Surface chemistry of calcium aluminosilicate hydrate (C-A-S-H) for ions immobilization and transport in low carbon cementitious materials

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detailed in English.

Alumina-rich supplementary cementitious materials produces aluminium incorporated calcium silicate hydrate, C-A-S-H. The electrostatic properties of the C-A-S-H gel are significantly different from the conventional C-S-H, which may affect the durability performance. This research project focuses on the surface electrical properties mainly surface charge of C-S-H and C-A-S-H. A methodology was proposed to determine the properties from the experimental data and fitting the data to a surface complexation model. Subsequently, the model was verified with experimental data focused on chloride adsorption considering corrosion of reinforcement in concrete. The developed model were coupled with the hydration and reactive transport models to predict the ionic ingress in cementitious materials. The model was verified with experimental data for chloride ingress in slag-blended cementitious materials. The methodology will be applied to C-A-S-H to understand the its structure and the properties.

Cement chemistry Surface chemistry Ionic adsorption Diffusion C-A-S-H

Portland cement is responsible globally for approximately 6% of the total anthropogenic greenhouse gas emission. Reduction of CO_2 emissions associated with cement manufacturing process is very challenging for cement and concrete industry without decreasing the cement demand. A number of novel cement systems and low carbon concretes are currently being developed as alternatives for Portland cement. Some of these novel cements are in use on limited scale in some parts of the world; however, their performance compared to conventional Portland cement needs to be established for their large-scale applications. A partial replacement of PC by supplementary cementitious materials (SCMs), such as fly ash, ground granulated blast-furnace slag, and silica fume, has been considered for the development of low carbon cementitious materials and also for better performance (durability and strength) of concrete [1-2]. The main reaction product in PC with SCMs or Ca-rich modern cements is a calcium aluminosilicate hydrate (C-A-S-H) gel. The composition of C-A-S-H gel generally expressed by Ca/(Al+Si) and Al/Si stoichiometric molar ratios and the ratios are changed in the presence of Al-containing and Si-rich SCMs [3]. These changes in composition modify its structure and can affect durability and mechanical performance of the system in concrete [4].

Calcium silicate hydrate (C-S-H) has surface electrical properties such as surface charge due to dissociation its functions groups and the ionic adsorption on its surface [5]. The aluminium incorporation into C-S-H may alter the surface electrical properties and thus, show different ionic interaction behavior. However, surface electrical properties of C-A-S-H gel are not well characterized than other hydrous oxides. Only few studies have reported about the surface functional groups of calcium silicate hydrate (C-S-H) gel, which is found in hydrated PC system [5-6], and the silanol site (SiOH) has widely accepted as the main surface site based on its structure which has many similarities to 1.4 nm tobermorite or jennite crystal structure. ^{29}Si and ^{27}Al MAS NMR suggest that Al can subsitute Si in bringing and pairing positions [7], and this supposes the existense of aluminol surface site (=AlOH) together with silanol site (SiOH) in C-A-S-H. However, there is no proper model to determine the surface electrical properties of C-A-S-H.

The surface charge or electrical double layer formed at solid/solution interface have a direct influence on the ionic adsorption and diffusion. A few studies have qualitatively reported this effect in cementitious materials, but no quantitative accounting in models or analyzing data [8-9]. Therefore, more studies on surface chemistry of C-S-H/C-A-S-H is necessary to understand the ionic adsorption in not only Portland cement-based materials but also in SCMs-blended cementitious materials.

The aim of this research project was to estimate surface electrical properties of C-S-H and C-A-S-H as a function of their composition to quantify the effect of surface charge on ionic adsorption and diffusion in SCMs-blended cementitious materials. It was divided into three sub-objectives as follows:

o Determination of the surface functional groups densities and deprotonation equilibrium constants of synthesized C-S-H and C-A-S-H;
o Investigation on how the surface charge of C-S-H and C-A-S-H affect the ionic adsorption;
o Development of an ionic adsorption model for slag containing materials and its coupling with a reactive transport model for prediction of durability performance of the materials in variety of aggressive environments.

The research was initiated with C-S-H to determine the properties and to propose an integrated model. C-S-H was synthesized using $Ca(OH)_2$ and AEROSIL 200. After that, it was characterized by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The experimental procedures are described in the published paper.

Potentiometric titration for C-S-H suspension and zeta potential measurements of C-S-H in various electrolyte solution were conducted to determine the surface electrical properties through fitting with a surface complexation model. A batch experiment was performed with chloride and sulfate to determine their physical adsorption on the C-S-H surface. The details of the

experiments are also described in

The slag cement paste samples were prepared by mixing PC with 55% of slag by weight. A batch experiment was performed to determine the total binding of chloride on slag cement paste. In addition, chloride diffusion experiments were conducted, as given in , in Portland cement- and slag cement-based paste. These results were used to verify the chloride adsorption and diffusion model.

