameters such as exchange coefficients, the amount of exchange sites, and the diffusion coefficient of chloride ions in concrete. The diffusion coefficient was determined by a steady state migration test. Experiments for determining the chloride isotherm were carried out to determine the exchange coefficients and the capacity of exchange sites in hydrated cement paste.
- In Part 2, experiments were carried out to verify the approach. Chloride isotherms were experimentally determined for different temperatures and using two chloride ion sources. Chloride profiles were determined for samples with three different water-cement ratios. The results of these experiments were compared to simulated chloride isotherms to see if the proposed ion-exchange model can capture the effects of all those different parameters.

4.1 Materials and Equipment for Experimental Programme

4.1.1 Mix Preparation

Since the binding of chloride ions takes place in the cement paste phase of concrete, we restricted our experiments to only cement pastes with different water-cement ratios. The cement used for all the experiments was CSA Type 10 Portland cement. The typical chemical compositions of Type 10 cement are given in Table 4.1 and the typical mineral compositions are given in Table 4.2 (Zibara, 2001). Three different water cement ratios were used: 0.5, 0.6, and 0.7.

Table 4.1: Chemical composition of Type-10 cement.

Chemical Composition	% by weight
SiO_2	20.7
Al_2O_3	3.68
CaO	63
Fe_2O_3	2.95
MgO	4.21
Na_2O	0.14
K_2O	0.59
SO_3	2.62
Free CaO	1.02
Loss on ignition	2.7

Table 4.2: Mineral composition of Type-10 cement.

Composition	% by weight
C_3S	50
C_2S	24
C_3A	11
C_4AF	8

The cement paste preparation is very important because the shear history of a mixture will influence its rheological behaviour. Under normal field conditions, the rolling mass of aggregate in the concrete mixer homogenizes the paste as effectively as the most vigorous laboratory mixer. Hence, a high-speed blender was used (Figure 4.1) and the mixing procedures were as follows:

1. One litre of solution was prepared at a time since the volume of the blender was 1.2 litres.

2. One third of the distilled water was added, followed by one half of the cement, then one third of the distilled water, then the remaining half of the cement, and finally the last one third of the distilled water was added.
3. The blender was closed and mixing was started at low speed (10000 rpm) for one minute.
4. Then, the speed of the blender was increased to a higher speed (15000 rpm) and mixing was continued for two more minutes.

At the end of the mixing cycle, a check was made to ensure that there were no lumps of dry cement powder in the mix. If any lumps were left, they were crushed and mixed manually and steps 2 and 3 were repeated.

Figure 4.1. High Speed Blender used for mixing of cement paste

After mixing, the paste was cast in 500 ml plastic bottles with size of 6 cm diameter and 17 cm height. The casting was done in two layers; each layer was tapped fifty times at a rate of 2 taps/second. The tops of the bottles were covered with lids to prevent the evaporation of water. To prevent segregation, the bottles were placed in a rotating wheel (operated at 12 rpm) for 24 hours (Figure 4.2). Then, they were cured at room temperature in a humidity controlled (relative humidity 71%) room for two months.

4.1.2 Equipment For Measuring Chloride Concentration

The chloride concentration in all the experiments was measured using the CMT 10 Automatic Chloride Titrator manufactured by Rdiometer Copenhagen (Figure 4.3). The CMT10 titrator performs coulometric titration, i.e., titrations in which the titrating agent is produced in the solution by electrolysis, and the amount of agent required to complete a reaction is determined by measuring the number of coulombs expended in the electrolysis.

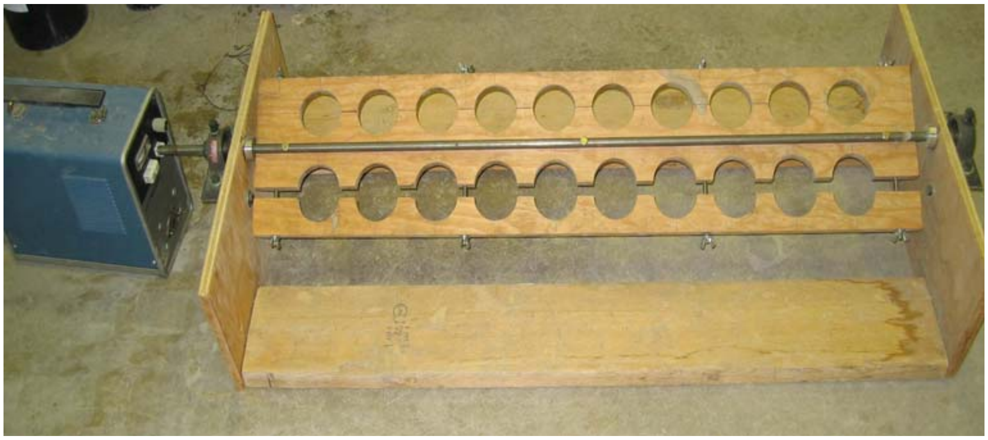

Figure 4.2: Rotating device used to prevent segregation

Figure 4.3: CMT10 Chloride Titrator used for the analysis of the chloride solutions.

4.1.3 Equipment For Measuring Solution pH

The pH of all the sample solutions was measured with a pH meter. The pH for all the sample solutions was above 12. Hence, the pH meter was calibrated using three buffer solutions of three pH levels: pH 7.0, pH 10.0, and pH 12.5. The buffer solution for pH 7.0 was prepared from 50 ml of 0.1M KH_2PO_4 + 29.1 ml of 0.1M NaOH. The solution for pH 10.0 was prepared from 50 ml of 0.05M Na_2HPO_4 + 3.3 ml of 1.0M NaOH. For pH 12.5, the buffer solution was prepared from 25 ml of 0.2M KCl + 3.3 ml of 0.2M NaOH.

4.2 Part One: Model Identification Experiments

To determine the exchange capacity and the equilibrium coefficient for the exchange reaction, the experiments were performed for the diffusion coefficient and chloride isotherms for samples of three different water-cement ratios (0.5, 0.6, and 0.7).

4.2.1 Experiment for Determining Diffusion Coefficient

The diffusion coefficient for chloride ions in cement paste was estimated using the Nernst – Planck equation that, for a steady state flux, is given by:

$$-J(x) = D_{eff} \cdot \frac{\partial C}{\partial x} + \frac{zF}{RT} D_e . C . \frac{\partial E}{\partial x} + C.V(x) \qquad \text{………………. (4.1)}$$

According to Truc *et al.* (2000), the influence of the activity coefficient on the flux of chlorides is negligible. It was found (Truc *et al.*, 2000) that the chloride binding effect does not modify the diffusion coefficient since it has no influence on chloride ion flux in the steady state. Chloride binding just leads to an increase in time lag. Since the concrete was saturated and the pressure gradient was negligible, the velocity of the solute was neglected. By assuming a constant electrical field across the sample, Eq (4.1) can be simplified for effective diffusion coefficient D_{eff} (Andrade, 1993), and it becomes:

$$\mathrm{D_{eff}} = \frac{\mathrm{J.R.T.l}}{\mathrm{z.F.C.E}} \qquad \text{………… (4.2)}$$

where *l* is the disc thickness.

In this equation, all the parameters are known and the chloride flux (J) was calculated using a steady state migration test. Two solutions with different chloride concentrations were separated with cement paste samples. Then, chloride ions moved from the higher concentration solution to the dilute solution, using only the process of diffusion as there was no head difference between the solutions. Potential difference of 25V was applied to accelerate the movement of ions. The chloride concentration at the anodic solution was measured and plotted as a function of time. The chloride flux (J) was calculated from the slope of the linear part of that plot.

4.2.1.1 Cement Paste Sample

After curing, the sample cylinders were demoulded from the bottles. Then, samples were cut into thin slices of about 6 mm in thickness so that a steady state flow could be achieved in a relatively short period of time. Special care was taken to maintain uniform thickness over the entire slice.

4.2.1.2 Electrolytic solutions and Electrodes

0.5 M of sodium chloride solution was used as the catholyte. The anolyte was distilled water instead of the NaOH solution recommended by Whiting (1981). This was based on the need to develop an active dissolution of the anodic electrode. The alkaline solutions that passivate the electrodes and the non-oxidable electrodes can develop a voltage in the electrodes that leads to water electrolysis and chloride evolution. Hence, chloride analysis in such an anodic solution gives erroneous results (Andrade and Sanjuan, 1994).

Finally, the two solutions, sodium chloride and water, were separated with the cement paste sample and, to avoid any advection, the heights of both solutions were kept the same.

4.2.1.3 Cell preparation

The schematic diagram of the diffusion cell used for the experiment is shown in Figure 4.4. To make the diffusion cell, two plastic cylinders of different diameters were used. The cylinder with the smaller diameter had both ends open with one end placed into the larger cylinder, which had one side open and the other side closed. The inside diameter of the smaller cylinder was the same as the diameter of the cement paste sample which was 6mm. The cement paste sample was sealed at one side of the smaller cylinder. Dow Corning 888 silicon joint concrete sealant was used to seal the sample to the plastic cylinder to prevent the movement of water and chloride ions between the sample and the surface of the cylinder.

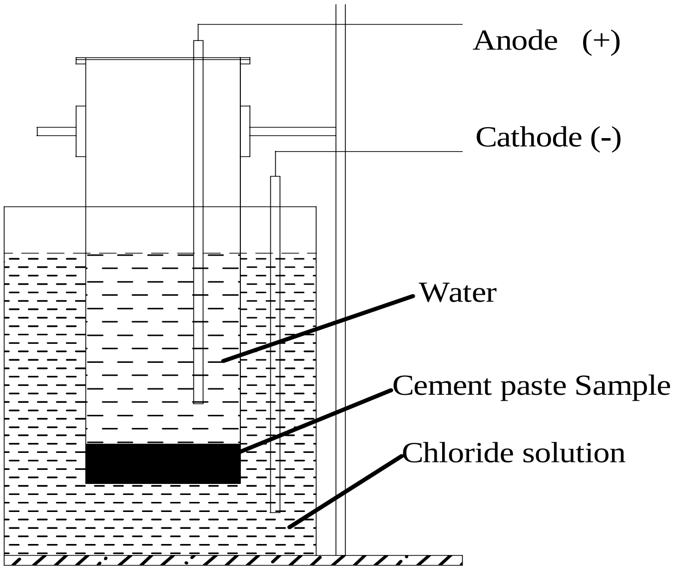

Figure 4.4: Schematic diagram of diffusion cell test

The outside cylinder was filled with 0.5 M sodium chloride solution and water was poured into the inside cylinder until the level was the same for both cylinders. The anode and cathode were added to the solution and a constant potential difference of 25V was applied between the two electrodes using a DC voltage source. Finally, the cylinders were covered to avoid any evaporation. The experimental set up is shown in Figure 4.5.

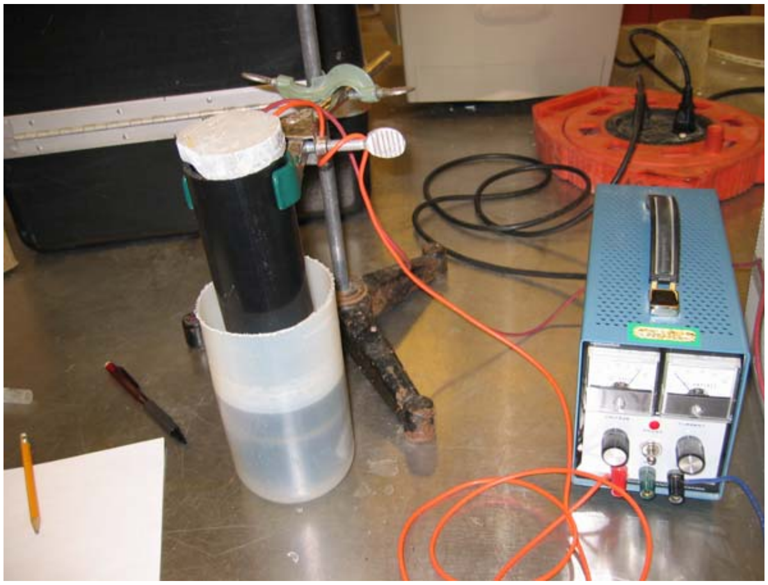

Figure 4.5: Experimental set up for migration test.

4.2.1.4 Measured Quantities

The concentration of chloride ions in the anolyte solution was measured using an automatic chloride titrometer. The measurement was done at intervals of 2 hours.

4.2.2 Determining Water Content

Knowledge of the water content of the cement paste is required in order to determine the concentration of free chlorides in the pore solution. It was assumed that the pore water inside the cement paste cylinder is equal to the evaporable water content. Thus, to convert the amount of chlorides from the concentration unit in a solution to a mass of chlorides per unit mass of the cement paste sample, the evaporable water content is required. To determine the evaporable water content, three cement paste cylinders were taken with three different water cement ratios. They were sliced into discs using a dry diamond blade and two discs from each water cement ratio were taken as samples. First, they were dried to a constant weight in an oven at a temperature of 105^{o}C. The dried weights of the samples were recorded (W_d). Following that, the samples were stored under water for 48 hours and the saturated weight was measured. Finally, they were stored under water for an additional 24 hours and the weight was again measured and it was found that the difference of this weight with the weight after 48 hours was negligible. Hence, that weight was recorded as the saturated weight of the sample (Ws). Using the following formula, the evaporable water content was calculated:

$$w_e = \frac{W_s - W_d}{W_d} \times 100 \qquad \text{…………} \; (4.3)$$

where w_e is the evaporable water content (g water / g sample)

4.2.3 Experiments for Chloride Isotherms

After curing for two months, the top part of the sample bottles were cut out. The cement paste samples were demoulded and then sliced into thin discs using a diamond saw. The discs were then dried in an oven for 7 days at a temperature of 80^{o}C. After drying, the discs were ground to powder using a grinding machine and mixed with a chloride solution inside glass bottles. The samples in each bottle were prepared as follows:

- The weight of the 125ml plastic bottle with the lid was taken.
- 25g of ground sample were placed into the bottle.

- The bottle was completely filled with a chloride solution and the lid was tightened so that there was no chance of carbonation. Then, the total weight was taken.
- The weight of the solution was determined by deducting the sample weight and the bottle weight from the total weight.

Chloride solutions of 9 different concentrations, 0.2M, 0.4M, 0.6M, 0.8M, 1.0M, 1.5M, 2.0M, 2.5M, and 3.0M, were prepared by mixing the required amounts of chloride salts with distilled water before they were saturated with calcium hydroxide to achieve the high pH level (pH = 12.5) typically found in concrete pore solutions. This was done to prevent the leaching of calcium hydroxide from the cement paste. These bottles were stored at room temperature for two weeks to allow the salt solution and the hydrated cement paste phases to reach equilibrium. After two weeks, the chloride concentration in each bottle was measured and the bottles were replaced in storage. The chloride concentration was again measured after one more week and compared with the previous one. If there was no difference in concentration, then it was assumed to have reached equilibrium.

