

Influence of Alkali Chloride on Surface Properties and Solubility of C-S-H

P. Henocq^{1,2}, E. Samson², J. Marchand^{1,2}

¹*Laval University, Québec, Canada;* ²*Simco Technologies inc., Québec, Canada*

Abstract

Alkalis adsorption on C-S-H surface can influence solubility and surface properties of C-S-H particles. For this work, C-S-H gels have been prepared at various C/S ratios in the presence of NaCl, LiCl and CsCl. Zeta potential of C-S-H suspensions in their equilibrium solution was measured. Surface properties did not appear significantly influenced by the nature of the alkali ion. Otherwise, C-S-H solubility was modified by the presence of salts, especially for low C/S ratios. It will be assumed that the equilibrium of ionic charges in solution is unbalanced by the important alkalis adsorption for low C/S ratios. The analysis of this behavior for low C/S ratios could be a way to determine specific surface area of C-S-H or to distinguish adsorption constant of Cs⁺, Li⁺ and Na⁺ ions.

1. Introduction

Calcium silicate hydrates (C-S-H) are the main component of the hydrated cement paste. Most of the mechanical properties of cementitious materials are induced by C-S-H. However, C-S-H remain difficult to characterize due to their disordered microstructure and their variable stoichiometry, which evolves as a function of their CaO/SiO₂ (C/S) molar ratio. The C/S range for C-S-H usually varies between 0.66 and 2.0 [1]. In this range of C/S values, the C-S-H structure and surface properties are a function of the C/S ratio and of the pore solution composition [2,3]. Moreover, the relationship between the calcium content in solution and the C/S ratio characterizes C-S-H solubility [1]. With this variable stoichiometry, it is difficult to clearly define solubility properties of C-S-H.

C-S-H are usually in the presence of alkalis due to small amounts of Na₂O and K₂O in cements or due to small NaCl concentration in water. During the service-life of a structure, alkalis can enter the material or, on the contrary, be leached out in the environment. It was shown that alkali ions are not incorporated in the atomic structure of C-S-H but are mainly adsorbed on C-S-H surface [4]. The presence of alkalis in the pore solution affects the C-S-H solubility, which can have an impact on the service-life modeling of a structure. This paper will present the influence of alkali ions, and especially their specific adsorption on C-S-H surface, on C-S-H solubility and on C-S-H surface charge. Some unexpected behaviors at low C/S ratios are highlighted and discussed.

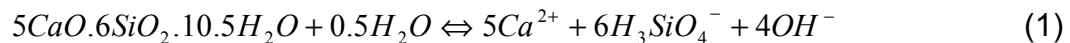
2. Methods

C-S-H gels were prepared from aerosil silica (Aerosil 200 Degussa) and from calcium oxide. Calcium oxide was thermally treated to prevent carbonation and hydration. Silica and calcium oxides were mixed in deionized and decarbonated water. Solutions were isolated from atmosphere to prevent carbonation. Precipitation of C-S-H gels in equilibrium solution was reached after three-weeks with daily stirring. Materials with different CaO/SiO₂ (C/S) ratio gels were prepared (from 0.6 up to 2.4). C/S ratios were varied by adjusting the CaO and SiO₂ content in order to have a constant initial solid mass of 2.0 g. The C-S-H gels were prepared at a liquid/solid ratio of 50. The C-S-H gel structure was analyzed by X-ray diffraction and NMR spectrometry after de-drying. Particularly, X-ray diffraction confirmed the absence of carbonation. C-S-H gels were also prepared in the presence of LiCl, CsCl and NaCl.

The calcium and alkali concentration in the equilibrium solutions were measured using the atomic adsorption (AAS) technique. Samples were centrifuged to extract the C-S-H gel from the equilibrium solution; a very small amount of C-S-H is re-introduced in solutions for preparing C-S-H suspensions. In these solutions, the liquid/solid ratio is approximately 5000 [5]. Solution conductivity and zeta potential were determined on C-S-H suspensions by a zetaphoremeter III model Z400 (Sephy/CAD) apparatus. The zetaphoremeter was calibrated based on conductivity measurements performed on a 0.01 M KCL solution. C-S-H particles were submitted to ultrasonic dispersions during 2 to 5 minutes before being introduced in the zetaphoremeteric cell. The automated measurement function of the apparatus allowed making reproducible and precise zeta potential measurements.

