Numerical Simulation of Chloride Ion Ingression in Mortar Incorporating the Effect of ITZ Using an Integrated COMSOL-IPHREEQC Framework

Siventhirarajah Krishnya[1](✉), Yogarajah Elakneswaran[1], Yuya Yoda[2], and Ryoma Kitagaki[1]

[1] Faculty of Engineering, Hokkaido University, Sapporo, Japan
krishnya1991@gmail.com
[2] Center for Construction Engineering, Shimizu Corporation, Shimizu Institute of Technology, Tokyo, Japan

Abstract. The prediction of chloride ingression in cement-based material has gained a great deal of interest among researchers as it causes long-term structural damage in buildings by chloride-induced reinforcement corrosion. The Cl^- diffusion in mortar is influenced by internal factors including pore-structure and hydrates which are determined by clinker properties, mixture recipe, and curing conditions and exposure conditions. The Cl^- penetration in mortar leads to the modification of the microstructure and pore-solution due to the disequilibrium of the hydrates-pore solution system. Considering the complexity of the process by incorporating all aforementioned factors and interaction of Cl^- with hydrates, a new model is herein proposed for predicting the microstructure of the mortar during the Cl^- diffusion. In this work, the microstructure of mortar is considered as a three-phase material: aggregates, interfacial transition zone (ITZ) and bulk paste, and ITZ is realistically considered as high W/C paste compared to the initial W/C. The developed COMSOL-IPHREEQC model involves hydration model for calculating the dissolution of clinker in bulk paste and ITZ, thermodynamic model including the surface complexation model to predict the hydrates and the Cl^- adsorption by hydrates, homogenization approach to compute the average hydrates, porosity, pore solution composition and diffusion parameters of the mortar and COMSOL Multiphysics to perform the transportation calculation. The predicted results are validated with experimental results available in the literatures to verify the reliability of the proposed model. The effect of ITZ on the penetration of Cl^- is also assessed in this work.

Keywords: Chloride ion diffusion · Hydration products · Interfacial transition zone · Porosity · COMSOL-IPHREEQC

A. Jędrzejewska et al. (Eds.): SynerCrete 2023, RILEM Bookseries 43, pp. 686–696, 2023.
https://doi.org/10.1007/978-3-031-33211-1_62

1 Introduction

The ability of concrete to withstand the chemical attack, weathering action or any other degradation process to maintain its original characteristics in connection with form, quality and serviceability while exposing to its envisioned service environment is commonly considered as the durability of the structure. The concrete degradation can be classified as chemical, mechanical and physical processes, in which the major durability issue associated with reinforcement corrosion is mainly caused by chemical deterioration such as chloride ion diffusion and carbonation [1]. It is pertinent to note that the chloride diffusion is the utmost serious deterioration process in the steel concrete structure among the varying chemical degradation processes, specifically the structures subjected to environments such as de-icing salts in cold regions and air-bone chlorides in marine regions [2, 3]. During the chloride ion ingression, the protective passive film covered on the reinforcement bars is destroyed by the diffused chloride ion in the pore solution after exceeding its threshold level, and finally, this leads to the initiation of reinforcement corrosion in the concrete structures [4].

The ionic transportation processes in the cement-based material not only depend on the exposure conditions but also on the morphology of the hydrated matrix i.e., porosity and pore network. The morphology of the hydrated cement matrix is mainly determined by several factors such as chemical and physical properties of cement, water-to-cement ratio (W/C), curing conditions, curing period, admixtures, exposure period and etc. [1]. The presence of aggregates in the cement mixture has modified the microstructure and diffusion properties of the matrix by a newly formed weakest region between the aggregate and bulk past referred as interfacial transition zone (ITZ). The general reason behind the formation of ITZ is the wall-effect originated by the aggregate surface that disturbs the general packing of clinker grains, i.e., small cement particles pack more easily adjacent to the aggregate surface compared to large particles [5]. As a result, the excess amount of porosity exists in the ITZ layer compared to that of bulk paste. It is believed that this weakest zone region in the mortar/ concrete has a major influence on the transport properties owing to its excess porosity and larger occupation in the total mortar or concrete.