One set of nine bottles, containing sample powders from the cement paste with a water-cement ratio of 0.5 and chloride solutions prepared with sodium chloride salt were stored at a temperature of 22^{o}C. After reaching equilibrium, the free chloride ion concentration of the solution in each bottle was measured. The reduction of chloride ion concentration in the solution was an indication that chloride ions were getting bound in the hydrated cement phase. The amount of bound chloride was determined from the initial and final chloride concentration, the volume of the salt solution, and the dry mass of the cement paste sample using the following equation:

$$C_b = \frac{\left(C_i - C_e\right) \times 35.5 \times V}{W_d} \qquad \text{………… (4.4)}$$

where:

C_b = Amount of bound chloride in mg Cl/ g of sample,

C_i = Initial chloride concentration of the external solution in mol/L,

C_e = Chloride concentration of the solution at equilibrium in mol/L,

V = Volume of external solution in mL, and

W_d = Dry mass of sample in *g*.

The free and bound chloride was plotted to determine the chloride isotherm. The same procedure was followed for two samples with two other water-cement ratios (0.6 and 0.7) to determine the chloride isotherm of these samples. The isotherms derived from these sets of samples were used to determine the exchange constants and exchange sites in cement pastes.

4.3 Model Verification Experiments

To verify whether the model produces realistic results, experiments were performed to determine the effect of temperature and chloride ion source on chloride isotherm. Experiments to determine the chloride profiles for the samples with three different water-cement ratios were also carried out to verify the proposed model.

4.3.1 Effect of Temperature on Chloride Ion Isotherm

To determine the effect of temperature on the binding of chloride ions, three different temperatures were selected: 5^oC, 22^oC, and 75^oC. Chloride isotherms were plotted at these temperatures following the same procedure as mentioned above (Section: 3.1.4.2). One set of nine sealed bottles with nine different chloride concentrations were stored in a refrigerator at a temperature of 5^oC and another set of bottles was stored in an oven at a temperature of 75^oC. These isotherms were compared with the isotherm determined at a temperature of 22^oC.

4.3.2 Effect of Chloride Ion Source on the Chloride Ion Isotherm

The binding of chloride ions in cement is known to depend on the source of the chloride ions. The cations associated with the chloride ions seem to play an important role in chloride binding. The amount of bound chlorides has been reported to be higher when using $CaCl_2$ as the de-icing salt than when using NaCl. To elucidate the effect of associated cations on chloride binding, one set of nine bottles containing calcium chloride salt solutions of nine different concentrations (0.1M, 0.2M, 0.3M, 0.4M, 0.5M, 0.75M, 1.0M, 1.25M, and 1.5M), with sample powders from cement paste with a water-cement ratio of 0.5, was stored at a temperature of 22^oC, and this isotherm was compared with the control paste isotherm.

4.3.3 Experiments for Chloride Profiles

The amount of free and bound chlorides along the depth of cement paste cylinders were measured after putting them in chloride solutions for a period of one year to determine the chloride profile.

4.3.3.1 Sample Preparation for the Chloride Profile

After curing for two months, the top portions of the bottles were cut out with a diamond saw. Then, the cement paste samples were demoulded and coated with paraffin wax on all sides except the cutting side, allowing chloride ions to penetrate into the cement paste sample in one direction only (Figure 4.6). The specimens were left for one day in the laboratory air to allow the wax to harden. Samples were then stored in a plastic container filled with 1 M sodium chloride solution saturated with calcium hydroxide (Figure 4.7). The container was then covered with plastic lid.

Figure 4.6: Sample cylinders coated with paraffin wax.

Figure 4.7: Sample cylinders stored in chloride solution

4.3.3.2 Slicing and Grinding

After one year of storage under the chloride solution, the cement paste cylinders were taken out and sliced into discs of 10 mm thickness from the exposed surface inwards to a depth of 60 mm before being ground into powders. Before grinding, the surrounding wax was removed so that wax did not contaminate the ground samples. The ground samples of the individual layers were stored separately in zip lock bags and the depths of the layers were marked on the bags.

4.3.3.3 Free Chloride Ion Measurement

The amount of free chloride was measured according to ASTM standard C1218, which is briefly described here.

From the ground samples of each layer, 5 g was placed into a beaker before adding 50 ml of water. The beaker was covered with a watch glass and boiled for 5 minutes using a hot plate. After removal from the hot plate, the sample was allowed to stay at room temperature for 24 hours before the mixture was filtered using filter paper placed in a funnel connected to a flask under a vacuum, and the filtrated solution was titrated to measure the free chloride concentration.

4.3.3.4 Total Chloride Ion Measurement

The amount of total chloride was determined according to ASTM standard C114-04, which is briefly described here.

Five grams of powdered samples were weighed into a 250 ml beaker before being mixed with 75 ml of water, and 25 ml of dilute (1+1) nitric acid was added with the sample. The beaker was covered with a watch glass and then boiled quickly for few seconds. The solution was then filtrated by suction through filter paper, and the filtrated solution was transferred for titration.

4.3.3.5 Bound Chloride Determination

Bound chloride concentration was determined by deducting the free chloride amount from the total chloride amount and then the concentration was converted to mass per kg of cement paste sample.

CHAPTER 5

Results and Analysis

Results from Part 1 of the experimental program were analysed and compared with the simulated data to determine the unknown parameters of the model from the best curve fit through an inverse modeling procedure. The main unknowns of the model, the exchange constant and the exchange capacity, do not lend themselves to easy direct measurement. Hence, these parameters were identified through an inverse modeling procedure in which these two parameters varied until the best fit with the experimental results was obtained. Part 1 of the experimental program (see chapter 4) was designed specifically for the purpose of model calibration and parameter identification. Then, using the resulting parameters, some other simulations were performed while varying different parameters and the results of the simulated data were verified with the experimental results from Part 2. After the model was verified against experimental data, some numerical parametric studies were carried out to see whether the proposed approach would be able to capture the effects of some parameters not previously tested in this study but reported in the published literature.

5.1. Model Parameters Identification Experiments

5.1.1. Experimental Result for Chloride Ion Diffusion Coefficient

The diffusion coefficient was determined by steady state migration tests. The diffusion coefficient of three samples with different water cement ratios, 0.5, 0.6, and 0.7, were estimated using the simplified form of the Nernst-Plank equation:

$$D = \frac{JRTl}{zFC_{Cl}\delta E} \text{ .... } (5.1)$$

The straight portions of these curves were plotted separately (Figure 5.2, Figure 5.4, and Figure 5.6) to determine their slopes. The slope of the straight portion of the curve was used to calculate the steady state chloride flux using the following equation:

$$J = \frac{1}{3600 \times 1000} \times \frac{S}{A} \text{ .... } (5.2)$$

After determining the chloride flux and the thickness of the sample, the diffusion coefficient of the chloride ion was calculated from the Nernst-Plank equation, and the results are shown in Table 5.1. The calculated values of the diffusion coefficients are plotted against water-cement ratios in Figure 5.7.

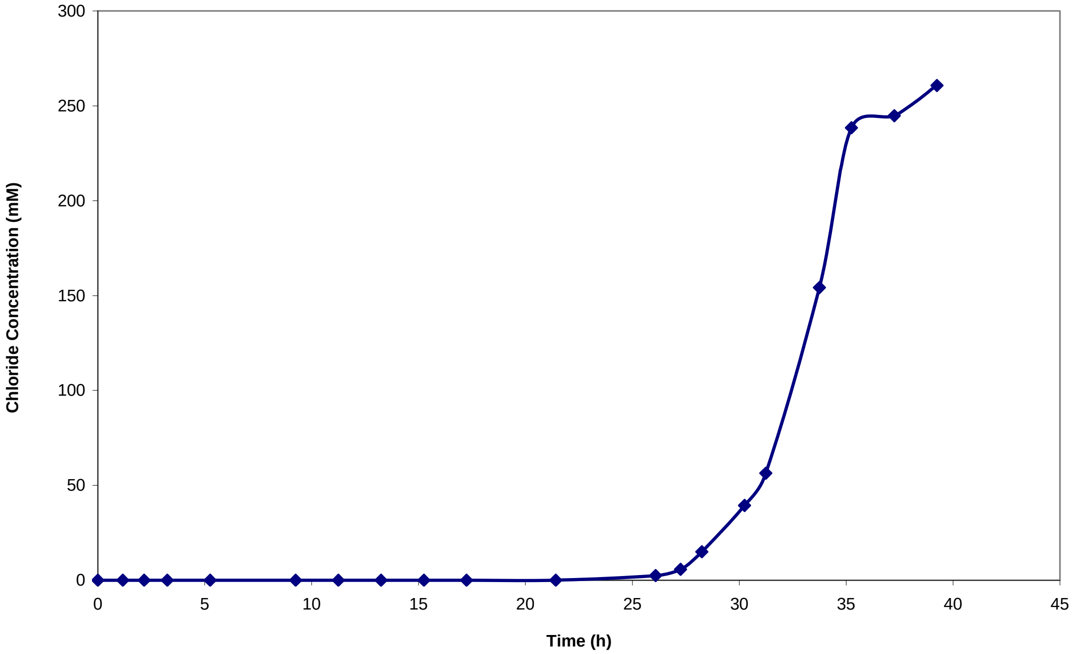

Figure 5.1: Increase of chloride concentration in the downstream solution with time for the sample with a water-cement ratio of 0.5

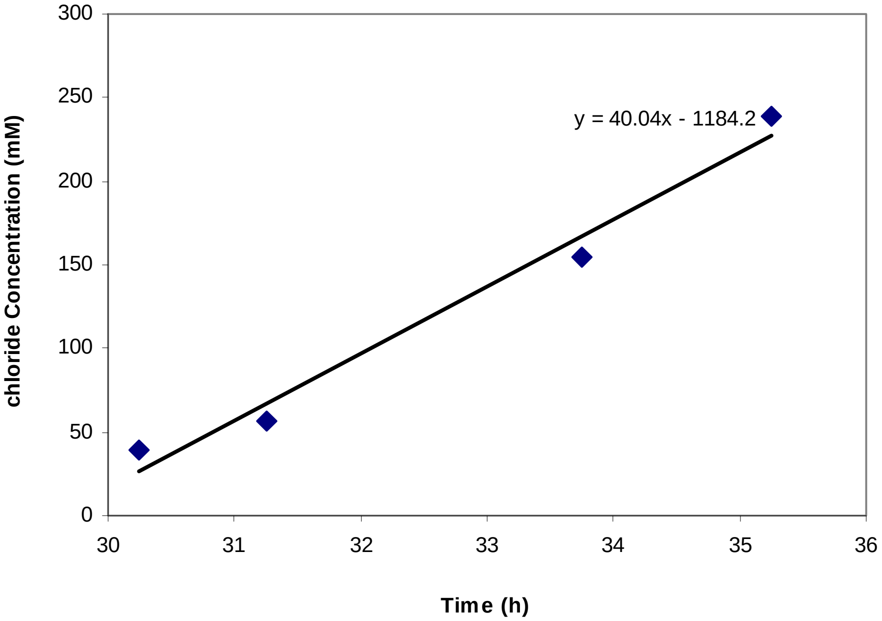

Figure 5.2: linear portion of the concentration curve for sample with a water-cement ratio of 0.5

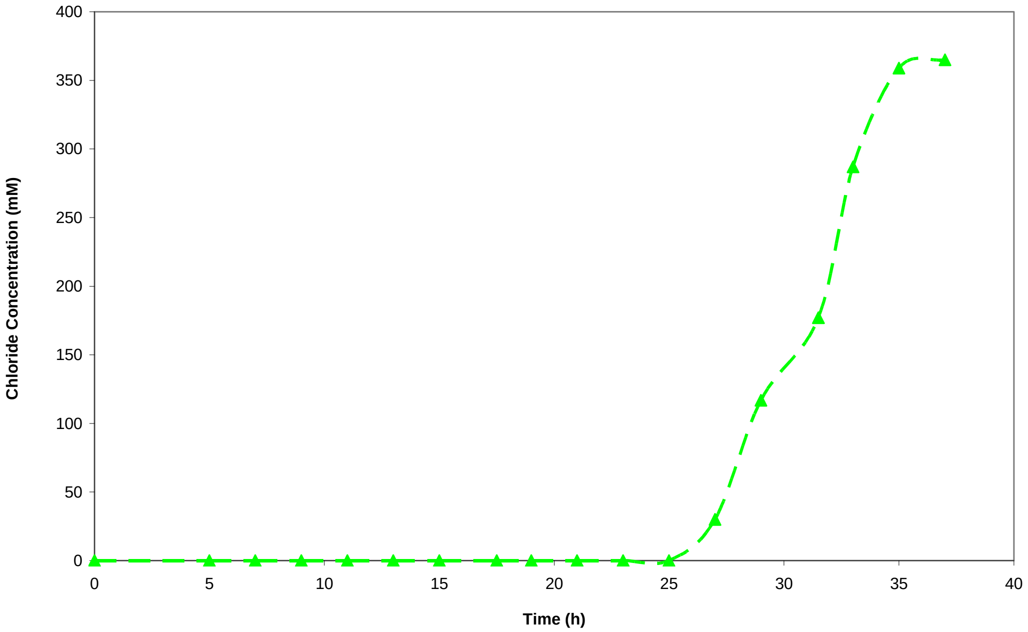

Figure 5.3: Increase of chloride concentration in the downstream solution with time for the sample with a water-cement ratio of 0.6

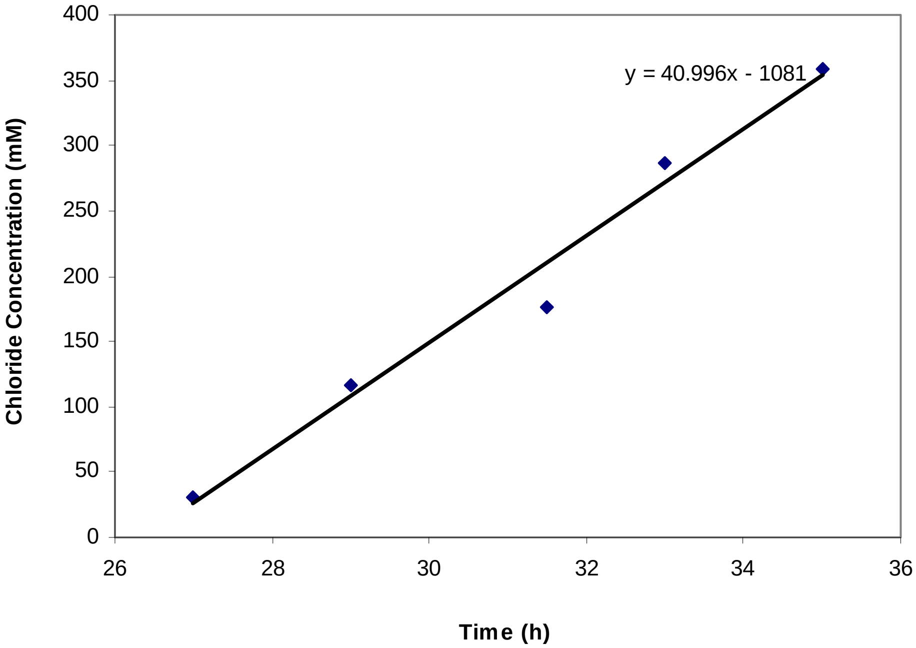

Figure 5.4: linear portion of the concentration curve for sample with a water-cement ratio of 0.6

