- Technical Paper -

COUPLED PHYSICAL AND GEOCHEMICAL MODEL FOR EXTERNAL SULFATE ATTACK IN CONCRETE

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ABSTRACT

In this study, a coupled physical and geochemical model was developed for predicting the durability of cementitious materials. DuCOM (Durability Concrete Model) and geochemical code PHREEQC were used for this purpose. The coupled model takes into consideration of hydration of cement particles, transport of multi species, and chemical interaction of ions with cement phases. The predicted pore solution composition successfully compared with reported experimental data. Further, the coupled model was applied to understand the external sulfate attack in concrete.

Keywords: DuCOM, PHREEQC, transport, modeling, Sulfate attack

1. INTRODUCTION

The durability of cementitious materials in aggressive environments is affected by numerous factors, leading to reduced service life. The durability of the materials must be ensured in both economically and environmentally responsible manner. Degradation of concrete due to ingress of detrimental ions from the environment plays an important role in durability of concrete structures. There are number of models have been developed to provide much information on the degradation behavior of concrete [1-4]. Further, many reports have been published multi-species transport and coupling the transport with geochemical models [1-3]. However, the developed models cannot predict the hydration and microstructure properties of cementitious with time, and they need a large amount of experimental data as the input for performance prediction. Evaluating the existing models make it clear that a proper model is necessary to predict the performance of concrete in various applications.

2. OBJECTIVES AND SCOPE

The primary objective of this study is to develop an accurate model to predict the performance of cementitious materials exposed to aggressive environment. This paper mainly describes the numerical framework of a coupled physical and geochemical model that can be used for multipurpose. The developed model considers the hydration of cement particles and the transport of multi-species into cementitious materials as well as the chemical interaction of multi-species with cement phases. Further, the model is able to predict spatial and time variation of physical and chemical properties of the materials as well as chemical degradation by ingress of detrimental ions. The computational platform of coupled model and the coupling procedures are described in detail in this paper. The predicted pore solution concentration and its comparison with experimental data are also presented. Further, the coupled model is used to understand the chemical degradation due to sulfate attack in concrete. The dissolution or precipitation of minerals as a result of geochemical reactions changes the pore structure of cementitious materials. This effect has not included in the current coupled model. In this study, the coupled modeling results have not compared with other modeling approaches reported in the literature as well as with experimental data. The detail verification of the coupled model for short and long term performances of cementitious materials in aggressive environments will be considered in the future. Although the constitutive models will carefully be verified in the future, in this paper authors show how the proposed platform is versatile and functions well.

3. THEORY

The transport of ions into concrete is due to advection and diffusion. The governing equation in this phenomenon can be expressed as follows [4]:

$$\frac{\partial(\phi \cdot S \cdot C_{ion})}{\partial t} + div J_{ion} - Q_{ion} = 0 \qquad (1)$$

Where,
Φ: porosity
S: degree of saturation of porous media
C_{ion}: concentration of an ion in pore solution
J_{ion}:   total flux of an ion
Q_{ion}:   Sink term

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In Eq. (1), the first term represents the rate of change in total amount of ion per unit time and volume, the second term gives the total flux due to both diffusion and advection, and the last term called the sink or source term which represents the rate of removed or precipitated ions by reactions. The Eq. (1) is to be solved for numerical analysis of ionic ingress into concrete. It is considered that the transport of ions in gel and capillary pores. Therefore, porosity, Φ, is the sum of gel and capillary porosities.

Diffusive flux of ions considering electrical potential gradient and activity coefficient in porous media can be expressed as follows (Nernst-Plank equation) [3]:

$$J_{ion} = -\phi \cdot S \cdot \left(\frac{D_{ion}}{\Omega} \cdot \delta\right) \cdot \left[\frac{\partial \ln(\gamma_{ion})}{\partial \ln(C_{ion})} + 1\right] \frac{\partial C_{ion}}{\partial x}$$
$$- \phi \cdot S \cdot \frac{F}{RT} Z_{ion} C_{ion} \left(\frac{D_{ion}}{\Omega} \cdot \delta\right) \frac{\partial \psi}{\partial x} + \phi \cdot S \cdot u \cdot C_{ion}$$

$$(2)$$

Where,
D_{ion}: Diffusion coefficient of an ion (m^2/s)
δ: Constrictivity
Ω: Tortuosity
R: ideal gas constant (J/mol.K)
T: absolute temperature (K)
F: Faraday's constant (C/mol),
Z_{ion}: ion valance
u: velocity of an ion transported by bulk movement of solution (m/s)

