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Mathematical Modelling of Chloride Penetration of Mortar (BTB-20)

Final Project Report

Mengheng, Ea

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Disclaimer

I declare this report to be my own work according to University academic integrity policy, unless otherwise referenced as per Harvard referencing guide UniSA.

Mengheng Ea

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Executive Summary

Owing to its durability, concrete is the most used material in construction industry and cement is an essential component in making concrete. However, production of clinker, a main component of cement is concerning to the environment as it releases a large amount of carbon dioxide (CO_2). Consequently, in order to reduce these greenhouse gas levels, addition of mineral material such as limestone might be adopted. A small proportion of cement kiln dust (CKD), collection of waste dust from the burning of the clinker in the rotary kiln, is also suggested as mineral addition to cement as to reduce the quantity of waste material being sent to landfill. Having said that, concrete durability, especially chloride resistance, should not be compromised because from preliminary investigation it is found that limestone could accelerate rate of chloride penetration resulting in corrosion of reinforcement plus there are chlorides present in CKD. These minerals are therefore suggested to be added in combination with fly ash to reverse this effect.

Data relating to the chloride penetration of mortar samples containing different percentages of limestone, CKD and fly ash has been tested using NT Build 443 test. This involves subjecting the specimens to immersion in a sodium chloride solution for 35 days and this is followed by determining the actual chloride content at various depths within the specimen by chemical titration.

In the proposed study, several research questions were addressed. The main objective is to establish a reliable model that can predict the rate of chloride penetration in the long term. Several existing models were used to analyse published data that were exposed for a number of years to determine their accuracy in predictions before choosing the most reliable one to analyse data from NT Build 443 test.

Based on the results, time-dependent Model 3, based on Aldridge, gives the most accurate prediction of chloride profiles of samples exposed up to 8 years. Results from analysis of Nord NT Build 443 test indicate that diffusivity of mortar increases with increasing level of limestone addition. However, the relationship is not yet distinct between rate of chloride penetration and addition of cement kiln dust and thus need further investigation. Furthermore, addition of 20% fly ash reduces the rate of chloride penetration significantly. But when a further 10% of fly ash is added, there is only slight decrease in diffusivity of mortar.

Contents

Disclaimer i

Acknowledgements ii

Executive Summary iii

Contents iv

Figures vi

Tables vii

Nomenclature viii

1. Introduction 1

   Background 1

2. Problem Statement 2

3. Research Questions 3

4. Literature Review 4

   Time dependency of chloride diffusion coefficient 4

   Time dependency of surface chloride concentration 9

   Effect of concrete properties and binder type on diffusion coefficients 11

   Existing modelling software packages 12

   Summary of literature review 13

5. Research Methodology 14

   Model 1 15

   Model 2 19

   Model 3 20

   Alternative Model 20

6. Results and Discussions 21

   Published Data 21

      6.1.1. Analysis by simplified model 24

      6.1.2. Analysis by Model 1, 2 and 3 26

   UniSA laboratory data from Nord NT Build 443 33

7. Conclusion 38

8. Recommendations 38

9. References 40

Appendices 43

   Appendix A: Results of published data by simplified model 43

   Appendix B: Results of published data by Model 1, 2 and 3 45

      B1 Portland cement concrete 45

B2 Fly ash concrete 46
B3 Slag concrete 48
Appendix C Results of UniSA laboratory data by simplified model 50

Figures

Figure 1: Chloride profiles of concrete and mortar (Dedicoat, Ramji & Zeng, 2013) 2
Figure 2: Time dependency of instantaneous diffusion coefficients calculated using short term penetration test (Luguang & Jianming 2012, p. 315) 7
Figure 3: Apparent diffusion coefficient calculated using the long term test (Luguang & Jianming 2012, p. 316) 7
Figure 4 Surface chloride content with time from a linear and square root build-up models, and the refined model (Song, Lee & Ann, 2008) 10
Figure 5 Average diffusion coefficients against exposure time 24
Figure 6 Chloride profiles by simplified model and experimental data of Portland cement concrete 25
Figure 7 Chloride profiles by simplified model and experimental data of fly ash concrete 25
Figure 8 Chloride profiles by simplified model and experimental data of slag concrete 26
Figure 9 Comparison between model 1 to 3 and experimental data for Portland cement concrete .. 27
Figure 10 Comparison between model 1 to 3 and experimental data for fly ash concrete 28
Figure 11 Comparison between model 1 to 3 and experimental data for slag concrete 29
Figure 12 Published data: change in diffusion coefficient with time... 30
Figure 13 Published data: predicted profiles at 50 years 31
Figure 14 Published data: depth of penetration at critical threshold level (0.12% mass of binder) 32
Figure 15 Diffusion coefficient at 0% fly ash, 0% CKD and different levels of limestone 36
Figure 16 Diffusion coefficient at 0% fly ash and different levels of limestone and CKD 36
Figure 17 Diffusion coefficients at 0% CKD with different levels of limestone and fly ash 37

Tables

Table 1: Regression parameters for 4% Limestone 17

Table 2: Values of D_{28} from the adjusted results 17

Table 3: Value of C_o from the adjusted results 18

Table 4: Value of k from the adjusted results 18

Table 5: Published data: concrete mixes (Thomas & Bamforth 1999) 21

Table 6: Published data: chloride concentration profiles (% mass of concrete) (Thomas & Bamforth 1999) 22

Table 7: Published data: chloride concentration profiles (% mass of binder) (Thomas & Bamforth 1999) 23

Table 8: 2013 mix details (Benn B.T., Baweja D. and Mills J.E. 2014) 33

Table 9 Illustration of unique mixed code (Jogi et al. 2013) 34

.... 34

Table 10: NT Build 443 test results 35

Table 11: Best fitted values of D_a and C_s of published data by simplified model 43

Table 12: Predictions of chloride contents by simplified model and experimental data of Portland cement concrete 43

Table 13: Predictions of chloride contents by simplified model and experimental data of fly ash concrete 44

Table 14: Predictions of chloride contents by simplified model and experimental data of slag concrete 44

Table 15 Comparisons between Model 1 and experimental data for Portland cement concrete 45

Table 16 Comparisons between Model 2 and experimental data for Portland cement concrete 45

Table 17 Comparisons between Model 3 and experimental data for Portland cement concrete 46

Table 18 Comparisons between Model 1 and experimental data for fly ash concrete 46

Table 19 Comparisons between Model 2 and experimental data for fly ash concrete 47

Table 20 Comparisons between Model 3 and experimental data for fly ash concrete 47

Table 21 Comparisons between Model 1 and experimental data for slag concrete 48

Table 22 Comparisons between Model 2 and experimental data for slag concrete 48

Table 23 Comparisons between Model 3 and experimental data for slag concrete 49

Table 24: Best fitted values of D_a and C_s of UniSA laboratory data by simplified model 50

Nomenclature

Symbol	Definition
$C(x,t)$	Chloride concentration measured at depth x and exposure time t
C_i , C_o	Initial chloride-ion concentration of the cementitious mixture prior to the submersion in the exposure solution
C_s	Surface chloride concentration or projected chloride concentration at the interface between the exposure liquid and test specimen that is determined by the regression analysis
D	Chloride diffusion coefficient
D_o	Instantaneous diffusion coefficient at the reference time of t_o
D_{28}	Diffusion coefficient at 28 days
D_a	Apparent diffusion coefficient
$D_{app(t)}$	Apparent diffusion coefficient at time t
$D_{ins(t)}$	Instantaneous diffusion coefficient at time t
D_{ref}	Diffusion coefficient at reference time t_{ref}
erf	Error function (table with values of the error function are given in standard mathematical reference books)
k	Time dependency factor of surface chloride concentration (C_s)
m	Time dependency factor of apparent diffusion coefficient using long term data
n	Time dependency factor of instantaneous diffusion coefficient using short term data
t	The exposure time
t_1	Age of concrete at the beginning of immersion period
t_2	Age of concrete at the end of immersion period
t_{eff}	Effective age of average diffusion coefficient from test
t_{ex}	Exposure time
t_{ref}	Reference time
x	Depth below the exposed surface (to middle of a layer)

1. Introduction

Corrosion of reinforcement has long been a costly issue leading to premature failure of concrete structures, especially in Australia as the majority of Australia's cities are located along the coastline. Every year corrosion costs Australia approximately A$13 billion (Manuel 2013). Chlorides are the primary cause of corrosion of reinforcement that leads to deterioration of the structures (Song & Shayan 1998; Robery 2005). Chlorides penetrate concrete cover and significantly increase the potential for corrosion of the steel reinforcement that eventually leads to loss of structural functionality. Therefore, it is essential to develop a reliable model for prediction of service life of concrete structures as this is necessary to provide sufficient cover in design stage. In addition it is necessary to ensure quality control in order to plan for regular maintenance to be carried out.

Through this study, it is anticipated that a reliable modelling method for chloride ingress prediction, where increased levels of limestone mineral addition has been incorporated into the cement, will be established, which will be used to analyse data generated in UniSA laboratory to predict its chloride penetration between 1 year and 50 years. These mortar specimens were made with cement containing different percentages of limestone mineral along with addition of varying percentages of cement kiln dust, fly ash and slag. Their results will be analysed as to reveal links between these mineral and rate at which chloride ions penetrate through mortars. Comparisons of service lives and chloride diffusion coefficients between these mortars will be done to achieve this.

Background

Chloride ions can be transported via three main mechanisms. One being diffusion where chloride ions are moved from high to low concentration regions under a concentration gradient, provided that adequate moisture is present. The second mechanism is called capillary absorption. This happens when chloride-containing water encounters dry surface of the concrete and this will be drawn into the concrete's porous matrix. However, the depth of penetration is generally not deep enough to reach reinforcement unless the concrete has very poor quality or shallow cover. Nevertheless, the chloride ingress is facilitated due to reduction of distance for chlorides to diffuse. Another mechanism is permeation. Chloride ions are driven into concrete matrix when hydrostatic pressure gradient is applied on one face of the concrete and this external hydraulic head can be sourced from wave actions in marine environments. Of all these mechanisms, diffusion is the principal one that can drive chlorides to the level of reinforcement, and hence will be used as a benchmark for purpose of results evaluation in this project (Stanish, Hooton & Thomas 1997). Nord NT Build 443 is believed to be the closest method in replicating a mechanism that involve diffusion only (Hamilton et al. 2007, p. 45). A study, which compares the results of chloride profiles of both mortar and concrete specimens containing 4% and 10% limestone mineral addition using Nord NT Build 443, found that there is a good correlation between the two types of specimens, thereby verifying that the test method is an appropriate testing for this research (Dedicoat, Ramji & Zeng 2013). Thus, in spite of its using mortar, the results obtained could be valid for concrete as well. The graph plotted the results of chloride profiles from this study is shown in Figure 1.

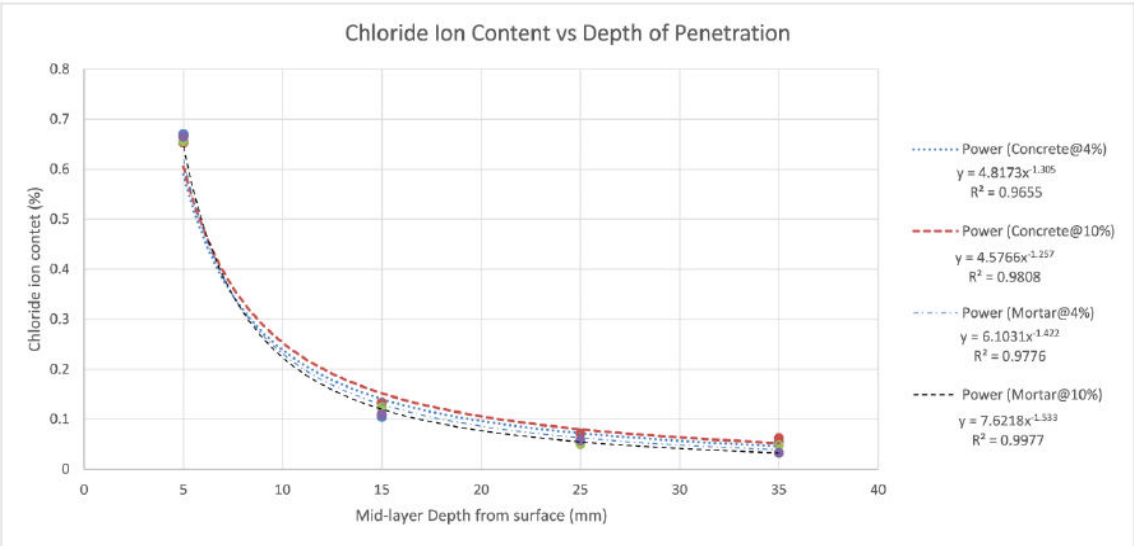

Figure 1: Chloride profiles of concrete and mortar (Dedicoat, Ramji & Zeng, 2013)

2. Problem Statement

There are a variety of models that have been developed based on Fick's second law. Nevertheless, it is noted that some of these models are incapable of accurately predicting chloride ingress in the long term and it has been suggested that this is due to lack of understanding of time-dependency of diffusion and surface chloride concentration. Due to this, it is noted that sometimes these time-dependency are not incorporated into the models altogether. Thus, it is vital to study this influence as one of the main objectives of this research is to be able to predict the long term rate of chloride penetration.

The results obtained from a suitable modelling method will be analysed in order to study the effects of mineral additions, present in the cement, will have on chloride ingress into concrete. Owing to its durability, concrete is the most used material in construction industry and cement is an essential component in making concrete. However, production of clinker, a main component of cement is concerning to the environment as it releases a large amount of carbon dioxide (CO_2). In fact, 0.9 tonnes of CO_2 is emitted for every one tonne of cement which needs 1.6 tonne of raw materials, proving this is significantly detrimental to the environment (McGrath, 2012). Consequently, in order to reduce these greenhouse gas levels, addition of mineral material such as limestone might be adopted. A small proportion of cement kiln dust (CKD), collection of waste dust from the burning of the clinker in the rotary kiln, is also suggested as mineral addition to cement as to reduce the quantity of waste material being sent to landfill. Having said that, concrete durability, especially chloride resistance, should not be compromised. Fly ash, a typical cement extender, which is shown to be beneficial in improving properties in cement such as workability, compressive strength, shrinkage reduction and in particular, its resistance to chloride ingress (Neville, 1995). Therefore, this investigation into the effect of additions of limestone and CKD as well as fly ash and slag have on chloride penetration of concrete is being undertaken. The information will be beneficial for cement industry that running test programs to reduce greenhouse gases by increasing the level of mineral additions above its current one. a revision in 2010 of the Australian Standard AS 3972 – General Purpose and Blended Cements allowed the mineral addition to be increased to 7.5%.