After entering the diffused chloride, the free chloride ion in the pore solution decreases due to different binding mechanism such as physical binding (chloride ion adsorption by hydrates surfaces) and chemical binding (chemical reaction between chloride ion and AFm phases in the cement matrix). The commonly available AFm phase in the ordinary Portland cement (OPC) is monosulfate, and it form as the result of the reaction between the aluminate (C_3A) and gypsum. In the presence of chloride ion, the sulfate ions in the monosulfate phase exchange with chloride ions and form as chloride containing AFm phases such as Friedel's salt. Besides the chemical binding of chloride, other chloride can be physically adsorbed on the C-S-H surface. Because C-S-H is the major hydration products in OPC and having high specific surface area. However, the physically and chemically bound chloride has no effect on the corrosion of steel bars. On the other hand, the free chloride moves through the pore solution and causes the reinforcement corrosion in the concrete structure.

Moreover, utilization of supplementary cementitious materials (SCMs) such as ground-granulated blast furnace slag, fly ash, metakaolin, silica fumes in concrete has been increased in recent decades to minimize the use of clinker and to improve the durability of the structures. The high alumina and silica content in SCMs helps to form more Friedel's salt by consuming chlorides, which delays the risk of corrosion [6]. And also, the use of SCMs limits the transport of ions, gas and moisture, as the permeability of the harden matrix is reduced by refining the microstructure. Therefore, understanding the chloride ion transport and binding mechanism are truly essential for the prediction of service life of a new building or existing concrete structure.

The aim of this research work is to propose a new modelling platform to predict the hydration products and porosity of mortar during the chloride ion diffusion. To capture the realistic behaviour, the ITZ is assumed as a third phase of the mortar matrix by considering the high W/C paste compared to the bulk paste. Moreover, all the possible hydration products including formation of two types of C-S-H and the physical and chemical binding mechanism of chloride ion with hydrates are also incorporated in this work.

2 Model Description

A new transport model developed to predict the hydration products, pore solution chemistry and porosity of the mortar exposed to an aggressive environment is presented in this study. The mortar matrix is considered herein as three phase material consisting of unreacted aggregates, interfacial transition zone (ITZ) and bulk paste. Figure 1 details the adopted procedures and phenomena of the developed transport model. The proposed framework is coupled with multiple constitutive models including several analytical models for the calculation of volume fraction of ITZ and bulk paste and computation of clinker content and W/C ratio in ITZ and bulk paste, cement hydration model, thermodynamic model, homogenization technique and transport model. The necessary parameters for the hydration calculation are chemical and physical properties of clinker, mixing proportions, boundary conditions and properties of aggregates, while ionic concentration in the exposure solution, beginning of transport reaction with respect to the hydration time domain and duration for transport calculations are the required parameters for the transport process. The details of cement paste model, calculation of volume fraction of ITZ and bulk paste and computation of clinker content and W/C in ITZ and bulk paste can be found in our previous works [7, 8]. The remaining thermodynamic model, homogenization method and transport model are comprehensively described in the following sub sections.