A generalized two-layer surface complexation model, built into PHREEQC, was used to determine the equilibrium constant values for dissociation surface sites of C-S-H as well as for adsorption of ions on its surface. The ionic adsorption model was coupled with reactive transport model to predict ionic diffusion in cementitious materials. In addition, the model was integrated with hydration model to predict the performance from the starting materials. Figure 1 gives an overview of the calculation procedure in the coupled model. The model considers the effect of surface charge on ionic diffusion as shown in Figure 2. The details are described in and .
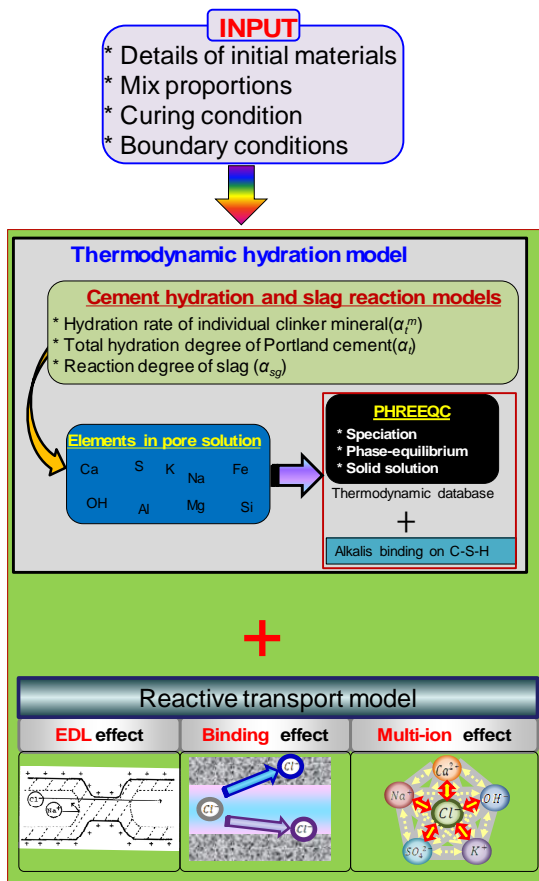

Figure 1: Calculation procedure of the model

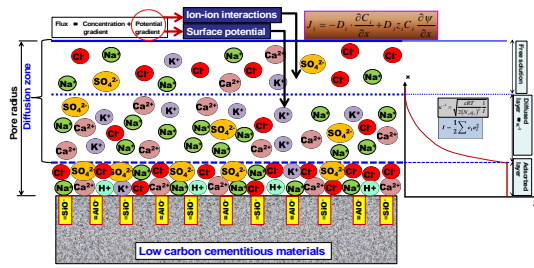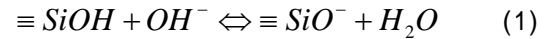Figure 2: Schematic representation of ionic ingress into free solution and diffuse double layer

4.1 Determination of surface electrical properties

The principal mechanism by which C-S-H acquires surface charge is the de-protonation of silanol sites as shown below

$$\equiv SiOH + OH^- \Leftrightarrow \equiv SiO^- + H_2O \qquad (1)$$

where K_{OH} is the intrinsic equilibrium constant for de-protonation, a_i is the activity of i (solution species or surface species), ψ_o is the surface potential (V), R is the universal gas constant equal to 8.31451 J/(mol.K), and T is the absolute temperature (K). The titration experiment can be simulated using the surface site density and the measured specific surface area to determine the surface charge density. The best fit of the experimental data as shown in Figure 3 provides equilibrium constant value, log_k of -8.65 to the equation 1 for the density of silanol sites 4.878 sites/nm^2.
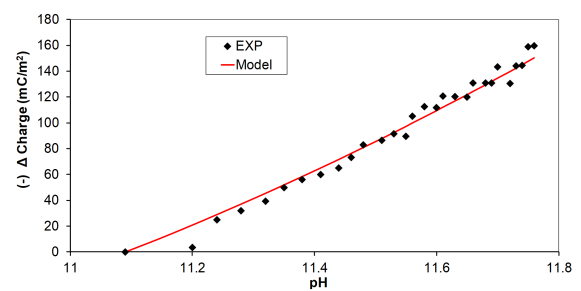

Figure 3: Measured and simulated relative surface charge densities of C-S-H as function of pH