3. Research Questions

The main objective of this research investigation is to find a reliable model, which can be used to predict chloride penetration of mortar specimens in a large research programme.

The research questions that will be as well deliberated are:

- What is the effect on mortar/concrete made with cements containing increased limestone additions, cement kiln dust regarding the rate of chloride penetration?
- Would fly ash mitigate the effect of chloride ingress in mortar/concrete?
- Is the time dependency of chloride diffusion coefficient and surface chloride concentration significant at this early age of the mixes?
- Up to what percentages of limestone and cement kiln dust present in cement would provide reasonable service life?

4. Literature Review

Over the years, many models have been developed in order to calculate chloride concentration within concrete cover in relation to time so that service life, defined as the time until corrosion initiation, can be predicted accurately. Diffusion into a material is explained by Fick's law and thus almost all models are based on this. However, since concrete is not a static material and has different properties from one structure to another, a simplified model that does not take these factors into account tends to underestimate or overestimate the chloride ingress. As shown across a variety of published literature, there is some discrepancy between actual chloride ingress in field data or experimental data and ones predicted by the models. This literature review was carried out in order to explore a variety of factors that can possibly cause these errors.

Time dependency of chloride diffusion coefficient

The most basic and simplest model developed is based on Fick's second law (Albridge, 2012a):

$$C(x,t) = C_s - (C_s - C_i)\mathrm{erf}(\frac{x}{\sqrt{4D}}) \qquad (1)$$

where

C(x, t) – chloride concentration, measured at depth x and exposure time t (% mass)

C_s – projected chloride concentration at the interface between the exposure liquid and test specimen that is determined by the regression analysis (% mass)

C_i – initial chloride-ion concentration of the cementitious mixture prior to the submersion in the exposure solution (% mass)

x- depth below the exposed surface (to middle of a layer) (m)

D- chloride diffusion coefficient (m^2/s)

t – the exposure time (sec)

erf – error function (table with values of the error function are given in standard mathematical references books).

Because this is a relatively simple mathematical expression compared to other developed models, it has been widely used for practical purposes by engineers despite its oversimplified assumptions which cause the model to be too conservative. This simplified model assumes that the chloride is penetrating the cover concrete by means of only pure diffusion and that the concrete is a static, homogeneous material. As mentioned by Luguang, Wei and Jianming (2012), since concrete material is not in fact static as assumed, the simplified model fails to take into consideration of the tightening of pore structure over time which in turn make it harder for chloride to penetrate into concrete as a result of blockage of hydration materials. Therefore, it is necessary to incorporate this time-dependency of chloride diffusion coefficient (D) in order to have a more accurate analysis.

This stated time dependency is further illustrated in a field studies of concrete exposed to marine environment in Norway carried out by Skjolsvold and Markeset (2010). In the studies, the graph where values of Dare plotted against their corresponding exposure periods of up to ten years clearly indicates that the chloride diffusion coefficient does decreases with time as also claimed by Luguang, Wei and Jianming (2012) and Tang and Gulikers (2007).

As the time-dependency of D has been proven by many data from various studies and experiments, it has prompted researchers to propose new mathematical expressions for the time dependency of D. The expression for this is (Stanish and Thomas, 2003):

$$D(t) = D_{ref}\left(\frac{t_{ref}}{t}\right)^m \quad (2)$$

where

D_{ref} is the diffusion coefficient at some time, t_{ref}

m is a variable to describe the rate of change of the diffusion coefficient.

t is the exposure period.

Chloride diffusion coefficient is determined by several test methods which can be divided into two main categories based on the duration of the test – long term and short term. The mathematical expression for D obtained from both tests have the same exponential function and many researchers have used both to calculate 'm', as if they have the same meaning. It is argued to be otherwise and it is claimed that D obtained from one test has different meaning to another (Luguang, Wei & Jianming, 2012). For instance, substituting time-dependency factor calculated from short term test into service life prediction model specifically developed for long term test or vice versa, leads to major errors. Thus, these have to be dealt with separately. According to Luguang and Jianming (2012, p.314), definitions of each diffusion coefficient are provided as below:

> …for long-penetration tests such as the natural immersion test or the field exposure test, because of its long immersion time, the diffusion coefficient is generally considered as an apparent diffusion coefficient or an effective diffusion coefficient (D_{app}), that is, the average diffusion coefficient within a certain period of time; but for the short term test, such as the rapid diffusivity tests, because of its short test time (usually continue a few hours to a day or two), the diffusion coefficient can be called the instantaneous diffusion coefficient (D_{ins}), that is, the diffusion coefficient of concrete at a certain time.

The time dependencies of instantaneous D and apparent D are presented graphically in Figure 2 and 3 respectively.

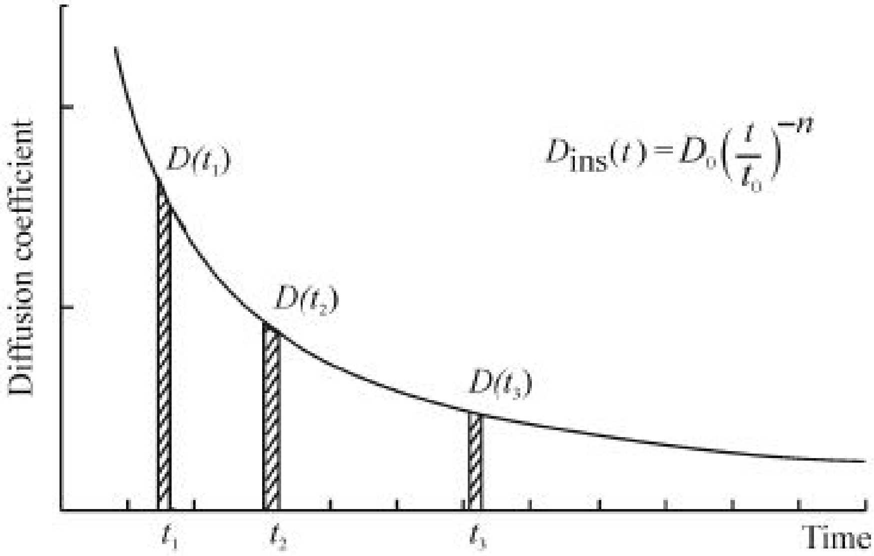

Figure 2: Time dependency of instantaneous diffusion coefficients calculated using short term penetration test (Luguang & Jianming 2012, p. 315)

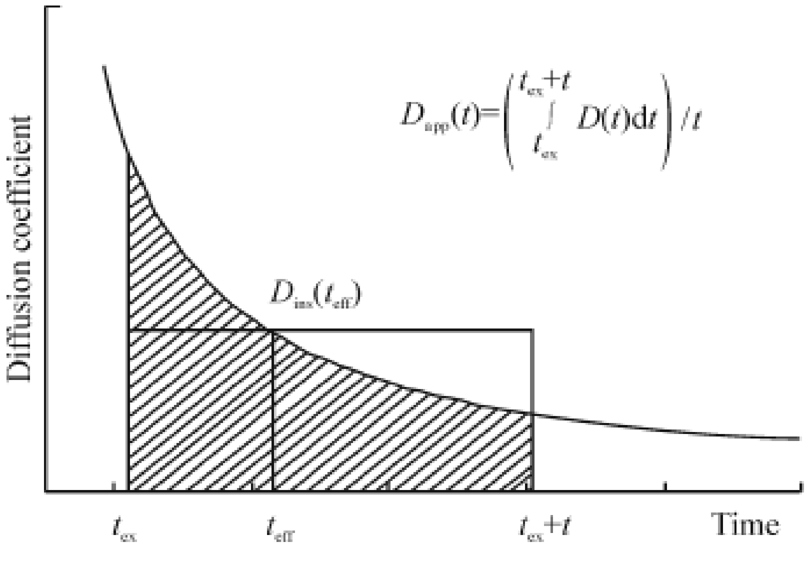

Figure 3: Apparent diffusion coefficient calculated using the long term test (Luguang & Jianming 2012, p. 316)

As noted in Nilson (cited in Luguang & Jianming 2012, p.316), after studying the relationship between the two, it is emphasised that if one of time dependencies expression is true, the other is not. A considerable number of data is needed, especially the ones from specimens exposed for a very long time in the field, in order to determine the validity of these time dependencies (Luguang, Wei & Jianming 2012).

Apart from the issue raised above, another possible error in service life prediction stems from the fact that the time-dependent D is substituted directly into equation (1). However, this is argued to be mathematically incorrect due to the fact that equation (1) is derived from Fick's first law with the assumption of constant diffusion (Luguang, Wei & Jianming 2012, Tang & Gulikers 2007, Petcherdchoo 2013). Therefore, Fick's second law should be solved with new boundary conditions. Hence, two proposed service life prediction models to be used for long term penetration test and short term penetration test are shown in equation (3) & (4) and equation (5) respectively (Luguang, Wei & Jianming 2012) and these also incorporate the effect of curing period.

$$C(x,t) = C_s(1 - erf\,\frac{x}{2\sqrt{T}}) \tag{3}$$

$$T = \frac{D_o}{1-n}.[\left(1 + \frac{t'_{ex}}{t}\right)^{1-n} - (\frac{t'_{ex}}{t})^{1-n}\,].(\frac{t'_o}{t})^n.t \tag{4}$$

where

D_o is the instantaneous diffusion coefficient at the reference time of t_o

n is the constant of the time dependency of instantaneous diffusion coefficient which calculated using short term test data from equation (2), but by replacing D_{ref} for D_o and m for n.

t_{ex} is the age of concrete at the start of exposure (curing period)

t is the duration of exposure

$$C(x,t) = C_s\left[1 - erf\frac{x}{2\sqrt{D_o'(\frac{t_o}{t})^m.t}}\right] \qquad (5)$$

where

D_o' is the apparent diffusion coefficient calculated from the long term test data from equation (2), but by replacing D_{ref} for D'_o.

To further reinforce the importance of accurately determining time-dependency factor, in the Skjolsvold and Markeset (2010) work; a probabilistic method was utilized to numerically study the sensitivity of all relevant parameters in the model and not surprisingly the age factor is found to be a dominant one. Just by solely varying mean values of age factors, the steel reinforcement within the concrete has a high probability of fifty percent to corrode.

Time dependency of surface chloride concentration

D is not the only parameter that depends on time. According to Skjolsvold and Markeset (2010), Figure 3 in the article illustrates the time dependency of surface chloride concentration (C_s) with exposure time. Similarly, Figure 7 and 8 within Tang and Gulikers (2007) studies also points out the same trend, notably even for concrete under submersion. The reason for this occurrence is suggested to have been caused by an increase in chloride binding capacity in relation to time. However, it is noted that there is no time-dependency of C_s in equation (4) and (5).

In a study by Song, Lee and Ann (2008), C_s predicted by models whose C_s expressions accounts for its increase over time, as in equation (6) and (7), are compared to the values of experimental data of C_s. The results showed that the models using these equations produce unrealistically low values of C_s at early exposure time and thereby underestimate it. Also, the model overestimate C_s at long-term exposure. A refined model results from empirical derivation of published data (equation 8), is then introduced. It includes the initial build-up of chlorides on the surface of concrete (C_o) and it is found that its prediction is closer to the measured data at an early age and rise to a constant value after 60 years. This is indicated in Figure 4.

$$C_s(t) = kt \qquad (6)$$

$$C_s(t) = k\sqrt{t} \qquad (7)$$

$$C_s(t) = C_o + k\ln(t) \qquad (8)$$

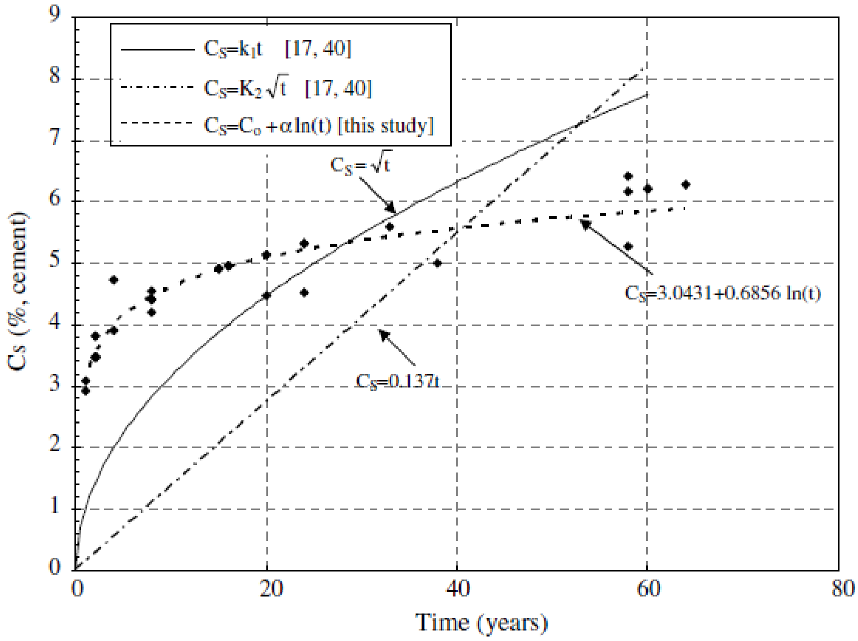

Figure 4 Surface chloride content with time from a linear and square root build-up models, and the refined model (Song, Lee & Ann, 2008)

In his paper, Aldridge (2012b) introduced a modelling method whose time dependency of C_s expressed in exponential form as indicated in equation (9). The prediction by this model has a fairly well-fitted curve to experimental data produced from Nord Build 443 test at a variety of exposure times. Nonetheless, the relationships between the model prediction and experimental data are not valid after 10 years and therefore it is suggested that this is the limit of the model's reliability, otherwise it would leads to overestimation of the service life of concrete at long times. The modelling equation used is (Albridge 2012b):

$$C(x) = C_o(t/t_o)^k\left(1 - \mathrm{erf}\left(\frac{x}{2\sqrt{tD_o\left(\frac{t}{t_o}\right)^{-m}}}\right)\right) \qquad (9)$$

Although Charlee et al. (cited in Petcherdchoo, 2013) proposed a model that takes into account of time-dependency of both D and C_s, the C_s term in the model's equation is proven to be mathematically incompatible when compared with numerical solutions by the finite difference method (Petcherdchoo, 2013).