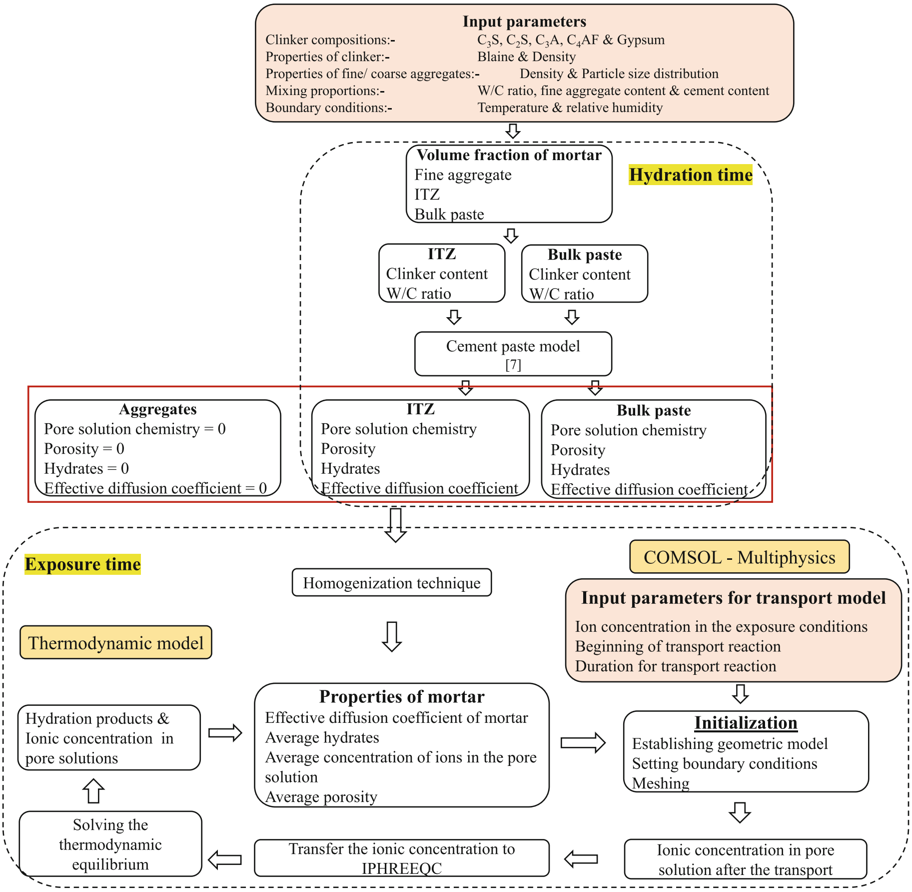

Fig. 1. Schematic diagram of the developed transport model for mortar

2.1 Thermodynamic Model

Thermodynamic model is used to predict the hydration products, concentration of ions in the pore solution and ions adsorption by hydrates of the mortar matrix. The thermodynamic calculations are performed using geochemical software called PHREEQC linked with precise thermodynamic database of Cemdata18 [9] and the default thermodynamic database of PHREEQC [10]. The reaction module, phase-equilibrium module and surface complexation module are used to define the hydrates and pore solution chemistry. The computed dissolved clinker phases from the cement hydration model (please refer for more details of the cement hydration model in our previous work [7]) are inputted in the reaction module for every time step. The phase-equilibrium calculations are performed to define the hydration products which react reversibly with pore solution to achieve equilibrium condition. C-S-H, portlandite, gypsum, ettringite, monosulfate, calcite, hemicarbonate, monocarbonate, hydrotalcite, brucite, stralingite, Fe-Al-silicieous hydrogarnet, Friedel's salt, amorphous silica and amorphous alumina gel are considered as equilibrium phases in the proposed model.

Numerous previous studies have been proved that the surface of C-S-H can adsorb the ions from the aqueous solution [11, 12]. Thus, the surface complexation module in PHREEQC is helped to determine the ions adsorption by the surface of C-S-H. Among the two types of surface sites in C-S-H such as silanol site ($\equiv SiOH$) and silandiol ($= Si(OH)_2$), silanol site is considered to be reacted with ions in the pore solution as per the previous studies [11, 12]. Table 1 shows the used site reactions of C-S-H silanol site and the equilibrium constants for this proposed frame work.

