

## **Durability of cementitious materials under combined sulphate attack and leaching: Development and application of a coupled physicochemical and geochemical model**

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### **ABSTRACT**

In this study, a coupled physicochemical and geochemical model is developed for the prediction of long-term performance of cementitious materials under combined effects of sulphate attack and leaching. DuCOM (Durability CONcrete Model) and geochemical code PHREEQC were used for development of the numerical framework. The coupled model retains all the capabilities of these models, and it allows predicting the spatial and time variation of minerals compositions, pore water concentrations, and other hydration and pore structures properties simultaneously. The coupled model was applied to understand the underlying mechanisms on sulphate attack and leaching. Further, the influence of bicarbonate ions on the dissolution and formation of sulphate phases is examined. The main simulation results agree qualitatively and quantitatively well with published experimental data in terms of hydrated cement products, porosity, pore solution chemistry, sulphate bearing products. The detailed experimental works have been considered for further verification of the model.

**Keywords:** Sulphate attack; Leaching; Physicochemical; Geochemical; Model

### **1. INTRODUCTION**

The problem posed by ingress of detrimental ions and consequent chemical reactions represents the greatest threat to durability of cementitious materials. Degradation of concrete in contact with sulphate bearing soils or groundwater is called "sulphate attack". Sulphate interaction with cement hydration products form expansive products such as ettringite and gypsum and resulting in spalling, swelling, cracking and eventual failure of the structure. Further, the formation of secondary sulphate phases can reorganize the internal microstructures of cement matrix in concrete. Simultaneous to sulphate ions ingress, leaching of ions mainly calcium and hydroxide from pore solution of cement matrix to external environments causes decalcification of cementitious material and thus increasing

porosity and permeability of the materials. Thus, it is necessary to evaluate the long-term performance of cementitious materials under these conditions. Over the last decade, a number of investigations have been reported on sulphate ingress into cementitious materials (Kunther 2013, Marchand 2002, Samson 2007, Sarkar 2010). Further, several numerical models have been developed to investigate the degradation processes of cementitious material under sulphate attack and leaching (Marchand 2002, Samson 2007, Sarkar 2010). Reactive-transport models are essential tool to evaluate the durability of cementitious materials in sulphate environments because degradation of the materials needs to be predicted precisely as a function of time and depth. However, different transport parameters and physicochemical properties of the cementitious materials have to be estimated in advance for the input of the model. Thus it is important to incorporate hydration cement particles, micro pore structure development, multi-ionic transport, degradation mechanism due to ingress of detrimental ions etc. into a single framework to accurately simulate the degradation of cementitious materials under combined sulphate attack and leaching. The main objective of this study is development of such numerical framework. A multi-scale simulator, which was developed in Concrete Laboratory at the University of Tokyo Japan, can predict the state of the concrete from its birth to entire life (Maekawa 2009). The simulator is able to predict the performance of concrete structures in aggressive environments. For very accurate prediction however, additional mechanisms and processes affecting the performance should also be incorporated into the multi-scale simulator. Durability concrete code DuCOM (Maekawa 2009) and geochemical transport code PHREEQC (Parkhurst 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 determining the chemical degradation due to sulphate transport and leaching. A brief description of the model and coupling DuCOM and PHREEQC are given. Validation of the model for predicting cement hydrates, porosity, and pore solution concentration are described. Finally, the model is applied to evaluate the degradation of concrete due to combined sulphate attack and leaching.

## 2. THEORY

DuCOM is developed by Concrete Laboratory at the University of Tokyo, Japan (Maekawa 2009). 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 1999). In this study, both DuCOM and PHREEQC were coupled to develop physicochemical and geochemical model. The basic theory behind ionic transport and geochemical reactions will be presented briefly in this paper. 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 2009, Ishida 2009):

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

where  $\Phi$  = porosity;  $S$  = degree of saturation of porous media;  $C_{ion}$  = concentration of an ion in pore solution;  $J_{ion}$  = total flux of an ion; and  $Q_{ion}$  = 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.

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 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  $D_{ion}$  = diffusion coefficient of an ion ( $m^2/s$ );  $\delta$  = constrictivity;  $\Omega$  = tortuosity;  $R$  = ideal gas constant ( $J/mol.K$ );  $T$  = absolute temperature ( $K$ );  $F$  = Faraday's constant ( $C/mol$ );  $Z_{ion}$  = ion valance;  $\gamma$  = activity coefficient; and  $u$  = velocity of an ion transported by bulk movement of solution ( $m/s$ ). The zero-charge flux,  $\sum_i J_i \cdot Z_i = 0$ , permits to determine the electrical potential gradient,  $\left( \frac{\partial \psi}{\partial x} \right)$ , as a function of other term in Eq. (2).

