



## C-S-H/solution interface: Experimental and Monte Carlo studies

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### ARTICLE INFO

#### Article history:

Received 3 June 2010

Accepted 27 October 2010

#### Keywords:

B: Calcium-silicate-hydrate (C-S-H)

Surface charge density (C)

Electrokinetic potential (C)

Cation (C)

Adsorption (C)

### ABSTRACT

The surface charge density of C-S-H particles appears to be one of the key parameters for predicting the cohesion strength, understanding the ion retention, the pollutant leakage, and admixture adsorption in hydrated cement pastes.

This paper presents a Monte Carlo simulation of the surface-ions interactions that permits the prediction of surface charge density ( $\sigma$ ), electrokinetic potential ( $\zeta$ ) and ions adsorption of mineral surfaces in equilibrium with a given electrolyte solution. Simulated results are compared to experimental data obtained by titration, electrokinetic potential measurements and ions uptake in the case of C-S-H suspensions. An excellent agreement is found between simulated and experimental results.

The wide spread idea that calcium is a potential determining ion in cement paste systems appears to be incorrect. Instead, the pH controls the charging behaviour of C-S-H nano-particles. This paper also shows to what extent the electrostatic interactions contribute to the measured Ca/Si ratio.

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### 1. Introduction

It is now well established that calcium-silicate hydrate (C-S-H) nano-particles are the main component of the cohesion of cement paste. Attractive forces between them [1–5] lead to aggregation and formation of the network that gives the mechanical and structural properties of the cement paste and of the final concrete construction. Recently, Delville et al. [6,7] and Jönsson et al. [8,9] have shown that this attraction occurring between highly charged C-S-H particles originates from the fluctuation of ion charges in the electric double layer (EDL), so-called ion–ion correlations [10,11]. Hence, the surface charge density of C-S-H particles appears to be one of the key parameters for predicting the cohesion strength [12] and the structure of the final concrete construction. On the other hand, the C-S-H surface charge density is also a determinant factor for understanding the ion retention and transport (diffusion and electro-migration), the pollution leakage, and admixture (polyelectrolytes and polymers) adsorption in cement materials [12–18]. But so far, little is known about the ionization equilibrium of the silanol groups present at the C-S-H/solution interfaces, i.e. variation of the C-S-H surface charge with pH, ion concentration and valency, and so forth.

In a recent paper [19], we have presented a Monte Carlo simulation (MC) method in the Grand Canonical (GC) ensemble [8,20,21], e.g. at constant volume ( $V$ ), temperature ( $T$ ) and chemical potential ( $\mu$ ), that permits the simultaneous prediction of surface charge density ( $\sigma$ ) and

electrokinetic potential ( $\zeta$ ) of mineral surfaces in equilibrium with an arbitrary electrolyte solution. The basic idea of the method is to describe the macroscopic measurable surface charge density of a mineral surface as the sum of the microscopic states of its surface titratable sites interacting between themselves and with the surrounding ions. In a close relation to the “real world”, the surface charge density of a mineral is thus determined by the probability to find an ensemble of titrating sites in a deprotonated state. Following this concept, a microscopic model of the solid/liquid interface have been developed and reduced to its more simple form, see Fig. 1. That is, the electrolyte solution is described by the primitive model where the ions are represented as explicit charged hard spheres while the water molecules are implicitly treated through a dielectric continuum. On the other hand, only the titratable sites from the known structure of the mineral surface are explicitly represented by charged or neutral spheres (depending on their ionization state). The electrostatic and hard-core interactions alone are considered in our approach. The electrostatic being the more long-range and dominating interaction, it is thought to be the main physical ingredient of a liquid system or a solid/liquid interface. During our simulations, in addition to the usual stochastic moves of a GCMC simulation (move of ion, exchange of a salt pair with an infinite bath), the surface sites are individually allowed to titrate. The MC simulations technique is described in numerous text books. For a complete description of MC method, see [22]. For each of these moves an associated energy is calculated which involves all hard-core and coulombic pair interactions (ion–ion, site–site, and ion–site). This constitutes the main difference with existing charging process models [14,23–25] where all interactions and titrations are averaged out through a mean field potential using the

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