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| 著者                              | ELAKNESWARAN Yogarajah, ISHIDA Tetsuya  |
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# DEVELOPMENT OF A PHYSICAL AND GEOCHEMICAL MODEL FOR LONG-TERM PERFORMANCE OF CEMENTITIOUS MATERIALS

Yogarajah ELAKNESWARAN \*, Tetsuya ISHIDA \*\*

Research Associate, Department of Civil Engineering, University of Tokyo, JAPAN\*

Associate Professor, Department of Civil Engineering, University of Tokyo, JAPAN\*\*

**ABSTRACT:** The deterioration of reinforced concrete is a major problem worldwide and hence the material issues are important in the entire process of infrastructures management. A simulation tool is necessary to evaluate the long-term performance of cementitious materials in various environments, consequently on safety assessment. This requires a good understanding of the underlying process affecting the performance of cementitious materials exposed to range of environmental conditions. The long-term performance of concrete structures do expose to aggressive environment has been investigating, however still more works are needed. A method is needed to take into account the fundamental physical and geochemical reactions resulting due to detrimental effects during the service-life of concrete structures. In this study, a coupled physical and geochemical model is developed for the prediction of long-term performance of cementitious materials. DuCOM (Durability CONcrete Model) and geochemical code PHREEQC were used for this purpose. 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. A part of simulation results have been compared with experimental data. The detailed experimental works have been considered for the further verification of the model. The sulfate ingress into concrete was analyzed in order to investigate the capability of the model. The simulation results are able to reproduce mineralogical alteration due to chemical reactions and sulfate ingress. It can be inferred that the developed model will be a useful tool to assess the performance of cementitious materials in aggressive environments, and thus provides a consistent platform in the management of concrete infrastructures.

**KEYWORDS:** Modeling, Durability, DuCOM, PHREEQC

## 1. INTRODUCTION

Planning, designing, constructing, and maintenance from a long-term aspect with technical and environmental point of view are the main considerations in the infrastructures management system. The advances in technology have increased the knowledge to create more and more concrete

infrastructures. The deterioration of cementitious materials in concrete structures is causing concern over the world today. Durability of cementitious materials is one of the most important properties to be considered in the design of concrete structures, so most of the research works have been directed on that. The durability of cementitious materials in aggressive environments is affected by numerous

factors, leading to reduce the service life. The different causes for the deterioration of cementitious materials are presented in Figure 1. It can be seen that the ingress of detrimental ions from the environment is a leading cause on the degradation of concrete. Various mechanisms and processes occur during the degradation of concrete. This involves complex chemical reactions and physical changes in the materials. The potential variation of chemical and physical properties of these materials with time is an important factor to maintain the performance over the time scale required. Therefore, a detailed knowledge on the underlying processes and mechanisms affecting the performance of concrete is essential. This knowledge need to be incorporated into models for understanding the phenomena and hence for predicting the actual service life of concrete structures in aggressive environments. Several modeling studies have been carried out to predict the performance cementitious materials (Elakneswaran, *et al.*, 2010, Ishida, *et al.*, 2009 Hosokawa, *et al.*, 2011, Maekawa, *et al.*, 2009, Marchand, *et al.*, 2002). These models are improving by understanding the degradation phenomena by considering different aspects of mechanisms and coupling between them. Reactive-transport models are essential to evaluate the durability of cementitious materials because degradation of the materials has to be predicted precisely with time at each point of the materials. Over the year, many reports have been published on multi-species transport and coupling the transport with geochemical models (Elakneswaran, *et al.*, 2010, Hosokawa, *et al.*, 2011, Marchand, *et al.*, 2002). A numerical model, called STADIUM, developed by Marchand *et al* considered the coupled transport of ions and chemical equilibrium of solid phases (Marchand, *et al.*, 2002 ). Further, Hosokawa *et al* establish multi-species transport model coupled with thermodynamic equilibrium model (Hosokawa, *et al.*,

2011). Elakneswaran *et al* used geochemical transport code PHREEQC to perform multi-species transport and geochemical calculation (Elakneswaran, *et al.*, 2010). However, in these investigations, the developed models unable to predict the hydration and microstructure properties of cementitious materials with time and they need a large amount of experimental data as the input to the model. Evaluating the existing models for predicting the long-term performance of cementitious materials, makes it clear that further investigation is necessary on this topic.