The sink term in Eq. (1) is considered as the rate of dissolved or precipitated ions due to geochemical reactions. The composition of equilibrating solution provides the information about the stability of the products. Comparing ion activity product (IAP) with solubility products gives the degree of over or under saturation of solids with respect the equilibrated solution. When 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 ions in IAP and in equilibrium. The rate of precipitated or dissolved ions can be written as follows:

$$\frac{\partial q_{ion}}{\partial t} = \frac{\partial q_{ion}}{\partial C_{ion}} * \frac{\partial C_{ion}}{\partial t} \quad (3)$$

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

$$Q_{ion} = \frac{\partial q_{ion}}{\partial t} = K * \frac{\partial C_{ion}}{\partial t} \quad (4)$$

### 3. THE COMPUTATIONAL PLATFORM

The new IPhreeqc module is designed for coupling of PHREEQC with other programming languages (Charlton 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. In this study, DuCOM is coupled with IPhreeqc (hereafter call PHREEQC) using FORTRAN programming language for the development of the computational platform. The coupled model retains all the capabilities of both DuCOM and PHREEQC, and it can be used not only for multi-species reactive transport but also other purposes. A basic framework of DuCOM-PHREEQC system is shown in Figure 1. DuCOM consists of several sub-models, which work together and are interlinked. PHREEQC has incorporated into DuCOM as a

model to perform speciation and geochemical calculation after hydration and microstructure computation as well as in each ionic model. It is known that PHREEQC perform variety of calculation, but in the coupled model DuCOM performs hydration, pore structure, multi-ionic transport calculation whereas PHREEQC performs only speciation and geochemical calculations. Therefore, each sub-model in the framework satisfies the governing equation (Eq. (1)) for FEM calculation through continuous iterations. Each gauss point in the finite element of DuCOM is represented by a single batch reactor for PHREEQC that contains minerals and solution elements, and PHREEQC performs speciation and geochemical calculations. 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. At the beginning of each time step, hydration and microstructure properties are computed in DuCOM and computed cement hydrates and porosity together with ionic concentrations are passed to PHREEQC. The input of ionic concentration is the preceding step of equilibrated concentration of ions from the last model (“K equilibrium and transport model” in Figure 1). In coupled model, PHREEQC has included in each ionic model and thus it uses the free concentration of ion as the input in the respective ionic model. Figure 2 shows the conceptual approach for data exchange between DuCOM and PHREEQC at each time step. The figure illustrates that the ions in pore solution (Such as  $[Na^+]$ ,  $[K^+]$ ,  $[Ca^{2+}]$ , etc.) are equilibrium cement hydrates (such as [C-S-H], [CH], [Aft], [Afm], etc.) before “SO<sub>4</sub> equilibrium and transport model”. The same values of concentration of ions and cement hydrates are given to PHREEQC in “SO<sub>4</sub> equilibrium and transport model” as input parameters. However, free concentration of sulphate ( $C_{SO_4^{2-}}$ ) in the governing equation (Eq. (1)) is the degree of freedom to solve FEM. Therefore, the equilibrated sulphate concentration ( $[SO_4^{2-}]$ ) before “SO<sub>4</sub> equilibrium and transport model” is given as sink term ( $Q_{SO_4^{2-}} = \Phi * S * \{ [C_{SO_4^{2-}}] - [SO_4^{2-}] \}$ ) to the “SO<sub>4</sub> equilibrium and transport model”. The degree of freedom ( $C_{SO_4^{2-}}$ ) is modified in FEM calculation using the sink term to satisfy the governing equation (Eq. (1)) for sulphate ion. Once the governing equation is satisfied, the output values equilibrated concentration of pore solution ( $[Na^+]$ ,  $[K^+]$ ,  $[Ca^{2+}]$ , etc.) and cement hydrates ( $[C-S-H]$ ,  $[CH]$ ,  $[Aft]$ ,  $[Afm]$ ) of “SO<sub>4</sub> equilibrium and transport model” are given to next model (“OH equilibrium and transport model”) as input parameters for PHREEQC in that model. These processes are continued until the last model (“K equilibrium and transport model” in Figure 1). The output of values of “K equilibrium and transport model” is given to “Hydration computation model” in the following step (see Figure 1). These steps of calculations are continued until total time. It can be seen that the output of PHREEQC in one model is passed to following model as the input of PHREEQC. However, free concentration of ion ( $C_{ion}$ ) are calculated in DuCOM according to the governing equation, and therefore PHREEQC uses the determined free concentration of ion for the calculation instead of output of PHREEQC in the previous model. This approach yields to perform PHREEQC calculation during iteration loop and required output values from PHREEQC is transferred to DuCOM via sink term in the governing equation. The amounts of dissolved and precipitated phases are passed to hydration and microstructure models, which update mineral composition and porosity and use them in the following time step. The main advantage of the current coupled system is the complete coupling between a full suite of geochemical reactions and multi-ionic transport. The coupled model does not need physical or chemical properties in advance as the input data to the model because those are calculating automatically in 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.

