



Interactions between calcium silicate hydrate (C-S-H) and calcium chloride, bromide and nitrate



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ARTICLE INFO

Article history:

Received 2 June 2016

Received in revised form 2 August 2016

Accepted 9 August 2016

Available online 30 September 2016

ABSTRACT

The interaction between C-S-H and anions, especially chloride, is already well documented. However, the conclusions vary from one author to another and a comparison of the obtained data is not always possible. Thus, this study aims to clarify this phenomenon and extend it to the case of bromide and nitrate. For this matter, a new analytical method has been developed in order to make the measurement directly in synthetic C-S-H suspensions, i.e. without any filtration, after calcium salt addition. Various parameters have been taken into account: the anion type and concentration, the Ca/Si of the C-S-H particles (ranging from 0.8 to 1.42) and the incorporation of aluminum inside the C-S-H structure. It has been found that there is no specific adsorption of chloride, bromide or nitrate by C-S-H. Calcium adsorption, which has been detected and measured, is limited, whatever the initial Ca/Si, and the presence of aluminum does not have any influence on it.

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1. Introduction

The study of the interactions between ionic species and products of hydrated portland cement is of primary importance. Indeed, the penetration of ions inside cementitious materials through the porosity plays an important part in the durability of such a material. In particular, links between the presence of anions and the durability of cement have been highlighted in the literature. For example, chlorides anion, present in the environment (sea water or de-icing agent) or directly in the binder (set accelerator), leads to the corrosion of the concrete rebars [1]. Then, the formation of corrosion products with higher volume will induce the cracking of the material [2]. Moreover, the bearing capacity of the reinforcement bars also decreased because of corrosion [3]. As calcium silicate hydrate (C-S-H) is the most abundant phase in a hydrated portland cement and develop the higher surface in interaction with solution, this study will focus on this hydrate. Several authors have already studied the interaction between C-S-H and anions, mainly sulphate and chloride. Concerning sulphate, the different studies are all in agreement: the adsorption of sulphate by C-S-H is specific and can be described as the formation of an ion pair “CaSO₄” at the surface of the particles [4–8]. The situation for chlorides is different, as the different available data concerning the interaction with C-S-H are not in agreement. Indeed, some authors consider such interaction as physical interaction [9–11] and some other as chemical interaction [12–14].

Even among the first group, the different authors disagree: Elakneswaran et al. [9] suggests an adsorption of chloride by non-ionized silanol groups; for Nguyen [11] Cl⁻ ions are trapped inside the interlayer of the C-S-H particles to compensate the charge after an adsorption of alkali ions; Hirao et al. [10] do not details the involved adsorption mechanism he considers. Concerning the second group of authors (chemical interaction), Ramachandran [14] distinguishes three different types of interactions between C-S-H particles and chloride (a chemisorbed layer at the surface, in the interlayer or intimately bound in the structure). Beaudouin et al. [12] clarify this study by separating the adsorbed chloride in two different groups: the first one is soluble in water and not in alcohol (and corresponds to the anions adsorbed at the surface and the interlayer) and the other one is soluble in alcohol but not in water (such chlorides are in minority and would be incorporated inside the structure).

Beyond those different hypotheses for explaining the chloride adsorption by C-S-H, experimental data have also been produced. Unfortunately, the data cannot be compared because those different studies had not been realized under the same conditions (method used to synthesize C-S-H, liquid to solid ratio (L/S) of the samples, Ca/Si ratio of C-S-H, temperature or type of added salt). Moreover, the adsorption data are not always represented in the same way: most of them are shown in terms of quantity of adsorbed chlorides by grams of C-S-H. Such a representation does not allow to make a comparison of all those data since the mass of synthetic C-S-H is only known after drying of the samples. This operation will not provide the same results depending on the drying method which has been used. Others authors prefer to represent the adsorption by the molar ratio Cl/Si, Cl representing the mole number of adsorbed chloride and Si the mole number of silica in the C-S-H. This

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representation seems more adequate in the case of an adsorption on C-S-H. Finally, the raw experimental data are not available, making impossible to convert a mode of representation to another.

Thus, this study aims to clarify the interaction between C-S-H particles and chloride anion but also bromide and nitrate, which could present specificity of adsorption. An experimental approach has been chosen, using a non-classical method: an in situ analysis has been developed and used in order to avoid the separation between solid and liquid prior to analysis. Indeed, previous experiments show that the use of a classical analytical method by first separating the solid from the liquid have a huge influence and leads to an important dispersion of the experimental results and thus to non-reliable data [15].

Different parameters had been taken into account: the initial Ca/Si ratio of the C-S-H, the anion concentration, but also the effect of insertion of aluminum in C-S-H. The different anions are added as calcium salt. The in situ analysis device allows to follow the evolution, versus time, of the concentration of different ionic species (Ca^{2+} , Cl^- and Br^-) in solution, and then, an adsorption of those species. The consequences of the adsorption on the solid/solution interfacial properties, if any, have also been investigated through zeta potential measurement on different samples.