In Eq.(2), the first and second terms are due to chemical and electrical potential gradients respectively while the third term represents the advection. The activity coefficients, γ, are calculated according to the extended Debye-Huckel [5]:

$$\log \gamma_{ion} = -\frac{A z_{ion}^2 \sqrt{I}}{1 + B a_{ion} \sqrt{I}} + b_{ion} I \qquad (3)$$

Where,
A and B: temperature dependent coefficients
a_{ion} and b_{ion}: ion-specific fit parameters.

Ionic strength, I, can be described as:

$$I = \frac{1}{2} \sum_{i=1}^{n} c_i z_i^2 \qquad (4)$$

The electrical potential gradient, $\left(\frac{\partial \psi}{\partial x}\right)$, is caused by different mobilities of ions in the solution. If there is no electrical current, $\sum_i J_i \cdot Z_i = 0$, the zero-charge flux permits to determine the electrical potential gradient as a function of other term in Eq.(2).

The sink term is considered as the rate of dissolved

or precipitated sulfate ions due to geochemical reactions. When ion activity product (IAP) is greater than solubility product or equilibrium constant, the ions in the solution start to precipitate. The amount of precipitated or dissolved ions can be given as the difference of sulfate in IAP and in equilibrium. The rate of precipitated or dissolved ions can be written as follows:

$$\frac{\partial q_{ion}}{\partial t} = \frac{\partial q_{ion}}{\partial C_{ion}} * \frac{\partial C_{ion}}{\partial t} \qquad (5)$$

For pure thermodynamic equilibrium, q_{ion} has a linear relationship with free concentration (C_{ion}). Therefore, sink term can be expressed as follows:

$$Q_{ion} = \frac{\partial q_{ion}}{\partial t} = K * \frac{\partial C_{ion}}{\partial t} \qquad (6)$$
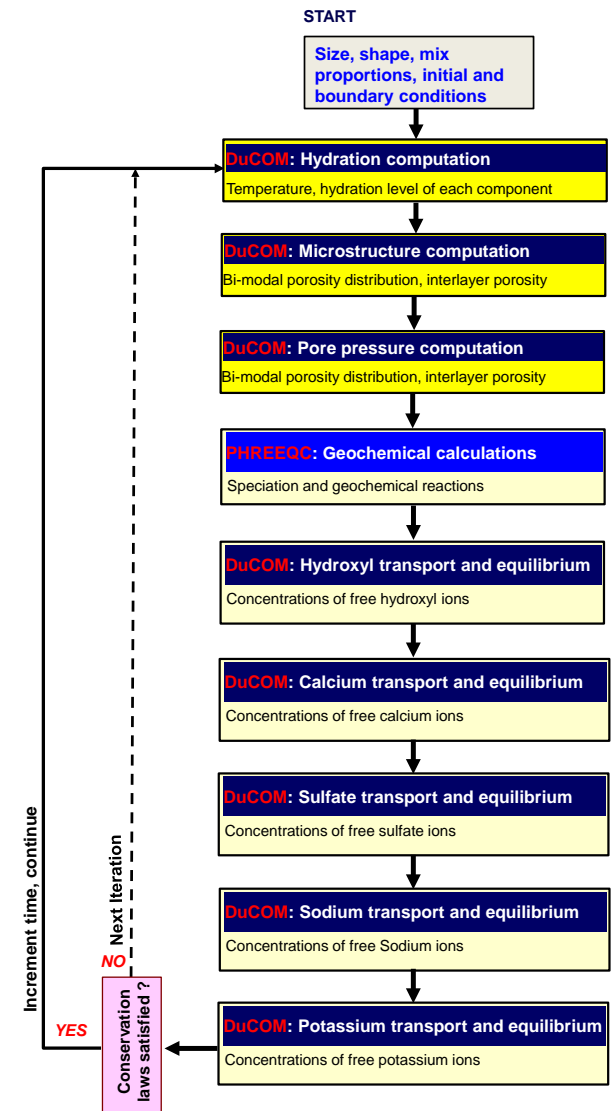
4. FRAMEWORK OF COUPLED MODEL