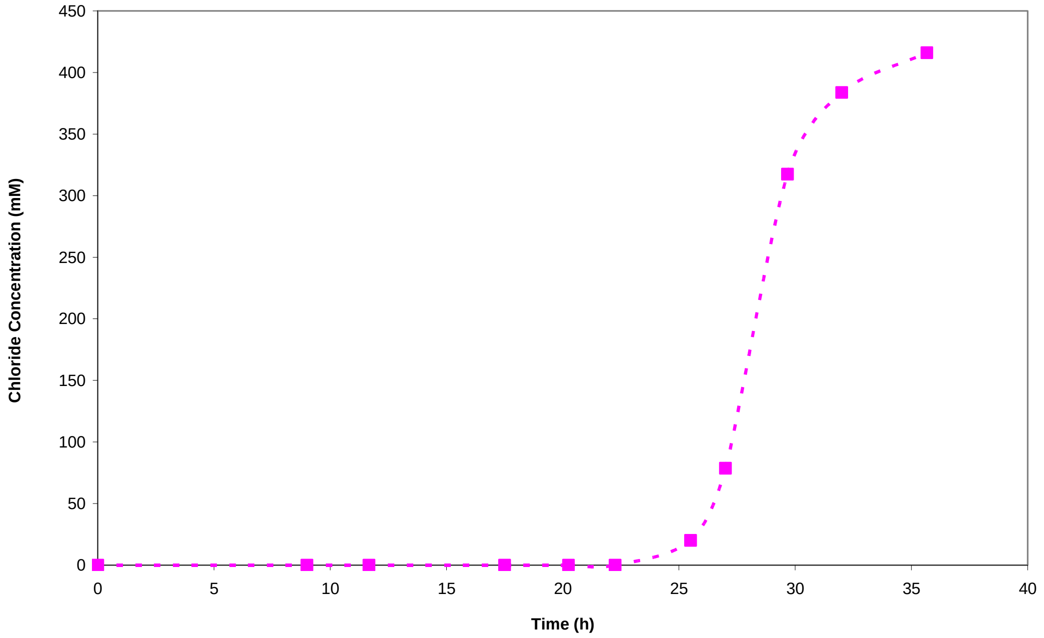

Figure 5.5: Increase of chloride concentration in the downstream solution with time for the sample with a water-cement ratio of 0.7

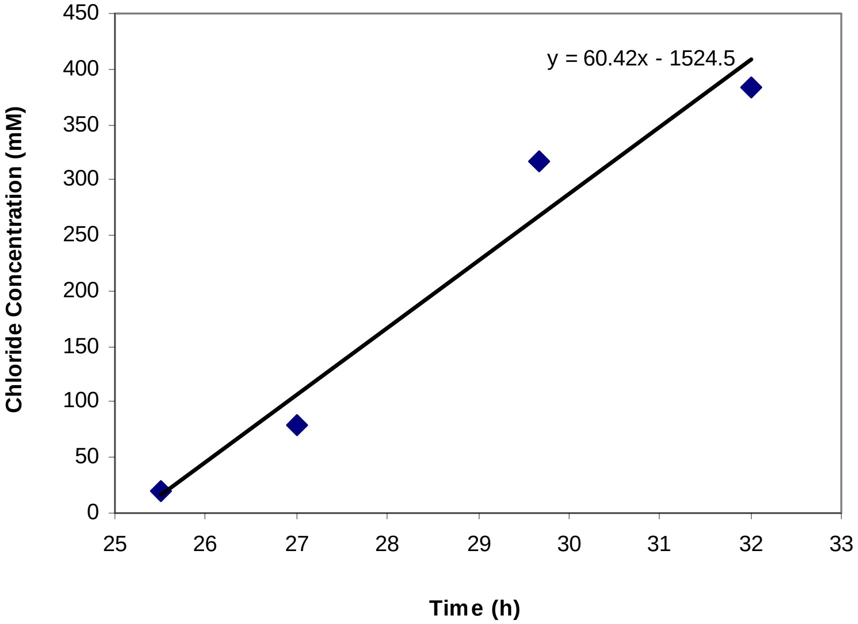

Figure 5.6: linear portion of the concentration curve for sample with a water-cement ratio of 0.7

Table 5.1: Experimental diffusion coefficients for different water-cement ratios

W/C Ratio	Average Thickness of Sample (cm)	X-Sectional Area (cm^2)	Slope of the straight portion of Con. Curve (mM/h)	Chloride Flux (J) (mol. Cm-2.s-1)	**Diffusion Coefficient (cm^2/s)**
0.5	0.767	29.24	40.04	3.82E-07	**5.933E-07**
0.6	0.962	28.27	40.99	4.01E-07	**7.851E-07**
0.7	0.741	28.40	60.42	5.91E-07	**8.902E-07**

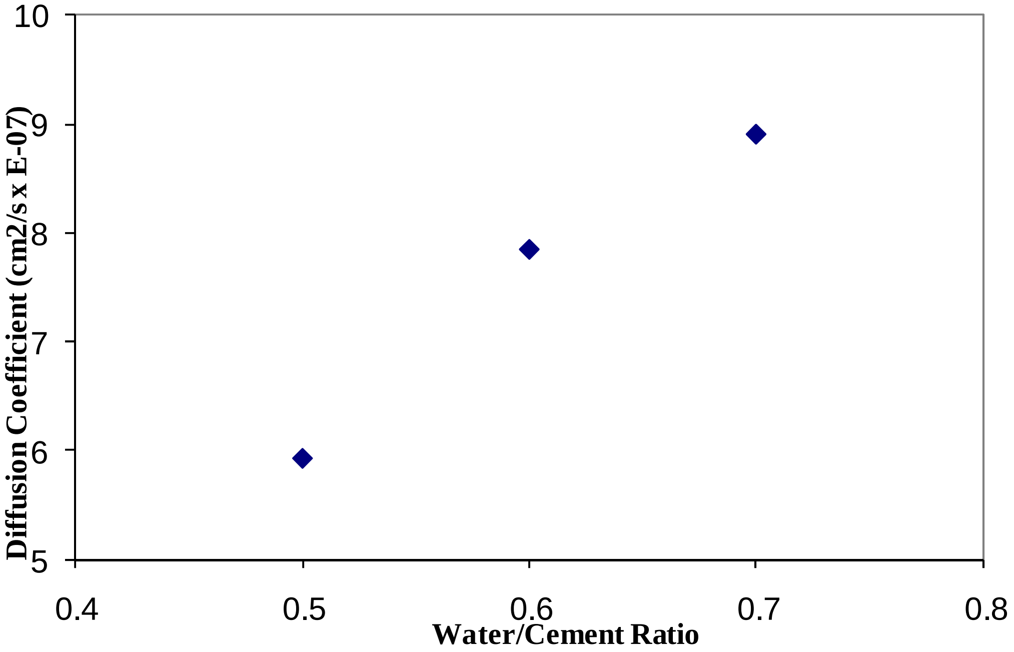

Figure 5.7: Experimental result of diffusion for samples with different water-cement ratios.

From the results of diffusion coefficients for different samples with different water cement ratios (Figure 5.7), one can easily see that the diffusion coefficient increases as the water-cement ratio increases. The diffusion coefficient of the sample with a water-cement ratio of 0.7 is 1.5 times the diffusion coefficient of the sample with a water-cement ratio 0.5. This is expected since greater water-cement ratios lead to higher porosities, which in turn lead to higher diffusion rates for same concentration difference. The values for the diffusion coefficient and the relationship of the diffusion coefficient with the water-cement ratio found in this study were reasonable compared to the results obtained by previous researchers (Page *et al.*, 1981).

5.1.2. Experimental results for water content

The experimental results for water content (Table 5.2) show that water content increases as the water-cement ratio increases. Thus, cement pastes with higher water-cement ratios are more porous and, hence, can contain more pore water.

Table 5.2: Experimental water contents of different water-cement ratios

Water Cement Ratio	Water Content (% g/g)
0.5	28.76
0.6	38.91
0.7	46.11

5.1.3. Estimation of Exchange Capacity and Exchange Coefficient

The exchange capacity of the hydrated cement paste and the coefficients for the exchange reactions are unknown for the proposed approach and need to be determined before any numerical simulations can be carried out. Given the lack of such data in the published literature and the difficulty of obtaining a direct measurement, those parameters were determined indirectly by using an inverse modeling approach. Chloride isotherms were simulated using different exchange capacities and exchange coefficients while keeping all other model parameters constant. The simulation results were then compared with the experimental data for chloride isotherms (Figure 5.8, Figure 5.9, and Figure 5.10). The values of these parameters that produced the best curve fits for the chloride isotherms were taken as the final values. The same procedure was followed for all the samples with three different water cement ratios. The equilibrium constant for the exchange reaction was found to be the same for all three water-cement ratios.

The main phases of cement paste are C-S-H, Portlandite ($Ca(OH)_2$), Monosulphate, Ettringite, and iron oxides. The dissolution of C-S-H is assumed to proceed by the release of calcium and hydroxide ions in a proportion of one calcium ion to two hydroxide ions in order to maintain the electro neutrality of the solution. This approach is in good agreement with the observed data (Marchand et. al., 2002). Assuming that C-S-H dissolves in water like portlandite, in our model, the pore solution is equilibrated with portlandite and monosulphate (AFm phase) as an exchange species (R-OH) to create appropriate initial pore solution conditions for the pore solution used in our simulations. In the case of carbonation, calcite was allowed to penetrate after formation. The different reaction used in the models together with their thermodynamic equilibrium constants are given in Table.5.3

Table 5.3: Chemical equilibrium expression for different phases

Reactions	Equilibrium Constant (log k)
$Ca(OH)_2 = Ca^{+2} + 2\ OH^-$	-5.19
$CaCO_3 = CO_3^{-2} + Ca^{+2}$	-8.406
$NaCl = Cl^- + Na^+$	1.570
$CO_3^{-2} + H^+ = HCO_3^-$	10.3393
$CO_3^{-2} + 2\ H^+ = CO_2 + H_2O$	16.6767
$NaHCO_3 = CO_3^{-2} + H^+ + Na^+$	-10.742
$CO_2(g) = CO_2\ (aq)$	-1.468

The values of the equilibrium constant and exchange capacity that gave the best curve fit with the comparison with the experimental results are tabulated in Table 5.4. From the values, we can observe that the exchange capacity of hydrated cement paste increases as the water-cement ratio of samples increases. Thus, higher amounts of chloride ions should be expected to bind in concrete with higher water-cement ratios. This is in agreement with experimental isotherms determined in this study and elsewhere in the published literature (Delagrave *et al.*, 1996; Mangat and Molloy, 1995; Tang and Nilsson, 1993).

The exchange coefficient for the carbonate ion was determined by comparing the simulated chloride isotherm in the presence of carbonation with the experimental data obtained from Zibara (2001) (Figure 5.11).

Table 5.4: Best fit values of Exchange Capacity and Equilibrium Constant for samples with different water-cement ratios.

Water/Cement	**Exchange Capacity (meq/100g)**	**log Exch. Coeft.** $R-OH+Cl^{-}=R-Cl$	**log Exch. Coeft.** $CO_3^{2-} + 2R^{+} = R_2CO_3$
0.5	8	-1.25	+3.25
0.6	10	-1.25	+3.25
0.7	11	-1.25	+3.25

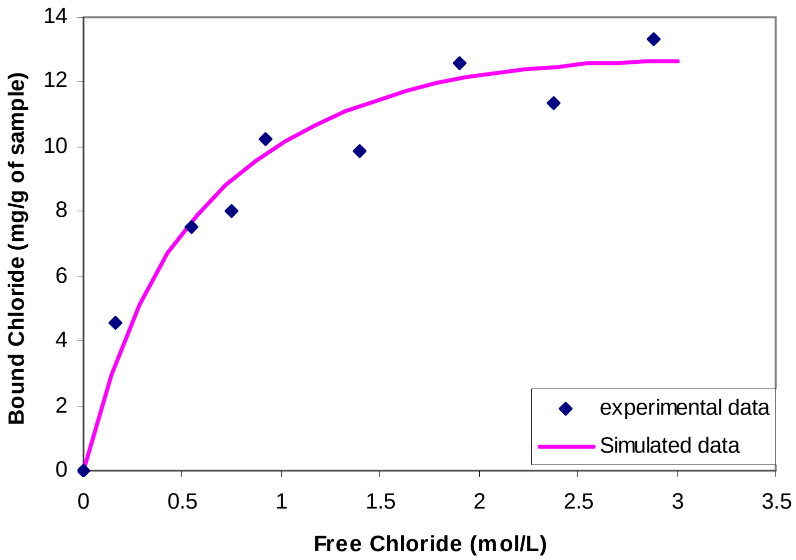

Figure 5.8: Chloride isotherms for samples with water-cement ratio 0.5.

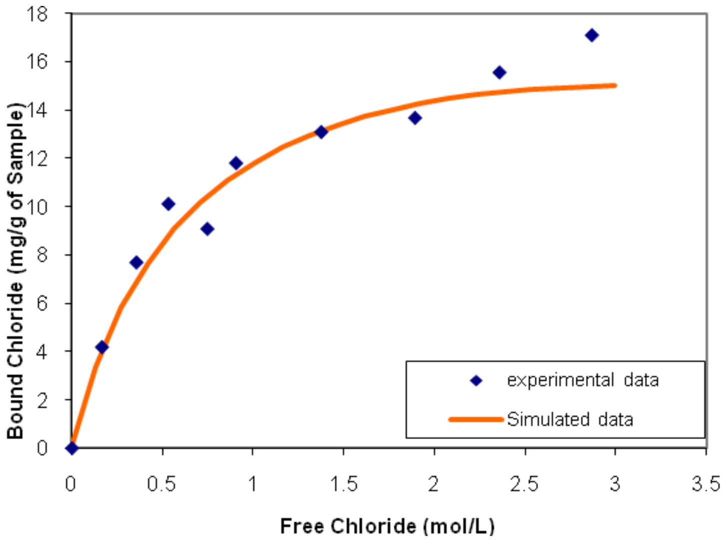

Figure 5.9: Chloride isotherm for samples with water-cement ratio 0.6.