3. Modeling the C-S-H solubility

The stoichiometry of C-S-H varies as a function of the C/S ratio. This variable stoichiometry leads to solubility properties that are evolving as a function of the C/S ratio. Different solubility models for C-S-H were presented in literature during the two last decades [6]. In this paper, the C-S-H solubility is modeled following the approach proposed by Berner [7]. This approach consists in considering C-S-H gels like a two-phase mixture. For the present study, it is assumed that C-S-H phase is made of tobermorite and also, depending on the C/S ratio, of silica or portlandite. The method consists in determining the solubility constant of each phase as a function of the C/S ratio. From experimental data given in the literature providing ionic concentrations at equilibrium, solubility constant K_{Tob} of tobermorite was calculated based on the following dissolution reaction:



Tobermorite has a C/S ratio of 5/6 (0.83). Based on this dissolution reaction, the solubility constant of C-S-H is then expressed as:

$$K_{Tob} = \frac{\{Ca^{2+}\}^5 \{H_3SiO_4^-\}^6 \{OH^-\}^4}{\{H_2O\}^{0.5}} \quad (2)$$

Ions and water activities were calculated by Mean Spherical Approximation (MSA) method [8]. The chemical equilibrium of species in solution was determined by considering the electroneutrality of the solution and the following ionic species (without alkalis): Ca^{2+} , $CaOH^+$, H_4SiO_4 , $H_3SiO_4^-$, $H_2SiO_4^{2-}$ and OH^- (Eq.3).

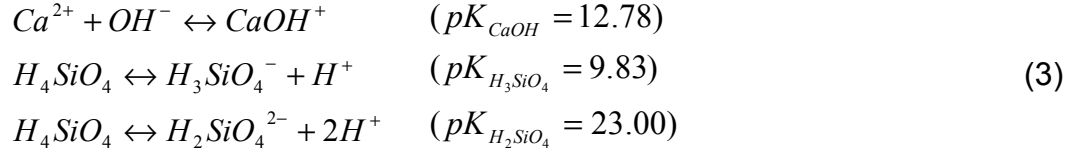


Figure 1 presents the evolution of K_{Tob} as a function of C/S. K_{Tob} was calculated from the experimental data published in reference [7].

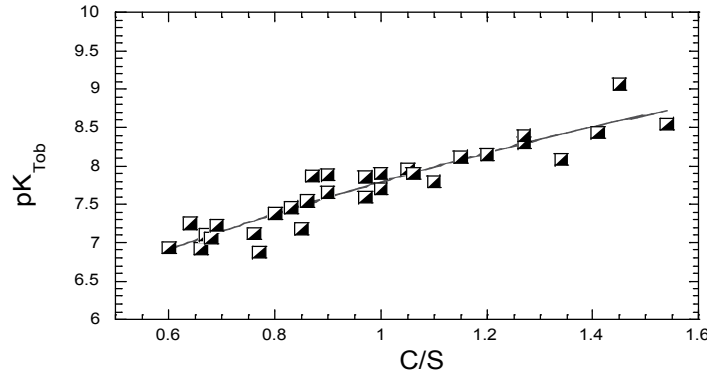
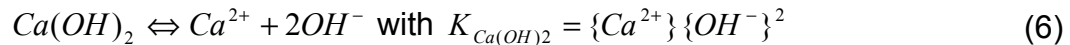
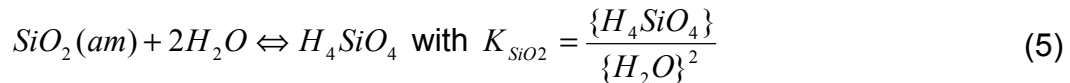


Figure 1. Evolution of pK_{Tob} ($-\log(K_{Tob})$) as a function of C/S

The evolution of pK_{Tob} is interpolated by the following equation:

$$pK_{Tob} = 5.29 + 3.01 \cdot C/S - 0.51 \cdot (C/S)^2 \quad (4)$$

The solubility constants of amorphous silica ($SiO_2(am)$) and portlandite ($Ca(OH)_2$), noted K_{SiO_2} and $K_{Ca(OH)_2}$ respectively, are evaluated using a similar procedure. The dissolution reactions associated to K_{SiO_2} and $K_{Ca(OH)_2}$ are:



Figures 2 and 3 present the values of pK_{SiO_2} and $pK_{Ca(OH)_2}$ as a function of the C/S ratio that were determined from data in Ref. [7].