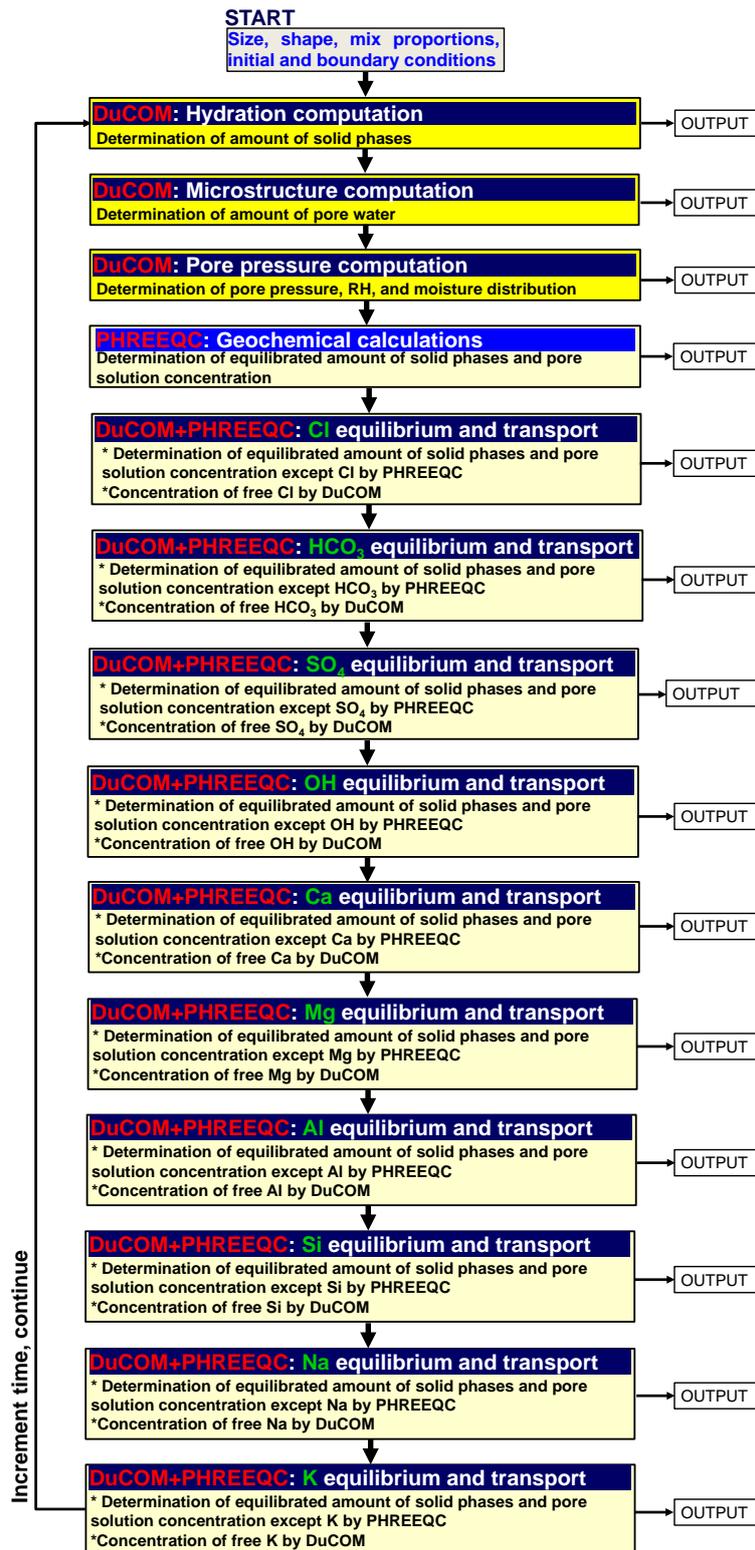


Figure 1 Framework of coupled DuCOM and PHREEQC. PHREEQC has incorporated into the system as a model after hydration and microstructure computation as well as in each ionic transport model.

