# Nanoscale investigation of particle interactions at the origin of the cohesion of cement

A. Nonat[1], I. Pochard[1], C. Labbez[2], C. Plassard[1], E. Lesniewska[1],
B. Jönsson[2],

[1]*University of Bourgogne, Dijon, France;* [2]*Chemical Center, Lund, Sweden*

## Abstract

The cohesion of cement grains is caused by surface forces acting between calcium silicate hydrate (C-S-H) nanoparticles in interstitial electrolytic solution. The influence of pH, cations valency and concentration on the stability of the final concrete construction is investigated both through Grand Canonical Monte Carlo (GCMC) simulations and force measurement experiments. Direct measurement of the interaction between two C-S-H surfaces, performed in different aqueous solutions by AFM, show that the cement cohesion is provided by both high calcium concentration and C-S-H surface charge density. GCMC simulations in the framework of the primitive model of electrolyte solution show that calcium ions have a strong physical affinity (in opposition to specific chemical adsorption) to the negatively charged C-S-H particles. The interaction between highly charged C-S-H particles in the presence of divalent calcium counterions is strongly attractive because of ion-ion correlations and a negligible entropic repulsion. These results allow one to confirm the pre-eminence of electrostatic forces in the cohesion (ion-ion correlations) of cement.

## 1. Introduction

Cement is one of the most widely used building materials in the world. The earliest known cements were made in Roman times from lime, volcanic ash and clay, so-called Pozzolanic cements. Amazingly, chemical and mechanical properties of cement are not fully understood.

During hydration, C-S-H precipitates on the surface of cement grains in the form of small sheets (typically 60 x 30 x 5 $nm^3$) [1,2]. Simultaneously to this chemical evolution, cement particles form a network established a few minutes after mixing [3-5]. Setting of the cement paste is due to strengthening of the cement grains network by C-S-H nanoparticles precipitating at the contact points between the cement grains. The strength of the cement paste increases during the hydration process because of the augmentation of the number of contact points between the cement grains by the multiplication of C-S-H particles. Although a fully hydrated cement paste can exhibit a high compressive strength (more than 100 MPa), its tensile strength is quite low (about 2 MPa) [6]. It is

probably due to the fact that the elastic limit of the material is small: the critical strain that cement paste can support without being destroyed is smaller than $10^{-4}$. It has been suggested by the fact that the cohesion of the network is due to short range surface forces between C-S-H particles [7].

Particle interactions in cement paste result from surface forces between negatively charged C-S-H particles in electrolytic solutions. According to the classical DLVO theory, the attractive part of the surface forces is due only to van der Waals forces and the repulsive part to the overlapping of the counterions cloud neutralizing the surface charges. However, as a consequence of the potentially high surface charge and the divalence of the calcium counterions, an attraction due to the ionic correlations may occur, which is neglected in the Poisson-Boltzmann equation. This was demonstrated by both anisotropic hypernetted chain (HNC) calculations and Monte Carlo simulations in a primitive model [8-12].

Force measurements between surfaces immersed in concentrated electrolytic solutions are not common. Kekicheff et al [13] demonstrated that it is possible to use an atomic force microscope (AFM) to measure forces between a mica surface and a silicon nitride tip immersed in concentrated calcium chloride solution. By this way, they experimentally evidenced for the first time an attraction driven by ionic correlation.

The aim of the present work is to investigate both experimentally and by simulation the forces between C-S-H particles that are immersed in electrolytic solutions. We will focus on the interaction between the C-S-H particles and how the interaction becomes attractive at high surface charge density and in the presence of divalent calcium ions. Finally, the cohesion under a variety of realistic conditions occurring during the evolution of cement paste will be described.

## 2. Materials and methods

### 2.1 Samples preparation and force measurements procedure

The experimental procedure consists of measuring the interaction forces acting between a probe and a substrate with an atomic force microscope in aqueous solution. Indeed, certain experimental conditions prove to be essential: the probe and substrate should not react with the solution in order to ensure the stability and reproducibility of force measurements. Moreover, the surface of the substrate must be atomically flat in order to avoid roughness effects.