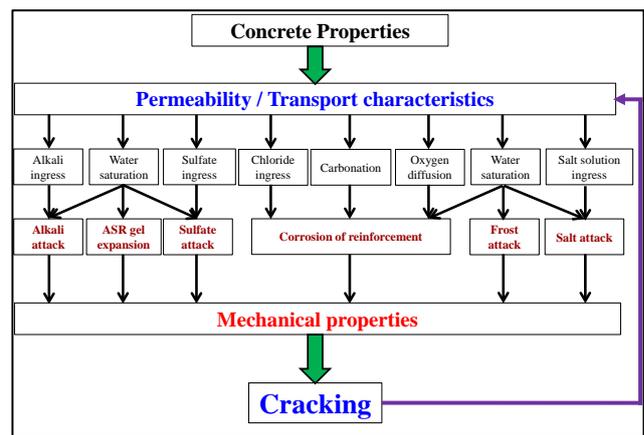


Figure 1 The deterioration of concrete structures (Ferreira, 2004 )

### 1.1 Objectives

The main objective of this study is development of a model, which can precisely predict the long-term performance of cementitious materials in various environments. Durability concrete code DuCOM (Maekawa *et al.*, 2009) and geochemical transport code PHREEQC (Parkhurst, *et al.*, 1999) will be used to achieve this purpose. The developed model will consider not only the hydration of cement particles and the transport of multi-species into cementitious materials but also the chemical interaction of multi-species with cement phases simultaneously. Further, the model is capable of predicting spatial and time

variation of physical and chemical properties of the materials as well as to determine chemical degradation by ingress of detrimental ions. The basic theory behind the ionic transport and geochemical reactions, framework of the model, and coupling procedures of DuCOM and PHREEQC will be presented briefly in this paper. In order to evaluate the model, some of simulation results will be compared with experimental data available in the literature. The developed model will also be used to understand the chemical degradation due to sulfate attack in concrete.

## 2. DESCRIPTION OF THE MODEL

DuCOM is developed by Concrete Laboratory at the University of Tokyo, Japan (Maekawa *et al.*, 2009). 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 (Parkhurst, *et al.*, 1999). In this study, both DuCOM and PHREEQC were used to develop a new model. In this section, set of equations that need to be solved for finite element analysis is briefly described.

### 2.1 Governing mass balance equation

The transport of ions into concrete is due to advection and diffusion. The ions are free to move in the liquid medium or bound to solid phase. The governing equation in this phenomenon can be expressed as follows (Maekawa *et al.*, 2009, Ishida, *et al.*, 2009):

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

Where,  $\Phi$  is the porosity,  $S$  is the degree of saturation of porous media,  $C_{ion}$  is the concentration of an ion in pore solution,  $J_{ion}$  is the total flux of an ion, and  $Q_{ion}$  is the sink term.

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,  $\Phi$ , is the sum of gel and capillary porosities.

### 2.2 Transport equation

The ions in a solution have an effect from the co-existing ions. Thus, diffusion coefficients of cations, anions, and neutral species in a solution have different values. However, most of the models to calculate the ionic transport into concrete assume the same diffusion coefficient for all the species. Diffusive flux of ions considering concentration and electrical potential gradients, and chemical activity effects in porous media can be expressed as follows (Nernst-Planck equation) (Appelo, *et al.*, 2007):

$$J_{ion} = -\phi \cdot S \cdot \left( \frac{D_{ion}}{\Omega} \cdot \delta \right) \cdot \left[ \frac{\partial \ln(\gamma_{ion})}{\partial \ln(C_{ion})} + 1 \right] \frac{\partial C_{ion}}{\partial x} - \phi \cdot S \cdot \frac{F}{RT} Z_{ion} C_{ion} \left( \frac{D_{ion}}{\Omega} \cdot \delta \right) \frac{\partial \psi}{\partial x} + \phi \cdot S \cdot u \cdot C_{ion} \quad (2)$$

Where,  $D_{ion}$  is the diffusion coefficient of an ion ( $\text{m}^2/\text{s}$ ),  $\delta$  is the constrictivity,  $\Omega$  is the tortuosity,  $R$  is the ideal gas constant ( $\text{J}/\text{mol}\cdot\text{K}$ ),  $T$  is the absolute temperature ( $\text{K}$ ),  $F$  is the Faraday's constant ( $\text{C}/\text{mol}$ ),  $Z_{ion}$  is the ion valance,  $u$  is the velocity of an ion

transported by bulk movement of solution (m/s). Diffusion coefficient of an ion,  $D_{ion}$ , in free water is expressed by (Maekawa *et al.*, 2009, Ishida, *et al.*, 2009):

$$D_{ion} = R \cdot T \cdot \frac{\lambda_{ion}}{z_{ion}^2 \cdot F^2} \quad (3)$$

$$\lambda_{ion} = \lambda_{ion_{25}} \cdot \exp\left\{-1700\left(\frac{1}{T} - \frac{1}{298}\right)\right\} \quad (4)$$