At high pH, the cation adsorption is possible on the silanol sites but anion adsorption is limited. Thus, the negatively charged C-S-H particles are compensated by calcium ions in the solution, and the strong affinity of calcium ions to the surface causes the charge reversal. Calcium ions lose some of their water molecules and make an ionic

bond with silanol sites through the reaction

$$\equiv SiOH + Ca^{2+} \Leftrightarrow \equiv SiOCa^+ + H^+ \qquad (2)$$
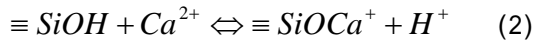
At Iso Electric point (IEP), the surface potential is zero and ($\equiv SiO^-$) and ($\equiv SiOCa$) are equal. Dividing Eq. (2) by Eq. (1) gives as:

$$\frac{K_{Ca}}{K_{OH}} = \frac{a_{SiOCa^+} * a_{H^+} * a_{SiOH}}{a_{SiOH} * a_{Ca^{2+}_{IEP}} * a_{SiO^-} * a_{H^+}} = \frac{1}{a_{Ca^{2+}_{IEP}}} \qquad (3)$$

The value around 0.3 mmol/l of calcium in concentration or 0.17 mmol/l of calcium in activity gives measured zero potential on C-S-H surface. Therefore, pK_{Ca} = pK_{OH} + Log(a_{CaIEP}) = 8.65-3.77 = 4.88. The predicted surface potential for the values of pK_{OH} and pK_{Ca} are agreed well with measured zeta potential for C-S-H suspension in varying calcium concentration, shown in Figure 4.
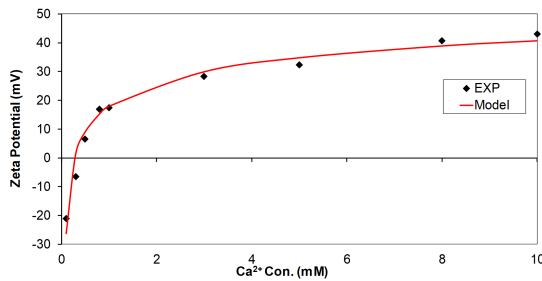

Figure 4: Measured zeta potential and simulated surface potential on C-S-H as a function of the initial concentration of calcium

The C-S-H 1.0 surface particles are highly charged by calcium at higher calcium concentrations (concentrations higher than IEP of calcium). Chloride ions can adsorb on the calcium adsorbed C-S-H surface through inner-sphere complexation reactions

$$\equiv SiOH + Ca^{2+} + Cl^- \Leftrightarrow \equiv SiOCaCl + H^+ \quad (4)$$

To further elucidate this, the two-layer surface complexation model was used to simulate chloride adsorption on the C-S-H surface with adsorbed calcium. The model uses the surface complexation parameters that are estimated in Equations (1-2) with the new equilibrium constant for Equation (4). The equilibrium constant value was derived by fitting the measured chloride adsorption data obtained in the experiments to the simulated results, the

estimated, log_K$_{CaCl}$ is equal to -4.05. Figure 5 shows the experimentally measured and simulated chloride adsorption on C-S-H for a constant concentration of calcium (5 mM Ca(OH)$_2$) with varying chloride concentrations. More detail description is given the published paper
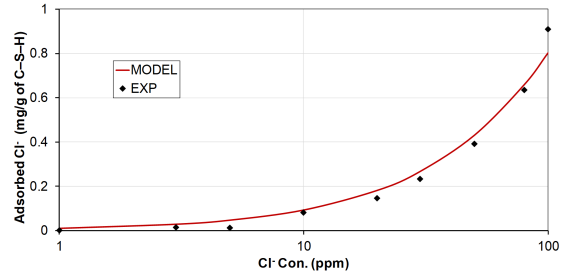

Figure 5: Measured and calculated adsorbed chloride on C-S-H as a function of the initial concentration of chloride. The suspension has a constant calcium concentration (5 mM Ca(OH)$_2$) with the chloride concentration varied.

4.2 Prediction of chloride adsorption on slag cement paste (SCP)

It is accepted that two types of C-S-H exist in the hydration products of slag-blended cementitious materials: low density C-S-H (LD C-S-H) and high density C-S-H (HD C-S-H). It is assumed that one of C-S-Hs is close to the C-S-H of hydrated PC while the other is near the C-S-H with Ca/Si of 1.0. The surface site density of silanol sites in both C-S-Hs equals to 4.878 sites/nm². The surface complexation parameters that are necessary to model ionic adsorption are determined in the previous section while the other surface complexation parameters were determined in the researcher's previous study.