*Substrate preparation*

To get atomically flat C-S-H surfaces in chemical equilibrium with solutions, freshly cleaved $\{10\bar{1}4\}$ face of calcite was immersed in a

sodium silicate solution ([SiO$_2$]/[Na$_2$O]=0.33, [SiO$_2$]=0.5 mol.l$^{-1}$, pH=14.2). The following chemical reactions then occur:

Partial dissolution of calcite substrate:

$$CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-} \tag{1}$$

Precipitation of C-S-H on the calcite cleavage plane by heterogeneous nucleation from calcium ions provided by the calcite dissolution and silicate and hydroxide ions contained in the solution according to:

$$2Ca^{2+} + 3H_2SiO_4^{2-} \ \square \ Ca_2H_2Si_3O_9, xH_2O + 2OH^- \tag{2}$$
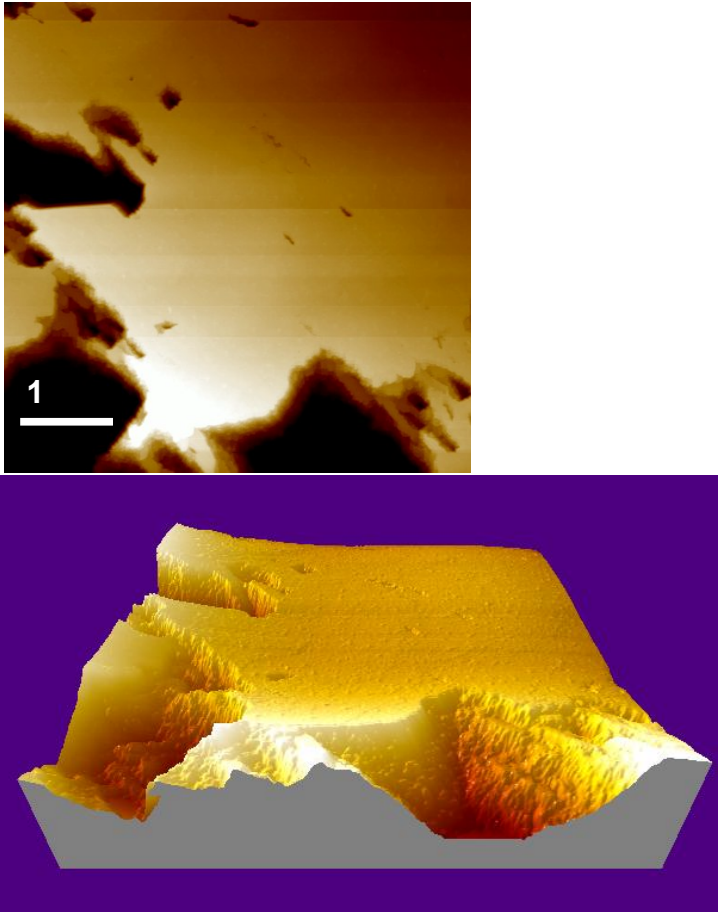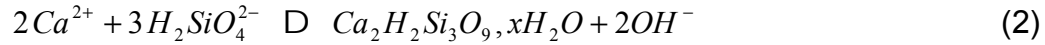


**Figure 1.** Atomic Force Microscopic image of a crystallized area of C-S-H obtained on a calcite monocrystal after equilibrium in solution (see text for details). (top) 2D image. Relative height : 200 nm. (bottom) 3D image.

The C-S-H growth on calcite was materialized by the aggregation of C-S-H nanoparticles of approximately 5 nm high and a developed face of 60 nm by 30 nm [14]. Then the calcite surface covered by C-S-H was immersed in various electrolytic solutions. These solutions were previously saturated with respect to C-S-H by adding C-S-H powder, previously synthesized as described elsewhere [14,15]. Solutions undergo equilibrium for one week prior to being filtered through 0.1 µm Millipore-system filtration. In such solutions, silica concentration is too low (few mmol/L or less) to displace the solubility equilibrium of calcite towards the

formation of C-S-H. C-S-H-covered calcite substrates were stored in these C-S-H equilibrium solutions for one month at 25°C in closed containers in order to avoid carbonation. Calcium and silicate concentrations of each solution were analyzed by ICP-OE Spectrometry (Vista pro, Varian) and the pH measured with a high alkalinity electrode (radiometer analytical high alkalinity combined pH electrode).

After one month, the samples are studied by AFM in their equilibrium solution for topographical and force investigations. The calcite surface is covered by micrometric atomically smooth C-S-H domains formed by Ostwald ripening (see Fig. 1), thus smoothing out the influence of roughness on force measurements. It should be mentioned that C-S-H nanoparticles are still present in the troughs. Atomic resolution imagings were made on the C-S-H microdomains. For $Ca(OH)_2$ concentrations ranging between 0.1 mmol.$L^{-1}$ and 20 mmol.$L^{-1}$ we noticed a structural evolution of the C-S-H surface as a consequence of the change of C-S-H stoichiometries with lime concentration in the equilibrium solution [16].