2. Materials and method

2.1. C-(A-)S-H synthesis

C-S-H samples, with Ca/Si of 0.8, 1.0 and 1.4, were synthesized using calcium oxide, aerosil silica and water according the protocol used by Haas et al. [16]. Calcium oxide was obtained after decarbonation of calcium carbonate (provided by Aldrich) at 1000 °C for 4 h. The amorphous precipitated silica Aerosil 200 have a specific area of 230 m²/g and an average primary particle size of 12 nm and was provided by Evonik industries. Before use, the water was freshly demineralized. Concerning the C-A-S-H samples (C-S-H containing aluminum), calcium aluminate has been added as the source of aluminum. The liquid to solid ratio (L/S) of those suspensions has been fixed to 20. This is high enough to ensure a good homogeneity of the product and low enough to obtain a substantial surface area to make the adsorption measurements sensitive. Different Ca/Si has been chosen to study the influence of the apparent surface charge on the anion adsorption. For C-A-S-H, only samples with Ca/Si = 1.0 and Al/Si = 0.05 (this last being close to the observed value in common hydrated OPC based systems) have been synthesized. The composition of the different samples is described in Table 1. Once the mix of the different reagents is made, the samples are put on an orbital shaking table for 4 weeks to ensure a complete reaction at the temperature of the laboratory. For C-A-S-H, this time has been extended to 6 months. The laboratory temperature was maintained at 23 °C. After that time, analyses of similar samples (composition of equilibrium solution, and X-ray diffraction) show that they are pure and have the desired composition and structure [16].

2.2. In situ analysis of the adsorption

2.2.1. Experimental device

The objective was to avoid any experimentalist intervention. For a proper analysis, the device needs to fulfill the following points:

- to be fully automated,
- to allow salt addition in a controlled way,
- to measure electrochemical signals in function of the ionic concentrations,
- to allow a controlled stirring of the suspension,
- to be controlled in temperature,
- to maintain an inert atmosphere above the suspension to avoid carbonation.

The device used for this study is presented in Fig. 1. It is composed with an automatic burette for salt addition, conductivity, pH and ion sensitive electrodes and a stirrer. The suspension is placed in a double-walled baker thermoregulated with a water bath (25 °C). The atmosphere of the reactor is maintained inert by using a nitrogen flow passing through a CO₂ trap. The control and data acquisition system, Titrand 905 with 856 conductivity module and Ti Stand 804 stirring module, is supplied by Metrohm. Stirring is provided by propellers which allow obtaining a more effective agitation than simple magnet bar without heat emission due to friction. The device is computer controlled using the Tiamo software.

A combined reference-pH electrode calibrated in the range 7–13 was used for all the experiments (Metrohm 6.0259.100) in combination with an ion-sensitive electrode, either calcium (Metrohm 6.0508.110), chloride (Metrohm 6.0502.120) or bromide ((Metrohm 6.0502.100). The chosen conductivity electrode is a two platinum plates type (XE161 Radiometer) calibrated using a 0.1 mol/L KCl solution ($\sigma = 12.88$ mS/cm at 25 °C). It is thus possible to measure simultaneously the activity of protons and calcium or chloride or bromide and the conductivity of the solution. The automatic burette (800 dosino Metrohm) allows the addition of a volume $V \leq 50$ mL of a salt solution (highly concentrated in order to not drastically change the liquid to solid ratio).

2.2.2. Methodology

Preliminary experiments showed that the presence of C-(A-)S-H particles has an influence on the response of the electrode dedicated to conductivity, as illustrated in Fig. 2. Under stirring, the conductivity of the suspension is stable (≈ 19 mS/cm). When stopping the agitation, the conductivity increases to reach a plateau (≈ 24 mS/cm). The lower conductivity under stirring is due to the presence of particles between the poles that could either modify the impedance because they are charged or simply decrease the effective surface of the electrodes or both. No influence of the presence of C-(A-)S-H particles has been noticed when using Ion Specific Electrode (ISE). A typical experiment follows different steps: once the signal of the electrodes is stable, the stirring is automatically stopped until the supernatant is clear and the signals constant. Then, known volume of the salt solution is added and the suspension is stirred again as long as the signals vary, then the stirring is stopped again and so on. 8 mL of concentrated salt solution are added in 10 steps (0.8 mL per step). According to the decantation time, an experiment takes between 7 and 10 days.

However, such a measurement system does not allow to access directly to the concentration of the species in solution. Indeed, the response of a specific electrode is not linked to the concentration of an anion but to its activity according to $U = A + \frac{RT}{zF} \log x$ where A is a constant depending on the electrode, F the Faraday constant, z the charge of the ion and x is activity.

Therefore, the response of the ISE depends also on the ionic strength of the solution. Furthermore, the ionic strength will evolve with each addition of salt solution. A specific calibration is thus required. Note that according to this equation, the potential increases with the activity in the case of cations and decreases in the case of anions.

2.2.3. Calibration

In order to access to the concentration in solution of the chosen species during the adsorption experiment, the same experiment is done

Table 1

Quantity of the different reagents introduced in 250 mL of pure water in order to have C-(A-)S-H suspensions with L/S = 20.

