

On the Formation of Cementitious C-S-H Nanoparticles: A Computational Bottom-up Approach

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Abstract: This work aims to highlight the importance of computational bottom-up approaches to describe the nanostructure of cementitious C-S-H gels. To this end two different ongoing studies will be presented. Firstly, the dependence of the mechanical properties upon the length of the silicate chains will be discussed with help of force-field calculations. Secondly, the underlying growth mechanisms which govern the formation of C-S-H nanoparticles will be studied by means of *ab-initio* and Molecular Dynamic calculations.

Introduction

The C-S-H (Calcium silicate hydrate) gel is definitely the most important hydration product of cement based materials. It constitutes about 60-70% of the fully hydrated cement paste, and is responsible for most of the properties of cement-based materials. From a compositional point of view, the C-S-H gel is often characterised by its Ca/Si ratio, which turns to be in the range that goes from 0.7 to 2.3. This variable composition explains why, though intensively characterised by techniques like SEM, TEM, NMR, etc [1], many features of the nanostructure of C-S-H gel remain un unravelled.

Much of the existing knowledge on the nanostructure of C-S-H gel has been gained from structural comparisons with crystalline calcium silicate hydrates. In fact, several models have been proposed so far [1, 3-6] that draw structural analogies with tobermorite and jennite crystals. From these models, C-S-H gel can be approximately viewed as a layered structure, in which calcium oxide sheets are ribbed on either side with

silicate chains, and free calcium ions and water molecules are present in the interlayer space.

This vision based on layered crystal-like structures has served as the starting point for the few existing computational works which deal with the C-S-H gel [7-13]. However, the experimental evidence shows that if the structure of the C-S-H gel is actually composed of C-S-H crystals, these ones should have multiple defects and imperfections. For instance, ^{29}Si NMR experiments find only finite silicate chain lengths [4,22]. These chains follow the rule $m=3n-1$, where m is the number of Si atoms and n an integer. Although longer chains can exist, it is well established that dimers ($m=2$) and pentamers ($m=5$) are the most relevant ones [23].

Thus, it is clear that complementarily to the numerical approaches that resort on comparisons with perfect tobermorite and jennite species, a new one based on small and distorted pieces of them is strongly required.

This work aims precisely to illustrate two ongoing studies where this new viewpoint (what we call “bottom-up” approach) has found to be crucial. First, we discuss the consequences of the finite length of the chains that make up the C-S-H gel on the mechanical properties of cementitious C-S-H gels. Second, we go further, and we explore the growth mechanisms that lead to the formation of mentioned tobermorite and jennite pieces.

1. Mechanical properties of short tobermorite and jennite pieces

To the best of our knowledge, only a couple of computational works have dealt with the mechanical properties of cementitious C-S-H gels. The first one centred its attention into tobermorite-like crystals, and by employing a potential minimisation calculations predicted a Bulk modulus of 71.8 GPa [1]. The second one used first-principles calculations for describing foshagite crystals $[\text{Ca}_4\text{Si}_3\text{O}_9(\text{OH})_2]$ and predicted an average Young's modulus of 110 GPa [3].

Although comparable Young's moduli to those obtained theoretically are obtained by nanoindentation experiments for synthetic C-S-H nanocrystals [4], the measurements over actual cementitious samples show much lower values. Mechanical experiments over macroscopical samples of cement paste showed Bulk modulus of 17-18 GPa [5]. Similarly, ultrasonic sound experiments obtained a Young modulus of 18 GPa for mature cement pastes [6,7]. In more detail, nanoindentation experiments [8,9] revealed similarly that the Young's modulus of cementitious C-S-H gels exhibits a bimodal distribution with centres at ~ 20 GPa and ~ 30 GPa. Finally, the inverse analyses performed in nanoindentation works [10,11]

for the C-S-H gel estimated Bulk and Shear modulus of 15 GPa and 9.7 GPa respectively for the C-S-H gel. In other words, the literature values of C-S-H crystals overestimate four or five times the experimental results of C-S-H gels.

In a recent work [26], we have explained the origin of such a discrepancy. In this new paper we will summarise the main conclusions of this work, and will provide new data concerning the effect of Al for Si substitutions.

To assess the influence of the silicate chain length on the mechanical properties of cementitious C-S-H gels we have introduced defects in the crystalline structures of tobermorite 14 A (T_{∞}) and jennite (J_{∞}) so that their silicate chains have a finite length. We have limited ourselves to the cases of dimers (T2 and J2) and pentamers (T5 and J5).