Table 1. C-S-H surface site reactions and equilibrium constants

Site reactions	$\mathrm{LogK_p}$
$\equiv SiOH + OH^- \leftrightarrow \equiv SiO^- + H_2O$	−12.7
$\equiv SiOH + Ca^{+2} \leftrightarrow \equiv SiOCa^+ + H^+$	−9.4
$\equiv SiOH + Ca^{+2} + Cl^- \leftrightarrow \equiv SiOCaCl + H^+$	−8.9
$\equiv SiOH + Na^+ \leftrightarrow \equiv SiONa + H^+$	−13.64
$\equiv SiOH + K^+ \leftrightarrow \equiv SiOK + H^+$	−13.64

2.2 Homogenization Method

To predict the effective diffusion coefficient of mortar, the generalized self-consistent theory was adopted in this study. The generalized self-consistent theory has been widely used to predict the effective properties of mortar and concrete in terms of elasticity, elastoplasticity and thermal behaviour [8, 13, 14]. In this research work, aggregate is assumed to be an inert material, thus the diffusion coefficient of aggregate (D_{agg}) is considered as zero.

$$D_{agg} = 0 \tag{1}$$

The diffusion coefficient of ITZ (D_{ITZ}) and bulk paste (D_{bp}) can be expressed in terms of diffusion coefficient of ions in free water (D_0), porosity of the matrix ($\phi_{ITZ/bp}$) and parameters of pore network such as tortuosity (δ) and constrictivity ($\mathcal{E}$) based on the Archi's law (Eq. 2) [4]. The considered diffusion coefficient of ions in free water are listed in Table 2.

$$D_{ITZ/bp} = D_0.\varepsilon_{ITZ/bp}.\phi_{ITZ/bp}^{\delta_{ITZ/bp}} \tag{2}$$

The porosity calculation of ITZ and bulk paste can be seen in our previous works [7, 8]. In the generalized self-consistent theory, aggregates and ITZ are initially considered to compute the effective coefficient of the aggregate-ITZ matrix as shown in Eq. (3).

$$D_{eff\_1} = D_{ITZ} + \frac{D_{ITZ}\cdot\frac{V_{agg}}{V_{agg}+V_{ITZ}}}{\frac{D_{ITZ}}{D_{agg}-D_{ITZ}} + \frac{1}{3.\frac{V_{ITZ}}{V_{agg}+V_{ITZ}}}} \tag{3}$$

Table 2. Diffusion Coefficient of ions in free water at 20 °C

Ion	Diffusion coefficient × 10^{-9} (m^2/s)
Ca^{+2}	0.793
Mg^{+2}	0.705
SO_4^{-2}	1.07
OH^-	5.27
Na^+	1.33
Cl^-	2.03
K^+	1.96

where, V_{agg} and V_{ITZ} are volume fraction of aggregate and ITZ in the mortar matrix respectively. The effective diffusion coefficient of mortar (D_{mor}) i.e., aggregates-ITZ matrix as inclusions embedded into the matrix of bulk paste can be computed based on Eq. (4).

$$D_{mor} = D_{bp} + \frac{D_{bp}.(V_{agg} + V_{ITZ})}{\frac{D_{bp}}{D_{eff\_1} - D_{bp}} + \frac{1}{3.(1 - V_{agg} - V_{ITZ})}} \tag{4}$$

The average hydrates, porosity and pore solution concentrations are calculated based on the volume fraction of the aggregates, ITZ and bulk paste.

2.3 Transport Model

The COMSOL Multiphysics adopted the finite element method is used herein to solve the transport calculation of ions between the pore solution and exposure solution. The calculated average ionic concentration, porosity and effective diffusion coefficient of the mortar matrix are the initial conditions for the transport calculation and they are transferred to COMSOL package via LiveLink for MATLAB offered in the COMSOL Multiphysics. The ion concentration profile of each ion in the pore solution and exposure solution are computed based on the defined boundary conditions and the time step. The critical expressions used in this research work to compute the transport problem are briefly described here. The Nernst-Plank equation is used to describe the ionic flux (J_i) in the pore solution as detailed in Eq. (5).