The surface complexation model was applied to predict the chloride-adsorption isotherm of slag cement paste. Both cations and anions in the solution compete for the adsorption on both C-S-Hs surface. It is assumed that C-S-H dominates the physical adsorption of chloride in SCP, and there is none or a negligible amount of physical adsorption of chloride on other cement hydrates. The difference between total and chemical binding of chloride (chloride in Friedel's salt determined by XRD-Rietveld analysis) is the physical adsorption of chloride. Figure 6 shows the predicted and experimentally determined adsorption of chloride on SCP along with the prediction results of chloride adsorption

considering only one C-S-H either C-S-H in hydrated PC or C-S-H with Ca/Si of 1.0. The model which considers two C-S-Hs in SCP predicts well the experimental adsorption of chloride. The amount of adsorbed chloride increases with concentration and follows a Freundlich isotherm. Thus, it can be inferred that the electrostatic adsorption of chloride in SCP is a combination of adsorption on C-S-H of hydrated PC or C-S-H with Ca/Si of 1.0. It is detailly described in the published paper
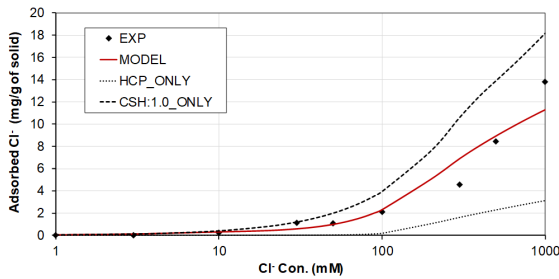

Figure 6: Measured and predicted adsorbed amount of chloride on SCP.

4.3 Prediction of chloride ingress in slag-blended cementitious materials

The surface electrical properties of C-S-H obtained in the previous sections were coupled with reactive transport model shown in Figure 1 to predict chloride ingress in SCP. The pore solution concentration and the amount of hydrates required for the simulations were calculated based on a hydration model. The size of the critical pore was assumed based on the pore size distribution and the surface areas of C-S-H. The pore consists of free water and diffuse double layer, and the volume of free water is used to calculate surface area.

The calculated total chloride content is compared with experimental values in Figure 7. There is good agreement between predicted and measured total chloride profile. The kinds of chloride such as chloride in the free water of the pore solution, diffuse double layer, chemically bound as Friedel's salt, and adsorbed on C-S-H surface are also presented in Figure 7. As can be seen the physical adsorption of chloride to a large extent controls the total content, which supports the findings of previous experimental studies in blended cements. The presence of AFm phases, which is more pronounced in slag-blended cements than conventional Portland cements, contributes to the chemical binding of

chloride. Slag replacement shows lower penetration rates than observed in conventional cement due to changes in the mineralogy and pore structure as more slag is added. Furthermore, high addition of slag leads to a better resistance against chloride transport.
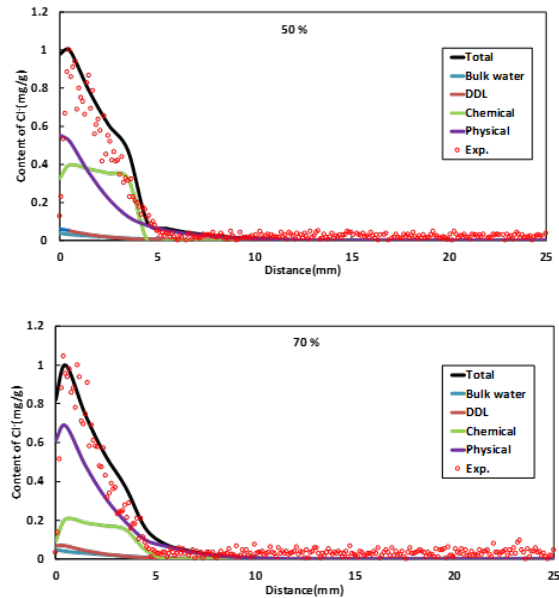

Figure 7. Comparison between measured and simulated chloride profiles of slag blended cement paste after 91 days of 0.5 M NaCl exposure. Exp.: Experimentally measured total Cl^-; Total: Predicted total Cl^-; Bulk water: Predicted free Cl^- in bulk pore water; DDL: Predicted free Cl^- in diffuse double layer; Chemical: Predicted chemically bound Cl^-; Physical: Predicted physically adsorbed Cl^- on C-S-H

Ion diffusion is taking place through the pores of inner and outer products of hydrates, and threshold pores exist in the inner products. It is reported that the effect of electrical charge exists at a distance five times of Debye length. The pores in the inner products are very small in size, and would be completely covered by the electrical double layer (EDL). The surface of hydrated PC with pore diameters less than 7 nm would be fully filled by an EDL, but this size is larger in SCP because of the lower ionic strength of the pore solution compared to hydrated PC. Ion diffusion through the pores of outer products experiences less effect from surface charge, but the diffusion is greatly affected by surface charge in the pores of inner products. When the pores of the outer and inner products are connected, diffusion through the inner products controls the overall diffusion rate due to

surface charge. This is a significant contribution in slag blended cement due to having large EDL thickness, high tortuosity, and small threshold pore size, which are changing with amount of slag addition to promote a lower chloride diffusion rate. The integrated reactive transport model and its verification in slag-blended cementitious materials were described in the published paper .

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