Fig. 1 Framework of coupled DuCOM and PHREEQC

Durability Concrete Model, DuCOM, is developed by Concrete Laboratory at the University of Tokyo, Japan [4]. The originality of this model comes from the fact that the DuCOM is a composite multipurpose model, which predicts the state of the concrete from its birth to its entire life. Geochemical code PHREEQC is designed to perform variety of geochemical calculations including equilibrium between minerals and solution, ion exchanges, surface complexes, solid solution and gases [5]. PHREEQC has been integrated with other programs to perform geochemical calculation. As described in ref. [6,7], PHREEQC has been coupled with other program in two different ways: hard and soft couplings. The first approach involves modification of source code either PHREEQC or other program to transfer data between those. It requires full knowledge of both programs' source code, and it is very difficult because of complexity in the programs. The traditional soft coupling is easy to implement, but the calculation time is long because of reading and writing of files, and repeated initiation calculation for each time step. The new IPhreeqc module is designed for coupling of PHREEQC with other programming languages [6]. IPhreeqc module can easily interface with other programming languages and PHREEQC can run without reading or writing files. The data can transfer between PHREEQC and other program through internal computer memory. This kind of process has merits on calculation time and programming because IPhreeqc preserve computed results between time steps rather than redefining PHREEQC for each time step.

Fig. 2 Conceptual coupling of DuCOM with PHREEQC at each time step

It has been proved that DuCOM can predict hydration, pore structure formation, ionic transport in cementitious materials, etc very well [4]. However, the current DuCOM system cannot perform geochemical reactions simultaneously with above calculations. On the other hand, PHREEQC can perform geochemical and speciation calculation. Further, it can do the same kind of calculation in cementitious materials also [3]. However, it cannot predict the hydration or pore structure formation in cementitious materials. In addition, it needs a lot of parameters such as physical and chemical properties (amount of cement hydrates, pore solution composition, etc.) as input to the model. Therefore, DuCOM needs to be coupled with PHREEQC to perform wide range of calculation and for the prediction of cementitious materials in aggressive environments.