Effect of concrete properties and binder type on diffusion coefficients

Moreover, water/binder ratios also plays a fairly substantial role in affecting chloride transport within concrete. For instance, it is found that upon measurement of D, chloride diffusivity varies considerably across different types of water/binder ratios (Page et al. cited by Aldridge 2012a, p.2). Consequently, on top of using time-dependent D and C_s, Life-365 model also relate its D to water binder ratio (Maheswaran & Sanjayan 2004, p.6). This model still has not considered all effects as it is widely known that due to the way the pore structure of different concrete mix proportion is formed differently, the effect of binder type is also attributed to time-dependency of D (Song, Lee & Ann 2008, p.115). For example, due to the nature of fine particle size distribution along with dense matrix in concrete containing pulverized fuel ash (PFA) and ground granulated blast-furnace slag (GGBS), the transportation of chlorides into this material is comparatively slower. Chloride diffusion is found to vary by an order of magnitude in concrete with different cement types (Hansson et al. cited by Aldridge 2012a, p.3). According to statements of the preceding two sources, it is obvious that the effect of binder type also accounts for the variation of D in concrete. Thus, it is important to not ignore this effect as shown in Tang and Gulikers (2007): when actual ingress profiles are compared with chloride profiles obtained from a model not accounting for binder replacement, although it can relatively predict the ingress well in Portland cement concrete, it leads to a considerable underestimation of chloride ingress in concrete containing fly ash.

In eliminating possible errors in the oversimplified model discussed so far that can cause inaccuracies in service life prediction, Petcherdchoo (2013) developed a model:

$$C(x,t) = C_o\left[erfc\left(\frac{x}{2\sqrt{D_a t}}\right)\right] + k \times \sqrt{t}\,[e^{-\frac{x^2}{4D_a t}} - \left(\frac{x\sqrt{\pi}}{2\sqrt{D_a t}}\right) erfc(\frac{x}{2\sqrt{D_a t}})] \qquad (10)$$

$$D_a = \frac{D_{28}}{1-m}\left[\left(1+\frac{28}{365t}\right)^{1-m} - \left(\frac{28}{365t}\right)^{1-m}\right].(\frac{28}{365t})^m \qquad (11)$$

where

D_{28} is diffusion coefficients at 28 days (mm^2/year).

k is a constant related to the rate of increase of surface chloride per square root of the exposure time.

x and t are the distance from concrete surface (mm), and the time after exposure (years), respectively.

m is age factor.

It is noted that this model requires two sets of measured data at two different times.

Nevertheless, Tang (2008) argues that empirical models based on Fick's second law in general are incorrect in the sense that the total chloride is taken as driving potential while in fact it is the free chloride and thus a physical and chemical based model is more appropriate, for instance, ClinConc model (Tang 2008). Plus, this model also considers the non-linearity of chloride binding capacity unlike other empirical models. Despite an attempt to modify the original ClinConc model to be more engineer-friendly with less sophisticated numerical evaluation, there are still a lot of parameters to be determined, in particular, chloride binding constants have to be determined from chloride binding isotherms. It should also be noted that data from short term test is required for this model.

Elsewhere, validation of another model using short term test data, DuraCrete model, results in a conclusion that it can predict chloride ingress fairly well provided that D at half a year is used as opposed to 28 days because with the latter, the chloride ingress is underestimated (Tang & Lindvall 2013).

Existing modelling software packages

Over the years, although Fick's-law-based models have been continuously modified and developed to eliminate the assumptions present in the model as shown in Equation (1), they still inevitably fail to consider several real-world factors which vary from one concrete structure to another such as concrete mixture proportions, different types of reinforcing bars and their coating materials. Furthermore, since these models use basic spreadsheet, they lacks the flexibility in updating material properties and boundary conditions using tedious iterative procedure. On the other hand, according to Bentz et al. (2014), models developed using powerful, advanced computer program are more flexible and accurate, because they are capable of solving the differential form of Fick's first law using finite-element analysis and permits implementation of real-world considerations. In the paper, an overview of existing modelling software packages were given. Firstly, Life-365 is able to model up to two dimensional chloride exposure and gives the options of selecting different materials (reinforcing bars and their corresponding coating materials), concrete mixture proportions. Another concrete-specific model mentioned was STADIUM 2.99. Not only is this model able to evaluate the effect of corrosion-protection measures (sealers, membranes and thick overlays), for different types of steel reinforcements, it holds a wide-range of databases of corresponding corrosion thresholds plus exposure conditions. Lastly, a generalized simulation and modelling package called the COMSOL Multiphysics is also able to predict concrete service life by linking its several modules such as transport/reaction module, mechanical/thermal response and corrosion modules.

Summary of literature review

The literature review discussed above has provided explanations as to why some of the existing models inaccurately predict the actual chloride ingress. Through various experimental studies and sensitivity analysis, even though time dependency expressions of D and C_s has to be accommodated for in the model to account for their effects, this should be integrated with correct boundary conditions from Fick's first law to ensure its mathematical compatibility. Otherwise, this will lead to errors.

Moreover, the literature has cleared confusion between meanings behind apparent and instantaneous diffusion coefficients. As chloride penetration test methods are predominantly classified into two main types based on duration of the test – short term and long term, choosing test data to be used in specific model has to be exercised carefully to avoid errors.

Furthermore, not only should a model contain an expression of C_s as time-dependent, but initial build-up of chlorides on the surface of concrete (C_o) and non-linearity expression of time should be accounted for, because time-dependent C_s is believed to be caused by chloride binding capacity and by nature this is not linear.

Although it is virtually agreed that D can be expressed in exponential form, there are a variety of model expressions for C_s and this might be due to lack of understanding of its actual physical process.

Last but not least, the effect of concrete properties such as curing, water/binder ratio and binder type should not be ignored either as it can significantly affect the accuracies of the model's prediction.

The models presented by equations (9) and (10) & (11) seem to be promising models to be used in this research investigation for long term test while DuraCrete model, on the other hand, is potentially a fairly good model to be used for short term test.

5. Research Methodology

This section detailed the research methodology that will be used to complete the objectives and answer research questions set out in Section 3.

Three potential models discussed in the literature are outlined below and will be utilised to analyse the published data in order to validate their reliability. The unknown regression parameters which are chloride diffusion coefficient at reference time (D_o or D_{28} if reference time is 28 days), initial surface chloride concentration (C_o) and their time-dependent factors (m and k respectively) are found using sum of square differences between the chloride profile from the regression analysis by experimental or field data and that by developed model. This common method of deriving the unknown parameters by regression analysis is shared among the models outlined and this can be done by just using readily available spreadsheet application, namely Excel. Any iterations required can be performed by Excel solver routine. The chloride profiles are created by plotting the chloride contents against their corresponding depths from the surface of the concrete.

Once these parameters are found, they are substituted back into original modelling equations along with exposure times and depths to get its corresponding chloride content. These can then be compared to the measured ones to determine the models' accuracies in their predictions. It is anticipated that among the three models, one or two better models are capable of reasonably predicting actual chloride content. These are then chosen to analyse the data produced in UniSA laboratory by Nord NT Build 443 test.

As has been discussed in the foregoing section, since the models chosen account for both time dependency of chloride diffusion coefficient and surface chloride concentration, at least two sets of data at different exposure times are needed for a successful regression analysis. Experimental data from specimens exposed for 35 days is available while ones exposed for 140 days is being generated and thus are viable to be analysed by the models.

As to evaluating the significance of time dependency of D and C_s at early age of the mixes, an observation of these values against time would provide the answers to this. Should the time dependency factors (m or n) of any mixes is made zero and still provide a good fit to actual chloride profiles, a conclusion could be drawn regarding how at this stage, D and C_s are not particularly dependent on time.

To predict the service life between 1 year and 50 years, values of critical chloride content and cover depth along with found parameters from regression analysis will be used to substitute into modelling equations to calculate time (t). This is the time before corrosion of steel reinforcement begins or in short is the service life. The critical chloride content and cover depth generally used in current practice in Australia will be modelled. As specified in AS 1379 (1998), critical chloride content that would take to initiate steel reinforcement corrosion is based on 0.8 kg/m^3 of concrete. With a typical density of concrete 2350kg/m^3, this equals to 0.034% chloride by mass of concrete and for a typical density of mortar at 2200kg/m^3, this equals 0.036% by mass of mortar. Finally, a conservative target of 0.034% has been chosen for this research or 0.012% by mass of binder. On the other hand, according to AS 3600 (2009), concrete members situated in coastal areas are considered to be in the B2 exposure classification according to Table 4.3 of the standard. With concrete strength of 40 MPa commonly used in durable concrete structures, the required cover is 45 mm.

Model 1

As discussed in literature review, both D and C_s vary with time. Thus this model is selected as it not only takes these into account but also is proven to be a mathematically compatible chloride transport model. This is because it is solved from Fick's first law with correct boundary conditions. Besides, in this model, $\sqrt{t}$ is chosen instead of a linear function due to its capability in expressing the rise of nonlinear surface chloride. Besides, C_o is also included in the model as it is known that as soon as concrete is exposed to marine environment, chlorides are bounded onto surface of concrete. The modelling equations are (Petcherdchoo 2013):

$$C(x,t) = C_o \left[erfc\left(\frac{x}{2\sqrt{D_a t}}\right)\right] + k \times \sqrt{t}\, [e^{-\frac{x^2}{4D_a t}} - \left(\frac{x\sqrt{\pi}}{2\sqrt{D_a t}}\right) erfc(\frac{x}{2\sqrt{D_a t}})] \qquad (10)$$

$$D_a = \frac{D_{28}}{1-m}\left[\left(1+\frac{28}{365t}\right)^{1-m} - \left(\frac{28}{365t}\right)^{1-m}\right] . (\frac{28}{365t})^m \qquad (11)$$

$$C_s(t) = C_o + k\sqrt{t} \qquad (12)$$

where k denotes time dependency factor of C_s.

Set out below are the steps used in regression analysis to find unknown parameters; several tables illustrated provide an explanation when taking mixes with different percentages of limestone as an example:

1. m = 2.5*(w/c) – 0.6 (Mangat & Molloy 1994)
2. D_{28} , C_o and k found from regression analysis for different exposure time and different percentages of mineral addition
3. To find these three regression parameters, the sum of the squared differences between the chloride profile from the regression analysis by published or experimental data and that by the developed model is minimized by adjusting the regression parameters.
4. After first regression analysis, k is expected to be found as 0. Time dependent effect vanishes because of analysis performed year by year. To avoid this, substitute C_o from initial results into C_s in equation (12) in addition to matching with their exposure time.
5. Plot C_s against $\sqrt{t}$, insert a trend line and then C_o can be found from intercept of the trend line on y axis.
6. Set C_o found, perform regression analysis again and adjusted results will be obtained.

Table 1: Regression parameters for 4% Limestone

Parameters	Initial Results		Adjusted Results	
	35 days exp.	114 days exp	35 days exp	114 days exp
D_{28}				
m				
C_o				
k				

7. Repeat this same procedure for concrete containing varying percentages of mineral additions (e.g. 4%, 10%, and 15%)
8. Average diffusion coefficients at 28 days over various exposure time (e.g. 35 days, 114 days) then plot them against amount of limestone (%LS)

Table 2: Values of D_{28} from the adjusted results

Mix No	D_{28}		
	35 days exp.	114 days exp.	Average (35 days to 114 days)
GP 4			
GP 10			
GP 10+5			

9. Insert trend line, get an equation representing D_{28} for different %LS. From this trend line equation D_{28} can be expressed in terms of %LS. (Note: adjust trend line equation accordingly (make it linear or non-linear, whichever fits with experimental data best)

10. Average C_o and k over exposure time and %LS

Table 3: Value of C_o from the adjusted results

Mix no.				
	35 days exp.	114 days exp	Average (35-114 days)	Average (4 – 20%LS)
GP 4				
GP 10				
GP 15				

Table 4: Value of k from the adjusted results

Mix no.				
	35 days exp.	114 days exp	Average (35-114 days)	Average (4 – 20%LS)
GP 4				
GP 10				
GP 15				

11. Plot $\log C_o$ against %LS and do the same plot for k and then add trend line to get the equation representing their relationships in terms of %LS and then substitute into equation (12)

Model 2

By using apparent diffusion coefficient at effective age (t_{eff}) rather than average diffusion coefficient, this model proves to produce more realistic results because according to (Stanish & Thomas 2003), when the latter is used in service life prediction, it is implicitly assumed that the age of concrete first exposed to chloride environment is the same during testing and in service. As a result, by using apparent diffusion coefficient, it is thought to depict a more realistic scenarios where conditions in service is not always similar to conditions during testing. However, since this model did not originally include time dependency of surface chloride concentration, it was modified by replacing its constant expression C_s by $C_o(t/t_o)^k$. Below sets out the steps used in regression analysis to find unknown parameters

1. For each exposure period (35 days and 114 days), calculate average diffusion coefficients (D_{avg}) which is the result of fitting the chloride profile to equation (13):

$$C(x,t) = C_s \text{erfc}\left(\frac{x}{\sqrt{4Dt}}\right) \quad (13)$$

2. Assume a value for time dependency factor of chloride diffusion coefficient (m)
3. For each exposure period (35 days and 140 days), calculate effective age from equation (14):

$$t_{eff} = \begin{cases} \left[\frac{(1-m)(t_2-t_1}{t_2^{1-m}-t_1^{1-m}}\right]^{1/m} , m \neq 0 , 1 \\ \\ \frac{t_2-t_1}{\ln(\frac{t_2}{t_1})} , m = 1 \end{cases} \quad (14)$$

4. Determine the logarithms of (D_{av}) and the effective ages from step 2
5. Determine the value of m from the negative slope of the line of best fit using the logs of the effective ages as the x-values, or in other word, negative slope $\log D_{avg}$ vs $\log t_{eff}$ This is based on equation:

$$D_{app} = D_{ref}\left(\frac{t_{ref}}{t_{eff}}\right)^m \quad (15)$$

6. Repeat step 3 through 5 with the new value of m. When the m value determined from step 5 is equal to the m value used in step 2, the value of m is established for the concrete.
7. The intercept of the line of best fit will be the log of the 1-day diffusion coefficient (if age is given in days). Correct to the reference age using equation (16)

$$D(t) = D_{ref}(\frac{t_{ref}}{t})^m \quad (16)$$

and the value of m just determined.