$$J_i = -D_{e,i} \cdot \nabla C_i - D_{e,i} C_i \cdot \frac{Z_i F}{RT} . \nabla \phi \tag{5}$$

where, C, D_e, Z, F, R, T and ϕ are respectively concentration of ion (mol/m^3), effective diffusion coefficient in liquid (m^2/s), electric charge number, the Faraday constant, the universal gas constant, absolute temperature and electrical potential (V). The governing equation for the transport problem of the porous matrix can be expressed in terms of ionic flux (J_i), porosity of the matrix (ϕ), concentration of ion (C_i) and sink term (S_i) (Eq. 6). The sink term is computed based on the dissolution and precipitation of phases during the thermodynamic equilibrium process by using PHREEQC.

$$\frac{\partial(\theta C_i)}{\partial t} + \nabla . J_i = S_i \tag{6}$$

The electrical current in the mortar matrix is zero during the ionic diffusion process. Hence,

$$\sum\nolimits_i Z_i j_i = 0 \tag{7}$$

In this study, the concentration profile of each ion in the pore system was computed by combining Eq. (4)–Eq. (7).

3 Results and Discussion

As the initial stage of the developed model, the chloride ion transportation in cement paste was verified with the experimental results reported by Mori et al. [15], for the W/C of 0.5 paste exposed in 3% NaCl solution for 91 days and the comparison between the predicted results and experimental results is depicted in Fig. 2. It should be noted that hydration products and porosity of the cement paste during the hydration reaction have been verified in our previous work [7]. The comparison between the predicted results of total chloride weight percentage and experimental results is illustrated for the mortar in Fig. 3. The experimental results reported in the previous study for W/C of 0.53, the fine aggregate to cement of 1.5, exposure solution of 5% NaCl and 100 days of exposure duration is compared with the predicted results of mortar [16]. As shown in Fig. 2 and Fig. 3, the predicted total Cl^- weight % results from the proposed model shows an excellent agreement with the experimental results for both cement paste and mortar. The weight percentage of total chloride is apparently high near to the exposed surface for all the cement-based matrix due to the high porosity and high concentration of the exposure solution. Large amount of total porosity close to the exposure side is due to the dissolution of hydrates, and which is induced by the leaching of ions in the pore solution. The effective diffusion coefficient increases with porosity. The diffusion of external ions depends on the concentration of the exposure solution. Because, the transport of ions in the porous matrix occurs due to the concentration gradient. Therefore, the diffusion rate and amount of chloride ion are observed high near to the exposure surface. The similar tendency is observed in both the experimental results.

The numerical results for the volume fraction of the 28 days hydrated mortar without aggregate (volume fraction of aggregate is approximately 0.41) exposed in 5% NaCl solution for 1 year is detailed in Fig. 4. In the proposed model, the formation of two types of C-S-H such as low-density C-S-H (LD CSH) and high-density C-S-H (HD CSH) is realistically considered to simulate the actual hydration behaviour of the hydrated matrix. The used characteristics of the two types of C-S-H are detailed in our previous work [7]. Due to the pH difference between the exposure solution (pH = 7) and the pore solution (pH ≈ 13.4), ions leach near to the exposure surface and it may be the

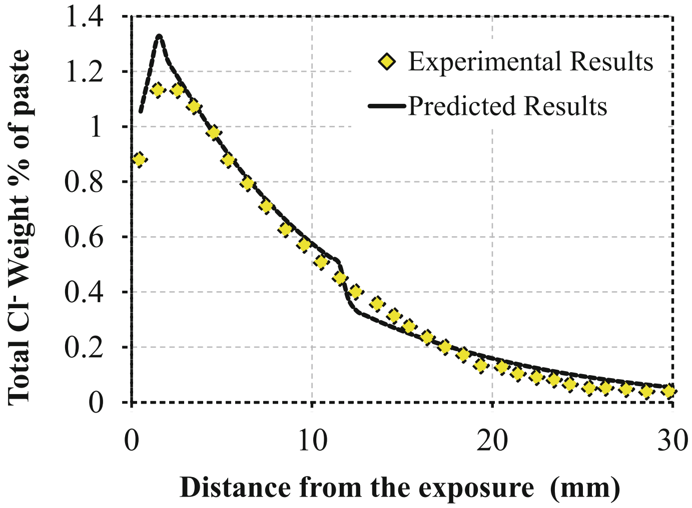

Fig. 2. Comparison of predicted total Cl^- profile with experimental results for cement paste