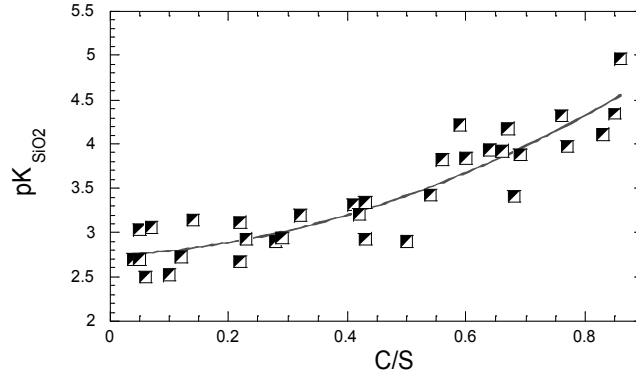


Figure 2. Evolution of pK_{SiO_2} as a function of C/S ratio

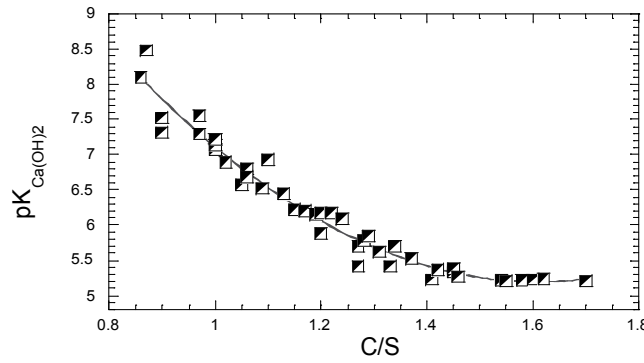


Figure 3. Evolution of $pK_{Ca(OH)_2}$ as a function of C/S ratio

Depending on the C/S ratio, the tobermorite coexists with amorphous silica or portlandite. The calcium and silicon contents in the solid (or in the solution) are the unknown values to solve by the two-equations system defined by $pK_{Tob}-pK_{SiO_2}$ or by $pK_{Tob}-pK_{Ca(OH)_2}$ as presented in Table 1:

Table 1. Solubility constants associated to $CaO.SiO_2.H_2O$ system dependently on C/S ratio

$C/S \leq 0.7$	$pK_{SiO_2} = 2.74 + 0.31 \cdot C/S + 2.08 \cdot (C/S)^2$ $pK_{Tob} = 7.50$
$0.7 \leq C/S \leq 1.5$	$pK_{Tob} = 5.29 + 3.01 \cdot C/S - 0.51 \cdot (C/S)^2$ $pK_{Ca(OH)_2} = 18.54 - 16.58 \cdot C/S + 5.15 \cdot (C/S)^2$
$C/S \geq 1.5$	$pK_{Tob} = 8.60$ $pK_{Ca(OH)_2} = 5.18$

The solubility model was applied on experimental results obtained for this study. The evolution of the C/S ratio as a function of the calcium content in solution, which is characteristic to the C-S-H phase, is modeled and

compared to experimental values obtained on C-S-H prepared in laboratory (Fig.4).

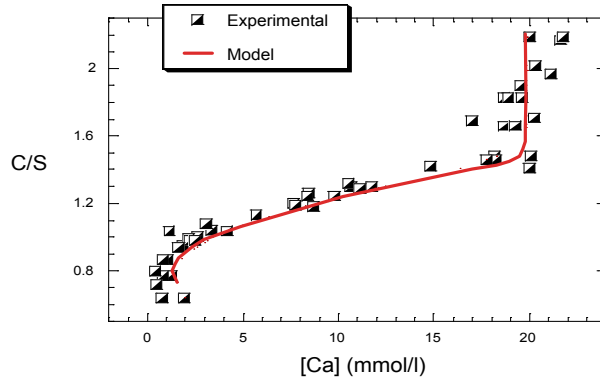


Figure 4. $C/S = f([Ca])$ relationship: experimental and modeling results

4. Results

This section presents experimental and modeling results on the influence of alkalis chloride (NaCl, LiCl, CsCl) on solubility and zeta potential measurements of C-S-H. Experimental data were obtained from lab-prepared C-S-H gel in alkali solutions.