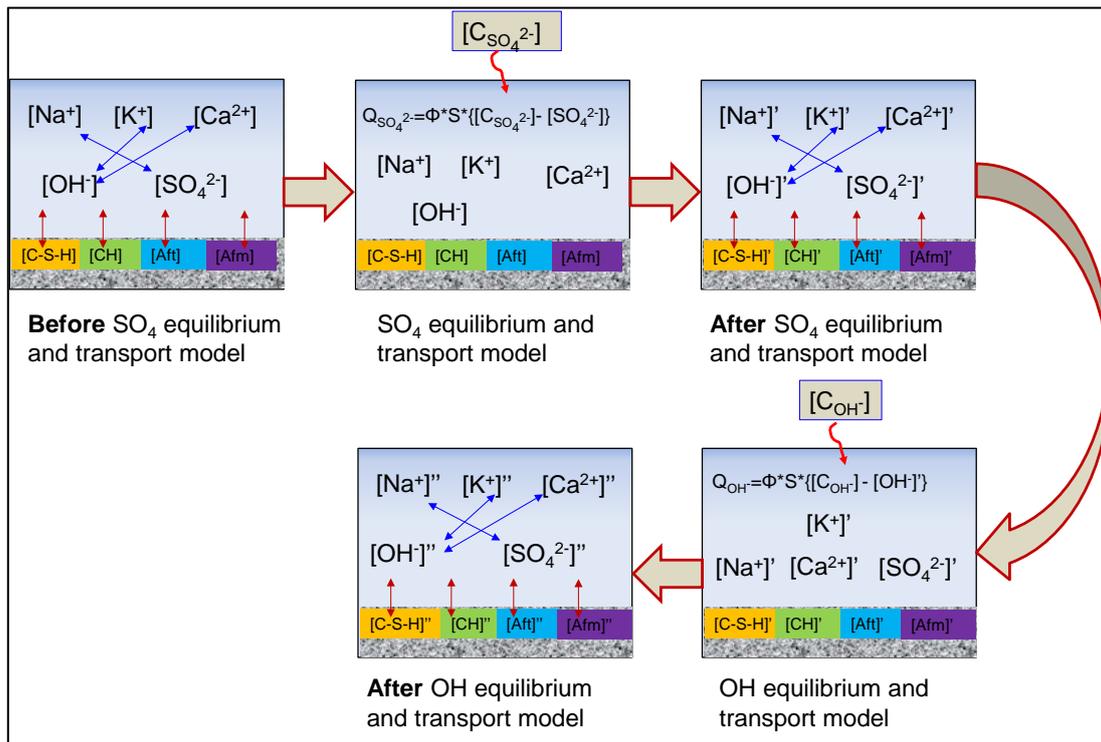


Figure 2 Conceptual coupling of DuCOM with PHREEQC at each time step

#### 4. SIMULATION RESULTS AND DISCUSSIONS

Simulation results provide many details such as 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 durability of cementitious materials under combined sulphate attack and leaching.

##### 4.1 Model validation

The coupled model was used to predict hydration of cement particles and the formation of porosity. The hydration and microstructure formation computations in the coupled model have been described in detail elsewhere (Maekawa 2009). The simulation result for hydrating Ordinary Portland Cement (OPC) with water to cement ratio (W/C) of 0.5 is shown in Figure 3. Beside some un-hydrated clinker, Calcium Silicate Hydrates (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 amount of C-S-H and portlandite continues to slowly increase with time. However, the formation of monosulfoaluminate does not change with time. 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 3. 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 3).

