

# A sorption model for alkalis in cement-based materials – Correlations with solubility and electrokinetic properties



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## ABSTRACT

In cement-based materials, radionuclide uptake is mainly controlled by calcium silicate hydrates (C-S-H). This work presents an approach for defining a unique set of parameters of a surface complexation model describing the sorption behavior of alkali ions on the C-S-H surface. Alkali sorption processes are modeled using the CD-MUSIC function integrated in the Phreeqc V.3.0.6 geochemical code. Parameterization of the model was performed based on (1) retention, (2) zeta potential, and (3) solubility experimental data from the literature. This paper shows an application of this model to sodium ions. It was shown that retention, i.e. surface interactions, and solubility are closely related, and a consistent sorption model for radionuclides in cement-based materials requires a coupled surface interaction/chemical equilibrium model. In case of C-S-H with low calcium-to-silicon ratios, sorption of sodium ions on the C-S-H surface strongly influences the chemical equilibrium of the C-S-H + NaCl system by significantly increasing the aqueous calcium concentration. The close relationship between sorption and chemical equilibrium was successfully illustrated by modeling the effect of the solid-to-liquid ratio on the calcium content in solution in the case of C-S-H + NaCl systems.

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## 1. Introduction

In radioactive waste repositories, the release of radionuclides from the waste canisters into the biosphere will be strongly controlled by the retention properties of the manufactured concrete materials. Cement-based materials such as concrete are extensively used in the context of nuclear waste disposal and related concepts. Concrete represents the first barrier preventing the migration of radionuclides from the waste canisters. A good understanding and characterization of the interactions between the radionuclides and the cementitious matrix is hence required. In long-term performance assessments, a distribution ratio ( $R_d$ ) approach is generally adopted to take into account the retention properties of each radionuclide in the various cementitious environments. As the cement-based materials are not thermodynamically stable in contact with the host-rock pore water, a leaching process will occur with time inducing the degradation of the cement-based materials. The retention properties of the radionuclides are then determined by four degradation states according to the pH evolution in the cementitious pore water as follows: state I

( $12.5 < \text{pH} < 13.5$ ), state II ( $\text{pH} = 12.5$ ), state III ( $10 < \text{pH} < 12.5$ ), and state IV ( $\text{pH} < 10$ ) (Ochs et al., 2016).

Nanocrystalline calcium silicate hydrates (C-S-H) are the main hydration phases from the reaction of cement and water (Taylor, 1997). Both in civil engineering as well as in more specific issues related to radioactive waste disposal, C-S-H phases were mainly studied during the last decades in conjunction with their role in the performance of the cement matrix as they account for cohesion of the material and contribute to its physical and chemical properties (Lothenbach and Nonat, 2015). In the framework of a radioactive waste repository, C-S-H are of concern due to their involvement in (1) the chemical degradation process of concrete structures which will occur with time and (2) the retention of radionuclides and toxic chemicals. These issues are related to the solubility and surface interaction mechanisms which were the focus of many studies. The solubility of C-S-H has widely been investigated since 1930–50s (Flint and Wells, 1934; Roller and Ervin, 1940; Taylor, 1950; Kalousek, 1952). It is still a matter of debate in terms of solubility models and measurements. Berner (1992) and more recently Walker et al. (2016) have outstandingly referenced experimental data on C-S-H solubility. C-S-H have a variable stoichiometry as a function of the Ca/Si ratio over the range [0.66–1.6]. Consequently, the solubility of C-S-H can be described by the relationship

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between the Ca/Si ratio of the solid and the calcium concentration in the equilibrium solution, or by [Si] vs [Ca] and pH vs Ca/Si ratio as well. Regarding solubility model, various approaches have been proposed: (1) dissolution/precipitation (Roosz, 2016; Roosz et al., 2017), (2) solid solution (Walker et al., 2016), (3) apparent solubility products (Berner, 1992; Henocq, 2005), (4) surface model (Haas and Nonat, 2015). The dissolution/precipitation model induces a discretization of the C-S-H solubility depending on a number of C-S-H phases while the other models (2–4) are solid solution models and give a continuous calculated solubility.

On the other hand, the surface properties of C-S-H were extensively investigated by electrokinetic experiments such as zeta potential measurements (Nachbaur et al., 1998; Viallis-Terrisse et al., 2001; Henocq, 2005; Labbez et al., 2006, 2011; Haas and Nonat, 2015). It has been shown that the surface charge of C-S-H evolves as a function of the equilibrium solution mainly as a function of the calcium concentration. The analysis of these electrokinetic data led to several (more or less complex) C-S-H surface models. The surface interactions are mainly characterized by (1) surface complexation (Viallis-Terrisse, 2000; Henocq, 2005; Plusquellec, 2014; Haas and Nonat, 2015), (2) ion-exchange (Sugiyama, 2008), and (3) electrostatic interactions (Labbez et al., 2006, 2011). These approaches give a mechanistic model for representing retention phenomena related to C-S-H phases and can constitute a phenomenological support and/or an alternative way to the  $R_d$  assessment.

The distribution ratio  $R_d$  (or  $K_d$ ) approach is limited to specific conditions and the effect of perturbations cannot be predicted without specific measurements. A mechanistic approach is then considered for (1) reducing the uncertainties on the retention parameters and (2) for providing  $K_d$  values on a large range of systems. As aforementioned, the surface complexation model is a well-developed concept to describe sorption processes which can be estimated from zeta potential measurements in various salt and pH conditions from mass law equation models such as Phreeqc (Viallis-Terrisse et al., 2001; Henocq, 2005; Haas and Nonat, 2015). Nevertheless, a multiplicity of model parameters can be deduced from experimental data due to the large number of these parameters.