Where,  $\lambda_{ion}$  is the conductivity of an ion ( $\text{Sm}^2/\text{mol}$ ) and  $\lambda_{ion_{25}}$  is the conductivity of an ion at 25 °C ( $\text{Sm}^2/\text{mol}$ )

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,  $\gamma$ , are calculated according to the extended Debye-Huckel (Appelo *et al.*, 2009):

$$\log \gamma_{ion} = -\frac{Az_{ion}^2 \sqrt{I}}{1 + Ba_{ion} \sqrt{I}} + b_{ion} I \quad (5)$$

Where  $A$  and  $B$  are temperature dependent coefficients, and  $a_{ion}$  and  $b_{ion}$  are ion-specific fit parameters. Ionic strength,  $I$ , can be described as:

$$I = \frac{1}{2} \sum_{i=1}^n c_i z_i^2 \quad (6)$$

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;

$$\sum_i J_i \cdot Z_i = 0 \quad (7)$$

The zero-charge flux permits to determine the electrical potential gradient as a function of other term in Eq. (2).

### 2.3 Chemical equilibrium model

This model is used to define the amount the pure phases that can react reversibly with an aqueous phase to achieve equilibrium. The pure phases will dissolve or precipitate to achieve the equilibrium or will dissolve completely. The equilibrium reactions are expressed by mass-action equations (Appelo, *et al.*, 2009). In general, pure-phase equilibrium can be written as:

$$K_p = \prod_i (\gamma_i c_i)^{n_{i,p}} \quad (8)$$

where  $K_p$  is the thermodynamic equilibrium constant for the phase  $p$ ,  $\gamma_i$  is the activity coefficients of ion  $i$ ,  $c_i$  is the concentration of ion  $i$ , and  $n_{i,p}$  is the stoichiometric coefficient of ion  $i$  in the phase  $p$ . The sink term in Eq. (2) 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:

$$\frac{\partial q_{ion}}{\partial t} = \frac{\partial q_{ion}}{\partial C_{ion}} * \frac{\partial C_{ion}}{\partial t} \quad (9)$$

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

$$Q_{ion} = \frac{\partial q_{ion}}{\partial t} = K * \frac{\partial C_{ion}}{\partial t} \quad (10)$$

## 2.4 Coupling procedure

The new IPhreeqc module is designed for coupling of PHREEQC with other programming languages (Charlton *et al.*, 2011). 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. IPhreeqc provides direct access to geochemical processes in PHREEQC through a library.