8. The procedure to determine C_o and k is similar to model 1.

Model 3

Similarly, this model is based on Fick's second law. The main difference here is its time dependency of surface chloride concentration is expressed in exponential form. It is observed that there were no models that use this expression and hence it is worth finding out if this is the more accurate way of describing change in surface chloride concentration.

The modelling equation is as follows (Aldridge, 2012b):

$$C(x) = C_o(t/t_o)^k(1 - \mathrm{erf}(\frac{x}{2\sqrt{tD_o(\frac{t}{t_o})^{-m}}})) \quad (17)$$

m and D_o are found from regressions analysis on the plots of $\ln(D/D_{28})$ against $\ln(t/t_o)$, while k and C_o are found from regression analysis on the plots of $\ln(C_s/C_{28})$ against $\ln(t/t_o)$. Regression of these plots can be done on an Excel spreadsheet and their corresponding equation are shown in equation (18) and (19).

$$\mathrm{Ln}(D/D_{28}) = \mathrm{slope}_D \mathrm{Ln}(t/t_o) + \mathrm{Intercept}_d \ (18)$$

$$\mathrm{Ln}(C/C_{28}) = \mathrm{slope}_k \ln(t/t_o) + \mathrm{Intercept}_c \ (19)$$

$$m = -\mathrm{slope}_D,\ k=\mathrm{slope}_s,\ D_o = D_{28}*\exp(\mathrm{Intercept}_D)\ \&\ C_o = C_{28}*\exp(\mathrm{Intercept}_c)$$

Alternative Model

An alternative model, an engineering expression of the ClinConc model modified by Tang (2008), was considered. Among all models discussed in the literature review, this model is the only one that is based on physical and chemical process involve in diffusion of chloride into concrete. Furthermore, in the same study in which the model is modified, good correlations are found between the time dependent factors for chloride binding and for diffusion coefficient, as well as between the diffusion coefficient measured in the laboratory and the apparent one. However, it is decided this is not feasible because there are a number of unknown parameters that have to be determined from other tests, specifically, chloride binding isotherms.

6. Results and Discussions

Published Data

The published data shown in Table (5) (Thomas & Bamforth 1999) were analysed by simplified model and three time-dependent models, i.e. Model 1, 2 and 3. The published data were generated from fifteen cast reinforced concrete blocks that were exposed in the splash zone on the sea front at Folkestone on the southeast coast of England. This consists of three different mixes: concrete with Portland cement only, concrete with 30% fly ash (P/PFA) and 70% slag (P/GBS) as partial replacement for the Portland cement. Their detailed mix proportions and chloride concentration profiles are shown in Table 5 and Table 6 respectively.

Table 5: Published data: concrete mixes (Thomas & Bamforth 1999)

	Mix proportions (kg/m^3)		
Mix designation	PC	P/PFA	P/GBS
Portland cement	288	227	110
Fly ash	—	98	—
Slag	—	—	255
Total cementitious content	288	325	365
Water	190	170	177
Water-to-cementitious materials ratio	0.66	0.54	0.48
Stone	1240	1305	1240
Sand	660	585	600
28-day strength (MPa)	39.4	49.6	37.9

Table 6: Published data: chloride concentration profiles (% mass of concrete) (Thomas & Bamforth 1999)

Mix	Depth (mm)	Chloride content (percent mass of concrete)					
		6 month	1 year	2 years	3 years	6 years	8 years
PC	0-10	0.267	0.493	0.313	0.370	0.257	0.288
	10-20	0.140	0.193	0.273	0.273	0.237	0.264
	20-30	0.050	0.043	0.143	0.190	0.197	0.203
	30-40	0.010	0.017	0.093	0.117	0.153	0.183
	40-50	0.000	0.000	0.053	0.073	0.133	0.159
P/PFA	0-10	0.280	0.427	0.333	0.383	0.367	0.419
	10-20	0.087	0.097	0.160	0.173	0.193	0.308
	20-30	0.007	0.010	0.037	0.013	0.010	0.057
	30-40	0.000	0.023	0.010	0.010	0.010	0.012
	40-50	0.000	0.000	0.010	0.010	0.010	0.012
P/GBS	0-10	0.437	0.493	0.340	0.387	0.363	0.381
	10-20	0.173	0.140	0.173	0.153	0.227	0.216
	20-30	0.077	0.090	0.023	0.027	0.067	0.068
	30-40	0.027	0.073	0.010	0.013	0.040	0.035
	40-50	0.000	0.000	0.013	0.010	0.030	0.035

Before these data can be analysed by the model, the chloride contents were converted to percent mass of binder and this is shown in Table 7.

Table 7: Published data: chloride concentration profiles (% mass of binder) (Thomas & Bamforth 1999)

Mix	Depth (mm)	Chloride content (percent mass of binder)					
		6 month	1 year	2 years	3 years	6 years	8 years
PC	0-10	2.225	4.108	2.608	3.083	2.142	2.400
	10-20	1.167	1.608	2.275	2.275	1.975	2.200
	20-30	0.417	0.358	1.192	1.583	1.642	1.692
	30-40	0.083	0.142	0.775	0.975	1.275	1.525
	40-50	0.000	0.000	0.442	0.608	1.108	1.325
P/PFA	0-10	2.068	3.153	2.459	2.828	2.710	3.094
	10-20	0.642	0.716	1.182	1.278	1.425	2.274
	20-30	0.052	0.074	0.273	0.096	0.074	0.421
	30-40	0.000	0.170	0.074	0.074	0.074	0.089
	40-50	0.000	0.000	0.074	0.074	0.074	0.089
P/GBS	0-10	2.873	3.242	2.236	2.545	2.387	2.505
	10-20	1.138	0.921	1.138	1.006	1.493	1.420
	20-30	0.506	0.592	0.151	0.178	0.441	0.447
	30-40	0.178	0.480	0.066	0.085	0.263	0.230
	40-50	0.000	0.000	0.085	0.066	0.197	0.230

6.1.1. Analysis by simplified model

$$C(x,t) = C_s\left(1 - \mathrm{erf}\left(\frac{x}{2\sqrt{D_a t}}\right)\right) \qquad (20)$$

The line graph in Figure 5 plots best-fitted average diffusion coefficients (D_a), which were found from regression analysis by equation (20), against their corresponding exposure time. Their values can be found in Table 11 in Appendix A. The figure illustrates that values of D_a for concretes containing fly ash and slag plummet from 6 months to 1 year and continue to decrease steadily afterwards.

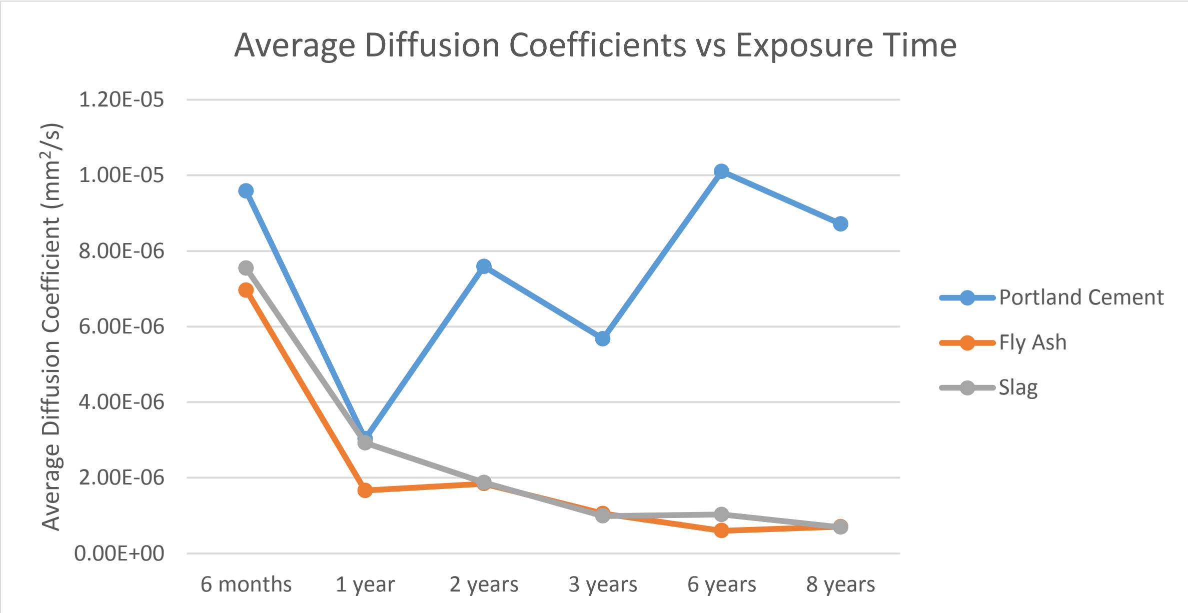

Figure 5 Average diffusion coefficients against exposure time

Equation 20 whose assumptions of constant D at 6 months, was fitted to the chloride profiles from experimental data tested at 6 months, 3 years and 8 years. These profiles are shown in Figure 6, 7 and 8. Their results can be found in Table 9, 10 and 11 in Appendix A. It is observed that for Portland cement concrete, errors between chloride profiles generated by equation (20) and that of experimental data are not great.

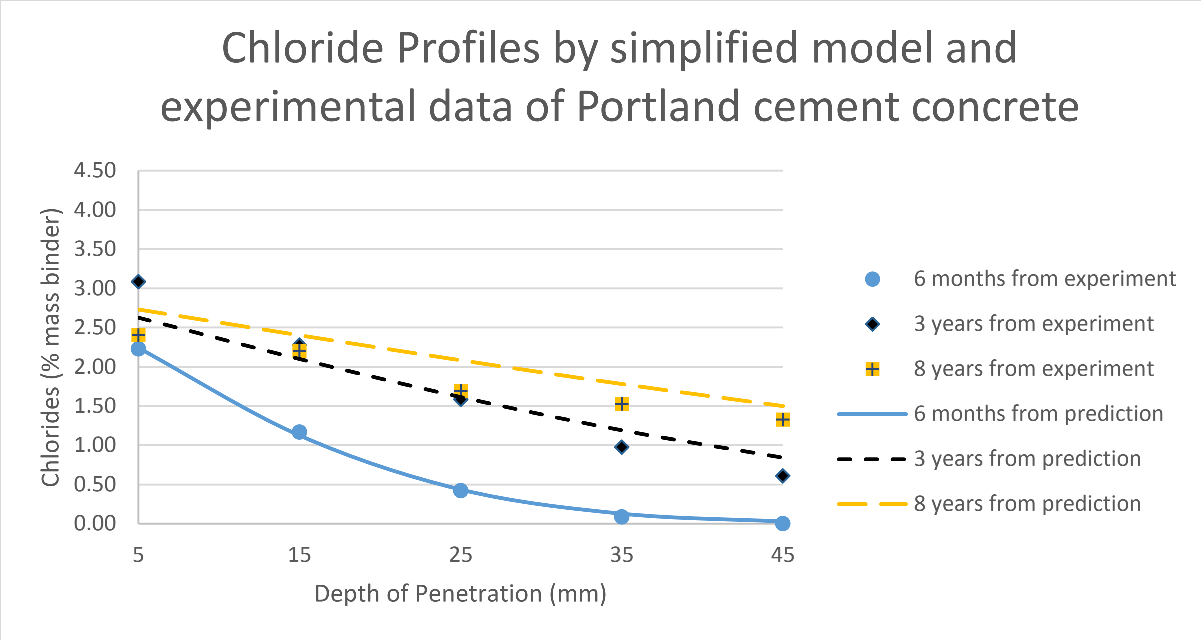

Figure 6 Chloride profiles by simplified model and experimental data of Portland cement concrete

However, this is not the case for fly ash and slag concrete as it can be seen from Figure 7 and 8 that these errors increases more and more significantly with increasing exposure time. This is expected because according to Figure 5, there is a decreasing trend in D_a of fly ash and slag concretes. In summary, this indicates that a model with assumed constant diffusion coefficient cannot predict future chloride penetration, especially for concretes containing fly ash and slag.

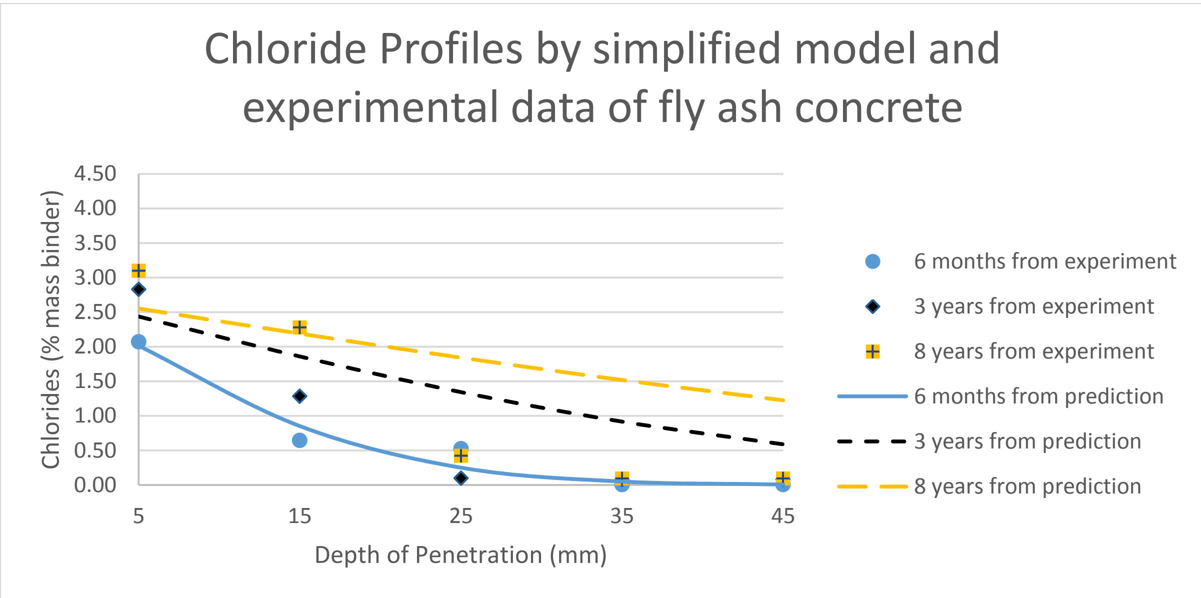

Figure 7 Chloride profiles by simplified model and experimental data of fly ash concrete