Sample	Ca/Si	Al/Si	CaO(g)	SiO ₂ (g)	CA(g)
C-S-H	0.8	-	5.6737	7.596	-
	1.0	-	6.115	6.4655	-
	1.2	-	6.828	5.9	-
	1.42	-	7.5107	5.1653	-
C-A-S-H	1.0	0.05	5.97	6.4655	0.4257

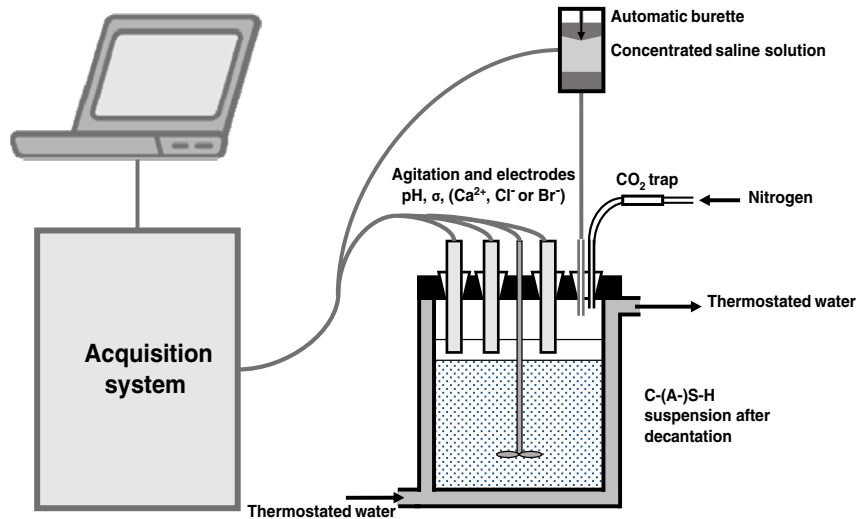


Fig. 1. Schematic representation of the device developed for in-situ analysis of ion adsorption.

first with a reference solution constituted by a solution in equilibrium with C-S-H from which the particles have been removed. That is, the same amount of salt solution is added step by step; at each step of the experiment (i.e. for each addition of the chosen salt solution) the exact concentration of each element is known and the response of each electrode is recorded. A relationship between the electrode potential and the concentration of the considered species can therefore be obtained. This relationship necessarily takes into account the ionic strength of the solution which is, at each step, the same as in the experiment with the C-S-H suspension. Thus, the potential obtained in the presence of C-S-H particles can be converted into concentration, and the ion adsorption by C-S-H can be calculated.

Table 2 shows the composition of the reference solution used in each case. The salt solutions (Table 3) are also enriched with lime and silica with the same concentration as the reference solution in order to avoid a decrease of their concentration in the C-S-H suspension which would lead to a partial dissolution of C-S-H. Note that no silica was added in case of Ca/Si = 1.0 and higher because the silica concentration is very low (tens of $\mu\text{mol/L}$ and less).

This protocol has been slightly modified for the study of a C-S-H with Ca/Si = 1.42. Indeed, such a C-S-H is in equilibrium with a saturated lime solution. Adding such a concentration of lime in the concentrated CaCl_2 solution is impossible. Therefore, the measurements were performed in saturated lime conditions: the reference consists in a saturated lime suspension and an excess of lime is introduced into the C-S-H

suspension before starting the measurement. No lime addition to the salt solution is therefore necessary.

2.3. Zeta potential

The evolution of the zeta potential of the different C-S-H samples with the addition of salt has been measured by acoustophoresis, using Zetaprobe from Colloidal Dynamics. The suspensions used in this part of the study were made exactly in the same way than for the adsorption measurements. The zeta potential decreasing strongly in absolute value with increasing ionic strength, C-S-H suspensions with low added salt concentration have been studied by acoustophoresis. The different anion concentrations are: 0.02, 0.04, 0.06 and 0.08 mol/L. The zeta potential measurement is done in three steps: 1) 10 measurements on the C-S-H suspensions are made successively to ensure a good reproducibility; 2) the liquid phase of the suspension is separated from the solid phase using a by filtration (sintered-glass filter (porosity P3)); 3) measurement of the equilibrium solution with the “background” mode. This last step corrects the value obtained in the first one (the ions contained in the solution may have an influence on the detector). It was noticed that this influence was more important when analysing the more concentrated samples.

3. Results

The evolution of the potentials measured by the electrodes with the addition of salt solutions is presented in Figs. 3 to 5 in both cases of reference solutions and C-S-H suspensions. The conductivity and the pH are reported in Figs. 6 and 7 respectively. The zeta-potential is

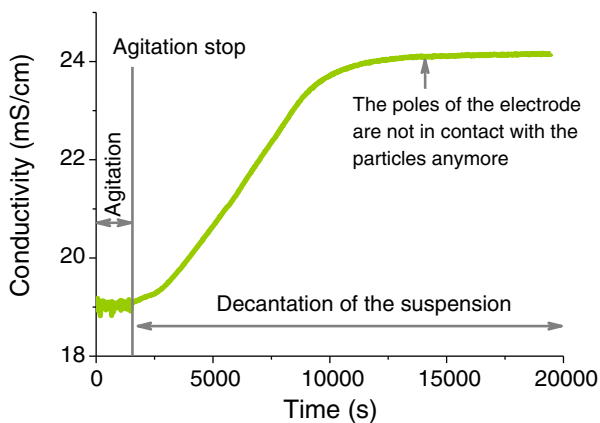


Fig. 2. Evolution of the conductivity of a C-S-H suspension mixed with CaCl_2 under stirring and during the decantation period (after stopping the agitation).