From a computational point of view, we have followed the same scheme employed in Ref. [27] to describe atomic interactions and to simulate lattice dynamics. These calculations were done with parameterised two-body and three-body potentials [27] as implemented in the GULP code [28].

The elastic constant tensor was calculated from the second derivative matrix at the optimised structures. Then, the Bulk (K) and the Shear (G) moduli were determined from the elastic constants. From them and following the experimental procedure, both the average Young's modulus (E) and the Poisson's ratio (ν) were determined through the standard relations

$$E = \frac{9G}{3+G/K} ; \quad \nu = \frac{3-2G/K}{6+2G/K} \quad (1)$$

that assumes an isotropic media.

Specie	K (Gpa)	G (Gpa)	E (GPa)
T2	29 (14)	14 (8)	36 (19)
T5	21 (10)	10 (5)	25 (14)
T_{∞}	46 (25)	39 (21)	91 (49)
J2	29 (13)	11 (6)	29 (16)
J5	29 (15)	19 (10)	47 (25)
J_{∞}	43 (22)	26 (22)	64 (35)

Table 1.- The calculated mechanical properties for T2, T5, T_{∞} , J2, J5 and J_{∞} . In parenthesis we write the results after the Mori-Tanaka scheme (see text for further details).

Our calculated mechanical properties are given in Table 1. Note that there is a large dependence of the mechanical properties on the length of the silicate chains. The mechanical properties of T2 and J2 are approximately 50% lower than those of their perfect crystalline counterparts (T^∞ and J^∞). Nevertheless, these K, G and E values fail to reproduce the magnitude found experimentally. Our computed values of the Bulk, Shear and Young's modulus lay in the range 21-29 GPa, 9-19 and 25-47 GPa respectively, and they overestimate slightly the experimental results, $K=18$ GPa, $G=9.7$ GPa and $E=20-30$ GPa.

We have achieved to rationalise this disagreement with the experimental values by taking into account the intrinsic gel porosity. Following the recipe found in Ref. [23,29], we employed a Mori-Tanaka scheme [30] to account for the void space. In this approach the Bulk and Shear modulus of the C-S-H gel ($K_{C-S-H \text{ gel}}$ and $G_{C-S-H \text{ gel}}$) were written as $K_{C-S-H \text{ gel}} = \phi(1-\alpha)/(1-\alpha\phi) K$; $G_{C-S-H \text{ gel}} = \phi(1-\beta)/(1-\beta\phi) G$, where ϕ is the packing factor, $\alpha = 3K/(3K+4G)$, $\beta = (6K+12G)/(15K+20G)$ and K and G stand for the Bulk and Shear modulus of the C-S-H crystals respectively. The respective Young's modulus and the Poisson's ratio of the C-S-H gel can be calculated with Eq. 1. The results of Table 1 presented in parenthesis stand for the values obtained by such a Mori-Tanaka scheme with a packing factor of 0.7. The first thing that is worth noting is that for perfect structures the computed values are again larger than the experimental values. However, when the finite length of the silicate chains is taken into account this discrepancy disappears.

Encouraged by the ability of this computational scheme to estimate and predict the mechanical properties of cementitious C-S-H gels, we have committed ourselves to extend this study to the case of C-S-H gels with high Aluminium content. In fact, our research is currently devoted to study the effect of substitutions of Si by Al on the mechanical properties of the C-S-H gels.

Since such substitutions are known to occur mainly at the bridging sites [31-35] only these replacements will be considered. Furthermore, and as starting point for ulterior calculations, we will assume that the bridging sites are always occupied by Al ions. Our simulations have followed the same force-field procedure presented in Ref. [26]. Some preliminary results are presented in Table 2. It is interesting to note that, in general, the mechanical properties of the jennite-like structures are almost not affected by the substitutions. Differently, tobermorite-like species present a curious behaviour. For infinite chains ($m=\infty$) the substitution entails a marked fall for the mechanical properties. Compare for instance the Young modulus of T^∞ , $E = 91$ GPa, with the one of $T^{(Al)\infty}$, $E = 61$ GPa. However, the values found for T5 species, i.e. $K=21$ GPa, $G= 10$ GPa,

and $E = 25$ GPa, are clearly exceeded by those of $T^{(Al)}_5$ species, namely $K = 27$ GPa, $G = 13$ GPa and $E = 35$ GPa. This result suggests that the substitution of Si by Al ions favours the cohesion of short tobermorite-like structures.

