

# ENHANCED PHYSICOCHEMICAL-GEOCHEMICAL MODEL COUPLED WITH MICRO-PORE STRUCTURE MODIFICATION TO EVALUATE CEMENTITIOUS MATERIALS IN AGGRESSIVE ENVIRONMENTS

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## ABSTRACT

A coupled physicochemical and geochemical model developed by the authors is extended in this paper by adding more sub-models for various ions to increase its capability and incorporating micro-pore structure modification resulting from mineralogical evolution. The model-based results for composition of cement hydrates, porosity, and ionic concentration in pore solution are quantitatively compared with experimental results obtained in the literature. The usefulness of the developed model in evaluating the degradation of cementitious components and leaching of ions are discussed.

Keywords: DuCOM, PHREEQC, transport, modeling, leaching

## 1. INTRODUCTION

Ensuring adequate durability of concrete structure in aggressive environments is a primary issue for engineers. The ability of cementitious materials to act as an effective barrier to the transport of aggressive substances is an important aspect on the durability. The performance of the materials in aggressive environments needs to be evaluated by both experiments and simulations. Several numerical models have been developed in the past to predict the performance of cementitious materials [1-3]. To our knowledge, the existing models need various transport parameters and physicochemical properties of cementitious materials in advance as the input of the model, and there is still a missing link among hydration of cement particles, micro-pore structure development, reactive transport, degradation of mechanism due to ingress of aggressive substances, etc. A coupled model was previously developed by authors incorporated the above features into a single framework [4]. The mineralogical composition of cement matrix changes with time because of precipitation and dissolution of several minerals. Therefore, the previous model is enhanced in this research work by considering more sub-models for various ions and incorporating the changes in micro-pore structure due to dissolution and precipitation of solids. This paper presents a brief description of the enhanced framework. Furthermore, a part of simulation results are verified with the experimental data available in the literature. The impact of micro-pore structure modification model in the framework is also discussed. Finally, simulations are performed to evaluate the performance of cementitious materials in various aggressive environments. Although it will be verified in the future, the simulation results show the influence of nature and composition of

aggressive solution on leaching of ions and mineralogical evolution of cement matrix.

## 2. OUTLINE OF THE MODEL

The physicochemical model DuCOM can simulate concrete behaviors during the hardening stage and deterioration during service-life [5]. 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 [6]. The authors coupled both DuCOM and PHREEQC for the development of a multi-scale physicochemical and geochemical model [4]. A detailed description of the developed model can be found in a previous work [4]. The governing equation which is to be solved by numerical analysis for transport of ions at pore scale can be expressed as follows [5]:

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

Where  $\Phi$  is the porosity (the sum of gel and capillary porosities),  $S$  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. In the governing equation, Nernst-Planck equation is used to express diffusive flux of ions considering electrical

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potential gradient and activity coefficient in porous media [7]. The sink term can be calculated as the rate of dissolved or precipitated ions due to geochemical reactions.

It has been reported that dissolution and/or precipitation of cement hydrates and minerals as a result of chemical reactions alter the pore structure of cementitious materials. The existing pore structure computation model in DuCOM is modified considering the dissolution and/or precipitation of cement phase assemblages due to thermodynamic equilibrium reactions. The micro-pore structure formation model is described detail elsewhere [5]; the main equations are described briefly here with modification. The porosity of cement paste matrix is divided into three main categories: interlayer, gel, and capillary porosity. Capillary porosity exists in the large inner space of powder particles, whereas gel and interlayer porosity exist in the interstitial spaces of gel products mainly C-S-H grains (Fig. 1). The volume of gel products,  $V_s$ , in a unit volume of paste at any arbitrary stage of hydration can be obtained as [5]:

$$V_s = \frac{\alpha W_p}{1 - \phi_{ch}} \left( \frac{1}{\rho_p} + \frac{\beta}{\rho_w} \right) \quad (2)$$