Table 2
Composition of the reference solutions.

	C-S-H 0.8	C-S-H 1.0	C-S-H 1.42	C-A-S-H 1.0/0.05
[CaO] (mmol/L)	1.0	4.0	Saturated	4.4
[SiO ₂] (mmol/L)	0.8	0	0	0

Table 3
Concentration of the saline solutions.

	CaCl_2	CaBr_2	$\text{Ca}(\text{NO}_3)_2$
Solution concentration (mol/L)	5.45	4.43	3.39

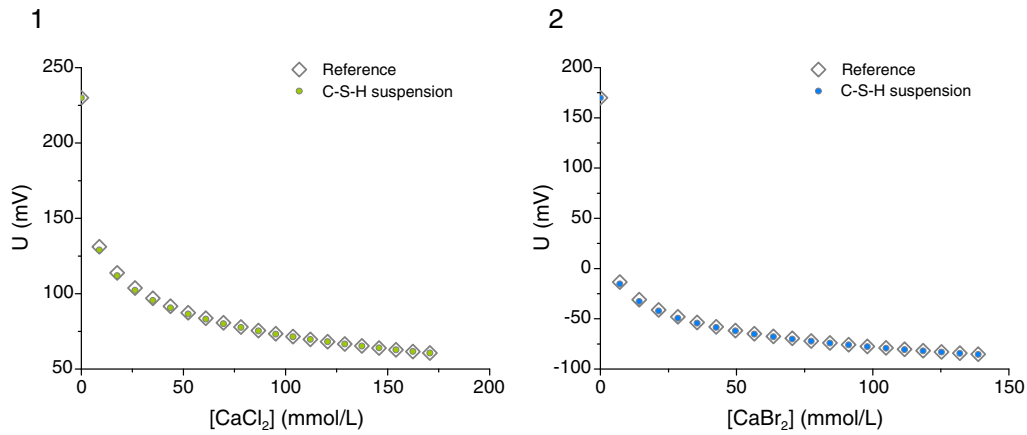


Fig. 3. Response of Cl and Br selective electrodes versus the concentration of added CaCl₂ (5.45 mol/L) (1) or CaBr₂ (4.43 mol/L) (2) during measurement of the reference solution and the C-S-H suspension (Ca/Si = 1.0).

represented in function of the concentration of anions and pH in Figs. 8 and 9 respectively.

There is absolutely no difference in the potential measured with the chloride and bromide electrodes in both C-S-H suspension and reference solution whatever the amount and the nature of the added salt solution (Fig. 3). A very tiny difference can be seen in the case of the calcium electrode for all Ca/Si and all the salts (Figs. 4 and 5). As far as the conductivity is concerned, the conductivity of the C-S-H suspension is slightly smaller than the one of the reference solution in the case of

addition of calcium chloride (Fig. 6). The most significant difference between the C-S-H suspension and the reference solution with salt addition is seen on the pH value (Fig. 7). Except in the case of the C-S-H of the highest Ca/Si for which the suspension is buffered with calcium hydroxide, the pH of the C-S-H suspension is smaller than the pH of the corresponding reference solution. The difference is bigger in case of chloride than bromide and nitrate. It should be noted that in case of reference solutions, the decrease of the pH for a same salt concentration is not identical for the three salts. The difference between salts is bigger at