### Probe preparation

Pyramidal silicon nitride $Si_3N_4$ tips fixed to commercial triangular cantilevers, double-side Au coated with a measured spring constant ranging from 0.06 to 0.6 N.$m^{-1}$ (Veeco Co., CA), were used. In order to obtain C-S-H coverage, the silicon nitride tips, which are naturally covered by a thin layer of silica (~5 nm thick), were immerged in a large volume (V = 50 ml) of a saturated calcium hydroxide solution at 25°C during 48 hours. Under these conditions, C-S-H precipitates on the tip apex from the silicate ions provided by the dissolution of silica in the alkaline medium and from the calcium and hydroxide ions from the solution (Fig. 2). After complete consumption of the silica layer, the probe was also rendered non-reactive, as long as the silicon nitride bulk was preserved from oxidation.



1 µm
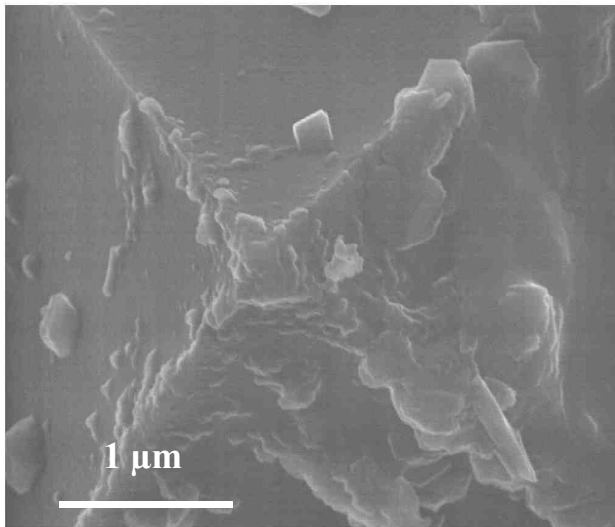
**Figure 2.** Scanning Electron Microscopic image of a silicon nitride tip after immersion during 48 hours in saturated calcium hydroxide solution: C-S-H nanocrystals are mainy precipitated on the edge and the top of the pyramid.

### *Force measurements*

Cantilevers with low spring constant values, typically in the range 0.6-0.1 N/m, have been chosen to be sufficiently sensitive to forces in liquid. In solution, the rate of the vertical motion performed during the approach-retract cycles was lowered to 50 nm.s$^{-1}$ to avoid changing the viscosity of the medium. The force versus separation curves presented in this paper are limited to the range 0-40 nm to increase the resolution of the measurements. However, in each case first measurements are performed with larger displacements (250 nm). The first retract curves were also recorded. In these conditions, the probe and the substrate are kept in contact until two seconds. The maximum force applied by the cantilever (k=0.6N.m$^{-1}$) reaches 10-20 nN. In the compliance regime, the deflection was always equal to the displacement without any instability proving there is no other interaction regime at shorter distance (see Fig. 3).
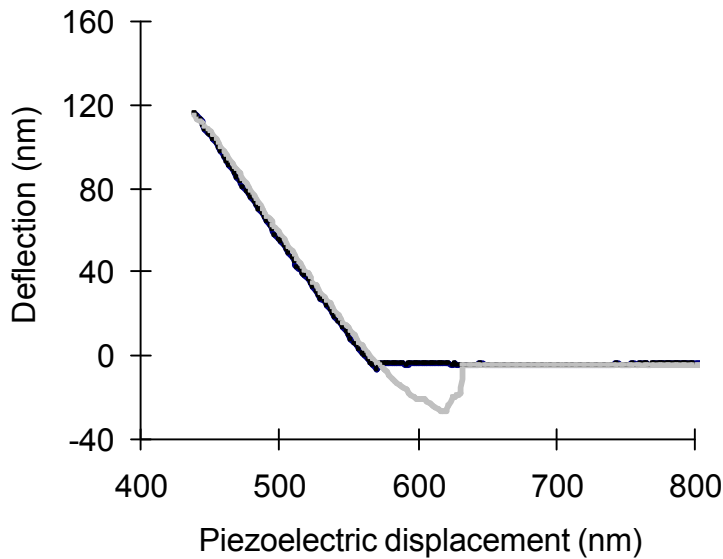


**Figure 3.** Deflection of cantilever against piezoelectric displacement. Substrate and tip are covered with C-S-H. Measurements in saturated calcium hydroxide solution.

Interaction forces were obtained with the usual calibration process in order to transform experimental cantilever deflection curves as a function of the vertical scanner displacement $\Delta z$ into force-distance curves [17]. Using the slope of the retraction deflection curves in the contact region, the cantilever deflection is then converted into a force using Hooke's law:

$$F = -k \Delta z. \tag{3}$$

where k is the stiffness constant of the AFM cantilever used, determined by resonant frequency method or thermal noise analysis. Force curves obtained give the force F (nN) against the tip-sample separation (nm). For each experiment, statistics of over 100 force measurements per sample were established by recording 5 force curves on 20 different locations from each sample. Five samples were analyzed for each different electrolytic solution.