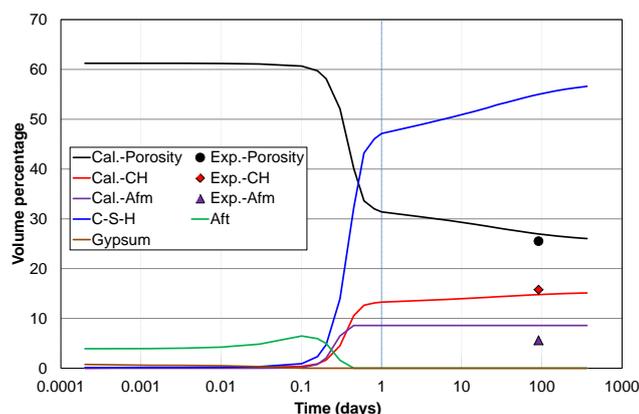


Figure 3 Hydrates and porosity changes as function of hydration time for OPC with W/C of 0.5 (Lines represent the simulated results while marks show the measured data (Elakneswaran, 2009) after 91 days of hydration)

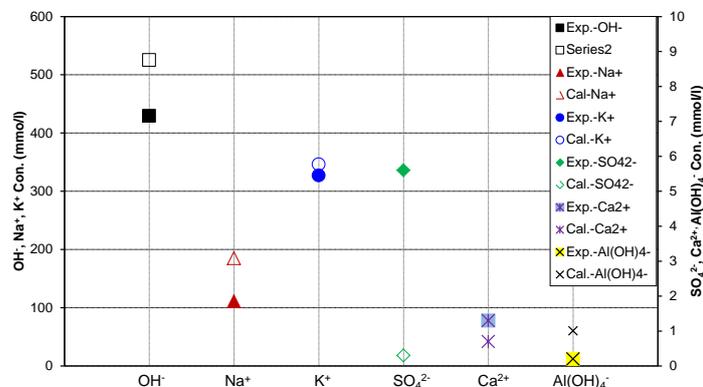


Figure 4 Comparison between predicted and measured (Samson 2007) pore solution concentration of OPC paste with W/C of 0.6

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 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 above model is incorporated into DuCOM-PHREEQC system (detail described in ref. (Elakneswaran 2012)). Figure 4 shows

the predicted ionic concentration in the pore solution of OPC paste with water to cement ratio 0.6 that compared with experimental data available in literature (Samson 2007). The simulated results show good agreement with measured pore solution data. Further, DuCOM-PHREEQC system was successfully applied to predict difference in the composition of pore solution for varying W/C ratios that agrees well with experimentally measured data (Elakneswaran 2012).

Table 1 Input parameters for simulation

Material	OPC concrete
Mineralogical analyses of OPC (%) By Bougue method	
-Alite	57.54
-Belite	14.88
-Aluminate	8.54
-Ferrite	9.42
-Gypsum	5.00
Composition of alkalis (%)	
-Na <sub>2</sub> O	0.20
-K <sub>2</sub> O	0.90
Characteristics of concrete mixtures	
-W/C	0.55
-Coarse aggregates (kg/m <sup>3</sup> )	1035.0
-Fine aggregates (kg/m <sup>3</sup> )	803.0
Specimen thickness	10 cm
Curing period and condition	28 days water curing
Exposure period	2 years
Temperature	20°C

#### 4.2 Application of the developed model: Long-term performance of cementitious materials under combined sulphate attack and leaching

The developed model was applied to investigate the alteration of cement hydrates during combined sulphate attack and leaching. The parameters needed to perform simulations are tabulated in Table 1. 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, other phases expected to form under these environment have also been taken into account. The used thermodynamic properties of various minerals and aqueous species were collected from the BRGM database (THERMOTDEM) (Blanc 2010). Figure 5 shows the simulation results for distribution of cement hydrates in terms of volume percentage. It can be seen that sulphate ions react with portlandite and monosulfoaluminate to form sulphate bearing products such as ettringite and gypsum close to the boundary surface, and

the dissolution and precipitation of solids are progressing with time. A similar phenomenon is usually observed for cementitious materials exposed to sulphate solution in laboratory or field conditions (Marchand 2002, Sarkar 2010). The stability of the phases is dependent on the conditions and concentration of exposure solution. In order to investigate the influence of bicarbonate ions on the deterioration, the simulations were performed with addition of bicarbonate ions in the exposure solution. The simulation results show that extensive dissolution of portlandite and gypsum does not form in the presence of bicarbonate ions (Figure 5 (C) & (D)). Further, the formation of calcite and monocarbonate were observed. These results are in agreement with recent experimental observation and thermodynamic modelling results (Kunther 2013). The dissolution and precipitation of cement hydrates will alter the microstructure of cement matrix. The dissolution and decalcification increase porosity, in turn, increase transport of ions that produces more phases which fills the pore space. Therefore, degradation of cement matrix depends on the relative rates of dissolution of cement hydrates and transport of ions.

