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# C-S-H sorption under temperature and relative humidity changes

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## ABSTRACT

Water vapor sorption measurements have positively contributed to the understanding of various phenomena affecting the durability and performance of cement-based materials. The temperature can have a great influence on these measurements. An in-depth research on the effect of temperature on sorption processes in cement-based materials informed by the molecular scale may offer new physical insights into understanding the phenomena. In this work, we aim to study water sorption in C-S-H. Specifically, we focus on the effect of temperature on water desorption in C-S-H at the molecular scale. Effective interactions and desorption isotherms are interpreted. Other features like water cavitation and stability under sorption are also analyzed. All these properties and features are investigated for temperatures between 27 and 150 °C through molecular simulation techniques. The influence of the pore size on the behavior of C-S-H under desorption is investigated. The effect of the temperature on the cohesion in C-S-H is also discussed. Cavitation shows a strong correlation with the temperature and the C-S-H pore size. The cohesion between the C-S-H layers increases with the temperature. These data can serve as valuable inputs for multi-scale models.

**KEYWORDS:** *C-S-H, Desorption, Temperature, Cavitation, Molecular simulations.*

## 1. Introduction

Moisture is a key factor in the durability of cement-based materials, as many processes affecting the durability of cement-based materials are moisture dependent (e.g., cracking, drying and autogenous shrinkage, creep, and fire spalling). Water vapor sorption isotherms describe the variation of the moisture content with the relative humidity (RH). The temperature can have a significant impact on the water sorption behavior of cement-based materials, which can consequently affect the shape of the sorption isotherm (Poyet (2009)). C-S-H (calcium silicate hydrate), is the primary porous element of Portland cement concrete contributing to sorption in the material. The effect of temperature on sorption in C-S-H at the molecular scale is not yet fully addressed, especially in what concerns the interplay between temperature and RH changes.

In this study, we investigate water sorption in C-S-H at different temperatures (27, 100, and 150 °C) and relative humidities (from 100 to 0 %) using molecular simulations. We consider C-S-H pores of sizes between 10 and 26 Å (i.e., in the domain of interlayer pores and small gel pores). We analyse the effective interactions, water desorption isotherms, cavitation, and stability under sorption. We also study cohesion in C-S-H and the effects of temperature and relative humidity on this property. The observables of this study can be used to develop a model of the behavior of cement-based materials at different scales.

## 2. Models and Methods

### 2.1. C-S-H atomic details and force field

This study uses the atomistic C-S-H model of Kunhi Mohamed et al. (Kunhi Mohamed et al (2018)), which features an orthogonal structure with two micropores of 13.7 Å interlayer distance each. In this work, one of the micropores has a constant size (13.7 Å interlayer distance), while the other one varies in size between 10 and 26 Å.  $\text{Ca}_{1.67}\text{SiO}_{3.7} \cdot n\text{H}_2\text{O}$  is the molecular formula of C-S-H. The interactions between atoms are elucidated using the ClayFF force field (Cygan et al (2004)) and the SPC/E water model (Berendsen & Grigera (1987)). Further details regarding the model can be found in (Honorio et al (2021), (2022); Masara et al (2023)). Figure 1 shows an atomic representation of one of the C-S-H pore sizes.

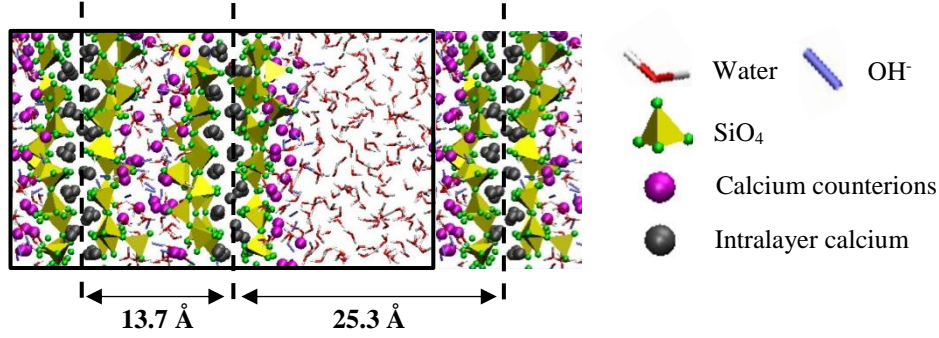


Figure 1: Atomic structure of the 25.3 Å interlayer distance pore at a  $T = 27^\circ\text{C}$  and  $\text{RH} = 100\%$ .