### Measurements environment

All experiments were performed in a $CO_2$ free glove box in order to prevent carbonation of hydroxide solutions. Inside, a commercial AFM (Nanoscope IIIa, Veeco Inst., Santa Barbara, CA) was used. For studies in aqueous solutions, an adapted commercial fluid cell was used. The temperature of the surrounding wall was maintained at 25°C and humidity controlled in order to avoid evaporation of the solution.

## 2.2 Model and simulations

We do not attempt to model the cement system in atomic details, but instead we aim at a mesoscopic model that contains the basic physical ingredients. The primitive model of electrolyte solution is such an alternative, where all ions are considered explicitly and water is treated as a dielectric continuum characterized only by its relative dielectric permittivity, $e_r$ = 78.5 (at room temperature). Furthermore, lacking detailed information on the geometry of the C-S-H nanoparticles, it is assumed that the interaction between them can be modeled as an interaction between two parallel planar walls, with a smeared out surface charge density. According to structural considerations, the surface charge density of C-S-H particles is supposed to reach 0.68 $C/m^2$ for extreme high pH. In the present work, reasonable surface charge densities have been chosen. That is, the latter are comparable with what can be measured in similar conditions (pH, ionic concentrations, etc.) [18]. The C-S-H platelets have limited dimensions, but the ratio between the extension of the platelets (300-600 Å) and the relevant separation between them, 10-20 Å, is such that the infinite system is a very good model for the interaction between C-S-H particles. The confined solution will contain an electrolyte solution with both counter- and co-ions whose average concentration will vary with the separation $h$. The assumption is that this solution is in equilibrium with an infinite bulk solution of known stoichiometric composition. That is, the concentration of the ionic species in the confined solution is not known beforehand but has to be determined from the chemical potentials imposed by the bulk solution in a Grand Canonical Monte Carlo (GCMC) simulation. This is done under the condition of electroneutrality. Cement paste can contain a variety of mono- and divalent cations as well as anions. In an attempt to minimize the number of parameters and maintain a simple model, we have set all ionic radii equal to 2 Å, that is, $d_{hc}$ = 4 Å.

Previous analyses of seawater also indicate that the appropriate variation of ionic radii is rather limited [19]. The osmotic pressure of the confined solution, from which the interacting force is deduced, is calculated according to a procedure described elsewhere [20]. As said earlier, the simulations are performed in the primitve model and, thus, only ion collisions (hard-core interactions) and electrostatic interactions contribute to the calculated osmotic pressure. That is, the van der Waals contribution to the osmotic pressure is neglected. However, it has been shown elsewhere [21] that in the present system, the latter is small. The force between the two parallel walls is calculated to be the net osmotic pressure (*i.e.* the osmotic pressure of the confined solution minus the bulk osmotic pressure) divided by the interacting surface area. An interacting surface area of 64 nm² has been chosen in agreement with the one measured by AFM [22]. These calculated force values can thus be compared to the experimental ones obtained by AFM.

## 3. Results and discussion

The experimental and simulated results obtained in the present work will be qualitatively compared along this section. The variation of cohesion force with bulk conditions is discussed for a number of technically important cases.
The varying parameters in simulations and experiments are not the same even if they are physically equivalent. This is surface charge density in simulations and pH in experiments. Consequently, the studied conditions (pH, surface charge density, concentrations) are not strictly the same for a set of simulated and experimental results. Nevertheless, the conditions are close enough for the purpose of this study.

## 3.1 Role of the pH and calcium concentration

It has previously been shown that it is only at high surface charge density and in presence of multivalent counterions that cohesion sets in [21;23-25]. The simplest solution simulating the pore solution of a hydrated cement paste is a calcium hydroxide solution. Fig. 4 shows how the attractive minimum is reduced when calcium hydroxyde concentration is reduced. Actually, it has been demonstrated by atomic force measurements that for very low calcium hydroxyde concentration, the attractive force vanishes and the interaction becomes purely repulsive [22]. That is, when both the surface charge density of the C-S-H nanoparticles and the calcium concentration are weak, no more ionic correlations occur and the cohesion is lost. The highest calcium hydroxyde concentration in Fig. 4 corresponds to a very high pH (>13) and gives a short range and strong attraction. This is in perfect agreement with the setting of the cement paste which is well known to occur in this high calcium hydroxyde concentration range. In these conditions, the high pH