where  $\alpha$  is the degree of hydration,  $W_p$  is the weight of powder materials per unit paste volume,  $\rho_p$  is the density of powder materials,  $\beta$  is the amount of chemically combined water,  $\rho_w$  is the density of chemically combined water, and  $\phi_{ch}$  is the characteristic porosity of gel products. It is assumed that C-S-H, portlandite, ettringite (Aft), monosulfoaluminate (Afm), and gypsum are the main hydrated products exist during the hydration of cement particles. Thus, the volume of C-S-H grains can be obtained as:

$$V_{C-S-H} = V_s - V_{CH} - V_{Aft} - V_{Afm} - V_{Gyp} + \Delta V_{C-S-H} \quad (3)$$

where  $V_{C-S-H}$ ,  $V_{CH}$ ,  $V_{Aft}$ ,  $V_{Afm}$ ,  $V_{Gyp}$  are the volume of C-S-H, portlandite, ettringite, monosulfoaluminate, gypsum in a unit volume of paste respectively produced during the hydration of cement particles and  $\Delta V_{C-S-H}$  is the volumetric change of C-S-H as a result of thermodynamic equilibrium reactions. The volume of other hydrated products except C-S-H grains can be calculated from hydration of cement particles and molar volume of respective products. As previously mentioned, the interlayer porosity ( $\phi_l$ ) and gel porosity ( $\phi_g$ ) mainly exist in the C-S-H grains, and they can be calculated as follows:

$$\phi_l = \frac{t_w s_l \rho_g V_{C-S-H}}{2} \quad (4)$$

$$\phi_g = V_{C-S-H} \phi_{ch} - \phi_l \quad (5)$$

where  $t_w$  is the interlayer thickness,  $s_l$  is the specific area of the interlayer, and  $\rho_g$  is the dry density of C-S-H.

It is expressed as:

$$\rho_g = \frac{\rho_p \rho_w (1 + \beta)(1 - \phi_{ch})}{(\rho_w + \beta \rho_p)} \quad (6)$$

The dissolved/precipitated of hydrated products and secondarily formed minerals affect the capillary porosity. The volume of products,  $V_p$ , a unit volume of paste resulting from both hydration and thermodynamic equilibrium reactions are computed as follows:

$$V_p = \sum_m (V_m + \Delta V_m) \quad (7)$$

where  $V_m$  is the volume of hydrated product except C-S-H produced from the hydration a unit volume of paste and  $\Delta V_m$  is the volumetric change of the product due to thermodynamic equilibrium reactions a unit volume of paste. The capillary porosity resulting from hydration and chemical reactions can be calculated as follows:

$$\phi_c = 1 - V_{C-S-H} - V_p - (1 - \alpha) \left( \frac{W_p}{\rho_p} \right) \quad (8)$$

The modified porosity directly influence on the transport of multi-species by modifying the porosity values in the governing equation (Eq. (1)).

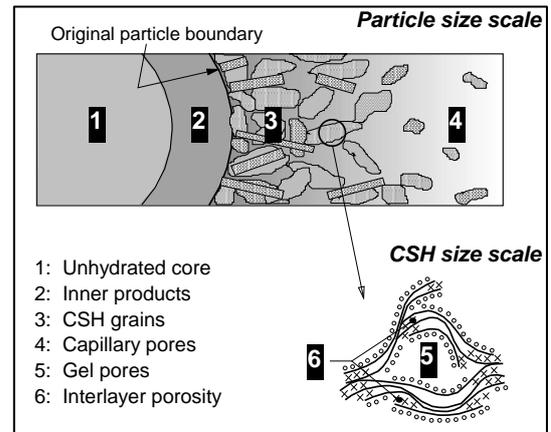


Fig. 1 Schematic representation of porosity component of mortar; adopted from ref. [5]