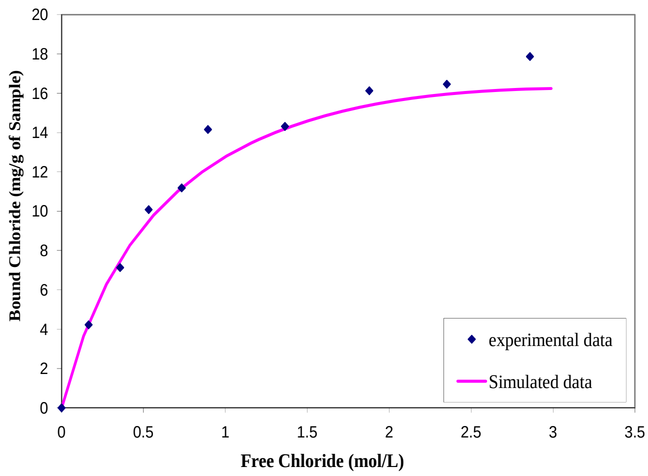

Figure 5.10: Chloride isotherm for samples with water-cement ratio 0.7.

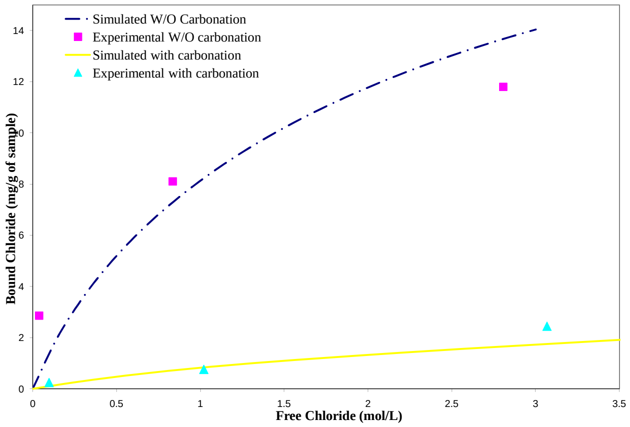

Figure 5.11: Chloride isotherm for carbonated and non-carbonated cement paste.
(experimental data from Zibara, 2001)

5.2. Model Verification Experiments

After determining all the unknown parameters necessary for model calibration in the previous section, the model is now ready to be used under arbitrary general conditions not representative of the tests used for calibration. This section serves the purpose of model verification against experimental results that can be achieved under general environmental conditions of interest. To verify the model, it has been experimentally determined the chloride isotherms while varying some environmental parameters, such as temperature and chloride source, and then compared them with the simulation result.

5.2.1. Effect of Temperature on Chloride Binding Isotherms

To observe the effect of temperature on chloride binding in a hydrated cement paste, chloride isotherms were experimentally determined at three different temperatures, 5°C, 25°C, and 75°C, and compared with three theoretical isotherms predicted by PHREEQC.

Figure 5.12 shows that the predicted isotherms agree very well with the corresponding experimental ones. Both the experimental and simulated isotherms show that chloride ions' binding is inversely related to temperature. That means that as the surrounding temperature decreases, the binding of chloride ions in cement paste increases. Hence, at higher temperatures, there are higher amounts of free chlorides in concrete pore solution, which increases the risk and rate of corrosion of embedded steel in concrete.

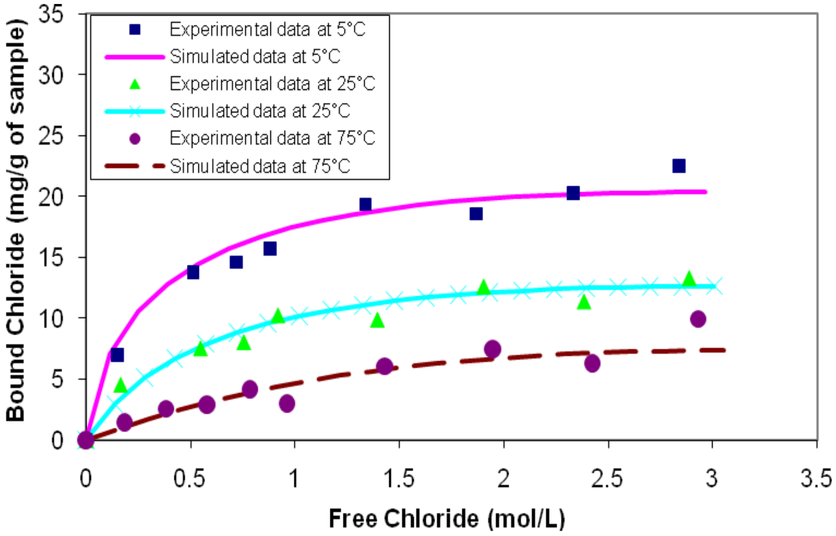

Figure 5.12: Experimental and simulated chloride isotherms at different temperatures.

One probable explanation for this phenomenon is that the exchange reaction for chloride ions over hydroxide ions is exothermic. Hence, at higher temperatures, fewer hydroxide ions can be exchanged by chloride ions, which results in a greater amount of free chloride in the solution.

5.2.2. Effect of Source of Chlorides on Chloride Binding Isotherms

Most experiments were carried out using sodium chloride as the source of chloride ions. However, one set of chloride isotherms experiments were conducted using calcium chloride as the source of chloride ions. The results of experiments for both sources of chlorides (NaCl and $CaCl_2$) were compared to each other and to theoretical isotherms predicted by PHREEQC, as shown in Figure 5.13.

Figure 5.13 clearly shows that the simulated curve is in very good agreement with the experimental data for both chloride sources. As expected, the amount of bound chlorides is higher when using calcium chloride as a source than when using sodium chloride as a source and the model has been able to capture this important feature.

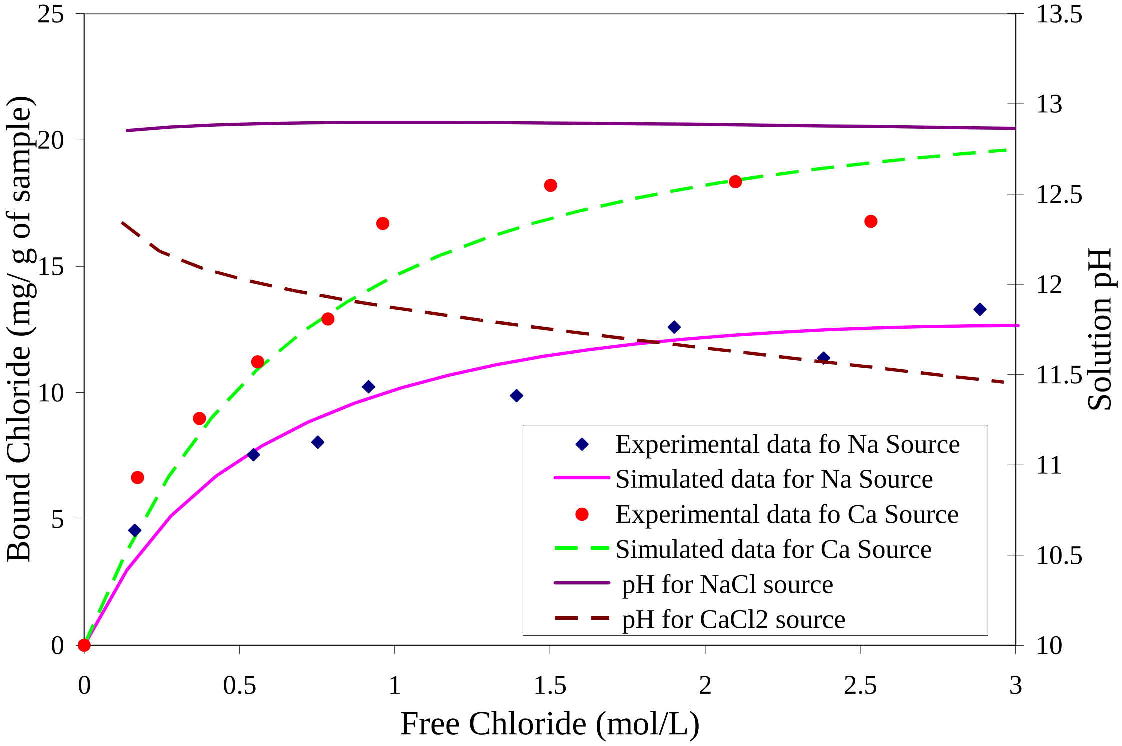

Figure 5.13: Experimental and simulated chloride isotherms using different chloride sources.

All results in the published literature have consistently shown that more chlorides are bound in concrete when $CaCl_2$ is used as a source than when used NaCl. However, and despite a very large body of published data, there is still some confusion as to what is causing this difference in behaviour, and various theories have been formulated to explain it.

1. Some researchers suggested that NaCl must first react with $Ca(OH)_2$ to form $CaCl_2$ before combining with aluminate phases to form Friedel's salt.
2. Others have proposed that it is probably the observed difference in pH values when using NaCl and $CaCl_2$ that is responsible for the difference in chloride binding.

Given the mechanistic nature of the proposed approach, it is tempting to use the detailed information generated by the numerical models can be used to try to shed some light on this question.

From the PHREEQC output file, a closer look into all the reactions taking place allows one to see that, in the case of calcium chloride, there is a formation of Portlandite ($Ca(OH)_2$) that consumes hydroxide ions from the solution. This leads to a decrease in hydroxide ions (i.e. a decrease in pH). However, in the case of sodium chloride, there is no formation of portlandite and no significant decrease of pH is observed. In Figure 5.16, we can see this difference in pH values for the two chloride sources. Hence, it is most likely that the second hypothesis is the mechanism controlling the difference in the amount of bound chlorides when using NaCl versus $CaCl_2$. This makes sense because, in case of the $CaCl_2$ source, fewer hydroxide ions are available to compete for binding sites with chloride ions, making it easier for chloride ions to bind since the bound chloride must also be in equilibrium with the free chloride in the solutions.

5.2.3. Effect of Concrete Quality (w/c) on Chloride Ingress

Since the w/c ratio is known to affect the porosity of cement-based materials and their transport properties (diffusion and permeability), it is expected to have a strong influence on the amount of free and bound chloride profiles.

As shown in fig. 5.14 simulated chloride profiles were compared against experimentally determined profiles for cement pastes with three different water-cement ratios (w/c = 0.5, w/c = 0.6, and w/c = 0.7). Figure 5.15, Figure 5.16, and Figure 5.17 show that the simulated profiles are in a very good agreement with the experimental data for both free and bound chlorides and for all w/c ratios considered.

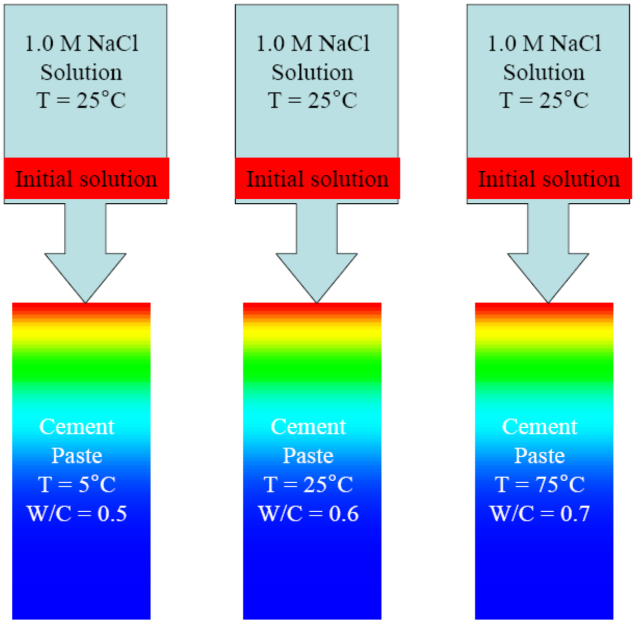

Figure 5.14: Simulation of chloride profiles for different water-cement ratios.

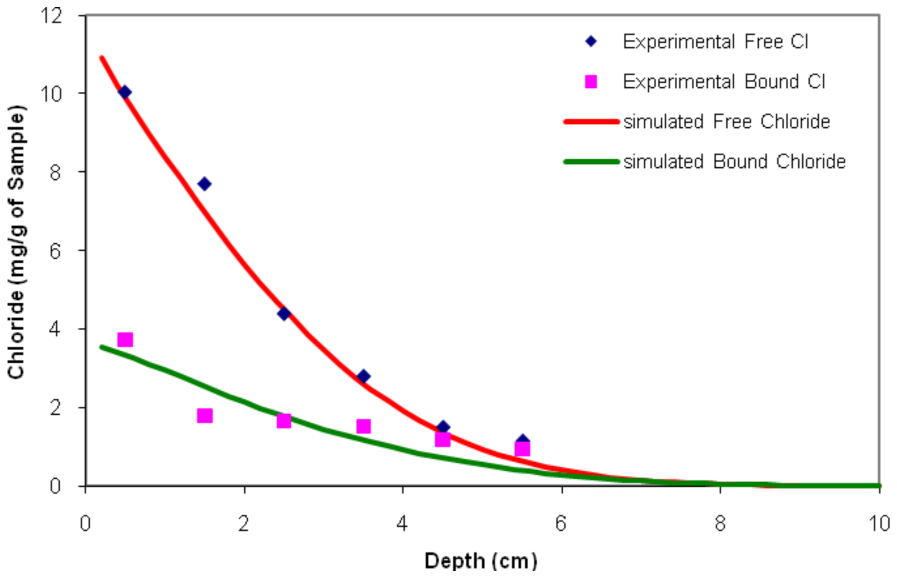

Figure 5.15: Comparison of simulated data with experimental result of chloride profile for samples with W/C ratio 0.5.

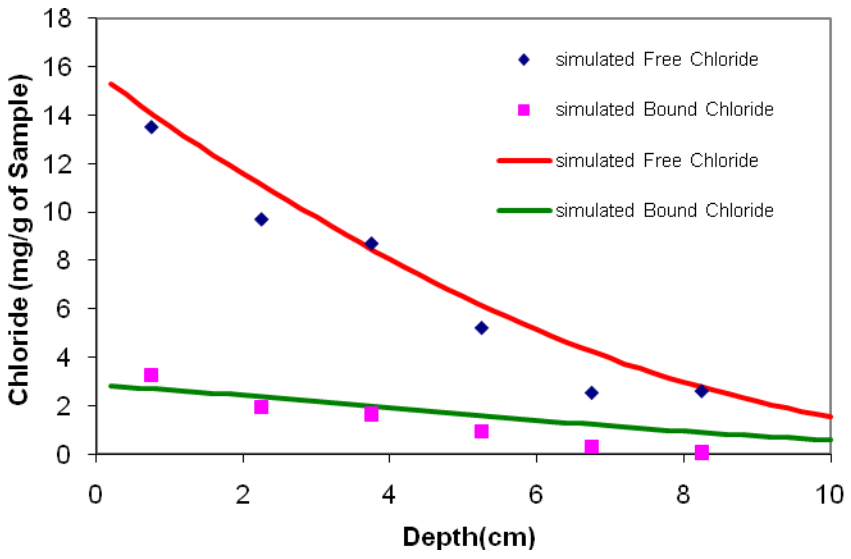

Figure 5.16: Comparison of simulated data with experimental result of chloride profile for samples with W/C ratio 0.6.