results in a high surface charge density of the C-S-H nanoparticles while the calcium ions accumulate near the negatively charged surfaces leading to attractive ionic forces [20]. Comparing the experimental and calculated results, a very good agreement is found. But the forces are found to be shorter in simulations.
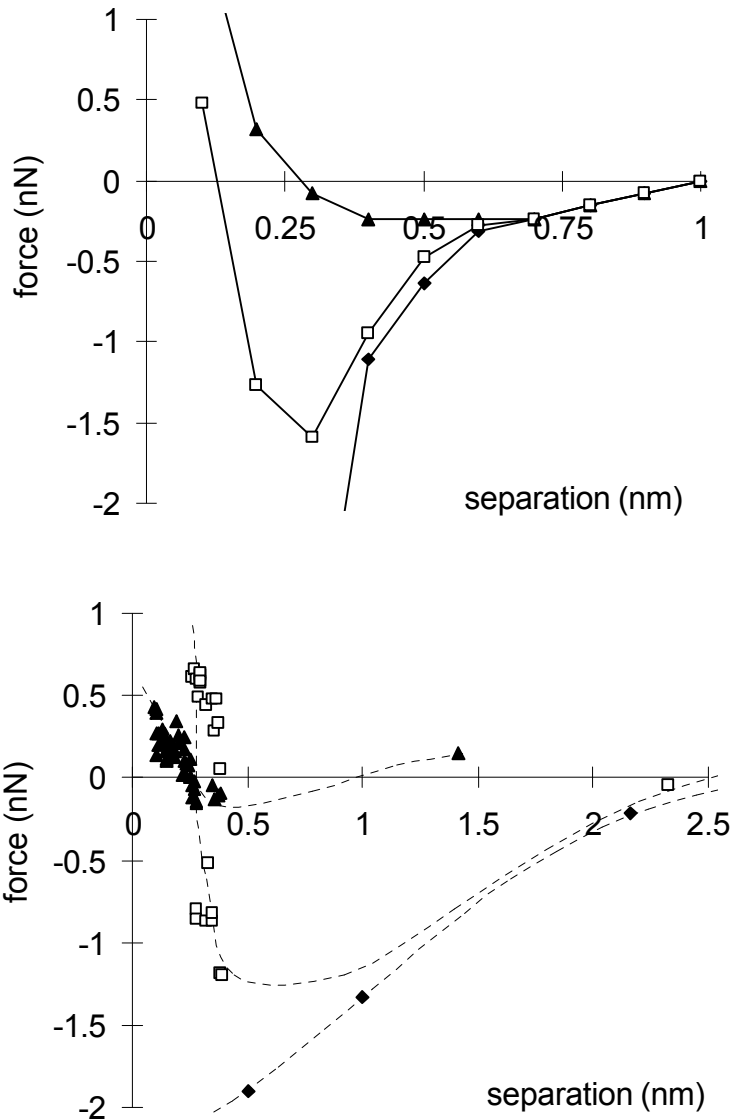


**Figure 4.** (top) Calculated interaction forces as a function of surface separation, varying charge density of C-S-H surface and bulk $CaX_2$ (X=OH or Cl) concentration: solid triangle: 0.16C/m² and 1 mM; open square: 0.32 C/m² and 20 mM; solid diamond: 0.57 C/m² and 20, 40 and 80 mM. In the latter case, the different $CaX_2$ concentrations give rise to three overlapping curves. (bottom) Mean interaction forces measured between micrometric flat C-S-H surface and a C-S-H nanocrystal at the top of an AFM tip immersed in $Ca(OH)_2$ solutions of different concentrations: solid triangle: 0.8 mM; open square: 10.3 mM; solid diamond: 19.1 mM. In the latter

case, $CaCl_2$ has been added up to 80 mM, and this gives rise to two overlapping curves. Lines are only guides to eyes.

The bulk calcium concentration has been enhanced for the highest pH studied in Fig. 4 in the simulated study as well as in the experimental one. This has been done by adding calcium chloride up to a total calcium concentration in the bulk of 80 mM. The whole results (experimental and calculated) give rise to overlapping curves whatever the calcium concentration is. Therefore, the addition of a calcium salt up to 80 mM not seems to improve the cohesion if the surface charge density is high.