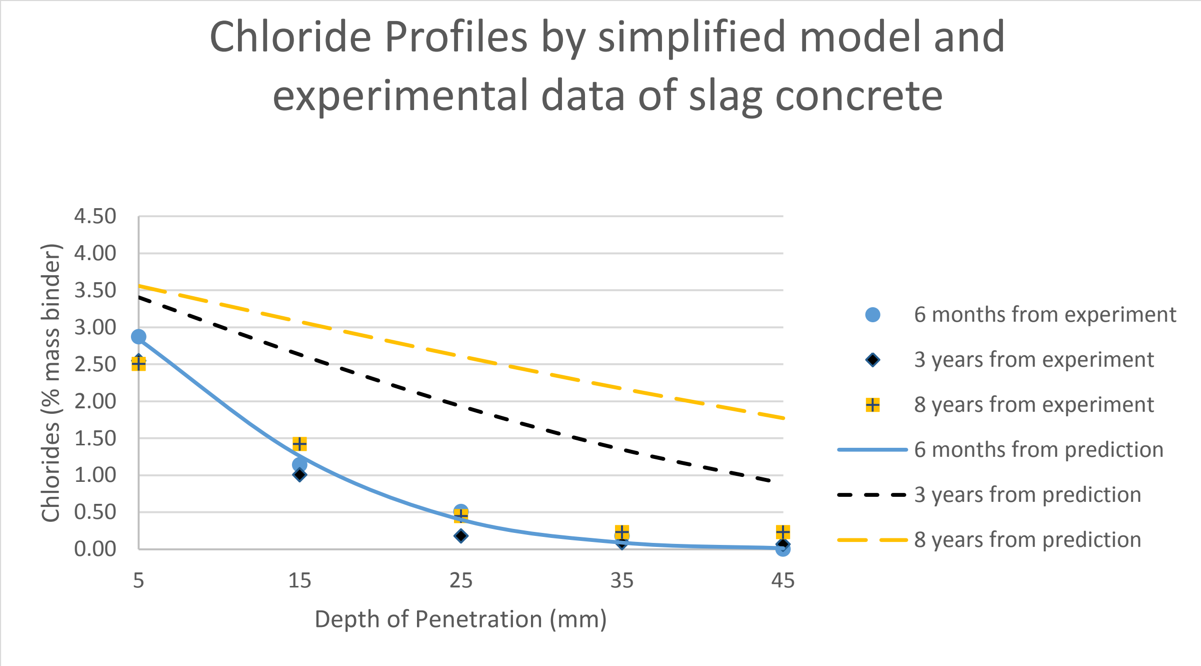

Figure 8 Chloride profiles by simplified model and experimental data of slag concrete

6.1.2. Analysis by Model 1, 2 and 3

Comparisons of chloride profiles predicted by the three models to that by experimental data of concretes containing only Portland cement, fly ash and slag are shown in Figure 9, 10 and 11 respectively. Their results are also shown in Appendix B.

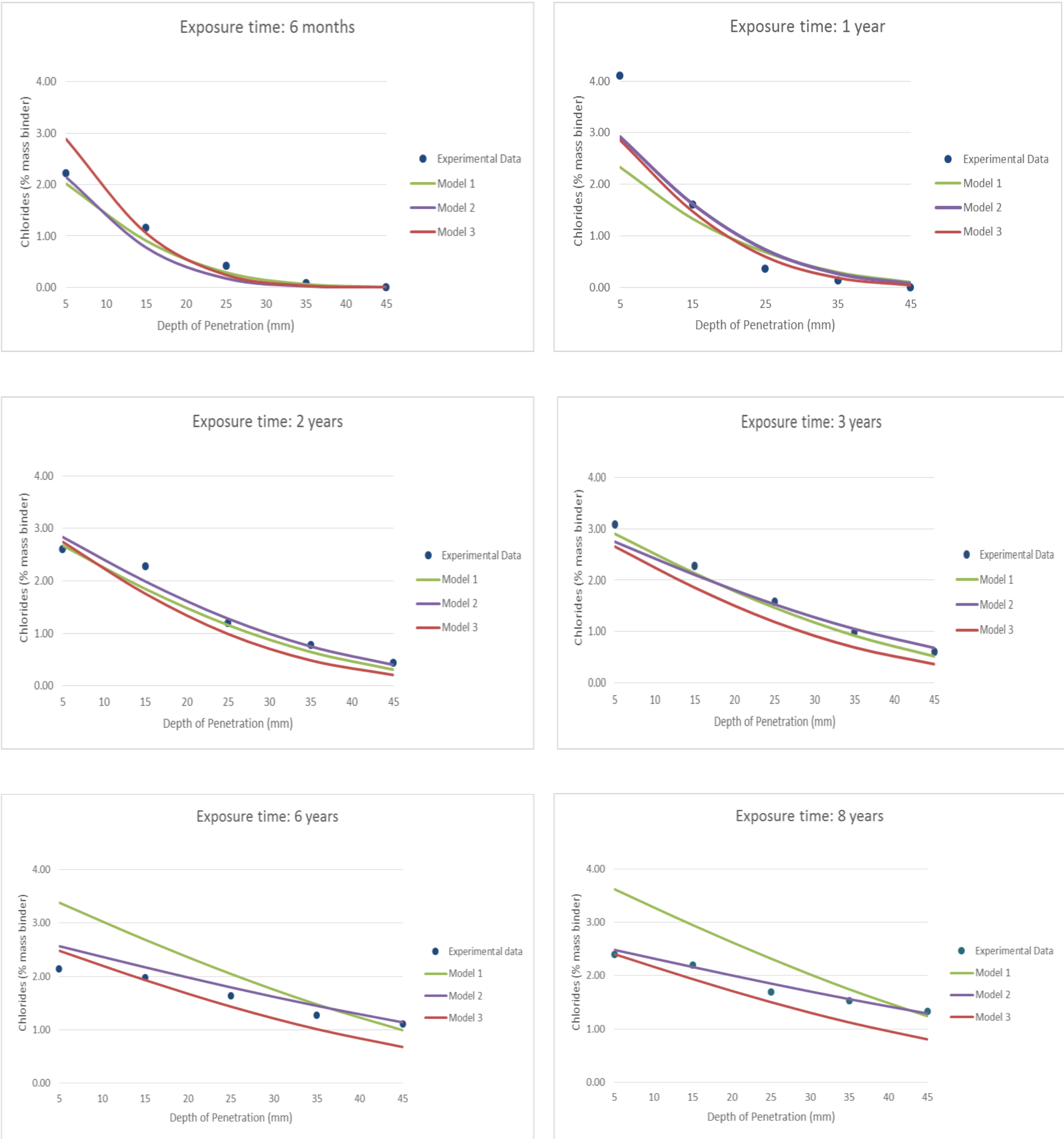

Figure 9 Comparison between model 1 to 3 and experimental data for Portland cement concrete

As illustrated in Figure 9, for Portland cement concrete, overall, Model 2 gives a relatively more accurate prediction than Model 1 and 3, especially at exposure time 6 years and 8 years where the chloride penetration predicted by Model 1 is considerably larger than that of experimental data.

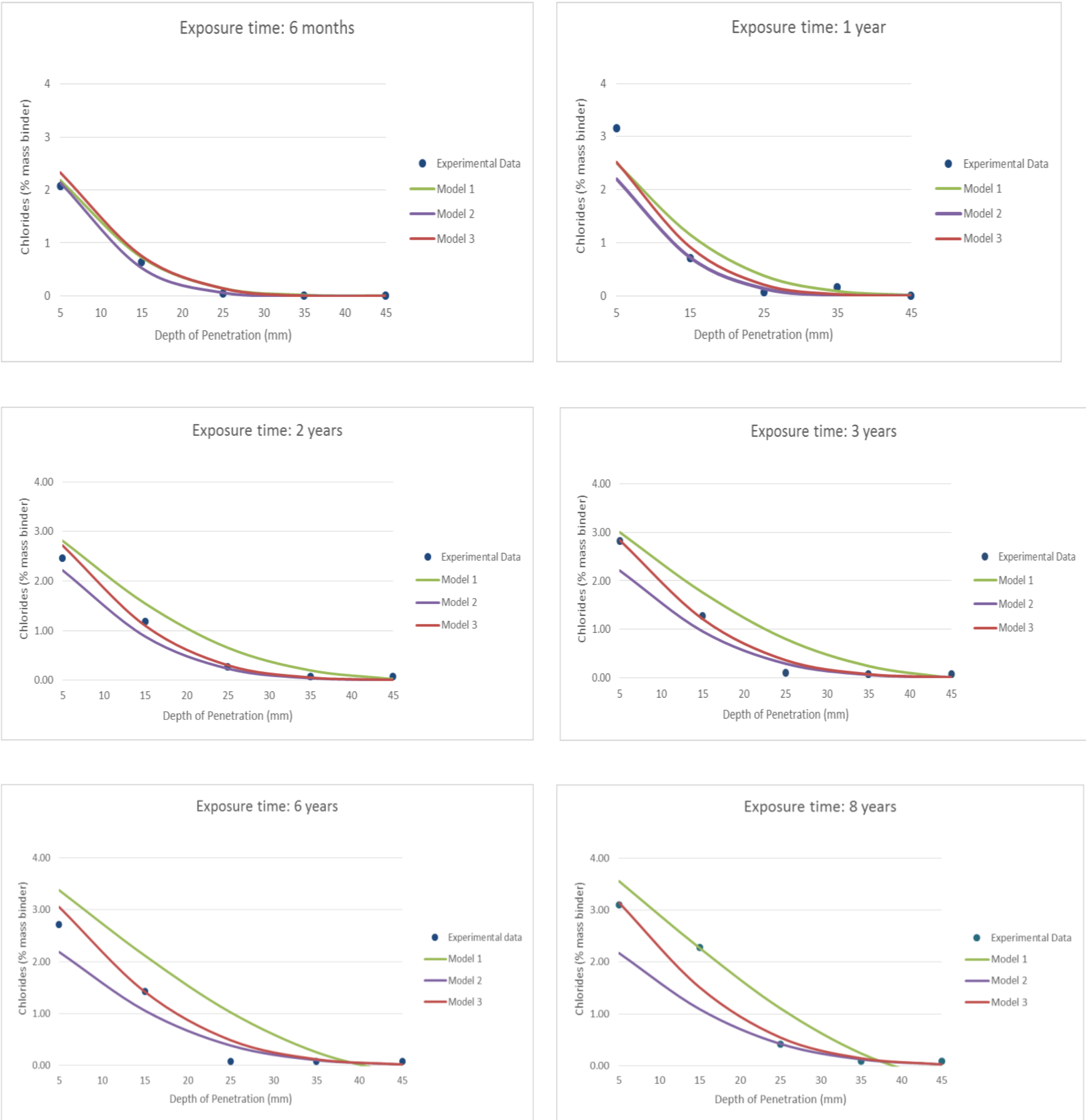

Figure 10 Comparison between model 1 to 3 and experimental data for fly ash concrete

Figure 10 indicates Model 3 estimates chloride profiles best for fly ash concrete among all models. On the other hand, Model 2 appears to underestimate chloride contents at shallower depth – from surface to around 25 mm, while Model 1 generally overestimates the chloride contents.

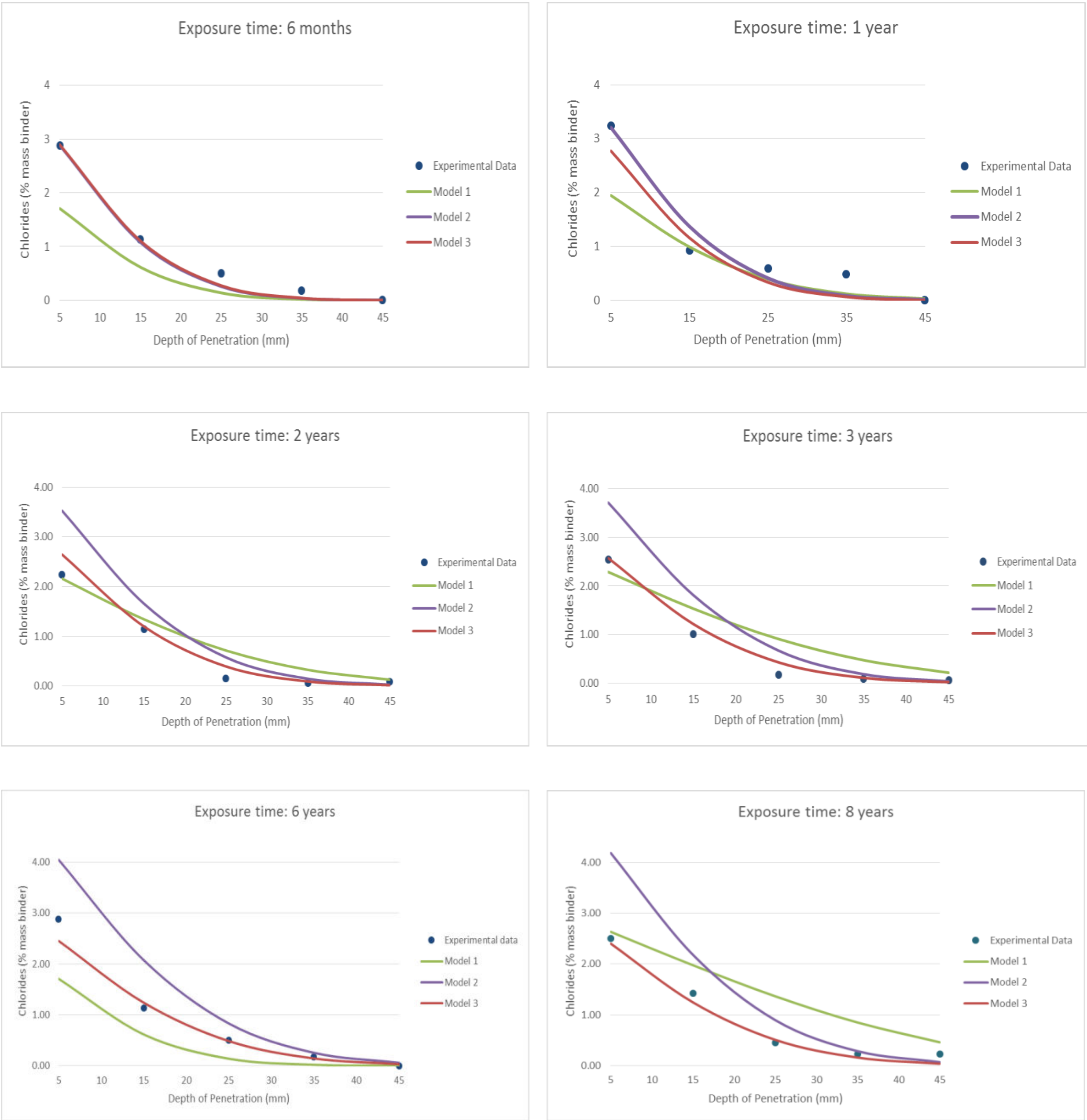

Figure 11 Comparison between model 1 to 3 and experimental data for slag concrete

Likewise, as shown in Figure 11 for slag concrete, in comparison to experimental data, Model 3 gives best prediction of chloride contents out of all models. To sum up, there is a better correlation between the Model 3 predictions and the experimental data than those by Model 1 and 2. Hence, this would be chosen to analyse UniSA laboratory data.