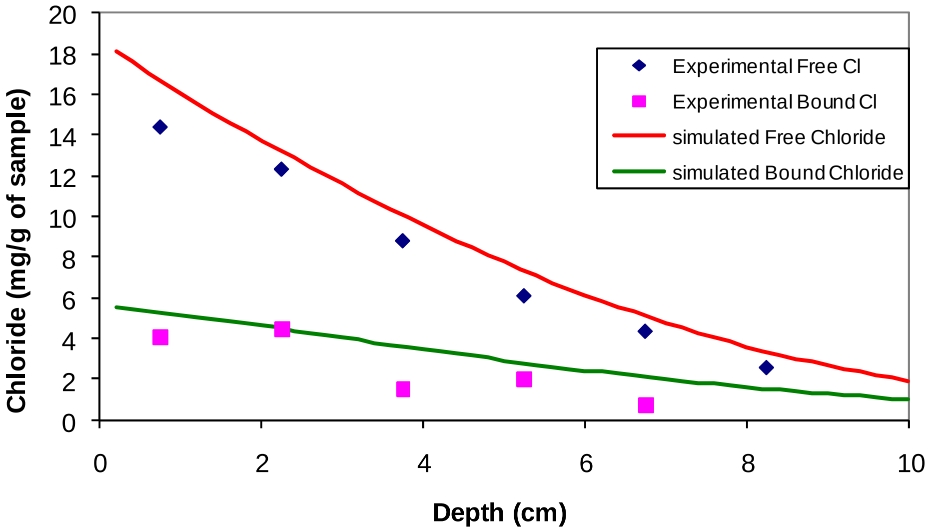

Figure 5.17: Comparison of simulated data with experimental result of chloride profile for samples with W/C ratio 0.7.

Figure 5.18 and Figure 5.19 display comparisons of the free and bound chloride profiles for different water-cement ratios. From these figures, it is clearly evident that as water-cement ratio increases, both free and bound chloride also increases. This is due to the increase in the diffusion coefficient with increasing water-cement ratios.

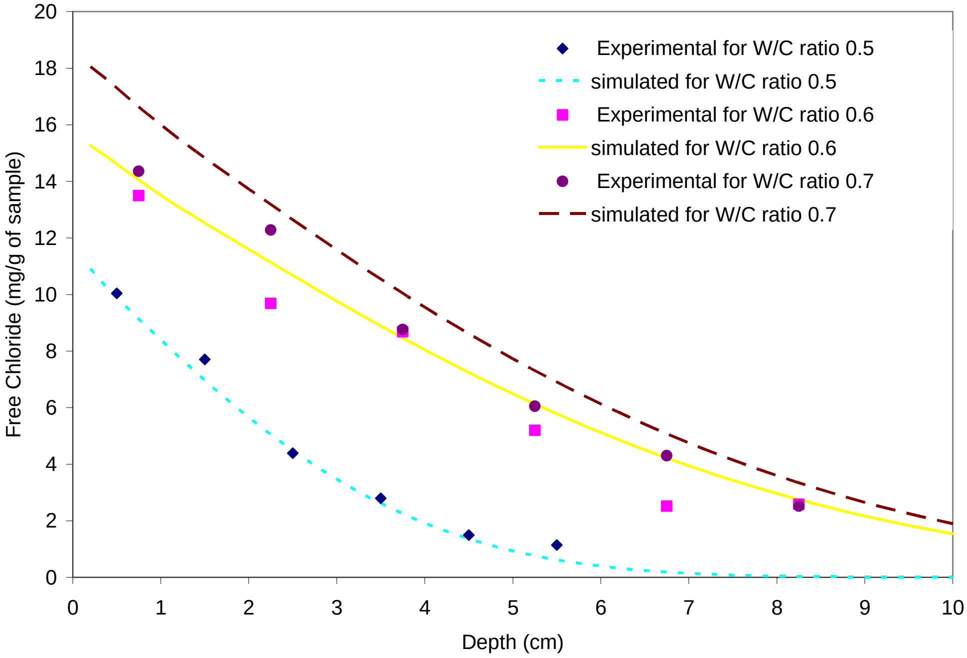

Figure 5.18: Comparison of free chloride profile for different W/C ratios.

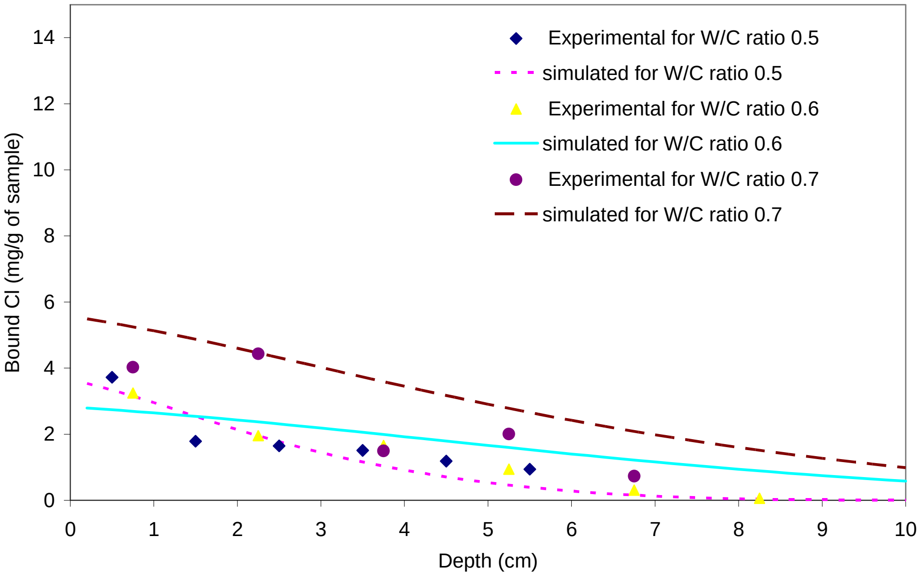

Figure 5.19: Comparison of bound chloride profile for different W/C ratios.

5.3. Numerical Parametric Study

Now that the model had passed the three verifications tests (testing the effect of temperature and the source of chlorides on the chloride binding isotherms, together with the effect of w/c ratio on chlorides ingress), parametric studies were conducted to determine whether the proposed approach would be able to capture the effects of some parameters not previously tested in this study but reported in the published literature.

5.3.1. Effect of pH on Chloride Binding Isotherms

To assess the effect of pH on chloride binding isotherms, numerical simulations were carried out at different values of the pore solution pH, and the results are compared to each other in Figure 5.20. From Figure 5.20, it is evident that chloride binding has an inverse relationship with the pH of the pore solution. In other words, the higher the pH, the lower the amount of bound chlorides. This trend agrees with the experimental findings of other studies in the published literature (Zibara, 2001).

A possible explanation for that behaviour is that, in case of higher pH, the amount of hydroxide ions present in the pore solution is higher, making it harder for the chloride ions to compete for the available exchange sites in the hydrated cement phases, and hence, leading to a higher amount of free chlorides and a corresponding lower amount of bound chlorides.

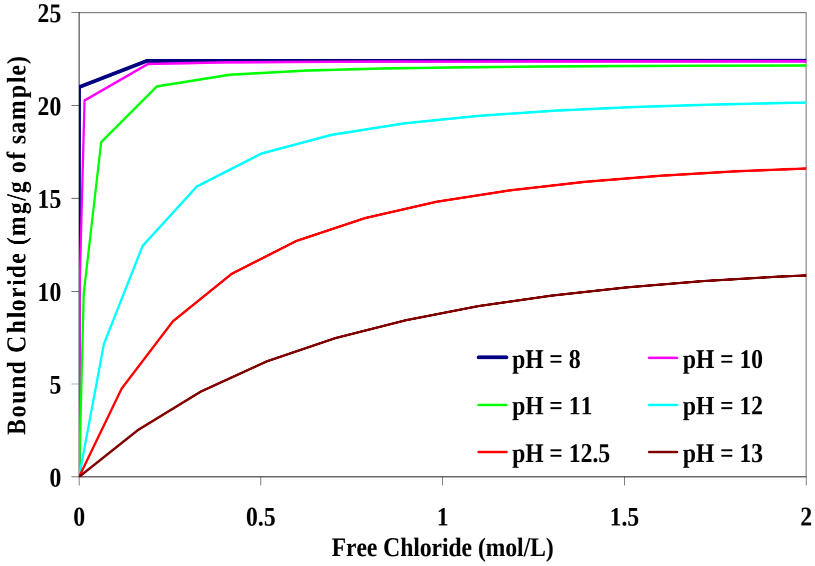

Figure 5.20: Comparison of simulated data of chloride isotherms at different pH valuess.

5.3.2. Effect of Carbonation on Chloride Binding Isotherms

The release of bound chlorides in carbonated concrete has often been associated with an accompanying drop in pH and a lot of controversy still exists about the causes underpinning that release. The fact that carbonation in concrete is always accompanied by a drop in pH has led many researchers in concrete technology to attribute the release of bound chlorides solely to that drop in pore solution pH. However, this explanation is in sharp contrast with some recent studies (Ishida, 2005) showing that the release of bound chlorides does takes place even at high pH values, typically on uncarbonated concrete.

Although the drop in pH in carbonated concrete can easily be explained by the fact that dissolved carbon dioxide converts to carbonic acid after reacting with hydroxide ions present in the pore solution, the reason for the release of bound chlorides is not so easily explicated. At least, it cannot be explained by the decrease in pH value because a decrease in pH should result in an increase inbound chloride . Another mechanism that might lead to the release of bound chlorides, and that did not receive enough attention, is the possible interference of carbonate ion, CO_3^{2-}, with Cl^- and OH^- by competing with them for the available exchange sites. Assuming that ion exchange is the only mechanism by which OH^-, Cl^-, and CO_3^{2-} can be bound or released, the following two numerical simulations were carried out to investigate the role of CO_3^{2-} on the release of bound chlorides in carbonated concrete:

a. Simulation 1 (see appendix A for PHREEQC input file):
   - Carbonation is allowed to take place
   - Only OH^- and Cl^- ions are allowed to compete for the available exchange sites ($R^+ + OH^- = R\text{-}OH$; $R^+ + Cl^- = R\text{-}Cl$)

b. Simulation 2 (see appendix A for PhreeQC input file):
   - Carbonation is allowed to take place
   - OH^-, Cl^-, and CO_3^{2-} ions are all allowed to compete for the available exchange sites. ($R^+ + OH^- = R\text{-}OH$; $R^+ + Cl^- = R\text{-}Cl$; $2R^+ + CO_3^{2-} = R_2\text{-}CO_3$)

The simulated results show that in both cases there is a drop in pH, but they have opposite trends for bound chlorides. Isotherms in Figure 5.21 clearly show that if carbonation were to occur without the possibility of CO_3^{2-} competing for the exchange sites, the amount of bound chloride is higher than the corresponding amount in uncarbonated concrete. This result is in agreement with the effect of a drop in pH on the amount of bound chlorides, as shown in Figure 5.20. If, on the other hand, CO_3^{2-} is allowed to compete for the exchange sites, we have both a drop in pH and a release of bound chlorides, as has been observed in a large number of past studies (Zibara, 2001). This result suggests that CO_3^{2-} probably plays a more significant role than the drop of pore solution pH in the release of bound chloride in carbonated concrete. Hence, one can argue that the reason behind the release of bound chloride due to a decrease in pH but the exchange of chloride ions by carbonate ions.

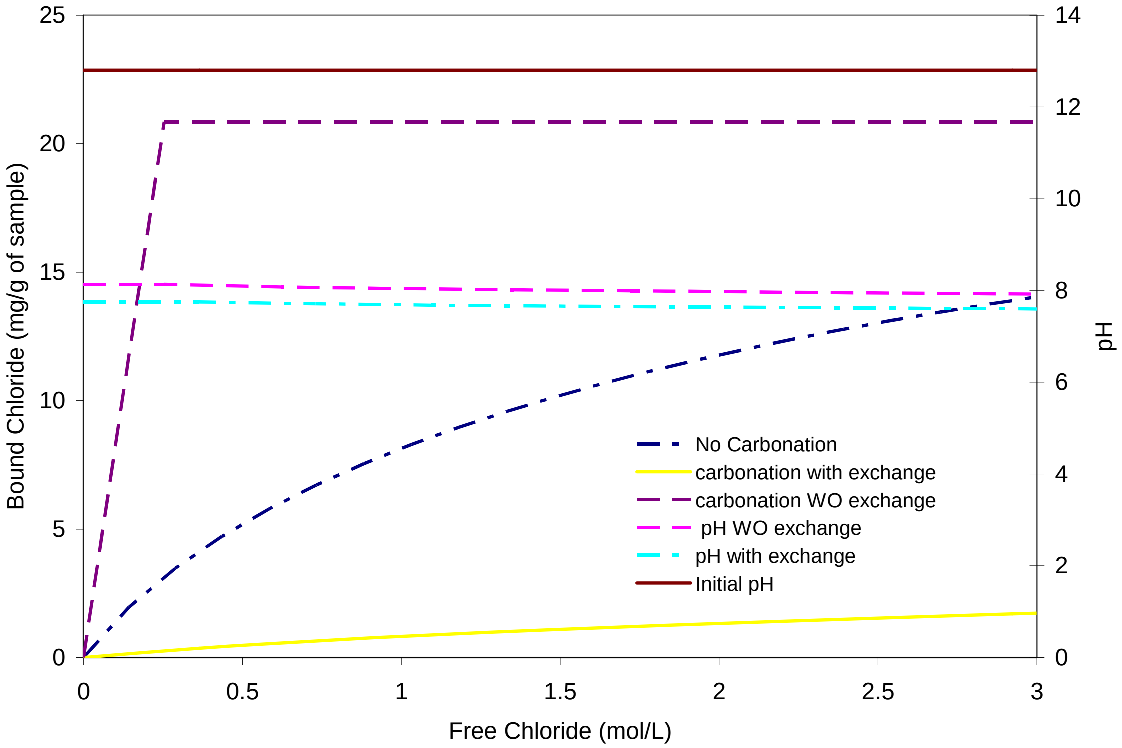

Figure 5.21: Simulated data for the effect of carbonation on chloride binding with and without carbonate exchange.