The framework of coupled physicochemical and geochemical model is shown in Fig. 2 (hereafter call DuCOM-PHREEQC). The DuCOM-PHREEQC model initially developed in the previous work [4], and it had PHREEQC as a model only after hydration and pore structure model to perform speciation and geochemical calculation. However, the current framework has PHREEQC incorporated into DuCOM as a model after hydration and microstructure computation as well as in each ionic model. Further, it is extended by incorporating more sub-models such as Cl,  $\text{HCO}_3$ , Mg, Al, and Si equilibrium and transport models and considering micro-pore structure changes resulting from the changes in solid composition. It is worth to mention that the porosity in the previous model [4] is a

constant and it did not change due to precipitation or dissolution of phases. However, the current model takes into account of the changes of porosity resulting from mineralogical evolution. Each sub-model in the framework satisfies the governing equation (Eq. (1)) for FEM calculation through continuous iterations. 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 model”. The input of ionic concentration is the preceding step of equilibrated concentration of ions from the last model (“K equilibrium and transport model” in Fig. 2). 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. Fig. 3 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 “ $SO_4$  equilibrium and transport model”. The same values of concentration of ions and cement hydrates are given to PHREEQC in “ $SO_4$  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 “ $SO_4$  equilibrium and transport model” is given as sink term ( $Q_{SO_4^{2-}} = \Phi * S * \{ [C_{SO_4^{2-}}] - [SO_4^{2-}] \}$ ) to the “ $SO_4$  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 “ $SO_4$  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 Fig. 2). The output of values of “K equilibrium and transport model” is given to “Hydration computation model” in the following step (see Fig. 2). 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 develop model can be used to predict

hydration of cement particles, multi-ionic transport, and geochemical reactions in cementitious materials simultaneously.

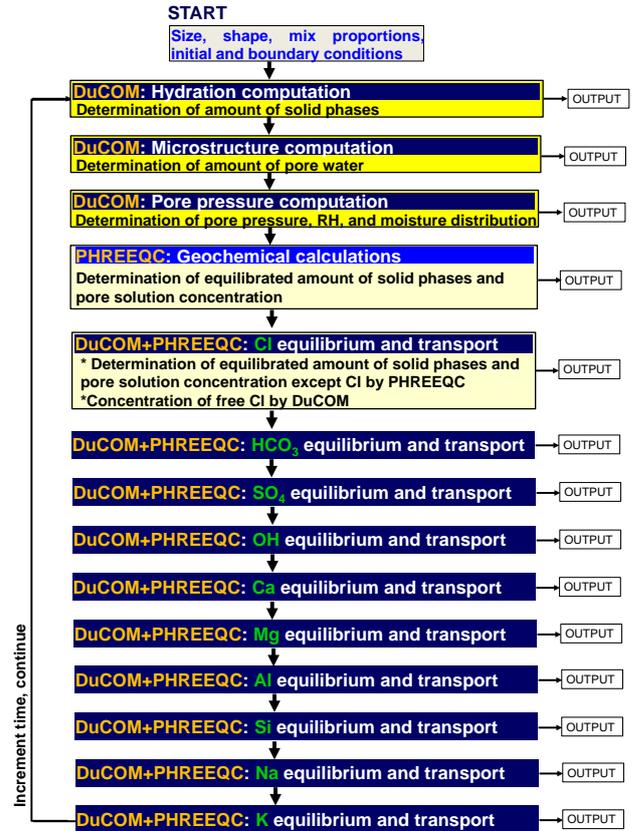


Fig. 2 Framework of coupled DuCOM and PHREEQC.