In this study, DuCOM and IPhreeqc (hereafter call PHREEQC) are coupled using FORTRAN programming language. The coupled model retains all the capabilities of these models, and it can be used for multipurpose. A basic framework of DuCOM system coupled with PHREEQC is shown in Fig. 1. PHREEQC has incorporated into DuCOM as a model to perform speciation and geochemical calculation. IPhreeqc provides direct access to geochemical processes in PHREEQC through a library. It is known that PHREEQC perform variety of calculation, but in the coupled model DuCOM performs hydration, pore structure, multi-ionic transport calculation while PHREEQC performs only geochemical calculation. Therefore, the coupled model satisfies the governing equation (Eq. (1)) for FEM in DuCOM. The necessary data to satisfy the governing equation are transferred to DuCOM from PHREEQC through the coupling. The coupling provides the internal data transfer between DuCOM and PHREEQC while they are running concurrently. Therefore, either DuCOM or PHREEQC neither writes nor reads files for coupling. Fig. 2 shows the conceptual approach for data exchange between DuCOM and PHREEQC at each time step. At each time step, first DuCOM perform hydration and pore structure computation then the computed cement hydrates, pore solution concentration and porosity are given to PHREEQC through computer memory as the input. Each gauss point in each finite element of DuCOM is represented by a single batch reactor for PHREEQC that contains minerals and solution elements, and PHREEQC performs the geochemical calculation through thermodynamic law. The porosity computation is performed at each time step based on the amounts of precipitated/dissolved minerals due to thermodynamic equilibrium. After PHREEQC geochemical calculation, the equilibrated pore solution composition, the amounts of precipitated/dissolved cement hydrates, and modified porosity are passed back to DuCOM. DuCOM perform the multi-ionic transport and other calculation to determine the physical properties. These steps are continued until to total time. The coupled model does not need physical or chemical properties in advance as the input data to the model. Therefore, input parameters for the coupled model are
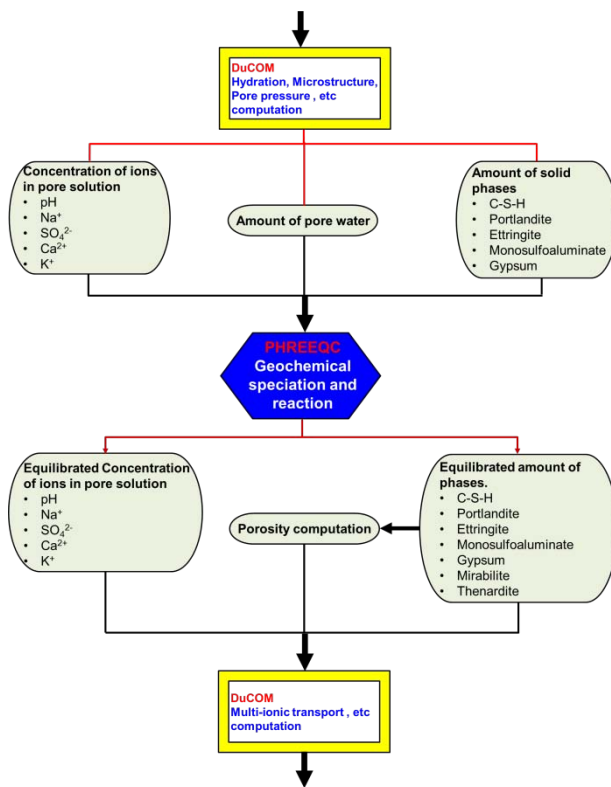
the same as the input of DuCOM. The coupled model described here can be used to predict hydration of cement particles, multi-ionic transport, and geochemical reactions in cementitious materials simultaneously. This strong coupling of geochemical processes with physical properties provides more information regarding the long-term performance of cementitious materials in aggressive environments.

5. SIMULATION RESULTS AND DISCUSSIONS

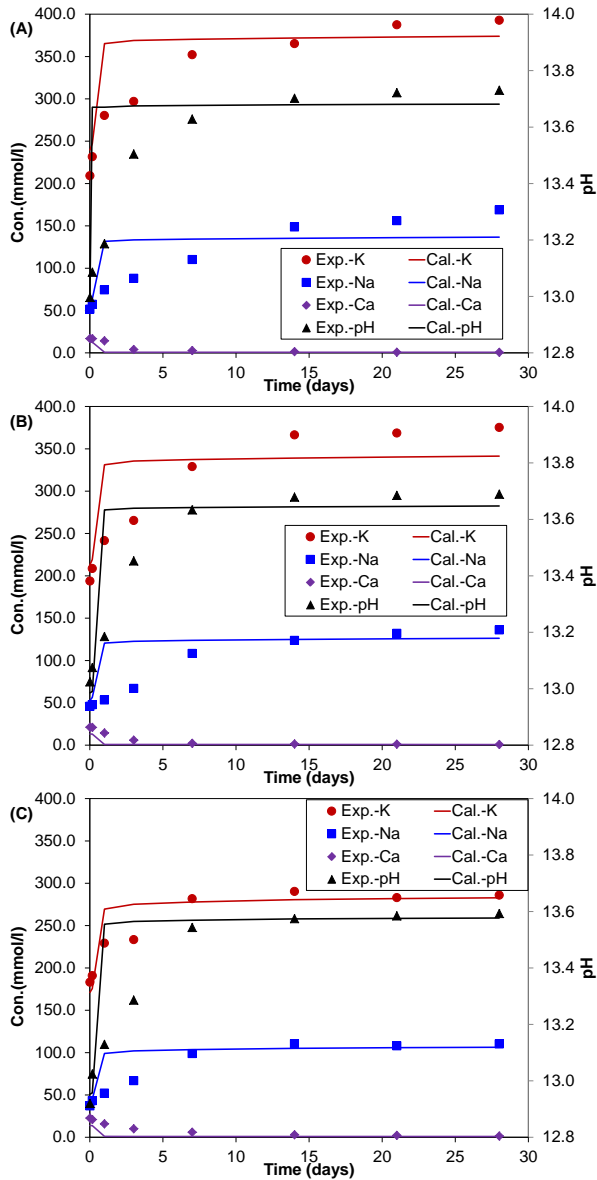### 5.1 Computation of pore solution concentration