5.3.3. Effect of Carbonation on Chloride Penetration Profiles

To assess the effect of carbonation on the ingress of chloride in concrete, simulations were carried out for chloride penetration into carbonated and uncarbonated concrete, and the results were compared for free chloride, bound chloride, and pH profiles. Figure 5.22, provides an illustration of both simulations.

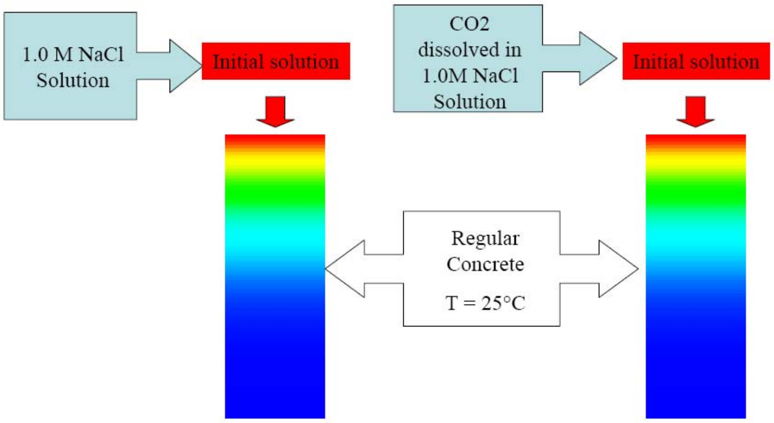

Figure 5.22: Schematic representation of the simulations for chloride and pH profiles in the a) absence of carbonation and b) presence of carbonation.

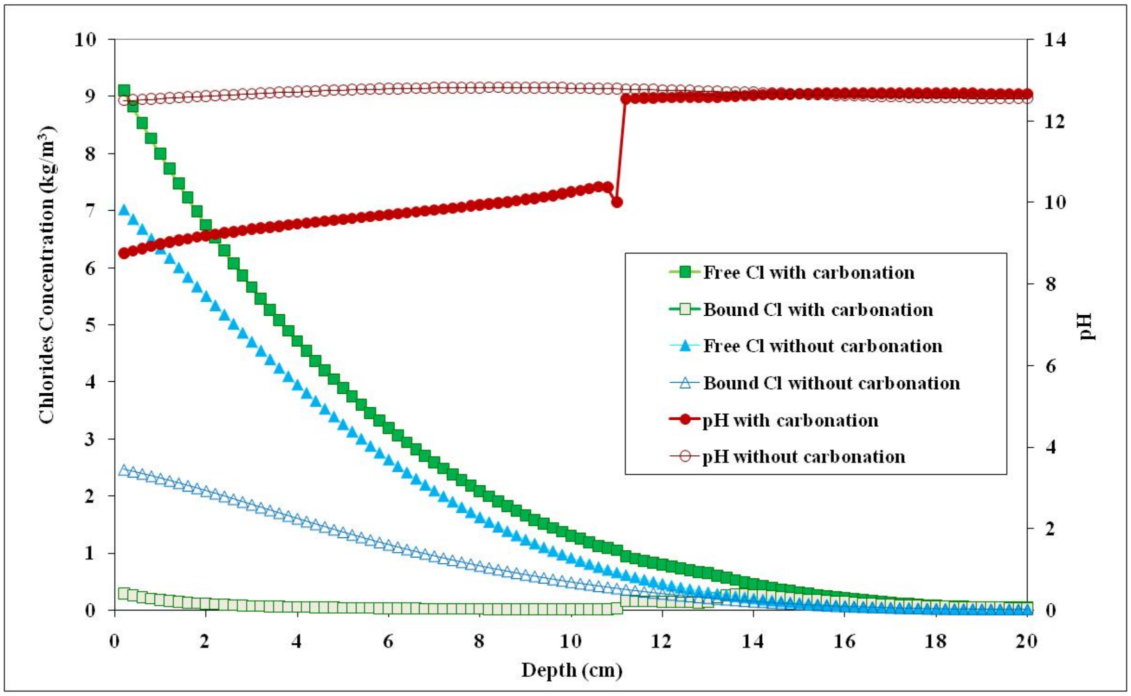

Figure 5.23: Simulation of chloride and pH profile after 10 years in the presence and absence of carbonation.

In the carbonation simulation, carbon dioxide, dissolved in a solution of one mol of chloride ions (in equilibrium with CO_2 at atmospheric pressure, $p_{CO_2} = 10^{-3.5} atm$), was allowed to penetrate into a concrete block at the same time as the chloride for a time period of 10 years. As can be seen in Figure 5.23, carbonation has a significant effect on chloride binding. Up to the carbonation front, the drop in pH is accompanied by a significant decrease in bound chloride and a corresponding increase in free chloride.

5.3.4. Effect of Chloride Source on Penetration Profiles

To assess the effect of the source of chloride on its ingress, chloride profiles were determined for two different chloride sources ($NaCl$ and $CaCl_2$). In the simulation with $NaCl$, one mol of sodium chloride was allowed to penetrate into hydrated cement paste for a period of 10 years, while in the simulation with $CaCl_2$, 0.5 mole of calcium chloride was allowed to penetrate into the same hydrated cement paste for the same period of time (see Figure 5.24).

Figure 5.25 clearly shows that the amount of bound chlorides is higher in the case of $CaCl_2$ than in the case of $NaCl$, as expected. However, the trend is reversed for the pore solution pH profiles. The drop in pH is higher in case of the calcium chloride source. To find an explanation for the observed behaviour, a detailed analysis was conducted for all the reaction products predicted by the model over the entire simulation period. The analysis showed that, in the case of calcium chloride, there is a formation of portlandite that is not dissolved in water. Hence, it seems like the hydroxide ions do precipitate by forming portlandite ($Ca(OH)_2$), which causes a decrease in pH due to the consumption of hydroxide ions. However, in the case of sodium chloride, there is no such precipitation of hydroxide ions and sodium hydroxide remains dissolved in solution. As the amount of hydroxide ions is lower in the pore solution in the case of $CaCl_2$ source, the exchange of hydroxide ions from the hydroxy AFm phase of hydrated cement paste by chloride ions is more likely, and hence, more chloride ions are bound into the cement paste phase.

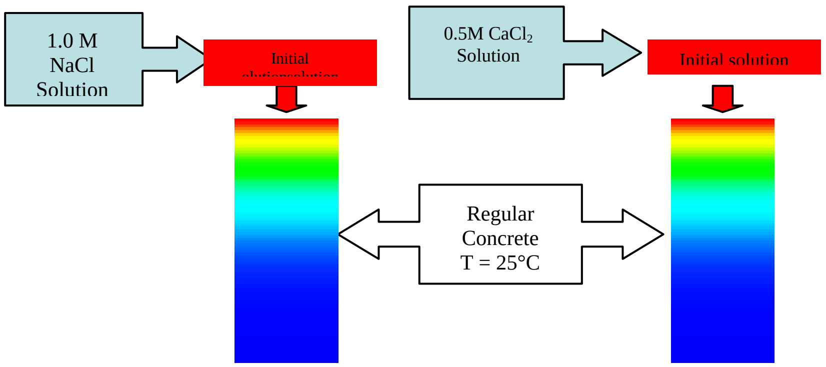

Figure 5.24: Simulation of chloride and pH profile after 10 years using different chloride sources.

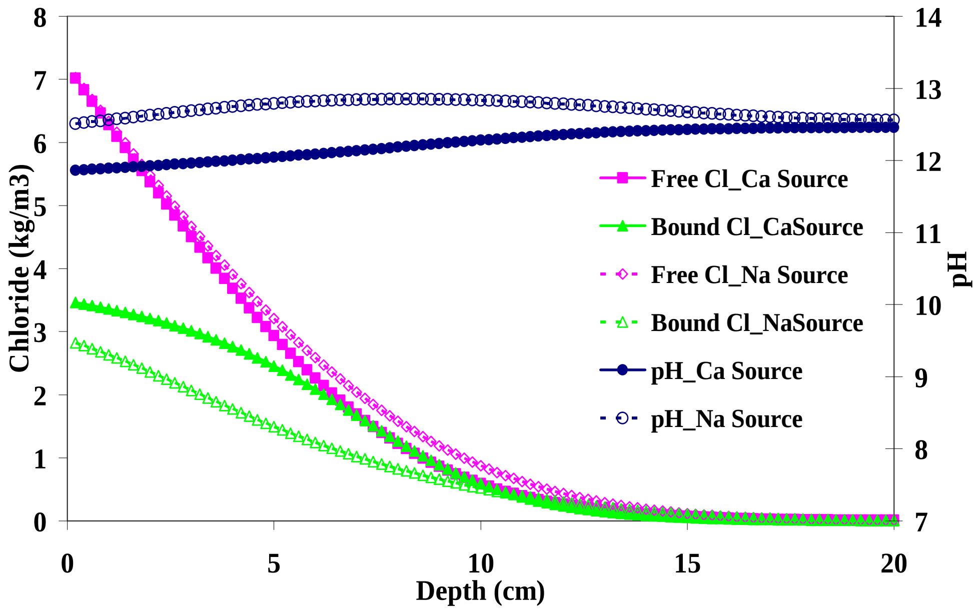

Figure 5.25: Comparison of simulated data of chloride and pH profile after 10 years using different chloride sources.

CHAPTER 6

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Conclusions and Future Recommendations

6.1 Conclusions

A reactive transport model has been proposed for modeling chloride ion ingress, carbonation, and the effect of the latter on the chloride ion profile in concrete. Although the model lies entirely within the framework of thermodynamic equilibrium (no kinetic analysis), it is able to capture the major aspects of the behaviour exhibited by cement based materials subjected to chloride ion ingress and/or carbonation, including the amount of bound chlorides, carbonation depth, the effect of carbonation on the liberation of bound chlorides, and the effect of concrete quality (through their transport properties).

The proposed model was calibrated for two unknown parameters, the chloride ion exchange capacity of the cement paste and the equilibrium coefficient of the exchange reaction, before being validated by comparing it with another set of experiments. Finally, a parametric study was carried out to illustrate the power and versatility of the proposed approach.

Since this model is rooted in first principles of chemistry for cementious materials, it can be and has been used to explain some unresolved issues by running virtual experiments in which detailed information about the major mechanisms and other controlling parameters can be obtained.

The most significant findings of this thesis are summarized in the following sections.

6.1.1 Important findings

1. Parameter identification tests

The main parameters of the proposed model that were determined in this study were the exchange capacity of hydrated cement pastes and the equilibrium constant for the exchange reaction. These parameters were estimated through an inverse modeling process in which the values of these two parameters that gave the best fit for the experimental isotherms to simulated isotherms were selected *a posteriori*. In other words, numerical simulations were run with all input parameters given fixed values, except for the exchange capacity and equilibrium constant, which were varied iteratively until a best fit was achieved.

To run the model, the diffusion coefficient for chloride ions in the cement paste samples was determined through migration tests for three different types of cement pastes with different water-cement ratios. The values of the diffusion coefficients determined from the experimental results were on the order of 10^{-7} cm^2/s, and it was also found that the diffusion coefficient increased as water-cement ratio increased. These results agree with published results in the literature (Sergi *et al.*, 1992; Truc *et al.*, 2000).

Experiments for chloride binding isotherms were carried out for three different water-cement ratios and, from the results, it was found that the binding of chloride increased as water-cement ratios increased. These results agree with the experimental results of previous researchers (Delagrave *et al.*, 1997; Mangat and Molloy, 1995; Tang and Nilsson, 1993).

The simulated chloride isotherms were compared with the experimental chloride isotherm data, and the exchange capacity and equilibrium constant were determined using an inverse modeling procedure. The results showed that the exchange capacity of the hydrated cement paste increased as water-cement ratio increased, while the equilibrium constant for the exchange reaction remained constant.

2. Validation tests

To verify the model, experiments that were different from the identification experiments were carried out. Chloride isotherms were simulated by varying important exposure conditions such as temperature and chloride sources. Experiments for chloride profiles were also carried out at three different water-cement ratios. All these experimental data agreed very well with the corresponding simulated results.

Chloride isotherms at different temperatures showed that increasing temperature decreased chloride binding in the cement paste.

Results from the experimental binding isotherms using two different chloride sources showed more extensive chloride binding when the source is sodium chloride rather than calcium chloride.

Results from the experiments for binding isotherms using samples with different water cement ratios showed that binding of chloride increases as water cement ratio increases.

3. Parametric study

The existing models for predicting chloride profiles in cement or concrete in the published literature are based on Fick's law and chloride isotherms. The chloride isotherms depend on the type of cement mixes and exposure conditions. Hence, those models cannot be used for any general exposure conditions or for all types of cement. By considering the specific mechanisms for the interaction of chloride ions with the cementious materials, the proposed reactive transport model can predict the amount of free and bound chlorides in concrete subjected to general exposure conditions, including differences in temperature, pH, chloride sources, and type of cement mixes, as well as interactions with other weathering phenomena such as carbonation.

The model is able to clarify some of the mechanisms controlling the interactions of cement based materials with the pore water, which have caused confusion and controversy in the literature until now. Two examples of such cases are given below.

A. Effect of pH on chloride binding isotherms.

From the simulations using proposed ion exchange theory it was found that chloride binding has an inverse relationship with the pH of the pore solution. In other words, the higher the pH, the lower the amount of bound chlorides.

B. Effect of chloride source on chloride binding

Most of the results in the published literature show that more chlorides are bound in concrete when using $CaCl_2$ than when using a NaCl source. However, there is confusion and no clear understanding about the reason behind that. Some researchers (Arya *et al.*, 1990; Ben Yair, 1974) suggested that NaCl has to react with $Ca(OH)_2$ to form $CaCl_2$ before combining with aluminate phases to form Friedel’s salt. However, according to other researchers, the difference in pH values in the pore solution with NaCl and $CaCl_2$ is responsible for the difference in chloride binding. Using the detailed information provided by the simulation results of the proposed approach, some insight into this problem has been achieved. A closer look at all the relevant reactions taking place allowed us to see that, in the case of calcium chloride, there is a formation of Portlandite ($Ca(OH)_2$) that consumes hydroxide ions in the solution. This leads to a decrease of hydroxide ions that compete for binding sites with chloride ions, which makes it easier for chloride ions to get bound.