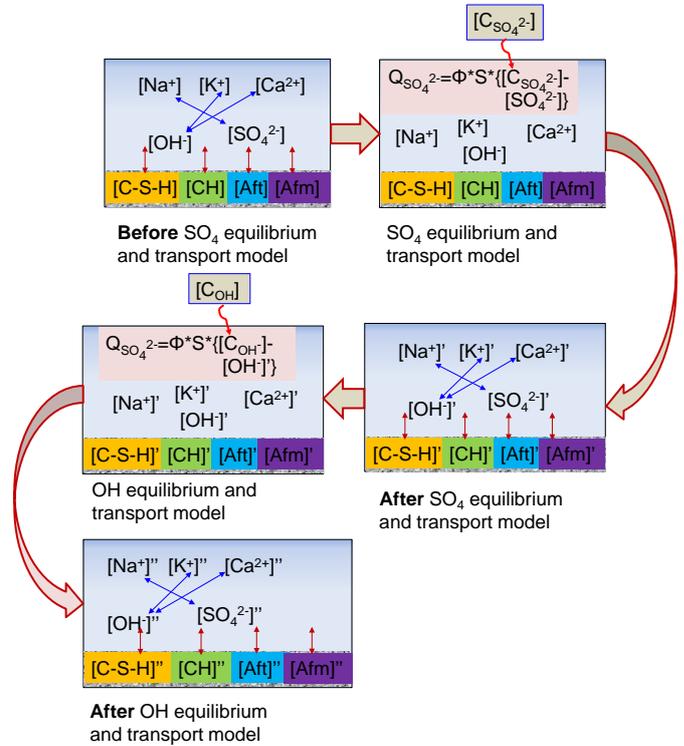


Fig. 3 Conceptual coupling of DuCOM with PHREEQC at each time step

### 3. SIMULATION RESULTS AND DISCUSSIONS

#### 3.1 Model validation

The simulation results from DuCOM-PHREEQC provide much information regarding the hydration of cement particles, micro-pore structure formation, concentration of ions in pore solution, multi-ionic profiles during transport, solid phase distribution, etc. as a function of time and depth. The validity of DuCOM-PHREEQC system is established by comparing simulation results with experimental data obtained from the literatures. The predictive capabilities of the model in terms of hydrated cement products and porosity are shown in Fig. 4 for hydrating OPC paste with W/C of 0.5. Beside some un-hydrated clinker, Calcium Silicate Hydrates (C-S-H), Ettringite (Aft), and monosulfoaluminate (Afm) are the main phases in the hydrated OPC. The simulated porosity (summation of gel and capillary) shows good agreement with measured total porosity by Mercury Intrusion Porosimetry (MIP) and nitrogen gas adsorption [3]. It can be inferred that the model accurately captures the hydration and micro-pore structure development of matured OPC paste. To provide further validation, DuCOM-PHREEQC system was tested against the composition of pore solution for varying W/C ratio. The predicted pore solution concentrations were consistent with experimental values for matured OPC paste and the results were reported in ref. [4].

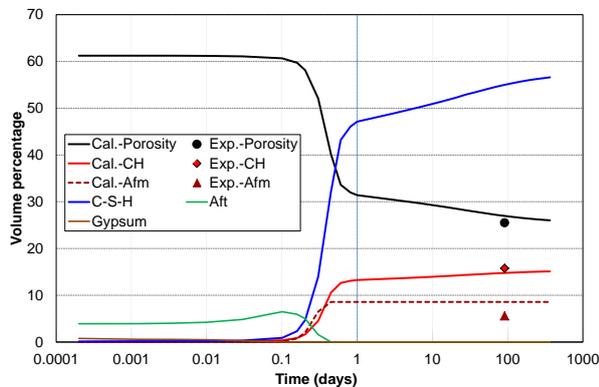


Fig. 4 Hydrates and porosity changes as function of hydration time for OPC with W/C of 0.5 (Lines represent the simulated results while marks show the measured data [3] after 91 days of hydration)

#### 3.2 Importance of micro-pore structure modification model

Simulations were performed to investigate the impact of micro-pore structure modification model which is incorporated into DuCOM-PHREEQC system. OPC paste exposed to a mixture of 500 mmol/l sodium chloride and 10 mmol/l sodium bi-carbonate solutions was considered as an example. The parameters needed to perform simulations are listed 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 this environment have also been taken into account. The used thermodynamic properties of various minerals and aqueous species were collected from the BRGM database (THERMODDEM) [8] and CEMDATA07 database [9].