## 3.2 Addition of alkaline ions

The competition between counterions of different valency is an important property, which has a profound influence on the cohesion of cement. Actually, concrete may contain reactive silica aggregates which, under basic conditions, form polysilicate ions in the solution and trap the calcium ions. In this extreme case, only monovalent counterions remain and the interaction turns repulsive promoting cracks in the structure. With the addition of small amounts of sodium salt in a C-S-H suspension, no major changes should be expected in the surface forces. With larger amounts, however, there ought to be a competition between calcium and sodium counterions for the surface, leading to a weakening of the cohesion. The interesting question is at which sodium salt concentration this becomes an important effect.
One set of experiment of interest is when calcium ions are replaced by sodium ions, keeping the hydroxyde concentration high. This means that pH and consequently the surface charge density are kept high, whereas the original divalent calcium counterions are replaced by the monovalent sodium ions. Fig. 5 shows that replacing calcium hydroxyde with sodium hydroxyde does not alter the cohesion unless the calcium concentration drops to submillimolar concentrations. If both the concentration of divalent cations in the bulk and the surface charge density are reduced and sodium ions are added (Fig. 6), then a weakened cohesion is seen and a primary maximum (repulsion) appears.
This reduction of the cohesion is a consequence of ion competition. That is, with increased bulk sodium concentration more monovalent counterions will enter the confined solution leading to an increase of the system entropy. At high surface charge density, calcium is favoured as counterions and a high bulk sodium concentration is needed to exchange the calcium ions in the confined solution. A high surface charge density favors calcium ions as counterions.
The general feature of adding salt is that nothing happens except under rather extreme conditions. That is, large amounts of a sodium salt are required to extinguish the cohesion, and at high pH, it is essentially impossible to salt out the attractive force, except if calcium concentration

tends towards zero. These features are in perfect agreement with which is empirically observed about concrete.
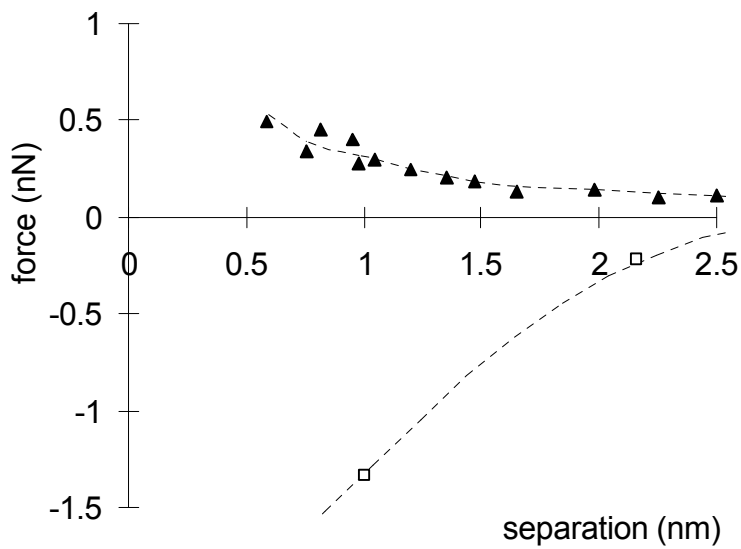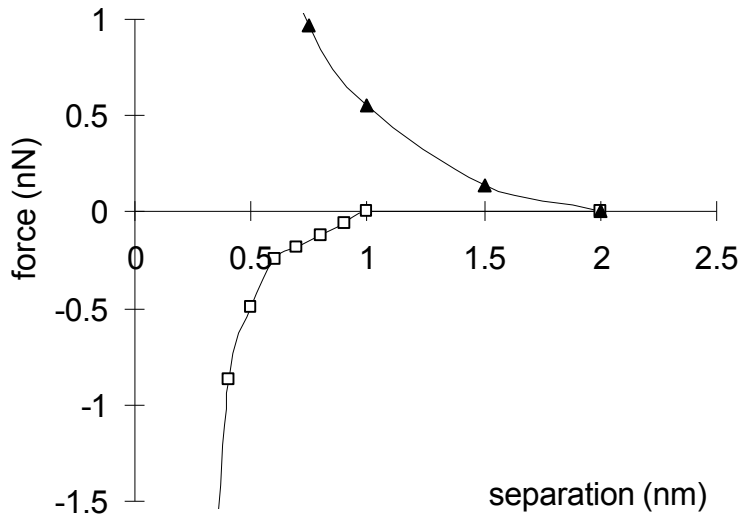