C. The effect of carbonation on chloride binding isotherm and ingress

It is well established that, in the presence of carbonation, there is a release of bound chlorides and a drop in pH. For a long time, it was speculated that the drop in pH is responsible for the release of bound chlorides. In their study, Saeki *et al.* (2001) related the carbonation release of chloride with pH. However, a more recent study by Ishida *et al.* (2005) disagreed with the relationship between pH of the liquid phase and carbonation of Friedel's salt. In their experiment, Ishida *et al.* found that, even at higher pH values, there is a release of bound chlorides. Using the proposed model, a rational explanation has been achieved. To clarify the effect of carbonation on the release of bound chlorides, two numerical simulations were carried out. In the first simulation, carbonation was allowed to take place and no exchange for CO_3^{2-} was allowed to take place. The results for this simulation show that there is a drop in pH and an increase in the bound chlorides. In the second simulation, exchange was allowed to occur, and it was found that CO_3^{2-} had to compete with Cl- and OH- for the available binding sites through the following half reactions:

$$R^+ + OH^- \Leftrightarrow R\text{-}OH; \qquad R^+ + Cl^- \Leftrightarrow R\text{-}Cl;$$
$$2R^+ + CO_3^{2-} \Leftrightarrow R_2\text{-}CO_3$$

From this investigation, we can conclude that the long studied phenomenon of bound chloride liberation by carbonation is more related to the exchange by CO_3^{2-} rather than a drop in pH.

6.2 Limitations of the Proposed Model

Although the proposed reactive transport model has the ability to simulate very general exposure conditions, it still has some limitations that are mentioned here:

1. In the case of chloride binding, only chemical binding has been considered here. Physical binding was neglected.
2. Water flow and the transport of chemical species is assumed to take place under fully saturated conditions.
3. Solute transport is assumed to take place under pure diffusion conditions.

6.3 Recommendation for future research

1. The proposed model includes the major part of chloride binding: chemical binding. Future research can be done to include physical binding into the model to make it more accurate.

2. This reactive transport model can predict the extension of chloride penetration into concrete under different environmental exposures. The next step of the chloride penetration is the corrosion of reinforcing steel, which is a chemical reaction between the chloride ions and reinforcing steel. This model can be extended to predict the rate and extent of corrosion in reinforced concrete by including the chemical reactions of corrosion.

3. The proposed transport model is applicable only under saturated conditions. Future studies can be done to include unsaturated conditions.

4. During the experiments for pore solution extraction, using a high-speed centrifuge to drive the pore solution out of the cement paste was considered. In that method, chloroform was used to drive the pore solution out of the cement paste sample using a high speed centrifuge. Chloroform was used because it does not mix with water. Thus, if chloroform can pass through the cement paste pores, it can take the pore solution along with it, and then the pore solution can be easily separated and analysed. Due to some difficulties related to the experimental set-up and a lack of time, this experiment was dropped. Hence, future research can be carried out to assess this approach as an easy method for pore solution extraction.

REFERENCES

Al-Hussaini, M.J., Sangha, C.M., Plunkett, B.A., and Walden, P.J., 1990, “The Effect of Chloride ion Source on the Free Chloride ion Percentages in OPC Mortars.” Cement and Concrete Research, V. 20, pp. 739-745.

Aitcin, Pierre-Caude, 2006, “Binders for durable and sustainable concrete” Modern Concrete Technology 16, pp 414

Andrade, C., 1993, “Calculation of chloride diffusion coefficients in concrete from ionic migration measurements.” Cement and Concrete Research, V. 23 No. 3 pp. 724-742.

Andrade, C., and Sanjuan, M.A., 1994, “Experimental Procedures For The Calculation Of Chloride Diffusion Coefficients In Concrete From Migration Test.” Advances in Cement Research, V. 6, No. 23, pp. 127-134

Appelo, C.A.J., and Postma, D., 2005, “Geochemistry, Groundwater and Pollution.” 2nd Addition, published by Leiden, New york

Arya, C., Buenfeld, N.R., Newman, J.B., 1987, "Assessment of simple methods of determining the free chloride content of cement paste," Cement and Concrete Research, V.17, No. 6, pp. 907-918.

Arya, C., Buenfeld, N.R., Newman, J.B., 1990, "Factors influencing chloride binding in concrete." Cement and Concrete Research, V.20, No. 2, pp. 291-300.

Arya, C. and Newman, J. B., 1990, "An assessment of four methods of determining the free chloride content of concrete." Materials and Structures, V. 23., pp 319 - 330

Barneyback, R.S., Diamond, S., 1981, "Expression and Analysis of pore fluids from hardened cement paste and mortars" Cement and Concrete Research, V.11, No. 2, pp. 279-285.

Ben-Yair, M., 1974, "The effect of chlorides on concrete in hot and arid regions." Cement and Concrete Research, V.4, No. 3, pp. 405-416.

Birnin-Yauri, U.A., and Glasses, F.P., 1998, "Friedel's salt $Ca_2Al(OH)_6(Cl,OH).2H_2O$: its solid solutions and their role in chloride binding." Cement and Concrete Research, V. 28., N. 12, pp. 1713 – 1723.

Bloom, S.A., and Mansell, R.S., 2001, " An Algorithm for generating cation exchange isotherms from binary selectivity coefficients." Soil Science Society of America Journal, V.65, pp 1426-1429.

Buenfled, N.R., Newman, J.B., 1984, "Permeability of concrete in a marine environment." Magazine of Concrete Research, V. 36, pp. 67-80

Byfors, K., Hansson, C.M., Trittihart, J. 1986, "Pore solution expression as a method to determine the influence of mineral additives on chloride binding" Cement and Concrete Research, V.16, No. 5, pp. 760-770.

Cerny, R., Pavlik, Z., and Rovnanikova, P., 2004, "Experimental analysis of coupled water and chloride transport in cement mortar." Cement and Concrete Composite,V. 26. pp 705 – 715.

Chatterji, S., and Kawamura, M., 1992, "Electrical double layer, ion transport and reactions in hardened cement paste." Cement and Concrete Research, V. 22, pp. 774-782.

Csizmadia, J., Balazs, G., and Tamas, F.D., 2001, "Chloride ion Binding Capacity of Aluminoferrites." Cement and Concrete Research., V. 31, pp. 577 -588

Delagrave, A., Marchand, J., Ollivier, J., Julien, S., and Hazrati, K., 1997 “Chloride binding capacity of various hydrated cement paste systems.” Advanced Cement Based Materials, V. 6, pp. 28 -35.

Delagrave, A., Pigeon, M., Marchand, J., and Revertegat, E., 1996, “Influence of Chloride ions and pH level on the durability of high performance cement pastes (Part II).” Cement and Concrete Research, V 26, N 5, pp 749 – 760

Detwiler, R.J., Kjellsen, K.O., Gjorv, O.E., 1991, “Resistance of Chloride Intrusion of Concrete Cured at Different Temperatures.” ACI Materials Journal, V. 88, pp. 19-24.

Dhir, R.K., Jones, M.R., Ahmed, H.E.H., 1990. “Determination of total and soluble chlorides in concrete.” Cement and Concrete Research, V. 20, pp. 579-590.

Diamond, S. 1986, “Chloride Concentrations in Concrete pore solutions Resulting from Calcium and Sodium Chloride Admixtures.” Cement , Concrete and Aggregates, V.8, No.2, pp.62-79

Enevoldsen, J.N., Hansson, C.M., Hope, B.B., 1994., “Binding of chloride in mortar containing admixed or penetrated chlorides.” Cement and Concrete Research, V. 24, N. 8, pp. 1525 – 533

Funahashi, M., 1990, “Predicting Corrosion-Free Service Life of a Concrete Structure in a Chloride Environment.” ACI Materials Journal, V. 87, no. 6, pp. 581-587

Geiker, M., Nielsen, E. P., and Herfort, D., 2007, “Prediction of chloride ingress and binding in cement paste.”, Material and Structures, V. 40, pp. 405 – 417

Glass, G.K., Hassanein, N. M., and Buenfield, N.R., 1997, “Neural Network modelling of chloride binding.” Magazine of concrete research, V 49, No 181, pp 323 – 335.

Glass, G. K., Wang, Y., Buenfeld, N.R., 1996, “An Investigation of experimental methods used to determine free and total chloride contents.”, Cement and Concrete Research, V. 26, N. 9, pp. 1443 – 1449

Goto, S., Roy, D.M., 1981, “Diffusion of ions through hardened cement pastes.” Cement and Concrete Research, V. 11, pp. 751-757

Hansen, T.C., Jensen, H., Johannesson, T., 1986. “Chloride diffusion and corrosion initiation of steel reinforcement in fly-ash concretes.”, Cement and Concrete Research, V. 16, pp. 782-784

Haque, M.N., and Kayyali, O.A., 1995, “Free and Water soluble chloride in concrete.” Cement and Concrae Reseach. Vol. 25. No. 3. pp. 531-542

Hussain, S.E., and Rasheduzzafar, 1993, “Effect of Temperature on Pore Solution Composition in Plain Cements.” Cement and Concrete Research, V. 23. pp. 1357-1368

Hussain, S.E., Rasheeduzzafar, Al-Mu&am, A., and Al-Gahtani, A.S. 1995, Factors effecting threshold chloride for reinforcement corrosion in concrete, Cement and Concrete Research, Vol. 25, No. 7. pp. 1543-1555.

Ishida, T., Kawai, K., and Sato, R., 2005, “Effects of carbon dioxide concentration in gas phase of pores on the decomposition rate of Friedel’s salt due to carbonation.” In Proceedings of the ConMAT Conference, in: N. Banthia et al. (Eds.), University of British Columbia, Vancouver, Canada.

Kayyali, O.A., and Haque, M.N., 1988, “Effect of Carbonation on the Chloride Concentration in Pore Solution of Mortars with and Without Flyash.” Cement and Concrete Research, Vol. 18, No. 4. pp. 636-648.

Kawamura, M., Kayyali, O.A., Haque, M.N. , 1988, “ Effect of a flyash on pore solution composition in calcium and sodium chloride-bearing mortars.” Cement and Concrete Research. V 18, No 5, pp. 763-773.

Kouloumbi, N., Batis, G., Malami, Ch. 1994, "The anticorrosive effect of Fly Ash, Slag and a Greek Pozzolan in reinforced concrete." Cement and Concrete Research, V.16, pp. 253-260.

Li, S., and Roy, D.M., 1986, "Investigation of relations between porosity, pore structure, and C1^{-} diffusion of fly ash and blended cement pastes." Cement and Concrete Research, V. 16, pp. 749-759

Luo, R., Cai, Y., Wang, C. and Huang, X., 2003, "Study of chloride binding and diffusion in GGBS concrete." Cement and Concrete Research. V 33, No 1 pp. 1-7.

Mangat, P.S., and Molloy, B.T., 1995, "Chloride Binding in Concrete containing PFA, gbs or silica fume under sea water exposure." Magazine of Concrete Research, V. 47, No. 171, pp. 129-141

Marchand, J., Samson, E., Maltais, Y. and Beudoin, J.J., 2002, "Theoretical analysis of the effect of weak sodium sulphate solutions on the durability of concrete." Cement and Concrete Composites, V. 24, pp. 317-329

Maslehuddin, M., Page, C.L., and Rasheeduzzafar, 1997, "Temperature effect on the pore solution chemistry in contaminated cements.", Magazine of Concrete Research, V. 49, No. 178, pp. 5-14

Mehta, P.K. 1977, "Effect of Cement Composition on corrosion of reinforcing steel in concrete." Chloride Corrosion of Steel in Concrete, ASTM STP 629, Edited by D.E. Tonini and S.W. Dean Jr., pp 12-19

Midgley, H. G.; Midgley, A., 1975, "Conversion of high alumina cement." Magazine of Concrete Research, v 27, n 91, pp 59-77

Midgley, H.G., Illston, J.M. 1984, "The penetration of chlorides into hardened cement pastes." Cement and Concrete Research, V.14, No. 4, pp. 546-558.

Nagataki, S., Otsuki, N., Wee, T., and Nakashita, K., 1993, "Condensation of Chloride ion in Hardened Cement Matrix Materials and on Embedded Steel Bars." ACI Materials Journal., V. 90, No. 4, pp. 323 – 332

Neville, A. 1995, "Chloride attack of reinforced concrete: an overview," Materials and structures, V. 28, pp 63-70

Nielsena, E.P., Herforta, D., Mette R. Geiker, M.R., 2005, " Binding of chloride and alkalis in Portland cement systems." Cement and Concrete Research., V. 35, pp. 117–123

Page, C. L., Short, N. R., and El Tarras, A. 1981, "Diffusion of chloride ions in hardened cement pastes." Cement and Concrete Research, V. 11, pp. 395-406

Papadakis, V. G., Vayens, C. G., and Fardis, M. N., 1981, “Fundamenta modeling and experimental investigation of concrete carbonation.” ACI Materials Journal, V. 88, pp. 363-373

Pruckner, F., Gjørv, O.E., 2004. “Effect of $CaCl_2$ and NaCl additions on concrete corrosivity.” Cement and Concrete Research, V. 34, pp. 1209-1217

Ramachandran, V. S., Seeley, R. C. and Polomark, G. M., 1984, “Free and combined chloride in hydrating cement and cement components.” Materials and Structures, V. 17, n 100, pp. 285-289

Rasheeduzzafar 1992, “Influence of Cement Composition on Concrete Durability.” ACI Materials Journal, V.89, No. 6, pp. 574-585.

Rasheeduzzafar, Hussain, S.E., and Al-Saadoun, S.S., 1991, “Effect of Cement Composition on Chloride Binding and Corrosion of Reinforcing Steel in Concrete.” Cement and Concrete Research, V. 21, pp. 777-794

Rasheeduzzafar, Hussain, S.E., and Al-Saadoun, S.S., 1992, “Effect of Tricalcium aluminate content of Cement on Chloride Binding and Corrosion of Reinforcing Steel in Concrete.” ACI Materials Journal, V. 89, No. 1, pp. 3-12

Roberts, M.H. 1962, “Effect of calcium chloride on the durability of the pretensioned wire in prestressed concrete.” Magazine of Concrete Research, V.14, No. 42, pp. 143-154

Saeki, T., Ueki, S., Yu, Q., and Shima, T., 2001, “A model for Predicting Concrete Deterioration due to the Compound Effect of Chloride Ions Ingress and Carbonation.” Creep, Shrinkage and Durability Mechanics of Concrete and Other Quasi-Brittle Materials, Edited by F.J. Ulm, Z.P. Bazant and F.H. Wittmann, pp. 431-436

Saito, M., Kawamura, M. 1992, “Effect of Sodium Chloride on the Hydration Products in the Interfacial Zone Between Cement Paste and Alkali-Reactive Aggregate,” Interfaces in Cementitious Composites, RIELM, Edited by J.C. Maso, E. & FN Spon, London, pp. 33-41

Sandberg, P., 1999, “Studies of chloride binding in concrete exposed in a marine environment.” Cement and Concrete Research, V. 29 pp 473–477

Sandberg, P., Larsson, J., 1993, “Chloride Binding in cement pastes in equilibrium with synthetic pore solutions”, Chloride penetration into concrete structures, Nordic miniseminar. Ed. L.O. Nilsson, pp. 98-107

Sergi, G., Yu, S.W., Page, C.L. 1992, “Diffusion of Chloride and Hydroxyl ions in cementitious materials exposed to a saline environment,” Magazine of Concrete Research, V. 44, No. 158, pp. 63-69.