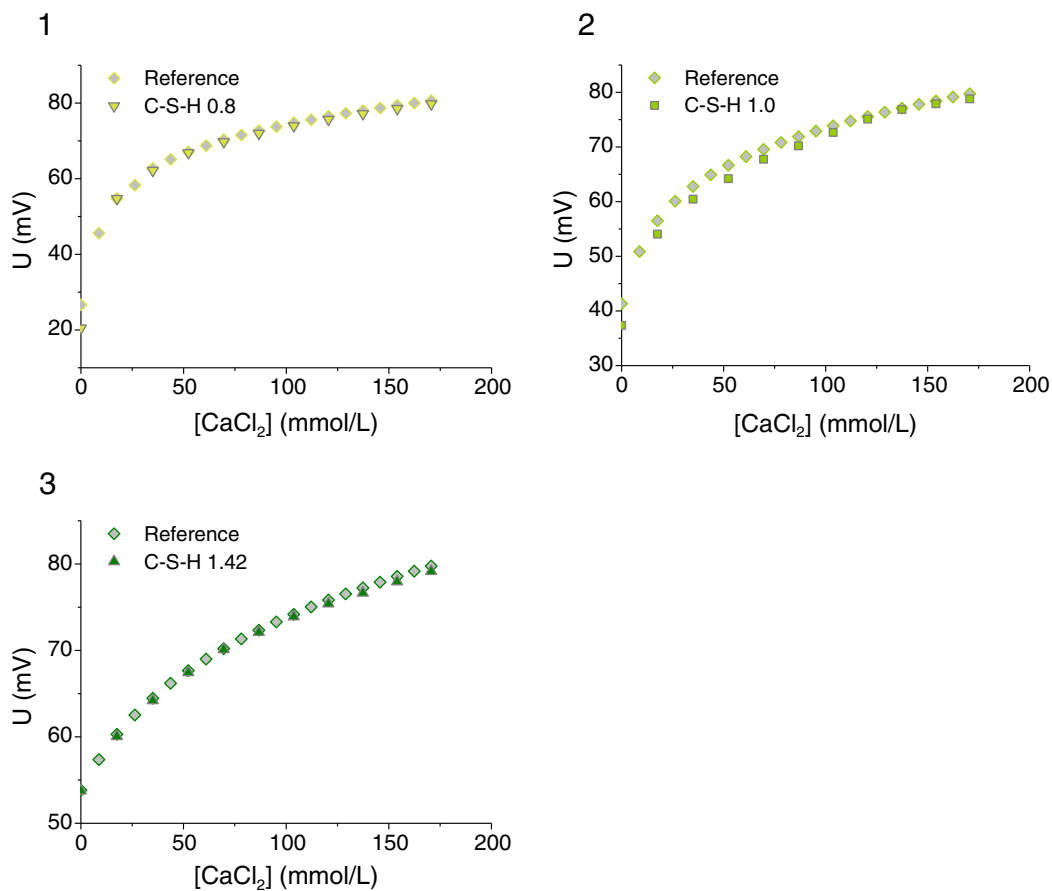


Fig. 4. 1, 2 and 3: Response of the calcium ISE versus the concentration of CaCl₂ added when measuring the C-S-H suspensions (Ca/Si = 0.8, 1.0 or 1.42) and the associated reference solutions.

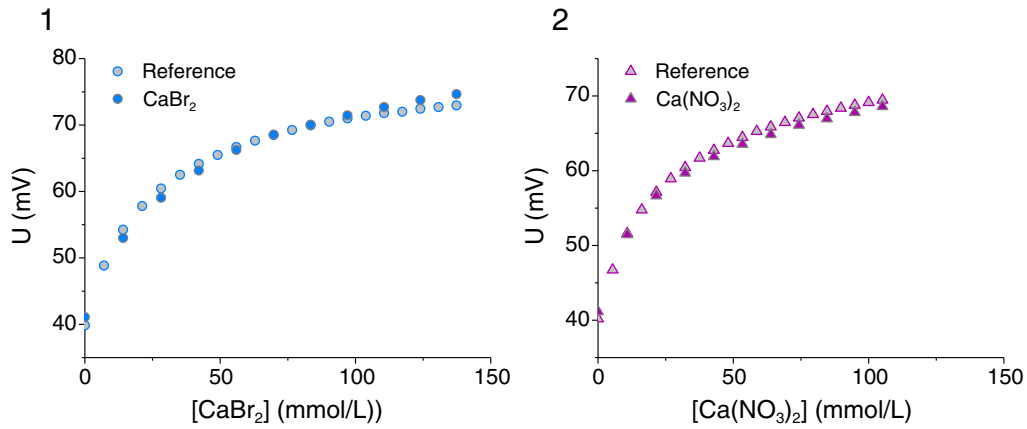


Fig. 5. 1 and 2: Response of the calcium ISE versus the volume of CaBr_2 or $\text{Ca}(\text{NO}_3)_2$ added when analysing the C-S-H suspensions ($\text{Ca}/\text{Si} = 1.0$) and the associated reference solutions.

high concentration. Contrary to the other salts, in the case of calcium bromide the decrease with concentration follows a linear trend at high concentration. The solution became cloudy after some salt solution additions, sign of a solid precipitation. At the end of the addition, the solid part which was present in very small quantity has been isolated by filtration and identified as portlandite by XRD.

Concerning the zeta potential measured after salt addition, it increases slightly with the calcium salts addition, whatever the initial Ca/Si of the C-S-H and the nature of the anion. In addition, it is also always higher for a same pH in presence of salt than without any addition.

4. Discussion

The C-S-H structure is composed by a calcium layer flanked on both side by parallel silicate chains [17–20]. Those last are made up of silica tetrahedra which can exhibit silanol group (SiOH) depending on their location in the silicate chains [21]. These silanol groups deprotonate to SiO^- with the increase of the pH associated with the increase of the calcium hydroxide concentration giving a negative charge to the C-S-H surface [5,22]. This negative charge is balanced by positive counterions [23]. As the number of the deprotonated silanol sites increases with pH, an increase of the density of the negative surface charge is observed, leading to a more important calcium adsorption and thus to an increase of the Ca/Si . The charge compensation by calcium can even lead to a reversal of the apparent surface charge (overcompensation) [22,24]. The addition of calcium chloride, bromide or nitrate, increases the calcium concentration and decreases the pH, it consequently modifies the

surface properties of C-S-H. In addition, aluminum is able to be incorporated in the C-S-H structure, leading to C-A-S-H [16,25–32].