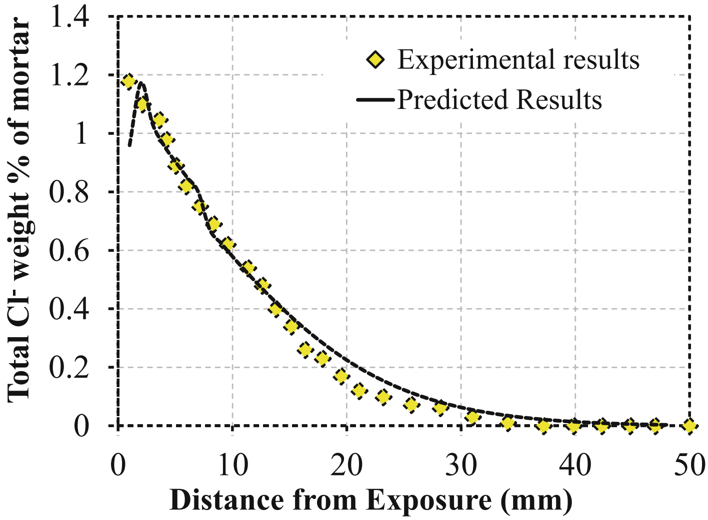

Fig. 3. Verification of total Cl^- weight % with distance from exposure for mortar

reason for dissolution of portlandite, ettringite and C-S-H. Consequently, the porosity of the system increases with the approach towards the exposure surface. Moreover, the diffused chloride ion reacts with monosulfate to form as Friedel's salt and small amount of ettringite as shown in Eq. 8 and Eq. 9 [17]. As a result, there is no monosulfate in the presence of Friedel's salt as depicted in Fig. 4. For instance, the precipitation of Friedel's salt is observed from 3 mm to 38 mm from the exposure surface while the formation of monosulfate occurs from 38 mm. The Friedel's salt formed upto 3mm is destabilized due to the leaching process. The dissolution of C-S-H and Friedel's salt leads to the formation of strälingite near to the exposure surface.

$$C_3A.CaSO_4.12H_2O + Cl^- \rightarrow C_3A.CaCl_2.10H_2O + SO_4^{-2} \tag{8}$$

$$C_3A.CaSO_4.12H_2O + Ca^{+2} + SO_4^{-2} \rightarrow C_3A.3CaSO_4.32H_2O \tag{9}$$

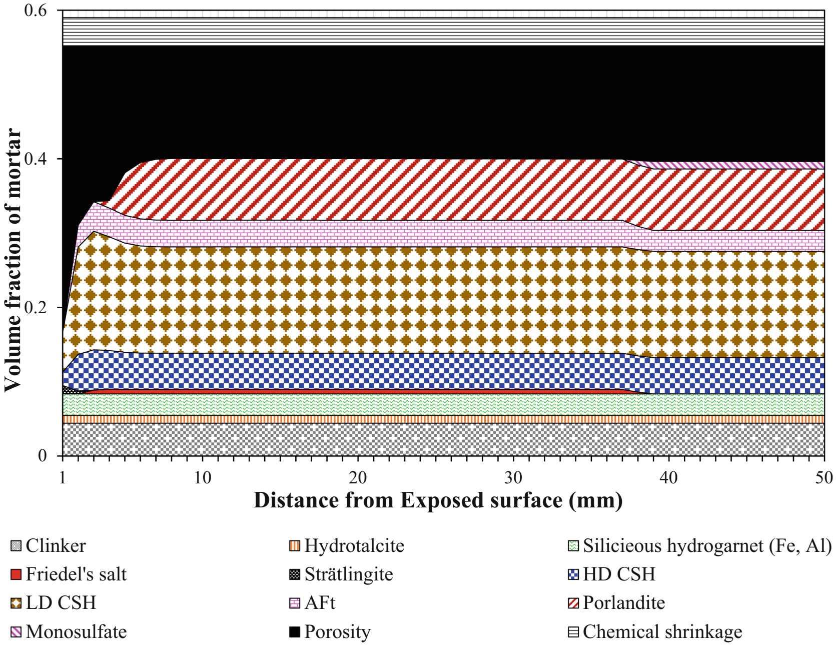

Fig. 4. Phase assemblage of mortar (without aggregate) exposed in 5% NaCl solution for 1 year