4.1. Influence of alkalis on solubility of C-S-H

Figure 5 presents the results of the C-S-H solubility in the presence of NaOH. The decrease of calcium concentration as NaOH content increases, mentioned by Ref. [9], is reproduced by the model. This evolution of calcium concentration as a function of NaOH content is due to the increase of OH^- concentration that involves a decrease of Ca^{2+} ions according to Eqs. 2 and 6. In this case, sodium ions, by their presence or by adsorption, have not a significant influence on solubility. Moreover, for the low C/S ratios, the calcium concentration becomes very low and it is difficult to see an effect of alkalis.

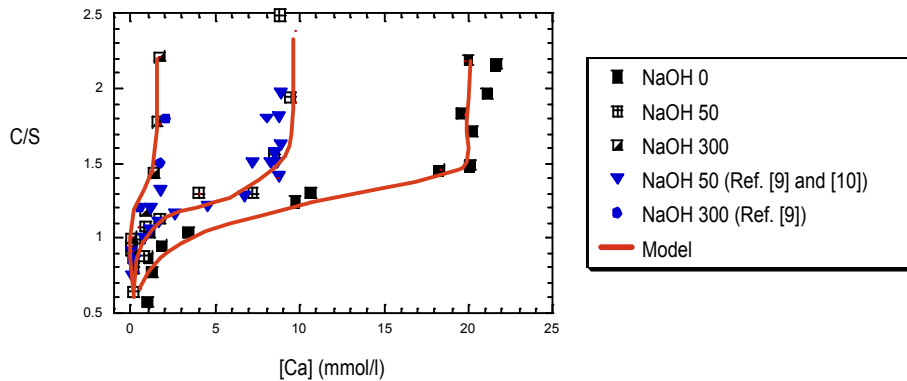


Figure 5. Modeling of the effect of NaOH on the solubility of C-S-H. References are Hong et al. [9] and Courault [10].

Figure 6 shows the influence of NaCl content on the $C/S=f([Ca])$ relationship. A shift of the $C/S=f([Ca])$ curves as a function of NaCl content is observed. The calcium concentration in equilibrium solution becomes higher as NaCl content increases.

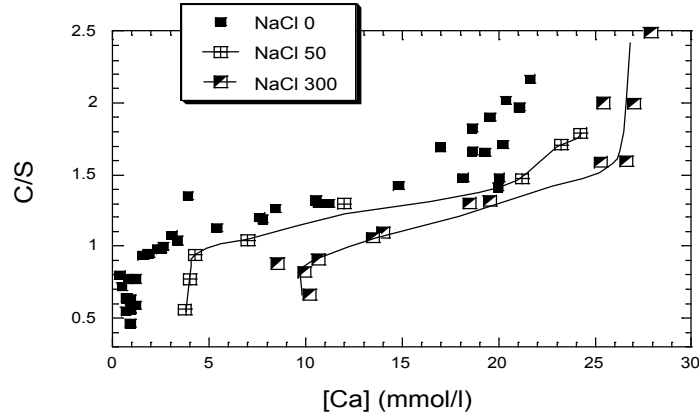


Figure 6. Influence of NaCl content on C-S-H solubility – Experimental results

The behavior described by Fig. 6 was expected. The NaCl content in solution modifies the ionic strength of the solution, and correspondingly affects the activity coefficients of the ionic species. The activity coefficients usually decrease for the NaCl contents applied in this work. In order for the ionic activity product to correspond to the solubility constant, the ionic concentrations increase (especially for calcium) to compensate for the reduction of the activity coefficient values. However, the shift observed for the lowest C/S ratio ($C/S < 0.9$) is higher than expected. Figure 7 shows this difference for the low C/S ratios between experimental and modeling results for NaCl=0.3 M. For higher C/S ratio ($C/S > 1.2$), the model is in agreement with the experimental data. The calculations were performed by assuming neutrality between sodium and chloride ions ($[Na^+]=[Cl^-]$).