Initially, the data that would be used is from work carried out in 2013 by Jogi et al. (2013) and more data was to be determined during the course of this semester. However, since only 2013 data is available and generation of 2014 data has not been completed, it is not possible to do regression analysis to predict chloride penetration between 1 year and 50 years and the mixes' service lives at critical chloride level as outlined in the objective of this project. This is due to two reasons. Firstly, to be able to use Model 3, at least two sets of data at two different exposure times are needed. In addition to this, from the results of analysis of published data, it is clear that diffusion coefficient does decrease with time, particularly with concretes containing mineral additions such as some of those used in the mixes from laboratory data, i.e. fly ash and slag. If average diffusion coefficients determined from simplified model were to be used to predict chloride penetration at 50 years, this would lead to an unrealistically short service life because diffusion coefficient at 50 years would be much lower than that at 35 days by several orders of magnitude. This is evident from line graph plotted in Figure 5. Assuming constant diffusion coefficient would lead to major errors in the prediction as concrete ages. Thus, only the available UniSA laboratory data which are from mixes exposed for 35 days were analysed using simplified modelling equation (20). Values of D_a acquired this way stand for the average diffusion coefficients of the mixes during 35 days period from the start of exposure to the time they were taken out of salt solutions. But it would be beneficial to further analyse published data since the mixes consists of fly ash and slag which are also present in laboratory specimens. By doing so, it provides better understanding of their influence and the results could be served as expected outcome for future studies.

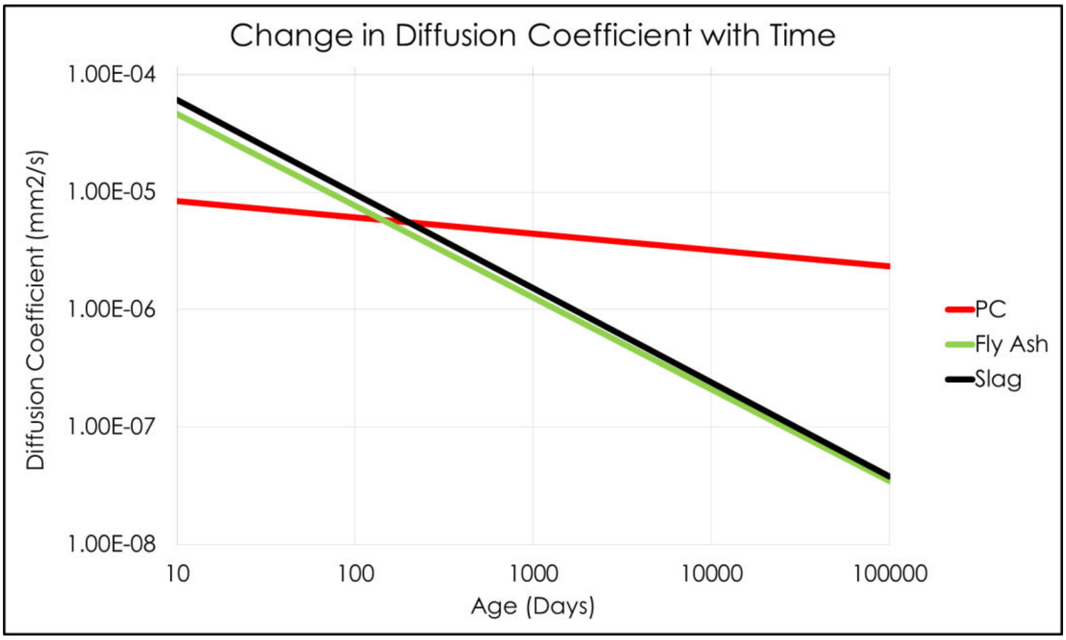

Figure 12 Published data: change in diffusion coefficient with time

Figure 12 shows the relationship between D and age of concrete. Although diffusivity of fly ash and slag started off with nearly an order of magnitude larger than Portland cement, after approximately 200 days they are the same and after 100 years diffusivities of fly ash and slag concretes are two order of magnitudes lower than Portland cement concrete. This indicates that D of concrete containing fly ash and slag is substantially more sensitive to aging than that of Portland cement concrete and shows how great an effect fly ash and slag can have on the chloride penetration of concrete in chloride environments in the long term.

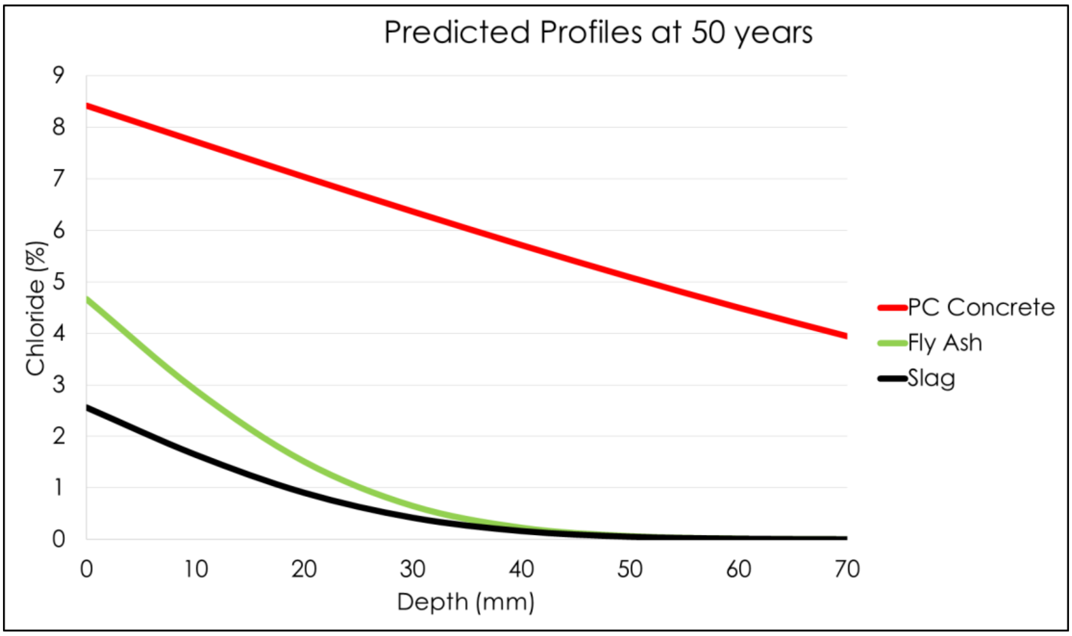

Figure 13 Published data: predicted profiles at 50 years

Figure 13 shows the predicted chloride penetration profiles at 50 years using Model 3. After 50 years of exposure and at 45-mm depth, chloride level is minimal in fly ash and slag concrete. On the contrary, at this same depth, there is a 5.4% mass of binder of chlorides present in Portland cement concrete which exceeds that of chloride level required to initiate corrosion.

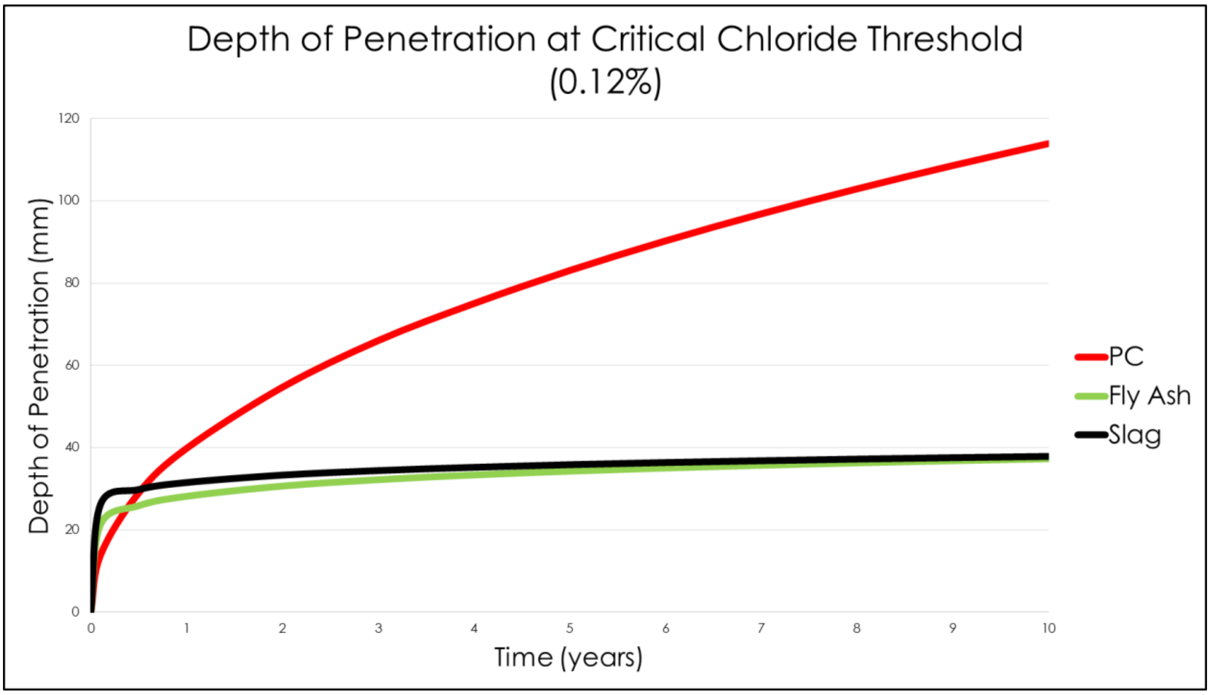

Figure 14 Published data: depth of penetration at critical threshold level (0.12% mass of binder)

Figure 14 shows the plot of depth of penetration against time at critical chloride level (0.12% mass of binder). Initially, at this level, the chloride penetration rate of all concrete types rise sharply. After that, for fly ash and slag, the rate increases only slightly with time to an almost constant depth 40mm after 10 years. However, this level of chlorides penetrates the Portland cement concrete and reaches 45mm after approximately only 1.5 years.

UniSA laboratory data from Nord NT Build 443

As have been previously mentioned, due to unavailability of chloride profiles of mortar samples exposed for 140 days, only the ones exposed for 35 days were analysed by simplified model. Table 8 shows these specimens' mix details. Their unique mix codes and NT Build 443 test are illustrated in Table 9 and Table 10 respectively. Their analysis results by simplified model are shown in Appendix C.

Table 8: 2013 mix details (Benn B.T., Baweja D. and Mills J.E. 2014)

Mix	Nominal limestone content	CKD content	Sand/binder ratio	Water/binder ratio
Cement only	4%	Zero, 2%, 5%	1.99	0.40
	10%	"	1.99	0.40
	15%	"	1.99	0.40
Cement with 20% FA	4%	"	1.93	0.40
	10%	"	1.93	0.40
	15%	"	1.93	0.40
Cement with 30% FA	4%	"	1.89	0.40
	10%	"	1.89	0.40
	15%	"	1.89	0.40

Table 9 Illustration of unique mixed code (Jogi et al. 2013)

Mix code	*M04.0.00*	*M04.2.00*	*M04.5.00*	*M04.0.20*	*M04.2.20*	*M.04.5.20*	*M04.0.30*	*M04.2.30*	*M04.5.30*
Percentages of limestone content by sample	4% (04)	4% (04)	4% (04)	4% (04)	4% (04)	4% (04)	4% (04)	4% (04)	4% (04)
Percentages of CKD content by sample	0% (.0)	2% (.2)	5% (.5)	0% (.0)	2% (.2)	5% (.5)	0% (.0)	2% (.2)	5% (.5)
Percentages of Flyash content by sample	0% (.00)	0% (.00)	0% (.00)	20% (.20)	20% (.20)	20% (.20)	30% (.30)	30% (.30)	30% (.30)
Mix code	*M10.0.00*	*M10.2.00*	*M10.5.00*	*M10.0.20*	*M10.2.20*	*M10.5.20*	*M10.0.30*	*M10.2.30*	*M10.5.30*
Percentages of limestone content by sample	10% (10)	10% (10)	10% (10)	10% (10)	10% (10)	10% (10)	10% (10)	10% (10)	10% (10)
Percentages of CKD content by sample	0% (.0)	2% (.2)	5% (.5)	0% (.0)	2% (.2)	5% (.5)	0% (.0)	2% (.2)	5% (.5)
Percentages of Flyash content by sample	0% (.00)	0% (.00)	0% (.00)	20% (.20)	20% (.20)	20% (.20)	30% (.30)	30% (.30)	30% (.30)
Mix code	*M15.0.00*	*M15.2.00*	*M15.5.00*	*M15.0.20*	*M15.2.20*	*M15.5.20*	*M15.0.30*	*M15.2.30*	*M15.5.30*
Percentages of limestone content by sample	15% (15)	15% (15)	15% (15)	15% (15)	15% (15)	15% (15)	15% (15)	15% (15)	15% (15)
Percentages of CKD content by sample	0% (.0)	2% (.2)	5% (.5)	0% (.0)	2% (.2)	5% (.5)	0% (.0)	2% (.2)	5% (.5)
Percentages of Flyash content by sample	0% (.00)	0% (.00)	0% (.00)	20% (.20)	20% (.20)	20% (.20)	30% (.30)	30% (.30)	30% (.30)