The effect of ITZ on the transport properties of mortar is depicted in Fig. 5. The mortar matrix with W/C of 0.6, fine aggregate to cement ratio of 4 exposed to 900 mol/m^3 NaCl solution for 1 year was considered for this simulation. As depicted in Fig. 5(a), due to the ignorance of ITZ in the mortar matrix, the without ITZ case shows considerably low chloride ion diffusion compared to the three-phase material i.e., with ITZ case. For instance, free chloride ion concentration at approximately 30 mm from the adjacent surface is 347 mol/m^3 and 260 mol/m^3 for the cases of with and without ITZ respectively. Based on this analysis, it can be found that maximum of about 25% deviation is observed, if the mortar is considered as two-phase material. Moreover, the effective diffusion coefficient of the two-phase matrix by neglecting the ITZ is reduced by 2 times compared to the three-phase material (refer Fig. 5(b)). As reported in the numerous studies, the ITZ is the weakest zone in mortar or concrete due to very high amount of porosity near to aggregate surface. Therefore, by ignoring the weakest zone in the matrix leads to reduction in the effective diffusion coefficient as it mainly depends on the porosity of the system.

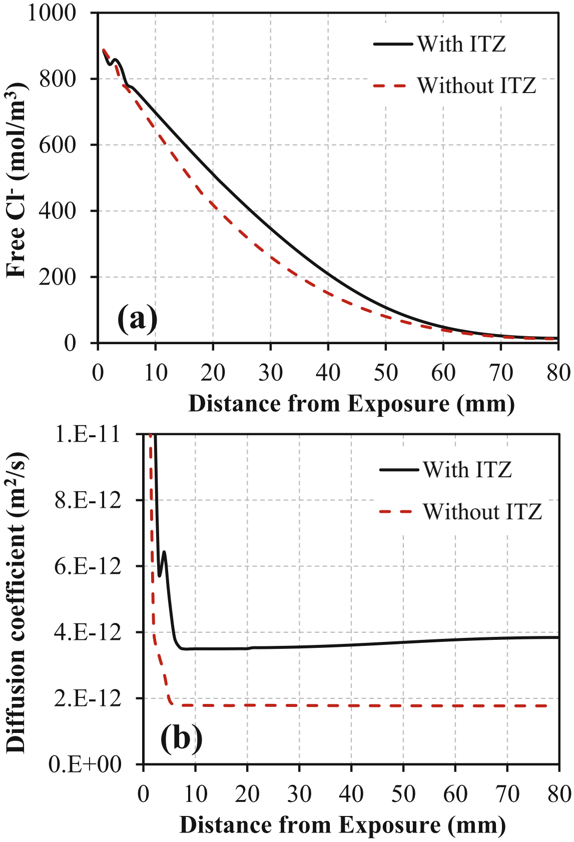

Fig. 5. Comparison of predicted (a) free Cl^- profile and (b) effective diffusion coefficient of mortar for the cases of with ITZ and without ITZ

4 Conclusion

A new integrated framework developed in MATLAB language is presented in this study to predict the microstructural changes of mortar due to the chloride ion diffusion. The mortar matrix herein is reliably assumed as three phase material consist of aggregates, ITZ and bulk paste. The developed model is coupled with cement hydration model, analytical relationship to compute the properties of ITZ and bulk paste, homogenization technique to compute the effective transport properties of mortar, thermodynamic model and transport model. The numerical prediction is verified with experimental results to demonstrate the predictability of the developed model. An excellent agreement between experimental results and predicted results were found comparing the total chloride ion profile with distance from the exposure. Furthermore, the effect of ITZ on transport properties were emphasized in this study. The predicted results via mortar as two-phase matrix reveals considerably lower chloride ion diffusion compared to that both predicted results from the three-phase model and the experimental results. However, the proposed framework needs further validations with different sets of experimental results including different W/C, aggregate content and exposure conditions to generalize the model.