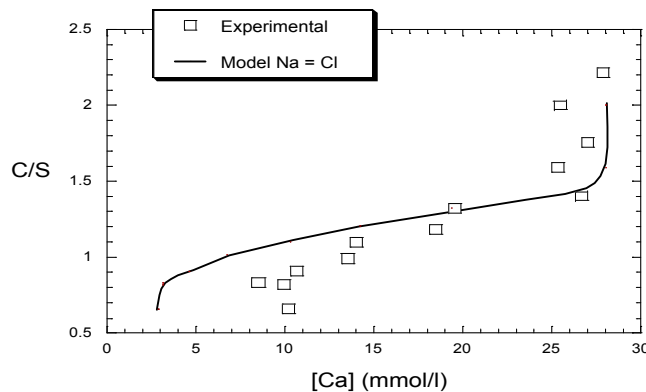


Figure 7. Modeling of solubility of C-S-H in the presence of 0.3 M NaCl assuming that $[Na^+]=[Cl^-]$.

After measuring sodium and chloride concentration in equilibrium solutions, it appeared that $[Na^+] \neq [Cl^-]$; sodium concentrations are lower than chloride concentrations. Na^+ ions are more adsorbed than Cl^- ions by C-S-H for low C/S ratio values (Fig.8).

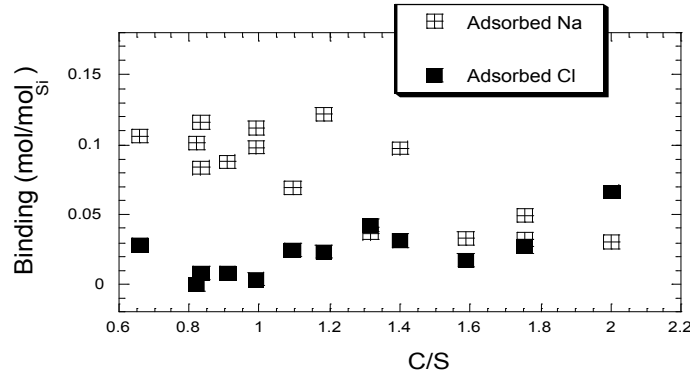


Figure 8. Sodium and chloride binding by C-S-H gel for $[NaCl]=0.3$ M

Figure 9 shows calculation results of C-S-H solubility that take into account the difference between chloride and sodium concentrations in equilibrium solution. The results show that the increase in calcium content occurs for verifying electroneutrality of the equilibrium solution which is unbalanced by different chloride and sodium concentrations.

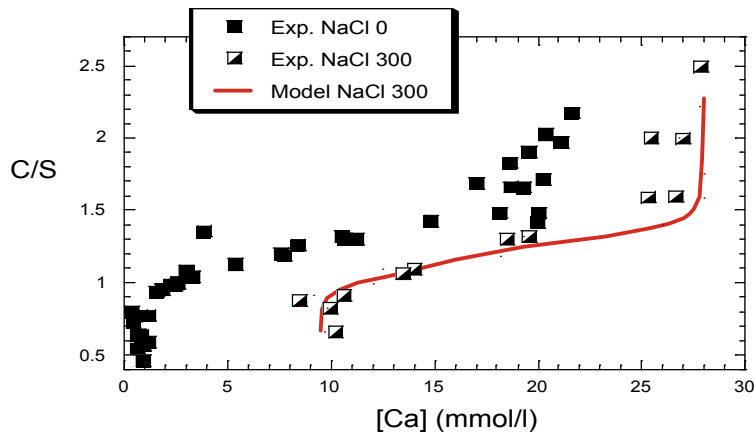


Figure 9. Modeling of solubility of C-S-H in the presence of 0.3 M NaCl by taking into account the difference between $[Na^+]$ and $[Cl^-]$.