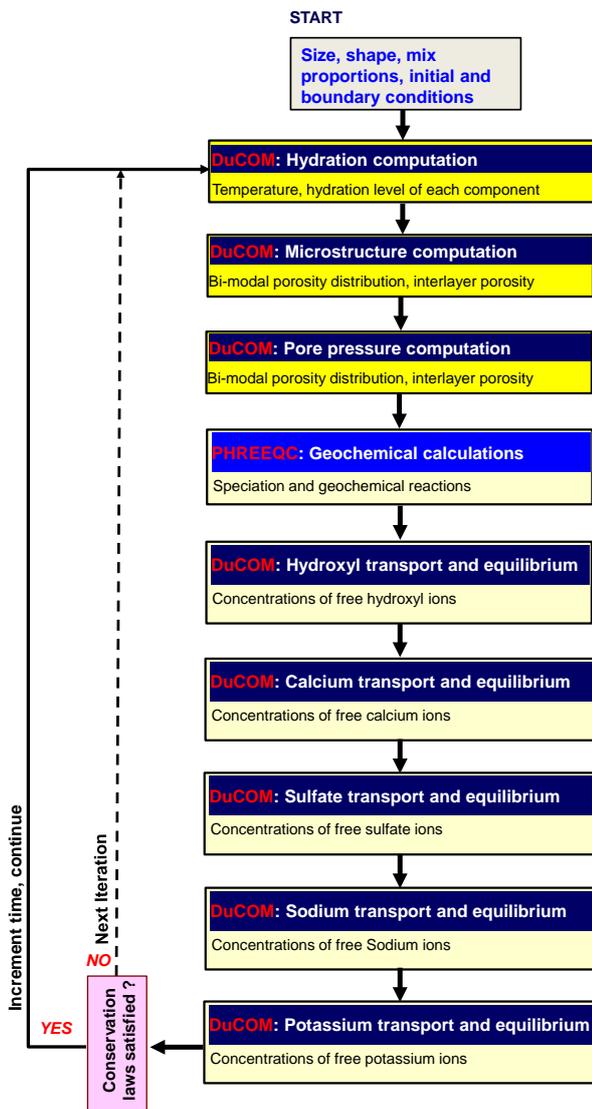


Figure 2 Framework of coupled DuCOM and PHREEQC

In this study, DuCOM is coupled with IPhreeqc (hereafter call PHREEQC) using FORTRAN programming language to solve multi-species reactive transport problems in cementitious materials. The coupled model retains all the capabilities of these models, and it can be used not only for multi-species reactive transport but also other purposes. A basic framework of DuCOM system coupled with PHREEQC is shown in Figure 2. PHREEQC has incorporated into DuCOM as a model to perform speciation and geochemical calculation. 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. Figure 3 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.

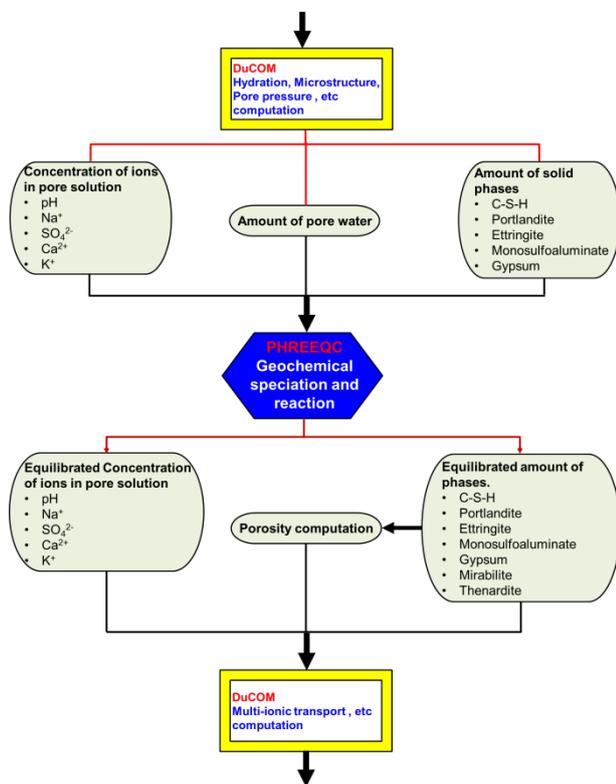


Figure 3 Conceptual coupling of DuCOM with PHREEQC at each time step

### 3. SIMULATION RESULTS AND DISCUSSIONS

#### 3.1 Verification of the proposed model

Various simulations have been carried out with the proposed model. It provides many details such as the hydration of cement particles, microstructure formation, pore solution concentration, ionic profiles during the transport, mineralogical distributions, etc. as a function of time and depth. The simulation results have been compared with experimental data available in the literatures in order to predict the long-term performance of cementitious materials.

#### 3.1.1 Composition of cement hydrates and porosity

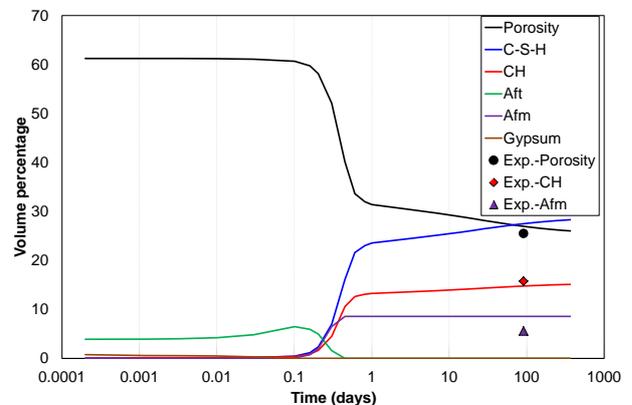


Figure 4 Hydrates and porosity changes as function of hydration time for OPC with W/C of 0.5 (Lines represent the simulate results while marks show the measured data (Elakneswaran, 2009) after 91 days of hydration)