Siegwart, M., Lyness, J. F. and Cousins, W., 2003, “Advanced analysis of published data on chloride binding in concrete.” Magazine of Concrete Research, V. 55, No. 1, pp. 41–52

Sumranwanicha, T., and Tangtermsirikula, S., 2004, “Time-Dependent Chloride Binding Capacity of Various Types of Cement Pastes.” Science Asia, V. 30, pp. 127-134.

Suryavanshi, A.K., Scantlebury, J.D., and Lyon, S.B., 1995, “The Binding of Chloride ions by Sulphate Resistance Portland Cement.” Cement and Concrete Research, V. 25, No. 3, pp. 581-592

Suryavanshi, A.K., Scantlebury, J.D., and Lyon, S.B., 1996, “Mechanism of Friedel’s salt formation in cement rich in tricalcium aluminate.” Cement and Concrete Research, V. 26, No. 5, pp. 729-741

Suryanvanshi, A.K., Swamy, R.N. 1996, “Stability of Friedel’s salt in carbonated concrete structural element” Cement and Concrete Research, V. 26, No. 5, pp. 729-741.

Tang, L., Nilsson, L.O., 1993, “Chloride Binding Capacity and Binding Isotherms of OPC Pastes and Mortars,” Cement and Concrete Research, V. 23, No. 2, pp. 247-253.

Tang and Nilsson, 1992, “Rapid Determination of the Chloride Diffusivity in Concrete by applying an Electrical Field,” ACI Materials Journal, V. 89, No. 1, pp. 49-53

Taylor, H.F.W. 1992, “Cement Chemistry”, 2nd edition, 475 p., Academic Press Ltd., London.

Trittihart, J., 1989, “Chloride Binding in Cement I. Investigations to Determine the Composition of Pore water in Hardened Cement.” Cement and Concrete Research, Vol. 19, pp. 586 – 594.

Truc, O., Ollivier, J.P., Carcasses, M., 2000, "A new way for determining the chloride diffusion coefficient in concrete from steady state migration test." Cement and Concrete Research, V. 30 No.2 pp. 217-226.

Tuutti, K. 1982, “Analysis of pore solution squeezed out of cement paste and mortar.” Nordic Concrete research, V. 1, pp. 25.1-25.16.

Weber, C.F., 2000, “Calculation of pitzer parameters at high ionic strengths.” Industrial Engineering Chemistry Research., V. 39, pp. 4422-4426

Wee, T.H., Wong, S.F., Swaddiwudhipong, S., and Lee, S.L. 1997, A Prediction Method for Long –Term Chloride Concentration Profiles in Hardened Cement Matrix Materials.

Zhu, C., and Anderson, G., 2002, "Environmental Application of Geochemical Modeling." Cambridge University Press.

Zibara, H., 2001, "Binding of External chloride by Cement Pastes." PhD thesis to University of Toronto.

Appendix A

Input file for Fick’s law simulation:

Chemistry input file:

```
SOLUTION 1
    temp      25
    pH        7
    pe        4
    redox     pe
    units     mol/kgw
    density   1
    Cl        1.0

    -water    1 # kg
SAVE solution 1
END
SOLUTION 2
    temp      25
    pH        7
    pe        4
    redox     pe
    units     mg/l
    density   1
    -water    1 # kg

SAVE solution 2
SELECTED_OUTPUT
    -file                 Chloride onlypit.xls
    -distance             true
    -time                 true
    -ph                   true
    -totals               Cl
    -molalities           Cl-  RCl  ROH R2CO3 CO3-2 R+
                          CO2
    -equilibrium_phases   Calcite  Portlandite
END
```

Transport Input File

```
TITLE
.      FICK'S LAW

SOLUTE_TRANSPORT                          true
   -diffusivity                          1e-12

STEADY_FLOW                               true
UNITS
        -time                               yr
        -horizontal                         m
```

```
        -vertical                            m
        -head                                m
        -hydraulic_cond                    m/s
        -specific_storage                  1/m
        -dispersivity                        m

GRID
        -uniform X  0  0.2                    101
        -uniform Y  0  0.02                   2
        -uniform Z  0  0.02                   2
        -chemistry_dimensions                 X
        -print_orientation                   XY


MEDIA
        -zone   0 0 0 0.2 0.02 0.02
                -Kx                        1e-10
                -Ky                        1e-10
                -Kz                        1e-10
                -porosity                   0.2
                -storage                      0
                -longitudinal_dispersivity  0.00000001
                -horizontal_dispersivity    0.00000001
                -vertical_dispersivity      0.00000001
FREE_SURFACE_BC false

SPECIFIED_HEAD_BC
        -zone   0 0 0 0 0.02 0.02
                -head                         0         0.02
                -fixed_solution               0         1
        -zone   0.2 0 0 0.2 0.02 0.02
                -head                         0         0.02
                -associated_solution          0         2
HEAD_IC
        -zone   0 0 0 0.2 0.02 0.02
                -head   X 0.02 0.0 0.02 0.2
CHEMISTRY_IC
        -zone   0 0 0 0.2 0.02 0.02
                -solution                      2

SOLUTION_METHOD
        -direct
        -space                              0.5
        -time                               0.5
TIME_CONTROL
        -time_step                            0       0.25 yr
        -time_end                           10 yr
PRINT_FREQUENCY
        0
        -hdf_chemistry                       05 yr
        -xyz_chemistry                        05 yr
END
```

Input file for simulation of analytical solution of pulse injection of solute that undergoes sorption and decay:

Chemistry input file:

```
TITLE
.       --Pulse of solute undergoing sorption and decay
.       Analytical solution from Quantitative Hydrogeology, de Marsily
#       Kd = 1 mol sorbed/mol dissolved
#       K  = 0.01 1/s   Decay constant
SOLUTION_MASTER_SPECIES
        A       A       0       A       1
SOLUTION_SPECIES
        A = A
        log_k   0
SURFACE_MASTER_SPECIES
        Surf    Surf
SURFACE_SPECIES
        Surf = Surf
                log_k 0
        Surf + A = SurfA
                log_k   -10
SOLUTION 1
END
SOLUTION 2
        A        1.0 mmol/kgw
END
SURFACE 1
        -no_edl
        Surf    1e10
END
KINETICS 1
        A_decay
        -formula A 1.0
        -m 0
RATES
        A_decay
        -start
10 rate = -(TOT("A") + MOL("SurfA")) * .01
20 moles = rate * TIME
30 SAVE moles
        -end
END
SELECTED_OUTPUT
        -file ex1.dummy.sel
        -reset false
USER_PUNCH
```

```
        -headings A SurfA SurfA/A
10 PUNCH TOT("A")*1000
20 PUNCH MOL("SurfA")*1000
30 IF TOT("A") > 0 THEN PUNCH MOL("SurfA")/TOT("A") ELSE PUNCH -1
END
```

Transport input file:

```
TITLE
.       --Pulse of solute undergoing sorption and decay
.       Analytical solution from Quantitative Hydrogeology, de Marsily
#       1D region       12 cm
#       Velocity       0.1 cm/s
#       Porosity       0.1
#       Dispersivity     1 cm    (isotropic)
#       120 s pulse,
SOLUTE_TRANSPORT                           true
STEADY_FLOW                                true
UNITS
        -time                               sec
        -horizontal                          cm
        -vertical                            cm
        -head                                cm
        -hydraulic_cond                    cm/s
        -specific_storage                  1/cm
        -dispersivity                        cm
GRID
        -uniform X  0 12                     61
        -uniform Y  0  1                      2
        -uniform Z  0  1                      2
        -chemistry_dimensions                 X
        -print_orientation                   XY
MEDIA
        -zone   0 0 0 12 1 1
                -Kx                        0.12
                -Ky                        0.12
                -Kz                        0.12
                -porosity                   0.1
                -storage                      0
                -longitudinal_dispersivity  0.1
                -horizontal_dispersivity    0.1
                -vertical_dispersivity      0.1
FREE_SURFACE_BC false
SPECIFIED_HEAD_BC
        -zone   0 0 0 0 1 1
                -head                         0         1
                -associated_solution          0         2

        -zone   12 0 0 12 1 1
                -head                         0       0.0
                -associated                   0         1
HEAD_IC
        -zone   0 0 0 12 1 1
                -head   X 1.0 0.0 0.0 12.0
CHEMISTRY_IC
```

```
        -zone   0 0 0 12 1 1
                -solution                     1
                -surface                      1
                -kinetics                     1
SOLUTION_METHOD
        -direct
        -space                              0.5
        -time                               0.5
TIME_CONTROL
        -time_step                            0       0.4 sec
        -time_end                           120 sec
PRINT_FREQUENCY
        0
        -hdf_chemistry                       10 sec
        -xyz_chemistry                        0 sec
        60
        -velocity                            60 sec
        -xyz_chemistry                       60 sec
        -force_chemistry_print               60 sec
END
```

Input file for chloride Isotherms:

Isotherm of chloride in cement paste with W/C ratio of 0.5 at 25C

```
SOLUTION 1
    temp      25
    pH        12.8
    pe        4
    redox     pe
    units     mg/l
    density   1
    -water    0.130 # kg

EXCHANGE_MASTER_SPECIES
    R             R+
EXCHANGE_SPECIES
R+ = R+
    log_k     0
OH- + R+ = ROH
    log_k     0
    delta_h   0 kJ
Cl- + R+ = RCl
    log_k     -1.25
    delta_h   -12 kJ

EQUILIBRIUM_PHASES 1

    Portlandite 0 0.34
```

```
EXCHANGE 1
    ROH     0.0154

REACTION 1
    NaCl       1
    0.40 moles in 20 steps
SELECTED_OUTPUT
    -file                 SapleA_1.xls
    -molalities           Cl-  RCl
END
```

Input file for Chloride Profile:

Chloride profile in cement paste with W/C ratio of 0.5

Chemistry input file:

```
SOLUTION 1
    temp      25
    pH        7
    pe        4
    redox     pe
    units     mol/kgw
    density   1
    Cl        1.125
    Na        1.125
    -water    1 # kg
EQUILIBRIUM_PHASES 1
    Portlandite 0 1
SAVE solution 1
END
SOLUTION 2
    temp      25
    pH        7
    pe        4
    redox     pe
    units     mg/l
    density   1
    -water    0.024 # kg
EXCHANGE_MASTER_SPECIES
    R            R+
EXCHANGE_SPECIES
R+ = R+
    log_k     0
OH- + R+ = ROH
```

```
    log_k     0
Cl- + R+ = RCl
    log_k    -1.25

EXCHANGE 2
      -equil with solution 2
    ROH     0.5246
EQUILIBRIUM_PHASES 2

    Portlandite 0 2.1
SAVE solution 2
SELECTED_OUTPUT
    -file                Chloride onlypit.xls
    -distance            true
    -time                true
    -ph                  true
    -totals              Cl
    -molalities          Cl-  RCl  ROH R2CO3 CO3-2 R+
                         CO2
    -equilibrium_phases  Calcite  Portlandite
END
```

Transport input file:

```
TITLE
.      CHLORIDE INGRESS

SOLUTE_TRANSPORT                          true
   -diffusivity                          6e-11

STEADY_FLOW                               true
UNITS
        -time                               yr
        -horizontal                         m
        -vertical                           m
        -head                               m
        -hydraulic_cond                   m/s
        -specific_storage                 1/m
        -dispersivity                       m

GRID
        -uniform X  0  0.2                   101
        -uniform Y  0  0.02                  2
        -uniform Z  0  0.02                  2
        -chemistry_dimensions                X
        -print_orientation                  XY


MEDIA
        -zone   0 0 0 0.2 0.02 0.02
                -Kx                       1e-10
                -Ky                       1e-10
                -Kz                       1e-10
                -porosity                  0.29
```

```
                -storage                      0
                -longitudinal_dispersivity  0.00000001
                -horizontal_dispersivity    0.00000001
                -vertical_dispersivity      0.00000001
FREE_SURFACE_BC false

SPECIFIED_HEAD_BC
        -zone   0 0 0 0 0.02 0.02
                -head                         0         0.02
                -fixed_solution               0         1
        -zone   0.2 0 0 0.2 0.02 0.02
                -head                         0         0.02
                -associated_solution          0         2
HEAD_IC
        -zone   0 0 0 0.2 0.02 0.02
                -head   X 0.02 0.0 0.02 0.2
CHEMISTRY_IC
        -zone   0 0 0 0.2 0.02 0.02
                -solution                      2
                -equilibrium_phase             2
                -exchange                    2
SOLUTION_METHOD
        -direct
        -space                              0.5
        -time                               0.5
TIME_CONTROL
        -time_step                            0       0.1 yr
        -time_end                           1.0 yr
PRINT_FREQUENCY
        0
        -hdf_chemistry                       0.2 yr
        -xyz_chemistry                        0.1 yr
END
```

Input file for Chloride isotherm in presence of carbonation without considering carbonate exchange (Simulation 1)

```
SOLUTION 1
    temp      25
    pH        12.8
    pe        4
    redox     pe
    units     mg/l
    density   1
    -water    0.130 # kg

EXCHANGE_MASTER_SPECIES
    R             R+
EXCHANGE_SPECIES
R+ = R+
    log_k     0
```

```
OH- + R+ = ROH
    log_k     0
    delta_h   0 kJ
Cl- + R+ = RCl
    log_k     -1.25
    delta_h   -12 kJ

EXCHANGE 1
    ROH     0.0154
EQUILIBRIUM_PHASES 1
    Calcite   0 0
    CO2(g)    -1.3 100000
    Portlandite 0 0.35
REACTION 1
    NaCl       1
    1 moles in 20 steps
SELECTED_OUTPUT
    -file                 iso_carbo ex.xls
    -molalities           Cl-  RCl
END
```

Input file for Chloride isotherm in presence of carbonation considering carbonate exchange (Simulation 2):

```
SOLUTION 1
    temp      25
    pH        12.8
    pe        4
    redox     pe
    units     mg/l
    density   1
    -water    0.130 # kg

EXCHANGE_MASTER_SPECIES
    R             R+
EXCHANGE_SPECIES
R+ = R+
    log_k     0
OH- + R+ = ROH
    log_k     0
    delta_h   0 kJ
Cl- + R+ = RCl
    log_k     -1.25
    delta_h   -12 kJ
CO3-2 + 2R+ = R2CO3
    log_k     +3.25

EXCHANGE 1
    ROH     0.0154
EQUILIBRIUM_PHASES 1
    Calcite   0 0
    CO2(g)    -1.3 100000
```

```
    Portlandite 0 0.35
REACTION 1
    NaCl       1
    1 moles in 20 steps
SELECTED_OUTPUT
    -file                 iso1_carbo.xls
    -molalities           Cl-  RCl
END
```