Fig. 3 Comparison between predicted and measured [10] pore solution concentration of OPC paste with W/C of (A) 0.4, (B) 0.45, and (C) 0.56 during the first 28 days

The concentration of alkali ions in pore solution in the saturated condition can be calculated according to the method proposed by Taylor (detailed in ref. [8]). It is based on mix proportion, the chemical composition of

cement, and hydration model. The calculation consists of release of alkali ions from cement and uptake of alkali ions by cement hydrates. When release and uptake of alkali are known, the concentration of Na^+ and K^+ in pore solution can be determined during hydration. The calculation method described in ref. [8] and briefly explained in here. The total concentration of Na^+ and K^+ can be computed from mass fraction and molecular weight. The calculation for Na^+ as follows:

$$Na_T = \frac{2 f_{Na_2O}}{M_{Na_2O}} \quad (7)$$

Where,

Na_T: Total Na content (mol/g)
f_{Na2O}: Na$_2$O mass fraction (g/g)
M_{Na2O}: Molecular weight of Na$_2$O (g/mol)

The total release of alkali is given by rapidly release of alkali from sulfate salt and progressive release of alkali during hydration. The released of Na^+ is calculated as follows:

$$Na^+_{released} = f_{Na,sulfate} * Na_T + \left(1 - f_{Na,sulfate}\right) * \alpha * Na_T \quad (8)$$

Where,

$Na^+{}_{released}$: Total release of Na^+ (mol/g)
$f_{Na,sulfate}$: Fraction of Na^+ in sulfate salt
α: Degree of hydration

According to ref.[8], the amount of alkali ions bound on calcium silicate hydrate (C-S-H) is proportional to the concentration present in the solution and the amount of formed C-S-H, thus:

$$Na^+_{released} m_{OPC} = [Na^+] V_w + Rd_{Na} [Na^+] m_{C-S-H} \quad (9)$$

Where,

m_{OPC}: Mass of ordinary Portland cement (g)
V_w: Volume of pore water (cm^3)
$[Na^+]$: Na^+ concentration in pore solution (mol/cm^3)
Rd_{Na}: Distribution ratio of Na^+ (cm^3/g)
m_{C-S-H}: Mass of formed C-S-H (g)

The fraction of alkalis in sulfate salt and the distribution ratio of alkalis are constant, and the values are given in ref. [8]. The above model is incorporated into the coupled model described in section 4 to determine the concentration of ions in pore solution. At each time step, the concentration of Na^+ and K^+ are calculated from the degree of hydration, porosity or pore water, and amount of formed C-S-H (according to Eqs. (7-9)). The concentration of other ions in pore solution such as Ca^{2+}, SO_4^{2-}, Al^{3+}, Si, OH^- are calculated based on the thermodynamic equilibrium between cement hydrates and pore water. The used thermodynamic properties of various minerals and aqueous species were collected from the BRGM

database (THERMODDEM) [9]. The computed element concentrations are compared with experimental data available in literature [10]. The coupled model simulations were performed for Ordinary Portland Cement (OPC) paste using the same cement composition and other experimental conditions adopted in ref. [10]. Fig. 3 shows the predicted concentration of Na^+, K^+, Ca^{2+} and pH in pore solution that compared with experimental data [10] for different water to cement (W/C) ratio. Very good agreement was obtained between experimental data and the simulation results after 7 days of hydration. However, the model predicts high concentration of ions at early ages. The model modification needs to be considered for the accurate prediction at the early age as well. It is well known that the W/C ratio influence not only the hydration of cement but also porosity or pore size distribution. Thus, pore solution composition is changed with W/C due to changes in the amount of formed C-S-H, porosity, hydration degree, etc (Fig. 3). The coupled model can successfully predict those changes also.