The simulation results for hydrating OPC with W/C of 0.5 is shown in Figure 4. Beside some unhydrated clinker, C-S-H, Ettringite (Aft), and monosulfoaluminate (Afm) are the main phases in the hydrated OPC. It can further be seen that the formation of monosulfoaluminate correlates with the disappearance of ettringite. The simulated hydrated

products are compared with experimental observations. The XRD Rietveld analysis in the hydrated OPC samples which cured until 91 days showed the same kind of phases as simulated one (Elakneswaran, 2009). The comparison of experimentally determined portlandite and monosulfoaluminate with the simulated results are shown in Figure 4. The simulated results agree well with experimental observation. However, quantitative comparison on C-S-H cannot be performed because it is an amorphous phase and hence cannot be determined with XRD Rietveld analysis. In order to determine the total (gel and capillary) porosity in hydrated OPC, Mercury Intrusion Porosimetry (MIP) and nitrogen gas adsorption were used (Elakneswaran, 2009). Very good agreement is obtained between experimentally determined and simulated porosity after hydration of 91 days for OPC sample (Figure 4).

### 3.1.2 Concentration of ions in the pore solution

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. (Brouwers *et al.*, 2003)). 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<sup>+</sup> and K<sup>+</sup> in pore solution can be determined during hydration. The calculation method described in Ref. (Brouwers *et al.*, 2003) and briefly explained in here. The total concentration of Na<sup>+</sup> and K<sup>+</sup> can be computed from mass fraction and molecular weight. The calculation for Na<sup>+</sup> as follows:

$$Na_T = \frac{2f_{Na_2O}}{M_{Na_2O}} \quad (11)$$

Where  $Na_T$  is the total Na content (mol/g),  $f_{Na_2O}$  is the Na<sub>2</sub>O mass fraction (g/g), and  $M_{Na_2O}$  is the molecular weight of Na<sub>2</sub>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<sup>+</sup> is calculated as follows:

$$Na_{released}^+ = f_{Na,sulfate} * Na_T + (1 - f_{Na,sulfate}) * \alpha * Na_T \quad (12)$$

Where  $Na_{released}^+$  is the total release of Na<sup>+</sup> (mol/g),  $f_{Na,sulfate}$  is the fraction of Na<sup>+</sup> in sulfate salt, and  $\alpha$  is the degree of hydration

Table 1 Thermodynamic properties of major cement phases at 25 °C used in calculations (Blanc, *et al.*, 2010(a), 2010(b))

| Phases             | Reaction  | log <sub>10</sub> K <sub>T</sub> | Δ <sub>r</sub> H <sup>0</sup> (kJ/mol) |
|--------------------|---|----------------------------------|--|
| C-S-H (C/S = 1.6)  | Ca <sub>1.6</sub> SiO <sub>3.6</sub> :2.58H <sub>2</sub> O + 3.2H <sup>+</sup> → 1.6Ca <sup>2+</sup> + 2.18H <sub>2</sub> O + H <sub>4</sub> SiO <sub>4</sub>   | 28.00                            | -133.31                                |
| Portlandite        | Ca(OH) <sub>2</sub> + 2H <sup>+</sup> → Ca <sup>2+</sup> + 2H <sub>2</sub> O  | 22.81                            | -130.11                                |
| Ettringite         | Ca <sub>6</sub> Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (OH) <sub>12</sub> :26H <sub>2</sub> O + 12H <sup>+</sup> → 2Al <sup>3+</sup> + 6Ca <sup>2+</sup> + 38H <sub>2</sub> O + 3SO <sub>4</sub> <sup>2-</sup> | 57.73                            | -389.36                                |
| Monosulfoaluminate | Ca <sub>4</sub> Al <sub>2</sub> (SO <sub>4</sub> )(OH) <sub>12</sub> :6H <sub>2</sub> O + 12H <sup>+</sup> → 2Al <sup>3+</sup> + 4Ca <sup>2+</sup> + SO <sub>4</sub> <sup>2-</sup> + 18H <sub>2</sub> O                 | 73.68                            | -553.08                                |
| Gypsum             | CaSO <sub>4</sub> :2H <sub>2</sub> O → Ca <sup>2+</sup> + 2H <sub>2</sub> O + SO <sub>4</sub> <sup>2-</sup>   | -4.607                           | -1.054                                 |
| Mirabilite         | Na <sub>2</sub> SO <sub>4</sub> :10H <sub>2</sub> O → 2Na <sup>+</sup> + 10H <sub>2</sub> O + SO <sub>4</sub> <sup>2-</sup>   | -1.230                           | 79.471                                 |
| Thenardite         | Na <sub>2</sub> SO <sub>4</sub> → 2Na <sup>+</sup> + SO <sub>4</sub> <sup>2-</sup>  | -0.356                           | -2.200                                 |