Adsorption of sodium ions has then a significant influence on C-S-H solubility, especially on the calcium content in solution, because the initial equilibrium $[Na^+]=[Cl^-]$ is unbalanced. Even if the adsorption of Na^+ ions is higher for NaOH systems than for NaCl systems [3], the influence of sodium adsorption has more significant consequences in the case of NaCl due to the ionic charges unbalance. By taking into account the measured Na and Cl concentrations, this behavior is predicted correctly by the model

of C-S-H solubility described above (Tab.1). Similar experiments were performed in the presence of CsCl and LiCl for studying the influence of alkali ions. Figure 10 compares the $C/S=f([Ca])$ relationship for C-S-H in the presence of NaCl, LiCl and CsCl; alkali chloride content was 0.1 M. No significant differences were observed on Fig.10 between the salts except for the low C/S ratios. In that case, the shift of the curves depends on the nature of the alkali ion. In the presence of LiCl, the calcium concentration is lower than for NaCl and CsCl, for which the calcium concentration of equilibrium solution is higher. That may reveal different adsorption properties between Li^+ , Na^+ and Cs^+ ions.

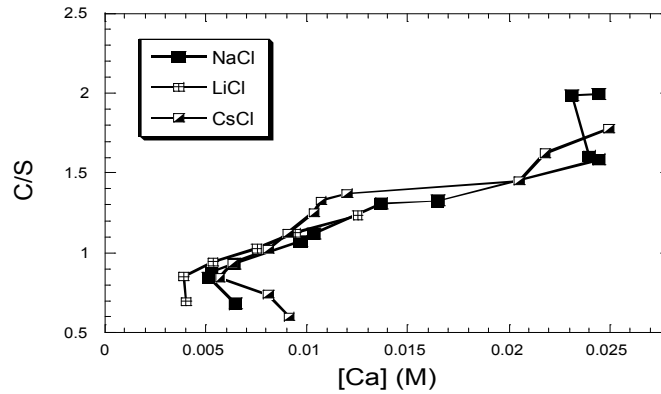


Figure 10. Influence of alkalis chloride on C-S-H solubility. Comparison between NaCl, LiCl and CsCl (0.1 M).

4.2. Zeta potential measurements

Zeta potential of C-S-H suspensions in the presence of NaCl was measured for each C-S-H preparation in their equilibrium solution. Figure 11 shows the influence of NaCl content on zeta potential values in comparison to pure C-S-H. Surface properties of C-S-H are characterized by an evolution of the zeta potential as a function of the calcium content.

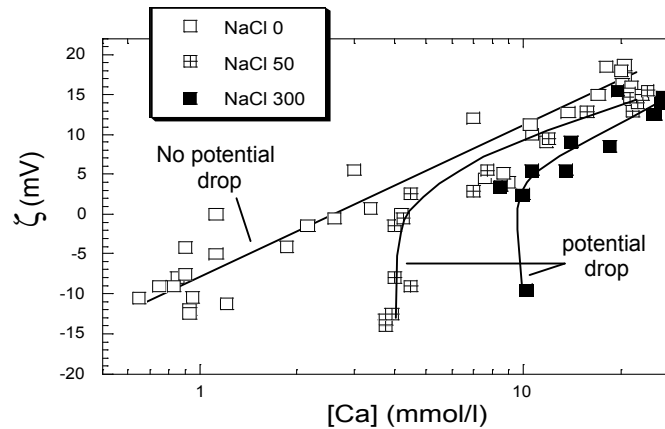


Figure 11. Zeta potential measurements on C-S-H suspensions in the presence of NaCl (50 and 300 mM) compared to pure C-S-H

The influence of NaCl induces a shift of the curves due to an ionic strength effect similar to the solubility case; specific adsorption of sodium or chloride can also influence zeta potential curve [3]. This curve shift is well obtained for the higher calcium content (that corresponds to the higher C/S ratios). However, for low calcium concentrations, i.e. for the low C/S ratios, a potential drop is observed for the both NaCl concentrations (50 and 300 mM). This potential drop was not expected because it can not be explained by solution composition (neither Ca concentration nor pH). Indeed, no significant changes of ionic concentrations were highlighted compared to pure C-S-H as seen in solubility study (Fig.6). The potential drop could be due to changes of surface properties.