4.1. Anions adsorption

Fig. 3 shows that the chloride and bromide electrodes potentials are strictly identical in the C-S-H suspension than in the corresponding reference solution. The activity of chloride or bromide is thus the same in both analysed systems. In both case, for a given concentration of added anion, with or without C-S-H particles, the activity coefficient which traduces the ion-ion and ion-surface interactions keeps the same value; one can conclude that there are no interactions between the surface of C-S-H and these anionic species or these interactions are not measurable. The zeta potential measurements (Fig. 8) are in agreement with this observation. Despite the increase of the ionic strength, zeta potential is increasing with the concentration of anions. If some anion adsorption would occur, the zeta potential should be smaller. This increase in the zeta potential reflects a calcium adsorption which thus provides a higher density of positive charges at the surface of the C-S-H particles. In case of the lowest Ca/Si ratio (0.8) which exhibits a negative zeta potential in its equilibrium solution without any addition, the lowest addition of CaCl_2 performed in this study ($[\text{CaCl}_2]_{\text{added}} = 10 \text{ mmol/L}$) is enough to reverse the sign of the zeta potential.

These experimental evidences clearly show that there is no adsorption of the anionic species studied here (chloride, bromide or nitrate) by the C-S-H particles. While the nitrate case has not been treated by the in situ measuring device, acoustophoresis did not reveal any difference in behaviour between the three types of salt. Chloride, bromide and nitrate

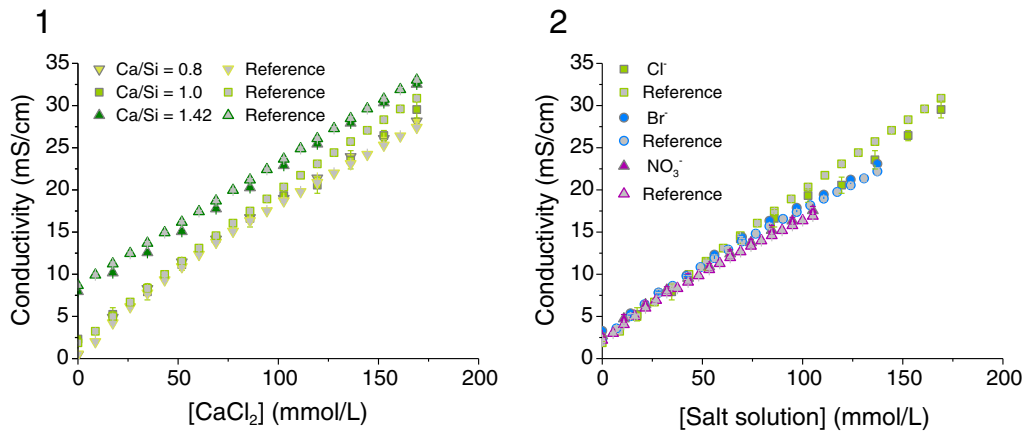


Fig. 6. Evolution of the conductivity of the C-S-H suspensions with the successive additions of salt solutions and comparison with the corresponding reference solutions: 1- CaCl_2 (5.45 mol/L) in the case of $\text{Ca}/\text{Si} = 0.8, 1.0$ and 1.42 . 2- CaCl_2 (5.45 mol/L), CaBr_2 (4.43 mol/L) and $\text{Ca}(\text{NO}_3)_2$ (3.39 mol/L) in the case of $\text{Ca}/\text{Si} = 1.0$.