According to Ref. (Brouwers *et al.*, 2003), 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:

$$Na_{released}^{+} m_{OPC} = [Na^{+}] V_w + Rd_{Na} [Na^{+}] m_{C-S-H} \quad (13)$$

Where  $m_{OPC}$  is the mass of ordinary Portland cement (g),  $V_w$  is the volume of pore water ( $cm^3$ ),  $[Na^{+}]$  is the  $Na^{+}$  concentration in pore solution ( $mol/cm^3$ ),  $Rd_{Na}$  is the distribution ratio of  $Na^{+}$  ( $cm^3/g$ ), and  $m_{C-S-H}$  is the mass of formed C-S-H (g)

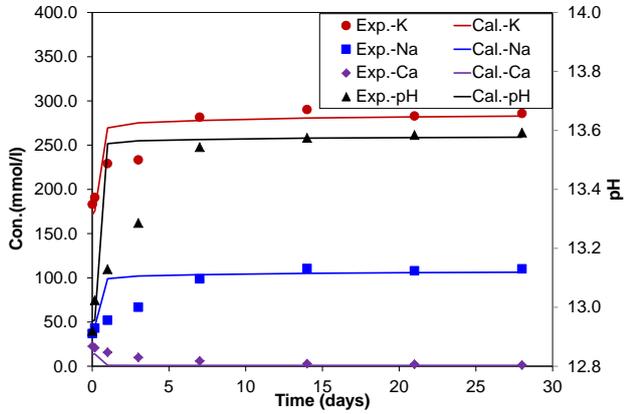


Figure 5 Comparison between predicted and measured (Larbi, *et al.*,1990) pore solution concentration of OPC paste with W/C of 0.56 during the first 28 days

The fraction of alkalis in sulfate salt and the distribution ratio of alkalis are constant, and the values are given in Ref. (Brouwers *et al.*, 2003). The above model is incorporated into the coupled model described in section 2 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. (11-13)). 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) (Blanc, *et al.*, 2010(a), 2010(b)). The thermodynamic properties of minerals considered in this simulation are tabulated in Table 1. The computed element concentrations are compared with experimental data available in literature (Larbi, *et al.*,1990). The coupled model simulations were performed for Ordinary Portland Cement (OPC) paste using the same cement composition and other experimental conditions adopted in Ref. (Larbi, *et al.*,1990). Figure 5 shows the predicted concentration of  $Na^{+}$ ,  $K^{+}$ ,  $Ca^{2+}$  and pH in pore solution that compared with experimental data (Larbi, *et al.*,1990) for a water to cement ratio (W/C) of 0.56. Very good agreement is 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.

Table 2 Input parameters for simulation

| Material   | OPC concrete         |
|--|----------------------|
| Mineralogical analyses of OPC (%) By Bougue method |                      |
| -Alite   | 52.06                |
| -Belite  | 22.45                |
| -Aluminate   | 9.67                 |
| -Ferrite   | 8.82                 |
| -Gypsum  | 3.87                 |
| Composition of alkalis (%)                         |                      |
| - $Na_2O$  | 0.26                 |
| - $K_2O$   | 0.38                 |
| 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 $Na_2SO_4$ |
| Temperature  | 20 °C                |

### 3.2 Application example: Sulfate ingress in OPC concrete

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 2. 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<sub>2</sub> 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<sup>+</sup>, K<sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, Ca<sup>2+</sup>, and OH<sup>-</sup> were considered. Porosity and pore structure modification due to precipitation or 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 given in Figure 6 and Figure 7. The alteration of C-S-H and portlandite is shown in Figure 6 while the distribution of ettringite and monosulfoaluminate is given in Figure 7. The coupled model results are compared with hydration and transport models of DuCOM. It can clearly be seen that the ingress of sulfate ions into concrete does not change the distribution of cement hydrates in the conventional models of DuCOM. In contrast, the coupled model results show the significant changes of cement hydrates as the result of sulfate ingress. As indicated in Figure 6, 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 Figure 6 and Figure 7, 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.