Table 1 Input parameters for simulation

Material	OPC Paste
Mineralogical analyses of OPC (%)	
-Alite	56.70
-Belite	17.81
-Aluminate	9.66
-Ferrite	8.42
-Gypsum	4.00
Characteristics of concrete mixtures	
-W/C	0.35
Specimen thickness	7 cm
Curing period and condition	91 days water curing at 50 °C
Exposure period	1 year
Temperature	20 °C

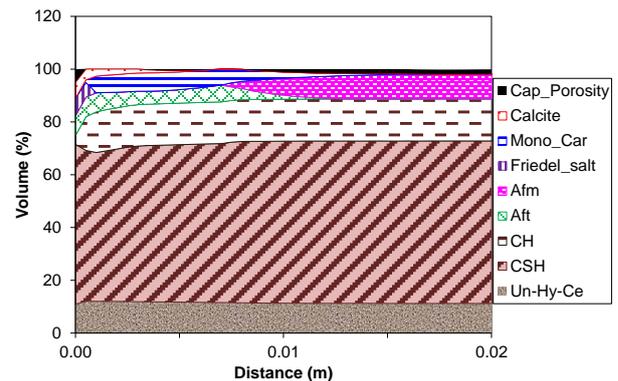


Fig. 5 Representation of the mineralogical distribution of OPC paste exposed to a mixture of 500 mmol/l NaCl and 10 mmol/l of NaHCO<sub>3</sub> for one year. Cap\_porosity: Capillary porosity; Mono\_Car: Monocarbonate; Afm: Monosulfoaluminate; Aft: Ettringite; CH: Portlandite; CSH: C-S-H with Ca/Si of 1.6; Un-Hy-Ce: Un-hydrated cement

The simulations were carried out with and without including the micro-pore structure modification model in DuCOM-PHREEQC. The solid phase distribution in terms of volume percentage inside the paste for the case with considering the micro-pore structure modification model is shown in Fig. 5. It shows that ingress of chloride and bi-carbonate ions lead to form Friedel's salt, monocarbonate, calcite, etc. close to the boundary. The positions of ettringite and monocarbonate front are correlates with the dissolution of monosulfoaluminate. It also shows the dissolution of portlandite and decalcification of C-S-H. The dissolution and decalcification increase porosity, in turn, increase transport of ions that produces more solid products

which fills the pore space. Fig. 6 shows the comparison of simulated results for the cases with and without considering the micro-pore structure modification model. It is important to note that complete dissolution of portlandite close to the boundary is shown in the result for the case without considering the model where the porosity is fixed. However, the results for the case with considering the model show the lower porosity due to filling up the pore with secondary products. This may retard calcium and hydroxyl ions leaching from portlandite. Simulation made with considering the micro-pore structure modification model showed that this plays an important role on diffusing and leaching of various species as well as on the microstructure of cement matrix.

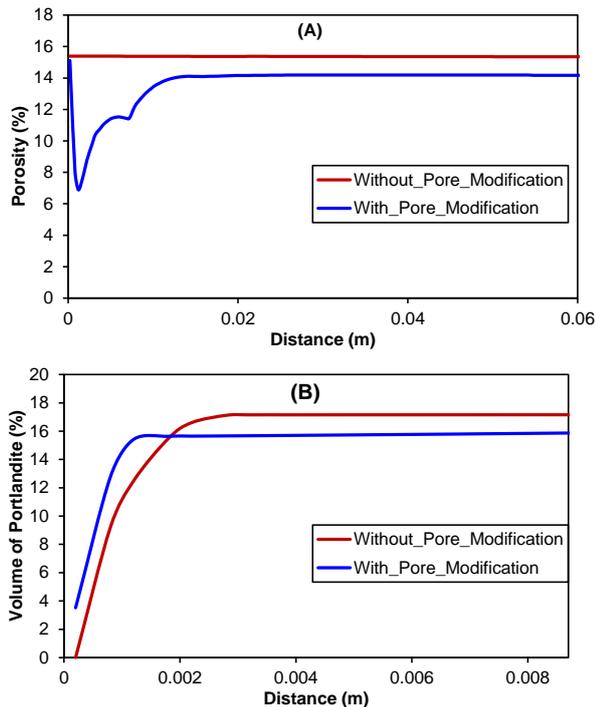


Fig. 6 (A) Sum of capillary and gel porosity profiles and (B) volume percentage of portlandite of OPC paste exposed to a mixture of 500 mmol/l NaCl and 10 mmol/l of  $\text{NaHCO}_3$  for one year.