C-S-H in presence of alkalis have been studied for investigating (1) the sorption properties (Faucon et al., 1997; Viallis-Terrisse, 2000; Landesman et al., 2001; Henocq, 2005; Bach et al., 2013; Plusquellec, 2014; Haas and Nonat, 2015; L'Hôpital et al., 2016), (2) the surface properties such as zeta potential (Nachbaur et al., 1998; Viallis-Terrisse et al., 2001; Henocq, 2005; Henocq et al., 2006; Haas and Nonat, 2015), and (3) their chemical reactivity (Sugiyama, 2008; Hill et al., 2006). These various studies have shown the influence of alkali species on the surface properties of C-S-H, but also on their equilibrium solutions. Nevertheless, it has been shown that alkali species do not incorporate the C-S-H structure. Only surface interactions have been observed (Viallis et al., 1999; Henocq, 2005). The presence of alkalis in the interlayer is debated; Bach et al. (2013) proposed a  $\text{Na}^+/\text{K}^+$  selectivity process to explain the different adsorbed amounts between Na and K.

In this paper, we propose to describe the alkali sorption on C-S-H by a combined approach linking a surface complexation model based on the CD-Music method in PHREEQC v3.0.6 and the electrokinetic properties of C-S-H. The goal of this approach is to determine the different surface complexation constants with an iterative approach from dedicated systems, such as pure C-S-H and C-S-H + NaOH, in order to analyze the C-S-H + NaCl system. The determination of the surface complexation constants is based on a combination of three experimental data: zeta potential, composition of the equilibrium solution, and sorption of sodium onto C-S-H surface. That study includes updated thermodynamic data recently

reported for C-S-H and advanced measurements of the specific surface area of C-S-H (Roosz et al., 2016). Experimental data on alkali sorption on C-S-H were interpreted using the proposed model over a large range of Ca/Si (C/S) ratios and water systems. This evolution of retention properties of C-S-H as a function of the C/S ratio is required for modeling the effect of the degradation of cement-based materials on radionuclide retention. As introduced previously, a discretized model based on four degradation states is commonly accepted for considering the degradation of cementitious materials regarding the behavior of the transfer properties of radionuclides. Alternatively, this work aims to develop a highly discretized model (pseudo-continuous model vs four-state degradation model) for taking into account the chemical evolution with time of the cement-based materials, in the radioactive waste repository context, on the transfer parameters such as solubility/speciation and  $K_d$  values.

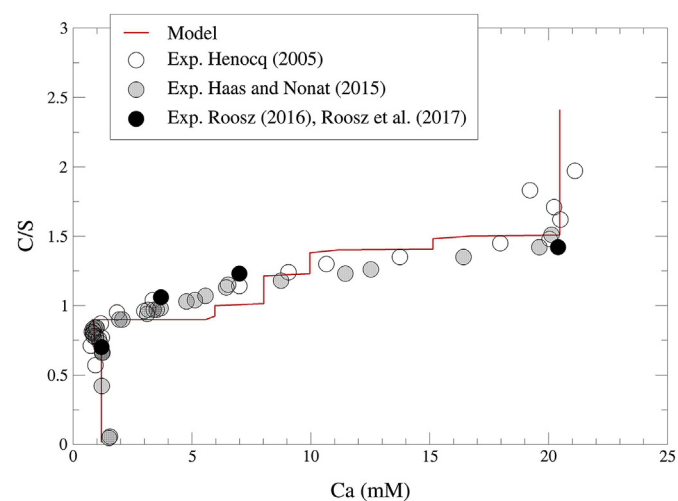
## 2. Geochemical model

### 2.1. Solubility model

The solubility of C-S-H was calculated from a dissolution/precipitation based model of which the solubility products ( $K_s$ ) were taken from Roosz et al. (2016, 2017).  $K_s$  values were determined by Roosz et al. on the basis of (1) measured thermodynamic parameters (heat capacity, entropy, Gibbs free energy), and (2) assessed water content in the C-S-H structure (Roosz et al., 2016). The following C/S ratios were used to characterize the whole domain of C-S-H: 0.70, 0.90, 1.06, 1.23, 1.42, and 1.50. The dissolution/precipitation model was assumed to be reliable for describing C-S-H solubility and the latter discretization of the C-S-H domain was assumed to be suitable for any C-S-H.

Phreeqc calculations were performed with the Thermochimie v.9b database including the Davies formalism for calculating the activity of species (<https://www.thermochimie-tdb.com>). The solubility of C-S-H is particularly characterized by the relationship between their C/S ratio and the calcium concentration in the equilibrium solution. This C/S vs [Ca] relationship was modeled as presented in Fig. 1.

The relevance of the thermodynamic model of C-S-H was also evaluated on the basis of nitric acid titration tests performed on C-S-H with C/S ratios of 0.7 and 1.23 by Pointeau (2000) (Fig. 2). pH



**Fig. 1.** Experimental and calculated relationship C/S vs Ca concentration in equilibrium solution. Experimental data are taken from Roosz (2016), Roosz et al. (2017), Haas and Nonat (2015), and Henocq (2005).

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