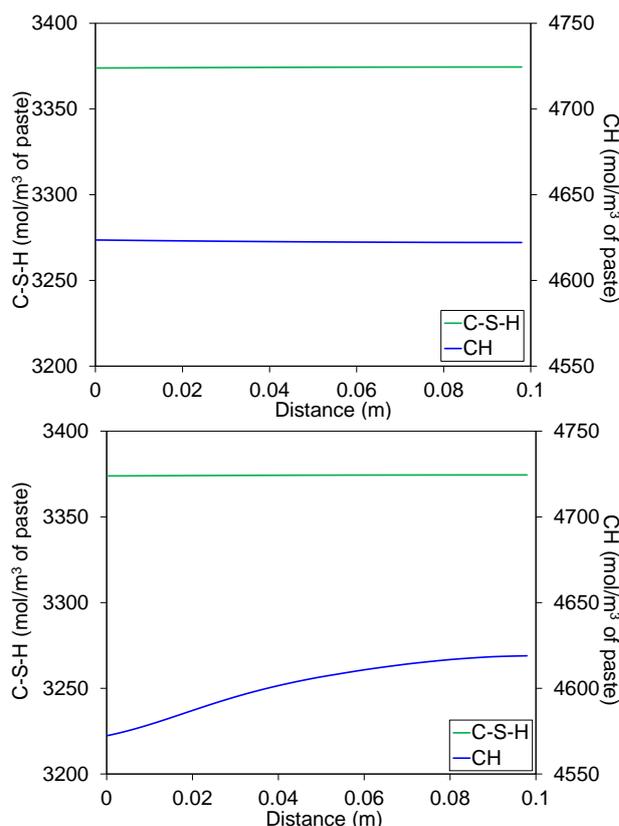


Figure 6 Representation of the distribution of C-S-H and portlandite after 10 years of sulfate ingress (Top: DuCOM only; Bottom: Coupled model)

### 3.3 Influence of various parameters on simulation results

The simulation results might be affected by various parameters or models. The capability of the proposed model is further investigated by identifying the parameters which affecting the sulfate ingress into OPC concrete. 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 2 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. Figure 8 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. It can be inferred that more porous mixtures are highly affected by the external sulfate ions ingress.

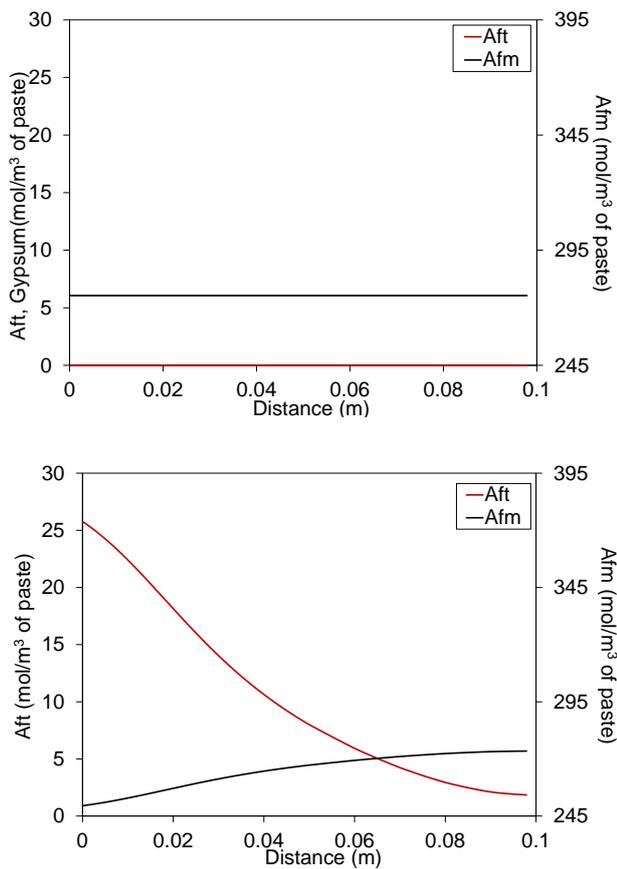


Figure 7 Representation of the distribution of ettringite and monosulfoaluminate after 10 years of sulfate ingress (Top: DuCOM only; Bottom: Coupled model)

The relevance of electrical potential gradient and activity effect on the mineralogical profiles of OPC

concrete due to sulfate ingress were evaluated. The input parameters to the simulation are the same as given in Table 2. The simulation results are shown in Figure 9 where lines represent “NO-MULTI” do not consider the effects of electrical potential gradient and activity. These effects influence formation of secondary ettringite and the dissolution of both portlandite and monosulfoaluminate (Figure 9). The inclusion of electrical potential gradient and activity of ions change the ionic profiles not only sulfate but also other ions in the pore solution. As a consequence, mineralogical distributions are affected. It can be emphasized that neglecting electrical potential gradients and activity effects in the diffusion process cannot predict the actual phenomena in cementitious materials and may lead to wrong decision on the performance assessment.