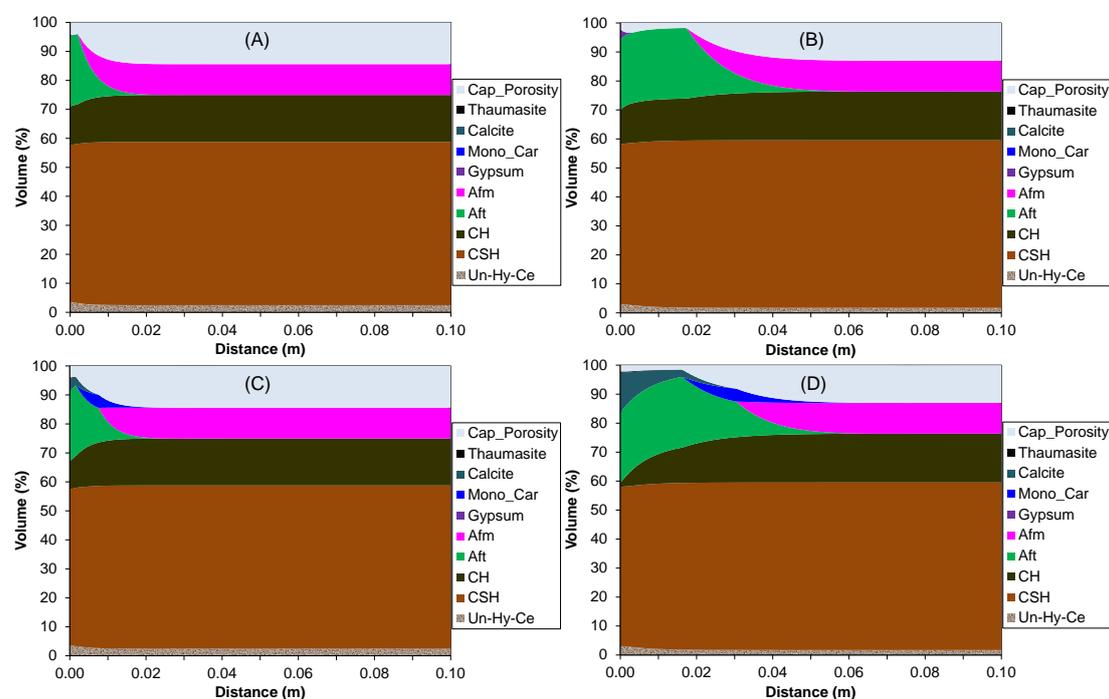


Figure 5 Representation of the distribution of phases for OPC concrete exposed to 0.2 mol/l  $\text{Na}_2\text{SO}_4$  (A: 91 days and B: 732 days exposure) and a mixture of 0.2 mol/l  $\text{Na}_2\text{SO}_4$  and 0.2 mol/l  $\text{NaHCO}_3$  (C: 91 days and D: 732 days exposure). Cap\_porosity: Capillary porosity; Mono\_Car: Monocarbonate; Afm: Monosulfoaluminate; Aft: Ettringite; CH: Portlandite; CSH: C-S-H with Ca/Si of 1.6; Un-Hy-Ce: Un-hydrated cement

## 5. CONCLUDING REMARKS

A coupled physicochemical and geochemical model for cementitious materials subjected to combined sulphate attack and leaching has been presented. A multi-scale model developed by Concrete Laboratory at the University of Tokyo (Maekawa 2009) is extended in this study by coupling an existing geochemical code PHREEQC to solve multi-species transport problems together with a comprehensive set of geochemical reactions. The resulting 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. In addition, it can capture the key aspects of combined sulphate attack and leaching in cementitious materials as observed in laboratory experiments or field conditions. The effect of bicarbonate ions on the dissolution and precipitation of phases in sulphate attack has been discussed. The results show that formation of calcite and monocarbonate resulting to extensive dissolution of portlandite and disappearance of gypsum. Finally, the simulation results of composition of cement hydrates assemblage, porosity, and pore solution concentration for mature ordinary Portland cement paste show good agreement with experimental results obtained in the literature. However, the coupled model needs to be validated under different conditions for better prediction, which will be performed in a future work.

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