Figure 12 presents zeta potential measurements on C-S-H suspensions in the presence of different alkali solutions (CsCl, NaCl and LiCl). No significant differences between NaCl, LiCl and CsCl were observed except for those due to calcium concentration differences for low C/S ratios as seen previously in Fig. 10. As for NaCl case, potential drop were observed for the CsCl and LiCl cases. The surface properties of C-S-H suspensions are not influenced by alkali ions, excepted for the lowest C/S ratios as mentioned previously.

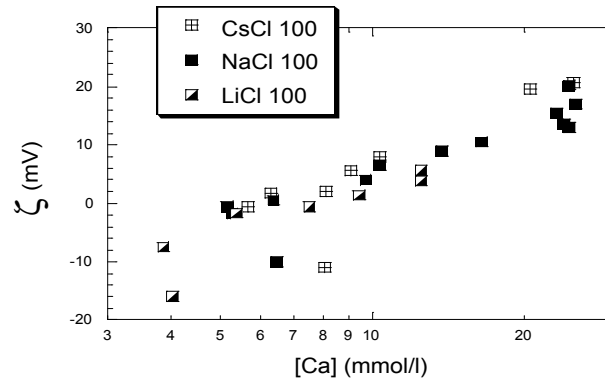


Figure 12. Influence of alkali ions (100 mM) on zeta potential values of C-S-H suspensions

5. Discussion

The experimental analysis of solubility and zeta potential have shown unexpected results concerning C-S-H with low C/S ratios in presence of alkalis. Alkalis adsorption, which is significant for low C/S ratios compared to chloride adsorption, influences the solubility of C-S-H by increasing the calcium concentration. This solubility behavior is coupled with a zeta potential drop. There is no obvious connection between those solubility and zeta potential behaviors. However, the potential drop was not observed when C-S-H suspensions were introduced in lab-prepared solutions (NaCl-based solutions other than equilibrium solution) [10].

Figure 13 compares zeta potential measurements of C-S-H suspensions in their equilibrium solution and in a laboratory solution. This last solution

was prepared with given calcium and NaCl concentrations. A very small amount of C-S-H was introduced in these solutions as described previously (liquid/solid ratio around 5000).

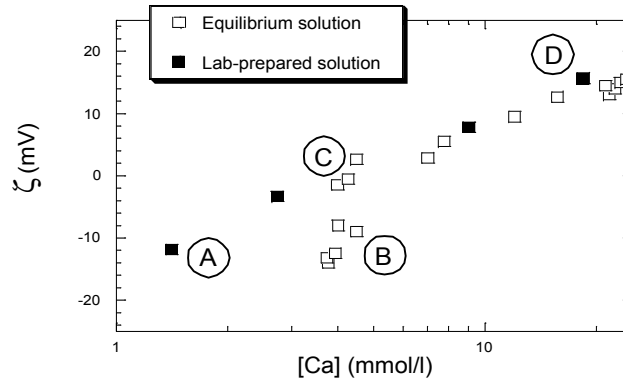


Figure 13. Zeta potential measurements on C-S-H suspensions in 50 mM-NaCl in equilibrium ($Na \neq Cl$) and lab-prepared solutions ($Na = Cl$).

The main difference between the equilibrium and lab-prepared solutions is the fact that sodium and chloride concentration are equal in the case of the prepared one. In this case, the small amount of C-S-H introduced in the solution implies a very small amount of adsorbed sodium ions. Accordingly, sodium and chloride concentrations in the lab-prepared solution will remain equal. On the other hand, in the case of equilibrium solution, the amount of C-S-H gel is clearly more significant and the adsorption of sodium ions will unbalance the solution to yield $[Na^+] < [Cl^-]$.