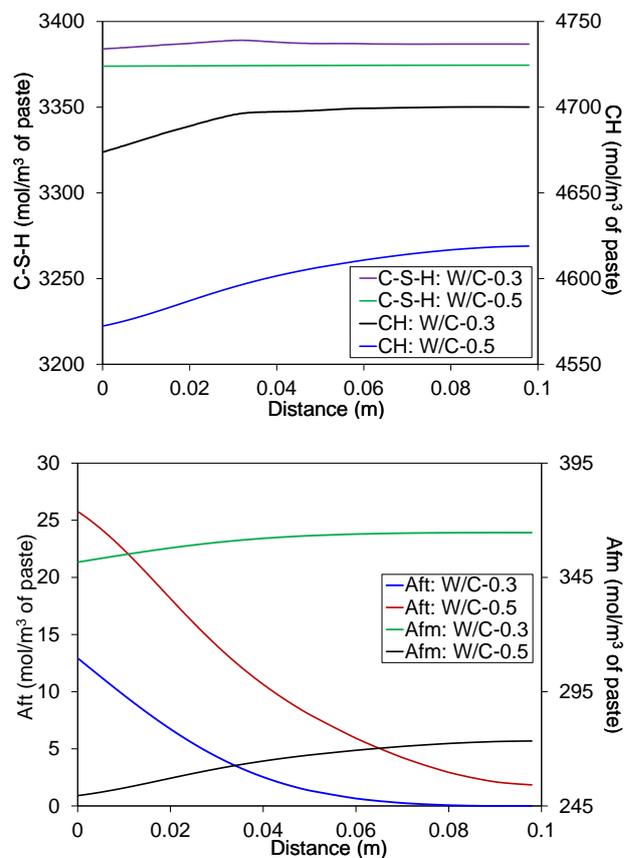


Figure 8 Influence of W/C on mineralogical distribution of OPC concrete after 10 years of sulfate ingress

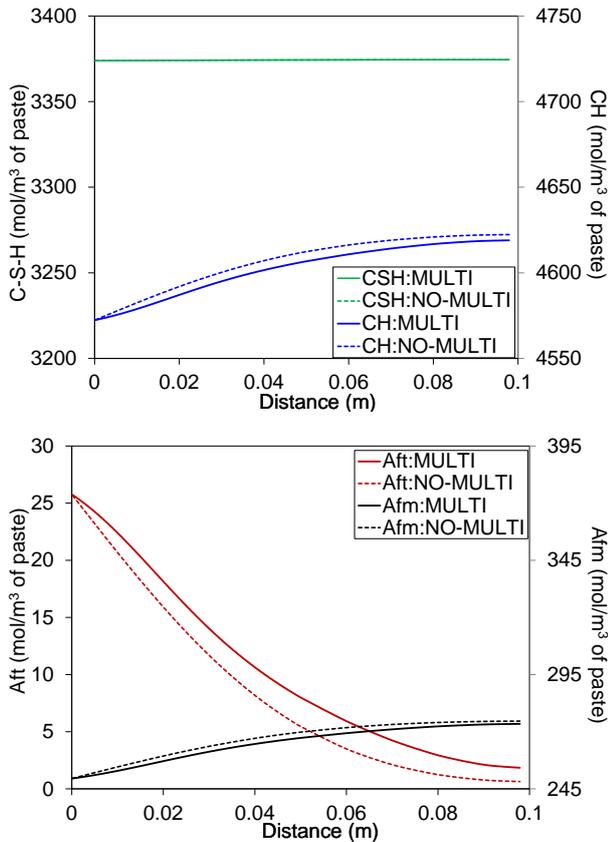


Figure 9 Effect of multi-species transport on mineralogical distribution of OPC concrete after 10 years of sulfate ingress

#### 4. CONCLUDING REMARKS

A robust and reliable model is necessary to predict the long-term performance of cementitious materials on various environments. In this study DuCOM has been coupled with PHREEQC for the development of such a computational platform. The developed model capable of addressing physiochemical and geochemical processes in cementitious materials such as hydration of cement particles, pore structure formation, multi-species transport, activity effect, ionic interaction with cement hydrates, etc. It can be used to predict the physical and chemical properties of cementitious materials as well as to determine the degradation of the materials due to ingress of detrimental ions. Some of simulation results have been compared with published experimental data.

The predicted cement hydrates, pore solution concentration, and porosity for mature cement paste agree well with experimental data. However, the detail verification for short and long term performances of cementitious materials in aggressive environments remains to be done. The capability of the coupled model was investigated through sulfate ingress in OPC concrete. In addition, some of the parameters which affecting the simulation results have been highlighted.

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