### 3.3 Application of DuCOM-PHREEQC to describe the leaching of cementitious materials

The developed model can be used to study various problems not only multi-species reactive transport but also other purposes. In here, the model is applied to describe the degradation of OPC paste exposed to various exposure solutions. The parameters needed to perform simulations are tabulated in Table 1 except the type and concentration of ions in exposure solution. Three types of solution were considered for the simulation: pure water, 500 mmol/l NaCl, a mixture of 500 mmol/l NaCl and 10 mmol/l  $\text{NaHCO}_3$ . Simulated results for distribution of cement hydrates in terms of volume percentage inside the paste are shown in Fig. 5 and Fig. 7. Figures indicate the reorganization of cement hydrates due to ingress and leaching of various species and equilibrium between solids and solution.

During the time frame of one year, C-S-H is more resistant to leaching of ions but partial dissolution of both portlandite and monosulfoaluminate producing more pores near to the boundary when the paste exposed to pure water (see Fig. 7 (A)). As observed in Fig. 7 (B), Friedel's salt and ettringite were formed from the reaction among diffused chloride ions and monosulfoaluminate. These secondary products tend to fill the pores and, as a consequence, on the decrease of the dissolution of portlandite. The influence of exposure solution on porosity of paste, calcium concentration in the pore solution, and pH of pore solution is shown in Fig. 8. The increase of porosity is related to dissolution of hydrates mainly portlandite, and precipitation of secondary products decrease the porosity. The dissolution of portlandite leaves calcium and hydroxyl ions in pore solution to leach out of the matrix. The leaching of ions strongly depends on the nature and composition of aggressive solution. The simulated results emphasized that the carbonated solution decrease the deterioration by precipitation of calcite, and pure water is the most aggressive in leaching. Thus, the simulation results provide useful insight into the degradation of cementitious components relating to mineralogical evolution and pore solution concentration with type of exposure solution.

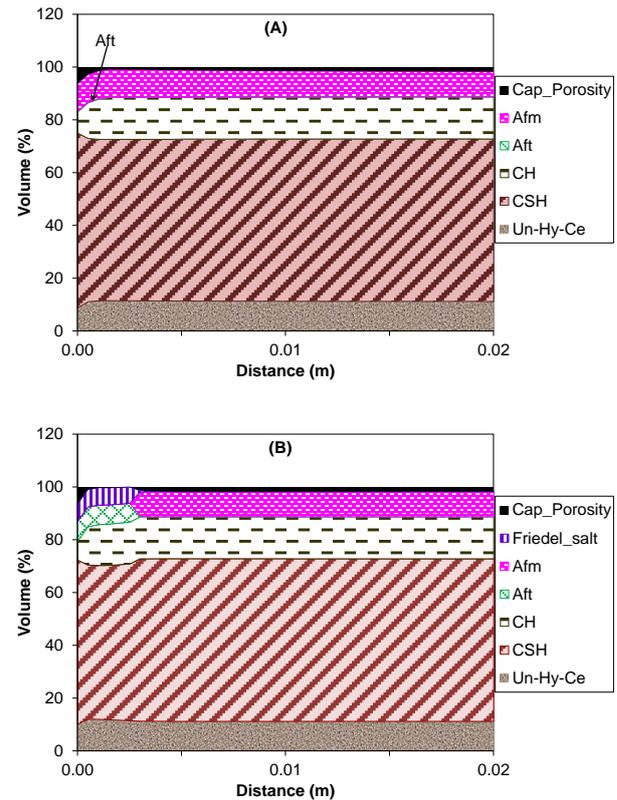


Fig. 7 Representation of the mineralogical distribution of OPC paste exposed to (A) pure water and (B) 500 mmol/l NaCl for one year. Cap\_porosity: Capillary porosity; Aft: Monosulfoaluminate; Friedel\_salt: Friedel's salt; CH: Portlandite; CSH: C-S-H with Ca/Si of 1.6; Un-Hy-Ce: Un-hydrated cement