**Figure 5.** (top) Calculated interaction forces as a function of surface separation with constant hydroxyde concentration equal to 40mM but a varying Ca/Na ratio in the bulk solution: open square: 20 mM $Ca^{2+}$ and no $Na^+$; solid triangle: no $Ca^{2+}$ and 40 mM $Na^+$. The surface charge density is 0.57 C/m². (bottom) Mean interaction forces measured by AFM at pH 12.5: open square: 19.1 mM $Ca^{2+}$ and no $Na^+$; solid triangle: 0.36 mM $Ca^{2+}$ and 33.78 mM $Na^+$. Lines are only guides to eyes.
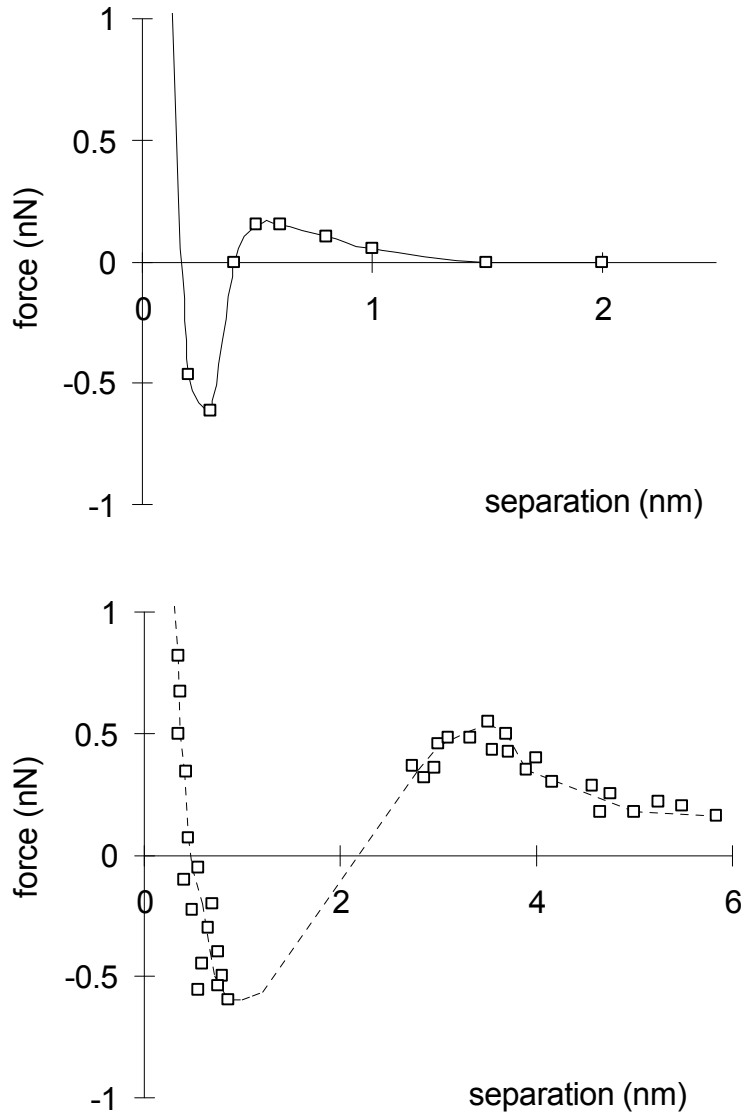
**Figure 6.** (top) Calculated interaction forces as a fu nction of surface separation when adding sodium nitrate: The surface charge density is 0.32 C/m². The concentrations of $Ca^{2+}$ and $Na^+$ are 1 and 100 mM respectively. (bottom) Mean interaction forces measured by AFM at pH 11. The concentrations of calcium hydroxyde and sodium nitrate are 4.4 and 20.98 mM respectively. Lines are only guides to eyes.

## 4. Conclusion

The present work describes the essential interactions that occur between particles in cement paste. In conditions representative of the pore solution of a cement paste, the pressure between C-S-H particles is about 30 MPa. The robustness of cement is explained by the Coulomb interactions between the charged surfaces of the C-S-H particles and the ions

confined between these surfaces. This finding may explain the robustness of setting and hardening of cement. Despite large variations in composition and environmental conditions, the cement cohesion is preserved except under rare extreme conditions. Pure repulsion can only occur if almost all calcium ions are replaced by sodium in the bulk solution. Calcium and sodium ions compete for the charged surfaces and the concentration ratio of $Na^+$ and $Ca^{2+}$ in the bulk has to be very high in order to destroy the cohesion, especially when the pH is high. It may be locally the case in concrete in which the alkali silica reaction occurs, promoting cracks in concrete.