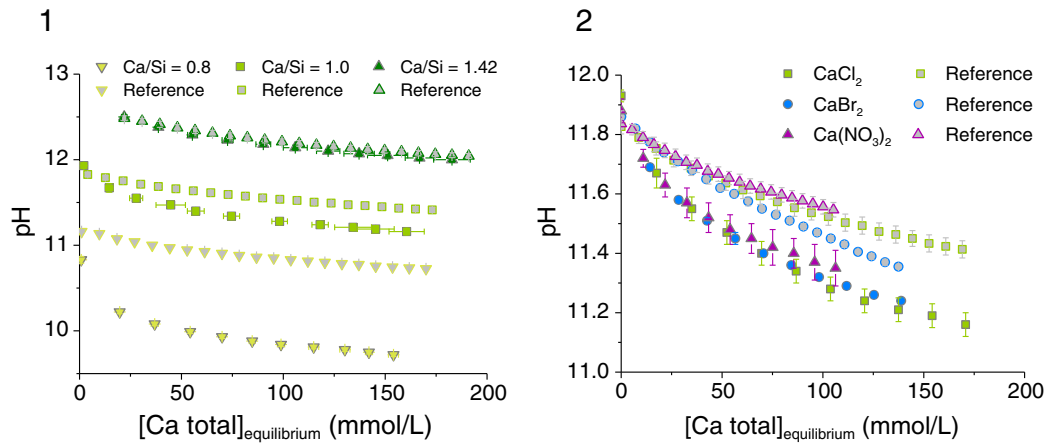


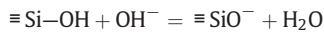
Fig. 7. Evolution of the pH of the C-S-H suspensions with the successive additions of salt solutions and comparison with the corresponding reference solutions: 1- CaCl_2 (5.45 mol/L) in the case of $\text{Ca/Si} = 0.8, 1.0$ and 1.42 . 2- CaCl_2 (5.45 mol/L), CaBr_2 (4.43 mol/L) and $\text{Ca}(\text{NO}_3)_2$ (3.39 mol/L) in the case of $\text{Ca/Si} = 1.0$.

just compensate the positive apparent surface charge of the C-S-H in the diffuse layer of the C-S-H particles as hydroxide ions in the case of pure C-S-H suspension.

However, an adsorption had been reported in previous studies. The common point of those studies is that the measurements were made after filtration of the C-S-H suspensions. Let us consider C-S-H particles in suspension with cations adsorbed in the Stern layer and a plurality of cations and anions in the diffuse layer. After filtration, a part of the anions of the diffuse layer will be stuck to the surface particles in order to maintain a neutral charge of the solid part and thus be removed by filtration from the solution. A schematic view of this mechanism is provided in Fig. 9. A lack of anions will thus be measured in the filtrate, which was associated to an adsorption.

4.2. Calcium adsorption

The more positive zeta potential reveals unambiguously an extra calcium adsorption when a calcium salt solution is added. This extra calcium adsorption is the consequence of a deprotonation of the remaining silanol groups as shown by the more important decrease of the pH in presence of C-S-H particles according to:



This extra deprotonation could be surprising since the pH decreases (see Fig. 7). In fact, on such a protonated surface, it is easy to deprotonate

the first sites and it is more and more difficult to deprotonate a SiOH site close to a SiO^- site due to the resulting electrostatic repulsion. If the counterion balancing the negative site is divalent, the repulsion is vanished and the deprotonation becomes easier (see refs [22,33]). Also, the increase of the calcium concentration in solution favours the deprotonation of the silanols. Nevertheless, this adsorption, calculated after calibration of the calcium ISE, remains very weak (see Fig. 10).

4.2.1. Influence of the anion type

The evolution of the Ca/Si of C-S-H was calculated after calibration from the calcium potential in the case of the addition of calcium chloride, bromide and nitrate in the case of $\text{Ca/Si} = 1.0$ (not shown). No significant effect of the type of anionic species was noticed on the calcium adsorption. The most significant difference observed was in the pH evolution of the reference solutions (Fig. 7). It decreases more with calcium chloride than with calcium nitrate addition and portlandite precipitation is observed in case of calcium bromide. The same order is observed for the solubility of portlandite in sodium chloride, bromide and nitrate solution [34]. It should result from the slightly different anion-anion interactions between OH^- and respectively Cl^- , Br^- and NO_3^- .

4.2.2. Influence of aluminum insertion

The possible influence of the insertion of aluminum into the C-S-H structure has been investigated in the case of samples with $\text{Ca/Si} =$

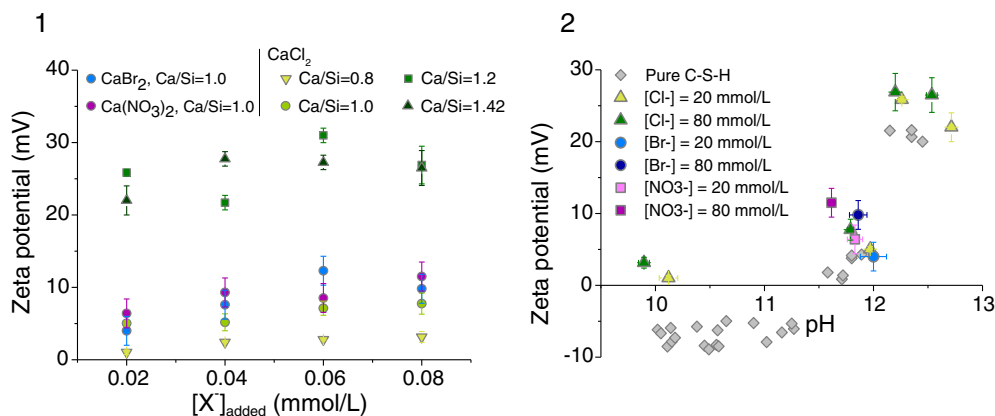


Fig. 8. Zeta potential of C-S-H particles with various Ca/Si in suspension with or without addition of calcium salt. The measurements of the so-called pure suspensions (i.e. without salt addition) come from Haas [16]. 1- the zeta potential is presented versus the concentration of the salt solution (expressed as the anion concentration). 2- the zeta potential is presented versus the pH of the equilibrium solution.