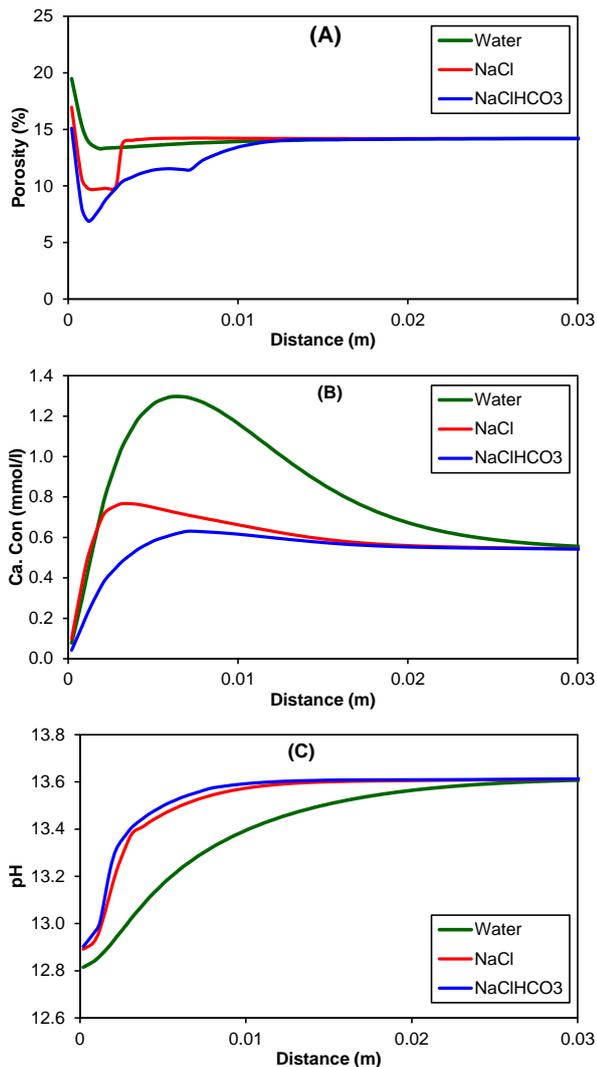


Fig. 8 (A) Sum of capillary and gel porosity, (B) Calcium ion concentration in pore solution, and (C) pH of pore solution profiles of OPC paste exposed to pure water, 500 mmol/l NaCl and a mixture of 500 mmol/l NaCl and 10 mmol/l of NaHCO<sub>3</sub> for one year

#### 4. CONCLUDING REMARKS

A computational platform developed by coupling of DuCOM and PHREEQC for addressing physicochemical and geochemical processes in a previous work is extended in this study. More sub-models for various ions and micro-pore structure modification resulting from dissolution and precipitation of solids are incorporated into the platform as the extension. Thus, the platform is a useful tool to assess the performance of cementitious materials in various aggressive environments. The main simulation results agree qualitatively and quantitatively well with published experimental data in terms of hydrated cement products, porosity, and pore solution chemistry. Additional validation experiments for short and long-term performance of cementitious materials in aggressive environments remains to be done. Simulations made with and without considering the

micro-pore structure modification model into DuCOM-PHREEQC system emphasized the importance of the model into the system. Finally, the platform is used to evaluate degradation of OPC paste in various leaching environments. The simulation results indicate that pure water is more aggressive than sodium chloride solution or a mixture of sodium chloride and sodium bi-carbonate solution. The bi-carbonate solution produces a stable product calcite and decreases the porosity and leaching of ions.

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