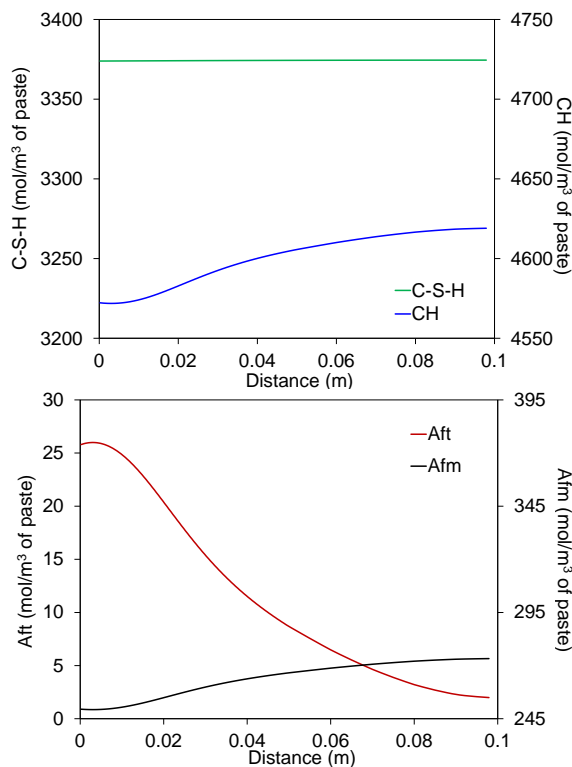5.2 Application of the coupled model for external sulfate attack in OPC concrete

Fig. 4 Representation of the mineralogical distribution after 10 years of sulfate ingress

In order to investigate the capability of the model, the simulation was carried out for sulfate ingress in OPC concrete as an example. The required input parameters for the simulation are tabulated in Table 1. In the simulation, one side of the concrete was considered to be contact with exposure sulfate solution and the other side was free. A one-dimensional multi-ionic transport coupled with geochemical reactions was considered. The hydration products are dominated by C-S-H (with CaO to SiO_2 ratio of 1.6), portlandite, ettringite, monosulfoaluminate, and gypsum. In addition to these hydrates, thaumasite, mirabilite, and thenardite were considered in the simulation. As for the multi-ionic transport, the main ions in pore solution and exposure sulfate solution such as Na^+, K^+, SO_4^{2-}, Ca^{2+}, and OH^- were taken into account. Porosity and pore structure modification due to precipitation/dissolution of minerals have not considered in the simulation. Further, the effect of carbonation is neglected in the simulation and hence formation of thaumasite cannot be expected. The mineralogical distribution of cement phases after 10 years of sulfate ions transport are shown in Fig. 4. It can clearly be seen that the coupled model results show the significant changes of cement hydrates as the result of sulfate ingress. Fig. 4 indicates that C-S-H is a stable phase during the transport of sulfate ions. However, the dissolution of portlandite can be observed near to the exposure surface. The dissolution is mainly due to leaching of calcium and hydroxyl ions. As can be seen in Fig. 4, the secondarily formed ettringite is closely related to the dissolution of both portlandite and monosulfoaluminate. The leached ions from portlandite and monosulfoaluminate have resulted in the formation of ettringite in the presence of diffused sulfate ions. The simulation results do not show any formation of gypsum, mirabilite, or thenardite.