Table 10: NT Build 443 test results

GP Cement with 4% limestone									
Mix Code	M04.0.00	M04.2.00	M04.5.00	M04.0.20	M04.2.20	M.04.5.20	M04.0.30	M04.2.30	M04.5.30
Initial Cl content	0.0189	0.0258	0.0203	0.0206	0.0218	0.0208	0.0176	0.0176	0.0182
2 - 8 mm	0.6832	0.6484	0.6301	0.5910	0.5440	0.6328	0.4437	0.3555	0.3223
8 - 14 mm	0.2737	0.2347	0.1819	0.0681	0.0960	0.0927	0.0313	0.0332	0.0570
14 - 20 mm	0.0762	0.0965	0.0544	0.0413	0.0537	0.0621	0.0353	0.0375	0.0434
20 - 26 mm	0.0411	0.0402	0.0380	-	-	-	-	-	0.0413
26 - 32 mm	0.0367	0.0329	0.0351	0.0342	0.0388	0.0317	0.0252	0.0268	0.0313
GP Cement with 10% limestone									
Mix Code	M10.0.00	M10.2.00	M10.5.00	M10.0.20	M10.2.20	M10.5.20	M10.0.30	M10.2.30	M10.5.30
Initial Cl content	0.0186	0.0189	0.0197	0.0175	0.0196	0.0195	0.0172	0.0178	0.0195
2 - 8 mm	0.7376	0.7645	0.6900	0.7829	0.5221	0.6285	0.3698	0.3627	0.4019
8 - 14 mm	0.3073	0.3346	0.2884	0.1168	0.0838	0.1189	0.0534	0.0532	0.0564
14 - 20 mm	0.0930	0.0860	0.0973	0.0817	0.0700	0.0564	0.0462	0.0376	0.0473
20 - 26 mm	-	-	0.0657	-	-	-	-	-	0.0347
26 - 32 mm	0.0707	0.0510	0.0487	0.0510	0.0490	0.0600	0.0303	0.0312	0.0398
GP Cement with 15% limestone									
Mix Code	M15.0.00	M15.2.00	M15.5.00	M15.0.20	M15.2.20	M15.5.20	M15.0.30	M15.2.30	M15.5.30
Initial Cl content	0.0167	0.0200	0.0211	0.0165	0.0197	0.0207	0.0159	0.0178	0.0207
2 - 8 mm	0.8862	0.8646	0.8818	0.6921	0.7038	0.8960	0.7512	0.9068	0.9780
8 - 14 mm	0.3906	0.4072	0.3683	0.0778	0.0964	0.2467	0.1690	0.2285	0.2703
14 - 20 mm	0.1065	0.1157	0.1152	0.0334	0.0643	0.0669	0.0529	0.0603	0.0759
20 - 26 mm	-	-	0.0488	-	-	-	-	-	0.0631
26 - 32 mm	0.0590	0.0526	0.0544	0.0397	0.0513	0.0483	0.0367	0.0508	0.0483

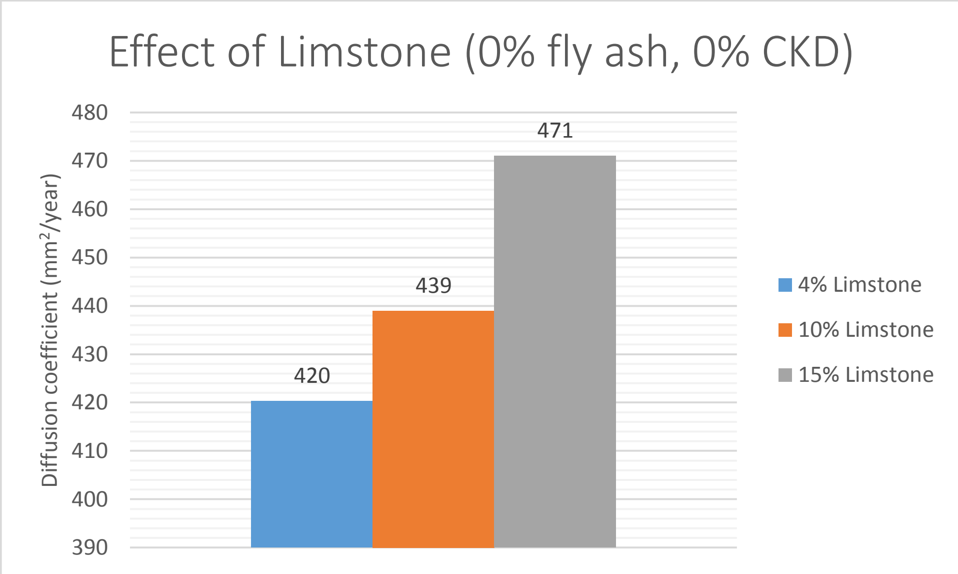

Figure 15 Diffusion coefficient at 0% fly ash, 0% CKD and different levels of limestone

Figure 15 shows average diffusion coefficient of mortar samples with 0% fly ash, 0% CKD and different percentages of limestone. Increasing levels of limestone in cement give rise to rate of chloride penetration through mortar.

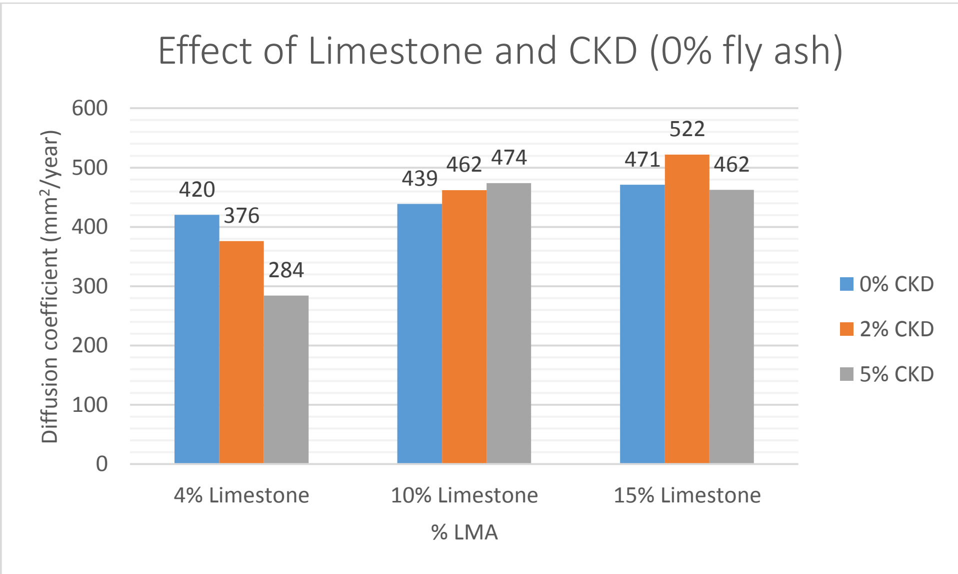

Figure 16 Diffusion coefficient at 0% fly ash and different levels of limestone and CKD

Figure 16 illustrates diffusion coefficient of mortar samples with no fly ash addition and different levels of limestone and CKD. Although the rate of chloride penetration is increasingly slower with each incremental additions of CKD at 4% limestone, it reduces steadily at 10% limestone and there is no clear increasing or decreasing trend at 15%

limestone. To sum up, no distinct relationship between CKD and diffusivity of concrete can be established yet.

On the other hand, looking at combination of limestone and CKD mineral additions, it appears to accelerate chloride penetration with one exception. First of all, without addition of CKD, increasing levels of limestone in cement give slight increase to rate of chloride penetration through mortar from 420 mm^2/year at 4% limestone to 471 mm^2/year at 15% limestone. Similarly, by adding 2% of CKD to the binder, diffusivity of mortar still increase with increasing levels of limestone, and the amount of growth in diffusivity is even greater than when there is no presence of CKD. However, at 5% CKD, although there is an even greater amount of increase in diffusivity of mortar from 284 mm^2/year at 4% limestone to 474 mm^2/year at 10% limestone, it then fell slightly to 462 mm^2/year at 15% limestone. It seems that combined additions of limestone and CKD do not always lead to higher diffusion coefficient.

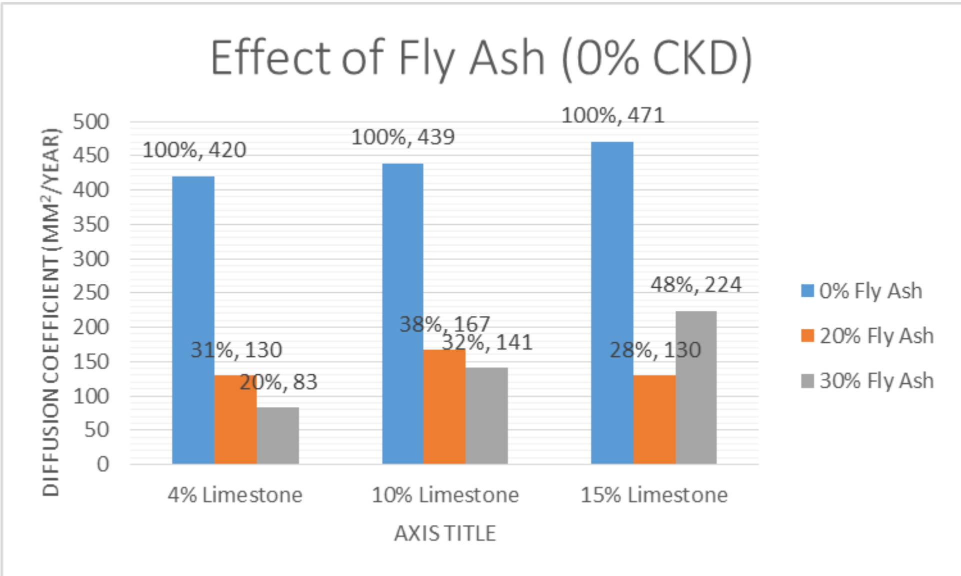

Figure 17 Diffusion coefficients at 0% CKD with different levels of limestone and fly ash

Figure 17 indicates diffusion coefficients of mortar samples with no CKD addition and different levels of limestone and fly ash. There is virtually a decrease in diffusivity of mortar samples with increasing additions of fly ash. At all levels of limestone with addition of 20% fly ash, diffusion coefficients are three times lower than when there is not fly ash present. With further increase to 30% fly ash, the rates of chloride penetration continue to drop by another 11% and 6% for mortar samples with 4% limestone and 10% limestone respectively. At this percentage of fly ash addition, however, diffusion coefficient of mortar sample containing 15% limestone unexpectedly rises by 20% from 130 mm^2/year (20% fly ash) to 224 mm^2/year (30% fly ash).

It is noted that although increasing levels of limestone increase diffusion coefficient, by adding 20% fly ash, the diffusivity in mortar sample at 15% is still comparatively much lower than that of mortar sample with 4% limestone but without fly ash.

7. Conclusion

- Which model(s) give reliable prediction of chloride penetration?

According to analysis of published data, simplified model is not able to predict long term chloride penetration. Among the three time-dependent models chosen, Model 2 is able to fit chloride profiles from Portland cement concrete exposed for up to 8 years while Model 3 gives most accurate prediction of chloride profiles for concrete containing fly ash and slag.

- What is the effect on mortar made with cements containing increased limestone additions, cement kiln dust regarding the rate of chloride penetration?

Results from analysis of Nord NT Build 443 test indicate that diffusivity of mortar increases with increasing level of limestone addition. However, the relationship is not yet clear between rate of chloride penetration and addition of cement kiln dust.

- Would fly ash mitigate the effect of chloride ingress in concrete?

Yes, addition of 20% fly ash reduces the rate of chloride penetration significantly. But when a further 10% of fly ash is added, there is only slight decrease in diffusivity of mortar.

8. Recommendations

At this stage, the results of analysis indicate that up to 15% limestone mineral addition, which is higher than current allowance, could be permitted as long as there is also addition of 20% fly ash to reverse the effect of acceleration of chloride penetration rate associated with addition of limestone. However, these results of diffusion coefficients was analysed by simplified model and can be considered as average diffusion coefficients within 35 days exposure period only. According to analysis of published data, fly ash would reduce diffusivity in the samples even more dramatically at longer exposure time. If this is the case, this allowance of mineral additions is still valid. Nevertheless, effect of limestone and CKD on rate of chloride penetration has not been thoroughly investigated yet. Therefore, once more data at longer exposure periods are obtained, Model 3 should be used to analyse these data, similar to how it was done to published data, to predict how these mixes perform in the long term regarding the effect of their chloride penetrations.

Furthermore, the results also show that acceleration of diffusivity in mortar with increasing levels of limestone holds at 0% and 2% CKD, but this trend fell short when 5% of CKD is combined with 15% limestone. It is thus recommended that higher percentage of CKD addition combined with limestone should be investigated further before determining whether this is an outlier caused by errors during testing and mixing, or addition of 5% and higher percentage of CKD actually gives a reversal effect to what have been found with addition of 2% CKD.

In addition, mixes with addition of 15% limestone should be repeated. As have been seen, the data obtained tend to produce odd results because they do not follow the trend found in lower percentages of limestone.