## 2.2. Simulation steps

In this study, LAMMPS (Plimpton (1995)) is used to conduct hybrid Grand Canonical Monte Carlo (GCMC)-Molecular Dynamics (MD) simulations in two different ensembles:  $\mu\text{VT}$  ensemble for water and NVT ensemble for all the remaining particles. The first ensemble implies that the number of water molecules can fluctuate (depending on the setted temperature and relative humidity). The second ensemble implies that the number of solid particles, calcium counterions and hydroxides is constant. Interlayer water molecules exchange with an infinite bulk water reservoir of a constant chemical potential  $\mu$  and temperature  $T$ . The chemical potential of the water reservoir, which depends on the temperature and relative humidity, is given as  $\mu \approx \mu_0(T) + k_B T \ln(\text{RH})$ , where  $\mu_0$  is the chemical potential when the system is saturated,  $k_B$  is the Boltzmann constant and  $\text{RH}$  is the relative humidity. The relationship between the temperature and vapor pressure (or the temperature and relative humidity) is expressed using the Clausius-Clapeyron equation (Fugel & Weiss (2017)). Periodic boundary conditions are used and the solid layers are immobilized to minimize the simulations time.

## 2.3. Effective interactions

The thermodynamic potential or the potential of mean force (PMF), describing the effective interactions in C-S-H, is calculated as a function of the interlayer distance using:

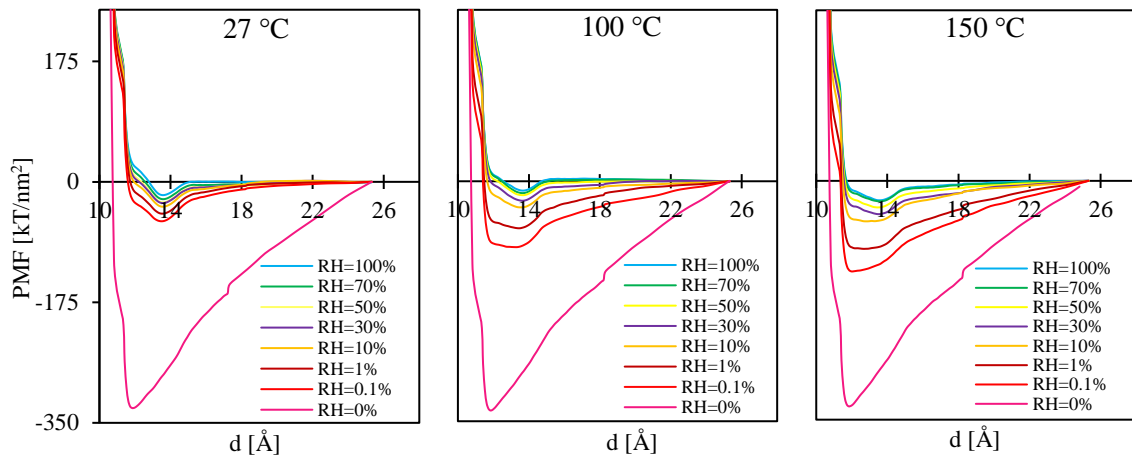
$$\Lambda(d) = \Lambda_0(d_0, \mu, T) - S_s \int_{d_0}^d P d(d) \quad (1)$$

where  $S_s$  is the surface area (constant),  $P$  is the confining pressure, and  $d$  is the imposed interlayer distance.

## 3. Results and discussion

### 3.1. Effective interactions

Figure 1 shows the evolution of the PMF with the interlayer distance from 100 to 0% relative humidity at 27, 100 and 150 °C.