# References

[1] S. Gauffinet, E. Finot, E. Lesniewska, A. Nonat, Observation directe de la croissance d'hydrosilicate de calcium sur des surfaces d'alite et de silice par microscopie à force atomique, Compte Rendu de l'Académie des Sciences de Paris 327 (1998) 231-236

[2] S. Garrault, A. Nonat, Hydrated layer formation on tricalcium and dicalcium silicate surfaces: Experimental study and numerical simulations, Langmuir 17 (2001) 8131-8138

[3] S.P. Jiang, J.C. Mutin, A. Nonat, Studies on mechanism and physico-chemical parameters at the origin of the cement setting, I. The fundamental processes involved during the cement setting, Cem Concr Res 25 (1995) 779-789

[4] S.P. Jiang, J.C. Mutin, A. Nonat, Studies on mechanism and physico-chemical parameters at the origin of the cement setting, II. Physico-chemical parameters determining the coagulation process, Cem Concr Res 26 (1996) 491-500

[5] L. Nachbaur, J.C. Mutin, A. Nonat, L. Choplin, Dynamic mode rheology of cement and tricalcium silicate pastes from mixing to setting, Cem Concr Res 31 (2001) 183-192

[6] J.C. Maso, Le béton hydraulique, Presses de l'Ecole Nationale des Ponts et Chaussées, Paris, 1982, pp. 275-293

[7] C.J. Rueb, C.F. Zukoski, Interparticle attractions and the mechanical properties of colloidal gels, Materials Research Society Symposium Proceeding, Pittsburg, (1991) 279-286

[8] L. Guldbrand, B. Jonsson, H. Wennerstrom, P. Linse, Electrical double layer forces. A Monte Carlo study, J Chem Phys 80(5) (1984) 2221-2228

[9] R. Kjellander, S. Marcelja, Inhomogeneous Coulomb fluids with image interactions between planar surfaces, J Chem Phys 82 (4) (1985) 2122-2135

[10] J. P. Valleau, R. Ivkov, G.M. Torrie, Colloid stability: the forces between charged surfaces in an electrolyte, J Chem Phys 95 (1991) 520-532

[11] A. Delville, Monte Carlo simulations of the mechanical properties of charged colloids, Langmuir 10 (1994) 395-402

[12] R. Pellenq, M. Crespin, N. Lequeux, C. Menager, L. Costalin, A. Delville, J.M. Caillol, H. Van Damme, A (NTV) Monte-carlo study of the stability of charged interfaces application to cement and clay minerals, Second Rilem Workshop on Hydrationand Setting, Rilem Editions, Dijon, France 1997, pp. 63-86

[13] P. Kékicheff, S. Marcelja, TJ. Senden, V.E. Shubin, Charge reversal seen in electrical double layer interaction of surfaces immersed in 2:1 calcium electrolyte, J Chem Phys 99 (1993) 6098-6113

[14] S. Lesko, E. Lesniewska, A. Nonat, J.C. Mutin, J.P. Goudonnet, Investigation by atomic force microscopy of forces at the origin of cement cohesion, Ultramicroscopy 86 (2001) 11-21

[15] H. Viallis-Terrisse, A. Nonat, J.C. Petit, Zeta-potential study of Calcium Silicate Hydrate interacting with alkaline cations, Journal of Colloid and Interface Science 244 (2001) 58-65

[16] C Plassard, E. Lesniewska, I. Pochard, A. Nonat, Investigation of the surface structure and elastic properties of calcium silicate hydrates at the nanoscale, Ultramicroscopy 100 (2004) 331-338

[17] W.A. Ducker, T.J. Senden, R.M. Pashley, Direct measurement of colloidal forces using an AFM, Nature 353 (1991) 239-241

[18] C. Labbez, B. Jönsson, I. Pochard, A. Nonat, B. Cabane, Surface charge density and electrokinetic potential of highly charged minerals: experimental and Monte Carlo simulations on Calcium Silicate Hydrate, Journal of Physical Chemistry B 110 (2006) 9219-9230

[19] M. Lund, B. Jönsson, T. Pedersen, Activity coefficients in sea water using Monte Carlo simulations, Mar Chem 80 (2003) 95-101

[20] B. Jönsson, A. Nonat, C. Labbez, B. Cabane, H. Wennerström, Controlling the cohesion of cement paste, Langmuir 21 (2005) 9211-9221

[21] B. Jönsson, H. Wennerström, A. Nonat, B. Cabane, Onset of cohesion in cement paste, Langmuir 20 (2004) 6702-6709

[22] C Plassard, E. Lesniewska, I. Pochard, A. Nonat, Nanoscale experimental investigation of particle interactions at the origin of the cohesion of cement, Langmuir 21 (2005) 7263-7270

[23] R. Pellenq, J. Caillot, A. Delville, Electrostatic attraction between two charged surfaces: a N,V,T Monte Carlo simulation, J Phys Chem B 101 (1997) 8584-8594

[24] A. Delville, R. Pellenq, J. Caillot, A Monte Carlo (N,V,T) study of the stability of charged interfaces: a simulation on a hypersphere, J Chem Phys 106 (1997) 7275-7285

[25] H. van Damme, in: Dekker (Eds), Encyclopedia of Surface and Colloid Science, New York (2002) p 1087