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Appendices

Appendix A: Results of published data by simplified model

Table 11: Best fitted values of D_a and C_s of published data by simplified model

Concrete mix	Exposure Time	Da (mm2/s)	Cs (% mass binder)
PC	6 months	9.581E-06	2.90
	1 year	3.031E-06	5.73
	2 years	7.587E-06	3.15
	3 years	5.675E-06	3.51
	6 years	1.01E-05	2.35
	8 years	8.712E-06	2.57
P/PFA	6 months	6.96E-06	2.74
	1 year	1.661E-06	5.04
	2 years	1.846E-06	3.45
	3 years	1.053E-06	3.96
	6 years	6.002E-07	3.74
	8 years	7.08E-07	4.13
P/GBS	6 months	7.54E-06	3.80
	1 year	2.924E-06	4.45
	2 years	1.875E-06	3.05
	3 years	9.9E-07	3.57
	6 years	1.03E-06	3.03
	8 years	6.94E-07	3.19

Table 12: Predictions of chloride contents by simplified model and experimental data of Portland cement concrete

Exposure Time	Depth (mm)	5	15	25	35	45	Sum Sq.
6 months	Cx (%)	2.225	1.167	0.417	0.083	0.000	0.005
	Cx Eqn	2.240	1.124	0.435	0.128	0.028	
1 year	Cx (%)	4.108	1.608	0.358	0.142	0.000	3.240
	Cx Eqn	2.429	1.569	0.895	0.447	0.194	
2 years	Cx (%)	2.608	2.275	1.192	0.775	0.442	0.186
	Cx Eqn	2.565	1.929	1.367	0.909	0.566	
3 years	Cx (%)	3.083	2.275	1.583	0.975	0.608	0.342
	Cx Eqn	2.625	2.098	1.613	1.190	0.841	
6 years	Cx (%)	2.142	1.975	1.642	1.275	1.108	0.709
	Cx Eqn	2.704	2.326	1.964	1.625	1.317	
8 years	Cx (%)	2.400	2.200	1.692	1.525	1.325	0.397
	Cx Eqn	2.730	2.401	2.083	1.780	1.499	

Table 13: Predictions of chloride contents by simplified model and experimental data of fly ash concrete

Exposure Time	Depth (mm)	5	15	25	35	45	Sum Sq.
6 months	Cx (%)	2.068	0.642	0.520	0.000	0.000	0.122
	Cx Eqn	2.013	0.852	0.250	0.050	0.007	
1 year	Cx (%)	3.153	0.716	0.074	0.170	0.000	1.533
	Cx Eqn	2.220	1.297	0.637	0.259	0.000	
2 years	Cx (%)	2.549	1.182	0.273	0.074	0.074	1.355
	Cx Eqn	2.369	1.676	1.091	0.650	0.352	
3 years	Cx (%)	2.828	1.278	0.096	0.074	0.074	3.019
	Cx Eqn	2.436	1.859	1.343	0.916	0.588	
6 years	Cx (%)	2.710	1.425	0.074	0.074	0.074	5.762
	Cx Eqn	2.523	2.107	1.713	1.355	1.041	
8 years	Cx (%)	3.094	2.274	0.421	0.089	0.089	5.650
	Cx Eqn	2.552	2.189	1.841	1.518	1.225	

Table 14: Predictions of chloride contents by simplified model and experimental data of slag concrete

Exposure Time	Depth (mm)	5	15	25	35	45	Sum Sq.
6 months	Cx (%)	2.873	1.138	0.506	0.178	0.000	0.035
	Cx Eqn	2.838	1.258	0.399	0.088	0.013	
1 year	Cx (%)	3.242	0.921	0.592	0.480	0.000	1.077
	Cx Eqn	3.115	1.870	0.957	0.413	0.149	
2 years	Cx (%)	2.236	1.138	0.151	0.066	0.085	5.829
	Cx Eqn	3.315	2.385	1.589	0.976	0.550	
3 years	Cx (%)	2.545	1.006	0.178	0.085	0.066	8.727
	Cx Eqn	3.404	2.630	1.933	1.347	0.888	
6 years	Cx (%)	2.387	1.493	0.441	0.263	0.197	12.017
	Cx Eqn	3.521	2.963	2.434	1.949	1.520	
8 years	Cx (%)	2.505	1.420	0.447	0.230	0.230	14.655
	Cx Eqn	3.559	3.074	2.607	2.170	1.772	

Appendix B: Results of published data by Model 1, 2 and 3

B1 Portland cement concrete

Table 15 Comparisons between Model 1 and experimental data for Portland cement concrete

Exposure Time	Depth (mm)	5	15	25	35	45	Sum Sq.
6 months	Cx (%)	2.225	1.167	0.417	0.083	0.000	0.124
	Cx Eqn	2.019	0.910	0.293	0.064	0.009	
1 year	Cx (%)	4.108	1.608	0.358	0.142	0.000	3.362
	Cx Eqn	2.334	1.333	0.686	0.294	0.103	
2 years	Cx (%)	2.608	2.275	1.192	0.775	0.442	0.224
	Cx Eqn	2.676	1.847	1.158	0.644	0.308	
3 years	Cx (%)	3.083	2.275	1.583	0.975	0.608	0.076
	Cx Eqn	2.906	2.136	1.465	0.920	0.515	
6 years	Cx (%)	2.142	1.975	1.642	1.275	1.108	2.256
	Cx Eqn	3.380	2.686	2.046	1.477	0.994	
8 years	Cx (%)	2.400	2.200	1.692	1.525	1.325	2.494
	Cx Eqn	3.620	2.948	2.318	1.744	1.239	

Table 16 Comparisons between Model 2 and experimental data for Portland cement concrete

Exposure Time	Depth (mm)	5	15	25	35	45	Sum Sq.
6 months	Cx (%)	2.225	1.167	0.417	0.083	0.000	0.219
	Cx Eqn	2.146	0.778	0.177	0.024	0.002	
1 year	Cx (%)	4.108	1.608	0.358	0.142	0.000	1.564
	Cx Eqn	2.924	1.620	0.734	0.267	0.077	
2 years	Cx (%)	2.608	2.275	1.192	0.775	0.442	0.144
	Cx Eqn	2.838	1.990	1.280	0.750	0.398	
3 years	Cx (%)	3.083	2.275	1.583	0.975	0.608	0.153
	Cx Eqn	2.751	2.106	1.529	1.050	0.679	
6 years	Cx (%)	2.142	1.975	1.642	1.275	1.108	0.273
	Cx Eqn	2.566	2.171	1.795	1.449	1.141	
8 years	Cx (%)	2.400	2.200	1.692	1.525	1.325	0.036
	Cx Eqn	2.482	2.161	1.852	1.560	1.291	

Table 17 Comparisons between Model 3 and experimental data for Portland cement concrete

Exposure Time	Depth (mm)	5	15	25	35	45	Sum Sq.
6 months	Cx (%)	2.225	1.167	0.417	0.083	0.000	0.482
	Cx Eqn	2.887	1.059	0.245	0.035	0.003	
1 year	Cx (%)	4.108	1.608	0.358	0.142	0.000	1.642
	Cx Eqn	2.858	1.474	0.597	0.186	0.044	
2 years	Cx (%)	2.608	2.275	1.192	0.775	0.442	0.471
	Cx Eqn	2.746	1.756	0.987	0.484	0.205	
3 years	Cx (%)	3.083	2.275	1.583	0.975	0.608	0.658
	Cx Eqn	2.657	1.855	1.186	0.689	0.363	
6 years	Cx (%)	2.142	1.975	1.642	1.275	1.108	0.412
	Cx Eqn	2.480	1.932	1.434	1.013	0.679	
8 years	Cx (%)	2.400	2.200	1.692	1.525	1.325	0.537
	Cx Eqn	2.402	1.935	1.503	1.123	0.806	

B2 Fly ash concrete

Table 18 Comparisons between Model 1 and experimental data for fly ash concrete

Exposure Time	Depth (mm)	5	15	25	35	45	Sum Sq.
6 months	Cx (%)	2.068	0.642	0.052	0.000	0.000	0.030
	Cx Eqn	2.183	0.730	0.145	0.017	0.001	
1 year	Cx (%)	3.153	0.716	0.074	0.170	0.000	0.713
	Cx Eqn	2.504	1.153	0.381	0.090	0.014	
2 years	Cx (%)	2.459	1.182	0.273	0.074	0.074	0.422
	Cx Eqn	2.814	1.547	0.654	0.196	0.023	
3 years	Cx (%)	2.828	1.278	0.096	0.074	0.074	0.797
	Cx Eqn	3.005	1.760	0.802	0.241	-0.007	
6 years	Cx (%)	2.710	1.425	0.074	0.074	0.074	1.919
	Cx Eqn	3.376	2.116	1.023	0.256	-0.176	
8 years	Cx (%)	3.094	2.274	0.421	0.089	0.089	0.856
	Cx Eqn	3.557	2.269	1.108	0.239	-0.295	

Table 19 Comparisons between Model 2 and experimental data for fly ash concrete

Exposure Time	Depth (mm)	5	15	25	35	45	Sum Sq.
6 months	Cx (%)	2.068	0.642	0.052	0.000	0.000	0.018
	Cx Eqn	2.141	0.529	0.062	0.003	0.000	
1 year	Cx (%)	3.153	0.716	0.074	0.170	0.000	0.931
	Cx Eqn	2.203	0.724	0.139	0.015	0.001	
2 years	Cx (%)	2.459	1.182	0.273	0.074	0.074	0.156
	Cx Eqn	2.218	0.881	0.233	0.040	0.004	
3 years	Cx (%)	2.828	1.278	0.096	0.074	0.074	0.523
	Cx Eqn	2.213	0.957	0.292	0.061	0.009	
6 years	Cx (%)	2.710	1.425	0.074	0.074	0.074	0.511
	Cx Eqn	2.186	1.057	0.386	0.104	0.020	
8 years	Cx (%)	3.094	2.274	0.421	0.089	0.089	2.257
	Cx Eqn	2.171	1.091	0.423	0.124	0.027	

Table 20 Comparisons between Model 3 and experimental data for fly ash concrete

Exposure Time	Depth (mm)	5	15	25	35	45	Sum Sq.
6 months	Cx (%)	2.068	0.642	0.520	0.000	0.000	0.224
	Cx Eqn	2.330	0.756	0.142	0.000	0.000	
1 year	Cx (%)	3.153	0.716	0.074	0.170	0.000	0.479
	Cx Eqn	2.521	0.920	0.211	0.029	0.000	
2 years	Cx (%)	2.549	1.182	0.273	0.074	0.074	0.042
	Cx Eqn	2.720	1.101	0.300	0.054	0.006	
3 years	Cx (%)	2.828	1.278	0.096	0.074	0.074	0.079
	Cx Eqn	2.841	1.214	0.363	0.074	0.010	
6 years	Cx (%)	2.710	1.425	0.074	0.074	0.074	0.294
	Cx Eqn	3.053	1.420	0.487	0.120	0.021	
8 years	Cx (%)	3.094	2.274	0.421	0.089	0.089	0.608
	Cx Eqn	3.143	1.511	0.546	0.145	0.028	

B3 Slag concrete

Table 21 Comparisons between Model 1 and experimental data for slag concrete

Exposure Time	Depth (mm)	5	15	25	35	45	Sum Sq.
6 months	Cx (%)	2.873	1.138	0.506	0.178	0.000	1.788
	Cx Eqn	1.709	0.616	0.139	0.020	0.002	
1 year	Cx (%)	3.242	0.921	0.592	0.480	0.000	1.854
	Cx Eqn	1.946	0.991	0.391	0.120	0.029	
2 years	Cx (%)	2.236	1.138	0.151	0.066	0.085	0.434
	Cx Eqn	2.163	1.343	0.715	0.325	0.127	
3 years	Cx (%)	2.545	1.006	0.178	0.085	0.066	1.052
	Cx Eqn	2.289	1.533	0.910	0.473	0.215	
6 years	Cx (%)	2.873	1.138	0.506	0.178	0.000	1.033
	Cx Eqn	1.709	0.616	0.139	0.020	0.002	
8 years	Cx (%)	2.505	1.420	0.447	0.230	0.230	1.854
	Cx Eqn	2.633	1.976	1.365	0.850	0.461	

Table 22 Comparisons between Model 2 and experimental data for slag concrete

Exposure Time	Depth (mm)	5	15	25	35	45	Sum Sq.
6 months	Cx (%)	2.873	1.138	0.506	0.178	0.000	0.085
	Cx Eqn	2.879	1.077	0.258	0.038	0.003	
1 year	Cx (%)	3.242	0.921	0.592	0.480	0.000	0.395
	Cx Eqn	3.206	1.372	0.411	0.084	0.011	
2 years	Cx (%)	2.236	1.138	0.151	0.066	0.085	2.133
	Cx Eqn	3.530	1.657	0.577	0.145	0.026	
3 years	Cx (%)	2.545	1.006	0.178	0.085	0.066	2.278
	Cx Eqn	3.717	1.812	0.670	0.184	0.037	
6 years	Cx (%)	2.387	1.493	0.441	0.263	0.197	3.258
	Cx Eqn	4.045	2.074	0.831	0.255	0.059	
8 years	Cx (%)	2.505	1.420	0.447	0.230	0.230	3.631
	Cx Eqn	4.184	2.181	0.897	0.286	0.070	

Table 23 Comparisons between Model 3 and experimental data for slag concrete

Exposure Time	Depth (mm)	5	15	25	35	45	Sum Sq.
6 months	Cx (%)	2.873	1.138	0.506	0.178	0.000	0.073
	Cx Eqn	2.897	1.107	0.275	0.043	0.000	
1 year	Cx (%)	3.242	0.921	0.592	0.480	0.000	0.517
	Cx Eqn	2.772	1.159	0.334	0.064	0.000	
2 years	Cx (%)	2.236	1.138	0.151	0.066	0.085	0.237
	Cx Eqn	2.648	1.199	0.393	0.091	0.015	
3 years	Cx (%)	2.545	1.006	0.178	0.085	0.066	0.111
	Cx Eqn	2.575	1.217	0.428	0.110	0.020	
6 years	Cx (%)	2.387	1.493	0.441	0.263	0.197	0.112
	Cx Eqn	2.452	1.239	0.485	0.145	0.032	
8 years	Cx (%)	2.505	1.420	0.447	0.230	0.230	0.086
	Cx Eqn	2.402	1.246	0.508	0.160	0.038	

Appendix C Results of UniSA laboratory data by simplified model

Table 24: Best fitted values of D_a and C_s of UniSA laboratory data by simplified model

Mix Code	% Limestone	% CKD	% Fly Ash	Diffusion (mm2/year)
M04.0.00	4	0	0	420
M04.2.00	4	2	0	376
M04.5.00	4	5	0	284
M04.0.20	4	0	20	130
M04.2.20	4	2	20	179
M04.5.20	4	5	20	159
M04.0.30	4	0	30	83
M04.2.30	4	2	30	94
M04.5.30	4	5	30	162
M10.0.00	10	0	0	439
M10.2.00	10	2	0	462
M10.5.00	10	5	0	474
M10.0.20	10	0	20	167
M10.2.20	10	2	20	169
M10.5.20	10	5	20	194
M10.0.30	10	0	30	141
M10.2.30	10	2	30	141
M10.5.30	10	5	30	141
M15.0.00	15	0	0	471
M15.2.00	15	2	0	522
M15.5.00	15	5	0	462
M15.0.20	15	0	20	130
M15.2.20	15	2	20	153
M15.5.20	15	5	20	275
M15.0.30	15	0	30	224
M15.2.30	15	2	30	251
M15.5.30	15	5	30	283