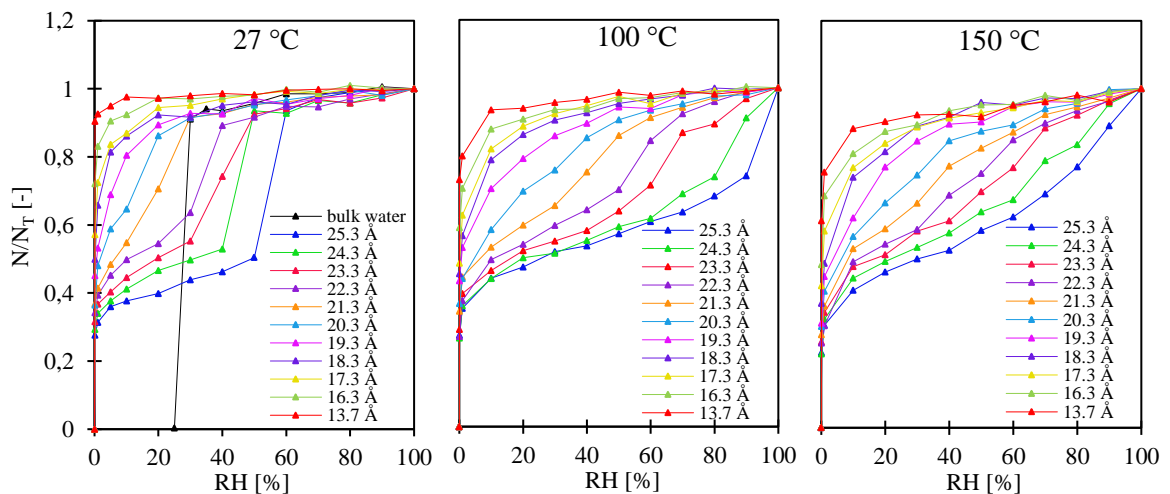


**Figure 2: PMF versus the interlayer distance for various RH upon desorption at 27, 100 and 150 °C.**

As shown in the figure, the shape of the PMF curve and the depth of the PMF well change with the relative humidity and the temperature. The minimum in the well refers to the most stable interlayer distance or the basal distance. At a given temperature, the basal distance decreases with the decreasing relative humidity. This implies the shrinkage of the pores upon desorption. The deepness of the PMF well increases when the relative humidity decreases with a jump occurring between 0.1 and 0 % relative humidity. The effect of the temperature on the depth of the PMF well is similar to that of relative humidity. At a constant relative humidity (range of relative humidities between 100 and 0.1%), the depth of the PMF well increases with the increasing temperature. For 0% relative humidity, the PMF well is independent of the temperature since water is totally desorbed at all the temperatures and the solid layers remain stable even when heated (the alteration of the solid layers upon heating is not simulated). The mobility of calcium counterions and hydroxides does not affect the PMF at this RH, which is an indication of the stability of microportlandite clusters with temperature increase. The observed increase in the PMF well depth with the increasing temperature or decreasing relative humidity indicates a greater level of cohesion in C-S-H.

### 3.2. Desorption isotherms

Figure 1 shows the desorption isotherms of C-S-H interlayer distances between 25.3 and 13.7 Å at 27, 100 and 150 °C.



**Figure 3: The water content evolution during desorption in C-S-H interlayer distances between 13.7 and 25.3 Å at 27, 100 and 150 °C.**

In all the examined pore sizes, the desorption isotherms demonstrate a noticeable dependency on the temperature. At 27 °C, the desorption isotherms for the interlayer distances  $\geq 20.3 \text{ \AA}$  exhibit a discontinuous pattern, where the sudden decay in the water content reflects cavitation. With an increase in the temperature to 100 °C, the cavitation relative humidity increases. As the temperature increases more (case of 150°C), the desorption isotherms display decreased discontinuity. For interlayer distances  $< 20.3 \text{ \AA}$ , the desorption isotherms show a continuous behavior at the three temperature values. The effect of temperature on the desorption behavior in these pore sizes can be seen as an increased water desorption (or decreased water content) at higher temperatures. The sensitivity of desorption isotherm to the temperature was also found in the work of Maruyama et al. (Maruyama et al (2018)). The authors of this work observed an increase in the cavitation relative humidity with the temperature for all the materials they tested (including concrete). The desorption isotherms in this work show as well a sensitivity to the pore size. This appears as a decrease in the cavitation relative humidity with the decrease in the pore size. The study of Rasmussen et al. (Rasmussen et al (2010)) on another microporous material reported a similar relationship.

#### 4. Conclusion

This study aims to understand the combined effect of the temperature and relative humidity on sorption in C-S-H interlayer micropores with the help of molecular simulations. The effective interactions show an elevated cohesion upon water desorption, either due to the increased temperature or decreased relative humidity. This implies an increase in the strength of concrete due to the higher cohesion in C-S-H upon heating. The desorption isotherms show a large dependence on the temperature and the pore size. Cavitation appears in small mesopores ( $\geq 20.3 \text{ \AA}$ ) and disappears in smaller pore sizes. For pores  $\geq 20.3 \text{ \AA}$ , the cavitation RH increases with the temperature. The observations of this study can give important physical insights into predicting the drying shrinkage and creep of cement-based materials through the understanding of the molecular processes at the level of C-S-H leading to these phenomena.

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