References

1. Patel, R.A., et al.: Diffusivity of saturated ordinary Portland cement-based materials: a critical review of experimental and analytical modelling approaches. Cem. Concr. Res. **90**, 52–72 (2016)
2. Ahmad, S.: Reinforcement corrosion in concrete structures, its monitoring and service life prediction-a review. Cem. Concr. Compos. **25**, 459–471 (2003)
3. Wang, K., Nelsen, D.E., Nixon, W.A.: Damaging effects of deicing chemicals on concrete materials. Cem. Concr. Compos. **28**, 173–188 (2006)
4. Hatanaka, A., et al.: The impact of tortuosity on chloride ion diffusion in slag-blended cementitious materials. J. Adv. Concr. Technol. **15**(1), 426–439 (2003)
5. Zheng, J., Zhou, X., Jin, X.: An n-layered spherical inclusion model for predicting the elastic moduli of concrete with inhomogeneous ITZ. Cem. Concr. Compos. **34**(5), 716–723 (2012)
6. Borade, A.N., Kondraivendhan, B.: Corrosion behavior of reinforced concrete blended with metakaolin and slag in chloride environment. J. Sustain. Cem. Based Mater. **8**(6), 367–386 (2019)
7. Krishnya, S., Yoda, Y., Elakneswaran, Y.: A two-stage model for the prediction of mechanical properties of cement paste. Cem. Concr. Compos. **115**, 103853 (2021)
8. Krishnya, S., Elakneswaran, Y., Yoda, Y.: Proposing a three-phase model for predicting the mechanical properties of mortar and concrete. Mater. Today Commun. **29**, 102858 (2021)
9. Lothenbach, B., et al.: Cemdata18: a chemical thermodynamic database for hydrated Portland cements and alkali-activated materials. Cem. Concr. Res. **115**, 472–506 (2019)
10. Parkhurst, D.L., Appelo, C.A.J.: A computer program for speciation, batch- reaction, one-dimensional transport and inverse geochemical calculations. USGS Report (1999)
11. Elakneswaran, Y., Iwasa, A., Nawa, T., Sato, T., Kurumisawa, K.: Ion-cement hydrates interactions governed multi-ionic transport model for cementitious materials. Cem. Concr. Res. **40**, 1756–1765 (2010)
12. Guo, B., Hong, Y., Qiao, G., Ou, J.: A COMSOL-PHREEQC interface for modeling the multi-species transport of saturated cement-based materials. Constr. Build. Mater. **187**, 839–853 (2018)
13. Sun, G., Zhang, Y., Sun, W., Liu, Z., Wang, C.: Multi-scale prediction of the effective chloride diffusion coefficient of concrete. Constr. Build. Mater. **25**(10), 3820–3831 (2011)
14. Herve, E.: Thermal and thermoelastic behaviour of multiply coated inclusion-reinforced composites. Int. J. Solids Struct. **39**, 1041–1058 (2002)
15. Mori, D., Yamada, K., Hosokawa, Y., Yamamoto, M.: Applications of electron probe micro-analyzer for measurement of Cl concentration profile in concrete. J. Adv. Concr. Technol. **4**(3), 369–383 (2006)
16. Fu, C., Li, S., He, R., Zhou, K., Zhang, Y.: Chloride profile characterization by electron probe microanalysis, powder extraction and AgNO3 colorimetric: a comparative study. Constr. Build. Mater. **341**, 127892 (2022)
17. Sui, S., et al.: Quantification methods for chloride binding in Portland cement and limestone systems. Cem. Concr. Res. **125**, 105864 (2019)