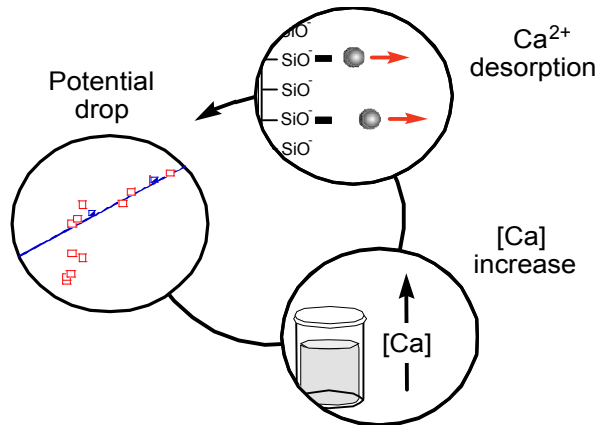


Figure 14. Relation between potential drop and increasing of $[Ca]$

Figures 6 and 13 show that the adsorption of sodium ions on C-S-H surface influences not only solubility of C-S-H but also their surface properties. The increase of calcium concentration for the low C/S ratios appears to be related to the potential drop. In fact, increasing the calcium content in solution is assumed to balance the solution (and the lack of cations Na^+) following the desorption of adsorbed cations Ca^{2+} . A

decrease of the surface charge will occur and the zeta potential will drop. Figure 14 summarizes this assumption.

We note that the expected value of point B in Figure 13 should be equivalent to point C (the same Ca concentration should give the same ζ value). Point B is not in agreement with surface properties related to zeta potential evolution (between point A and D). The potential drop is then associated to a modification in the adsorption of calcium ions. The transition from point C to point B is explained by a desorption of calcium ions. Accordingly with usual ionization constant of silicates given in literature [11,12], we assume that pH variation between point C and point B can not explain the zeta potential variation. As presented in Figure 13, the calcium concentration increase ($D[Ca]$) is defined by $D[Ca]=[Ca]_B-[Ca]_A$ where $[Ca]_A$ and $[Ca]_B$ are calcium concentration at point A and B respectively. The quantity $D[Ca]$ is related to surface charge density variation of adsorbed calcium between point B and C (DS_{Ca} in C/m^2). DS_{Ca} is defined by $S_{Ca}^C - S_{Ca}^B$. Equation 7 expresses the desorbed amount of calcium ions which is equal to an increase of calcium content in solution (expressed in mol per gram of C-S-H) :

$$\frac{\Delta[Ca] \times V}{m_{csh}} = \frac{\Delta S_{Ca} \times S}{z_{Ca^{2+}} F} \quad (7)$$

where V is the volume of solution, m_{csh} is the mass of C-S-H, S is the specific surface area of C-S-H, $z_{Ca^{2+}}$ is the valence of ions Ca^{2+} and F is the Faraday constant. The parameter m_{csh} does not correspond to the initial solid mass since CaO and SiO₂ have been hydrated; accordingly, V/m_{csh} is not the liquid/solid ratio.

The mechanism illustrated on Figure 14 is thus described by Eq. 7. By calculating the charge density S_{Ca} using an ionic surface interactions model [3], it is possible to determine the specific surface area S . The sodium adsorption which differs between points A and B in Figure 13 also has to be characterized. Preliminary results on C-S-H in the presence of NaCl were obtained; the specific surface area S was estimated around 300 m²/g which corresponds to data found in the literature [13,14].

The assumption summarized in Figure 14 could also provide data on adsorption of ions Li⁺ and Cs⁺ relative to solubility results on Figure 12 where shift of calcium concentration differs between LiCl, NaCl and CsCl. In this case, the zeta potential measurements may not provide enough precision to distinguish adsorption constants of Na⁺, Li⁺ and Cs⁺ as no significant differences were showed by these measurements. Moreover, chloride binding by C-S-H is equivalent in the presence of NaCl, LiCl and CsCl [15]. Obviously, alkalis binding measurements would give significant informations. However, some difficulties were faced in this study when measuring alkalis content due to their high ppm concentration (especially for Cs).

6. Conclusion

This work focused on the influence of alkali adsorption on solubility and surface properties of C-S-H with low C/S ratio. The proposed solubility model could be used to emphasize that alkali binding induces the solubility behavior which was observed for low C/S ratios. Moreover, this behavior seems to be related to surface properties evolution. Analysis of this coupled effect could be a way to determine specific surface area of C-S-H gel in solution or to evaluate adsorption constants of alkalis ions. Further work will be made to model ionic interactions on C-S-H surface and to measure alkali binding.

7. References

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