The numerical simulations are sensitive to several parameters or models. In order to understand the effect of W/C on the simulation results, the simulation with lower W/C was performed. The other input parameters to the model were the same as given in Table 1 where W/C of 0.3 was used instead of 0.5. The type of cement hydrates produced at W/C of 0.3 is similar to those produced at 0.5. Fig. 5 shows that the W/C significantly influences formation of both C-S-H and portlandite as well as dissolution of portlandite. The W/C shows a high impact on secondary ettringite. The secondarily formed ettringite is reduced to half by lowering the W/C to 0.3 from 0.5. The calculated initial porosity (both gel and capillary) from the coupled model, which is used for sulfate ingress, is 0.13 and 0.26 for W/C of 0.3 and 0.5 respectively. Lowering W/C is decreasing the concentration of sulfate ions in pore solution. Furthermore, the equilibrated sulfate ions concentration in both W/C is nearly equal to zero. As a matter of fact, the precipitation of secondary ettringite controls the equilibrated concentration of sulfate ions in pore solution. It can be inferred that more porous mixtures are highly affected by the external sulfate ions ingress.

Summarizing, the coupled model allows predicting the spatial and time variation of minerals compositions, pore water concentrations, and other hydration and pore structures properties. In addition, it provides to a better understanding of the underlying mechanisms, which govern the degradation of cementitious materials. Therefore, the coupled model will be a useful tool to assess the performance of cementitious materials in aggressive environments.

Table 1 Input parameters for simulation

| Material	OPC concrete
Mineralogical analyses of OPC (%)	
-Alite	52.06
-Belite	22.45
-Aluminate	9.67
-Ferrite	8.82
-Gypsum	3.87
Characteristics of concrete mixtures	
-W/C	0.5
-Coarse aggregates (kg/m^3)	1035.0
-Fine aggregates (kg/m^3)	803.0
Specimen thickness	10 cm
Curing period and condition	7 days sealed curing
Exposure period	10 years
Exposure solution	0.1 mol/l Na$_2$SO$_4$
Temperature	20℃
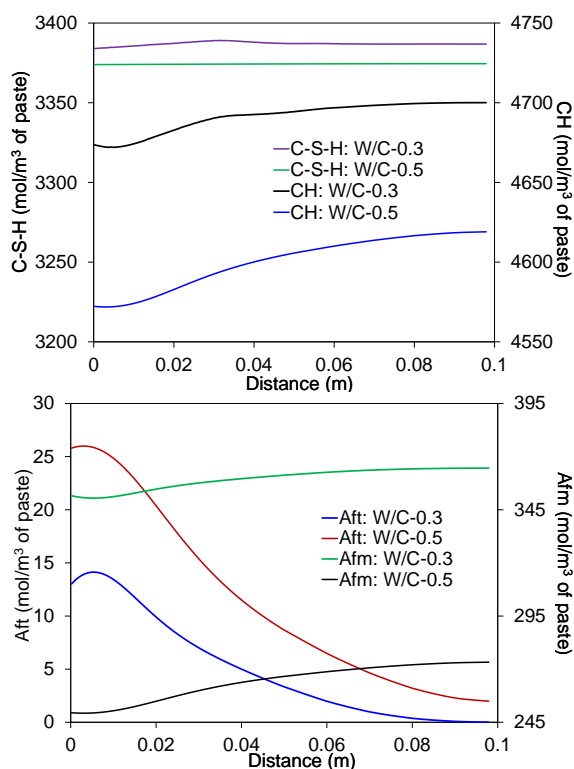
Fig. 5 Sensitivity analyses of mineralogical distribution on water to cement ratio after 10 years of sulfate ingress

6. CONCLUDING REMARKS

This study has revealed the capability of both DuCOM and PHREEQC to provide a coupled model for predicting the durability performance of cementitious materials in aggressive environment. The coupled model considers cement hydration, multi-species transport and ionic interaction with cement hydrates. The coupled model does not require physical or chemical properties of the materials in advance as input. The simulation gives many details not only hydration or pore structures properties but also mineralogical distribution and pore solution composition. The predicted pore solution composition agreed well with experimental data especially for matured cement paste. The capability of the coupled model was investigated through sulfate ingress in OPC concrete. It can be inferred that the simulation results are able to reproduce mineralogical alteration due to chemical reactions and sulfate ingress. It should be noted that there some aspects still require further investigation in order to develop a robust and reliable model for predicting the performance of cementitious materials in aggressive environments.

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