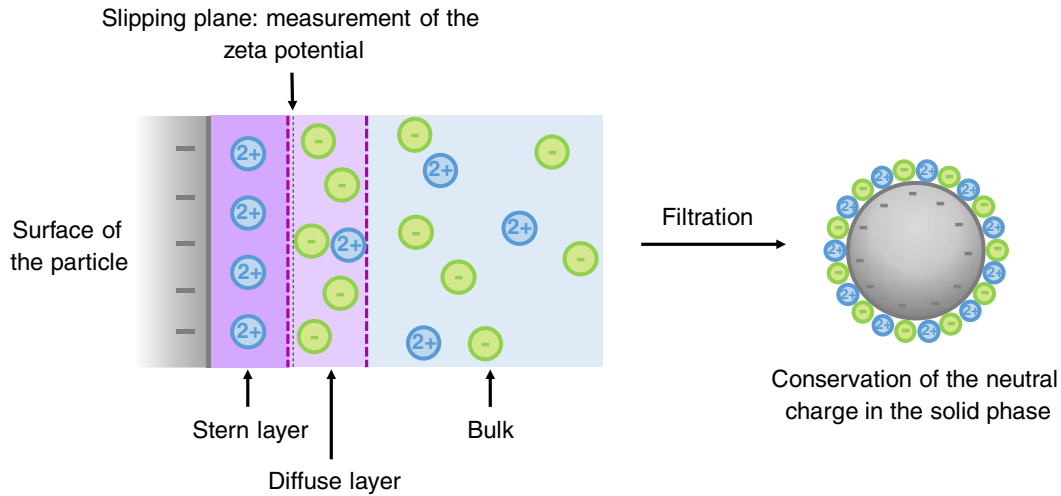


Fig. 9. Impact of the filtration on the ions contained in the double layer of C-S-H particles in suspension.

1.0 and $Al/Si = 0.05$. The analysis was done by using the in situ method with $CaCl_2$ additions. Under these conditions, no difference between C-A-S-H and C-S-H was observed (Fig. 11).

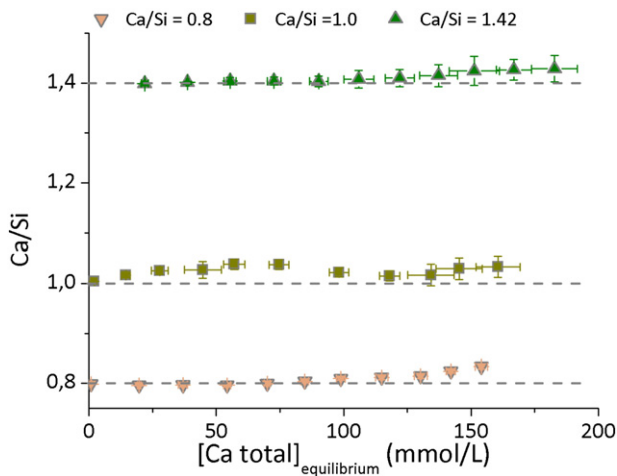


Fig. 10. Evolution of the stoichiometry of the C-S-H particles after successive additions of $CaCl_2$ in the suspensions.

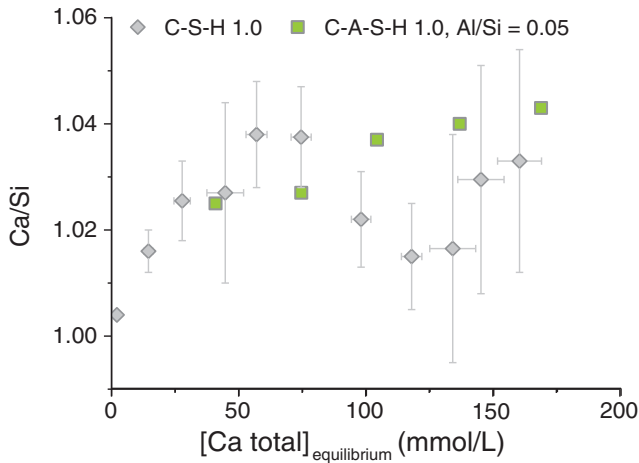


Fig. 11. Evolution of the stoichiometry of the C-S-H ($Ca/Si = 1.0$) and C-A-S-H ($Ca/Si = 1.0$ and $Al/Si = 0.05$) particles after successive additions of $CaCl_2$ in the suspensions.

5. Conclusion

An automatic in situ analysis method of colloidal systems has been developed for this study to overcome a problem of reproducibility. This method is based on the use of specific electrodes directly immersed in C-S-H suspensions and has been applied to the study of ion adsorption by C-S-H particles.

The main finding is that chlorides, bromides and nitrates do not adsorb on C-S-H particles although they tend to accumulate in the diffuse layer where they compete with OH^- . The addition of calcium salt increases very slightly the calcium to silicon ratio of the initial C-S-H particles.

The incorporation of aluminum the C-S-H structure has no influence on this calcium adsorption and therefore on the surface charge of the particles.

Acknowledgements

The financial support of Swiss National Foundation Sinergia grant no. 130419 is gratefully acknowledged.

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