Specie	K(GPa)	G(GPa)	E(GPa)
$T^{(Al)}_{\infty}$	38	25	61
$T^{(Al)}_5$	27	13	35
$J^{(Al)}_{\infty}$	38	24	60
$J^{(Al)}_5$	36	18	48

Table 2. Mechanical properties for tobermorite ($T^{(Al)}$) and Jennite ($J^{(Al)}$) with Al ions at the bridging sites. Both infinite ($m = \infty$) and short ($m = 5$) chains are considered.

2. Formation of T-like and J-like pieces.

This section aims to shed light on the mechanisms that take place in the formation of T-like and J-like unities, and combines some *ab-initio* simulations presented elsewhere [36] together with new molecular dynamic calculations.

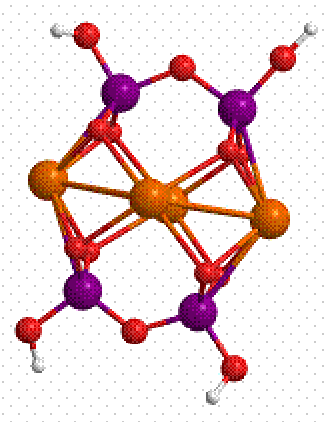


Figure 1. Ground state geometry of the inferred precursor (P) of tobermorite-like and jennite-like structures

As a first step to study the formation of small C-S-H pieces, an educated guess of a precursor (hereafter denoted by P) of both tobermorite-like and jennite-like dimeric structures has been selected. This structure is composed of two silicate chains sandwiched by a single calcium oxide layer, as seen in Fig. 1. From this P unit, increasingly complicated structures have been studied by aggregations of these units with Calcium ions. Basically two limit cases will be discussed. The first studied case (Subsection 2.1) corresponds to the aggregation of two P units with a

single calcium ion. This system, due to its Ca/Si=1.125 ratio, should lead to the appearance of T_2 units [18]. The second case (Subsection 2.2) aims to reproduce the formation J_2 units, so three more calcium ions have been incorporated into the simulations. The so formed system exhibits a Ca/Si ratio equals to 1.5. In both systems, hydrogen atoms have been conveniently removed to ensure electrical neutrality. Finally, Subsection 2.3 presents some preliminary molecular dynamic calculations which attempt to simulate the polymerisation of silicic acids ($\text{Si}(\text{OH})_4$) in presence of calcium ions.

2.1 Formation of T_2 -like units

To study the aggregation of two $\text{P}^{(-)}$ units and a single Ca^{++} ions, we have performed *ab-initio* calculations at the Hartree-Fock (HF) level with a DZV-d basis set and by means of GAMESS code [20].

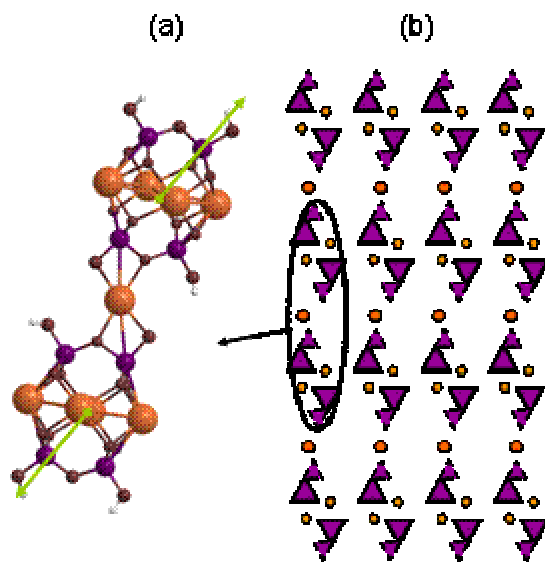


Figure 2. (a) Found relaxed geometry for the self-assembly of two $\text{P}^{(-)}$ units and one calcium ion. To stress the dipole-dipole origin of the so-formed structure, the dipole moments of the P units are indicated by arrows. (b) Schematic representation of a tobermorite crystal, where a piece as the one calculated in (a) is marked.

Ours simulations have revealed that, independently of the initial configuration, the reached stable morphology is the one showed in Fig. 2a. Different points should be discussed in view of it. First, we would like to draw the attention to the fact that the so formed structure reproduces indeed the basic morphology of a T_2 unit (see the schematic representation showed in Fig 2(b)). Secondly, it is remarkable that the existence of such a structure can be explained in terms of dipole- dipole

interactions. Both $P^{(-)}$ units have a quite large dipole moment (10.75 Debyes). Therefore, substantial energy gain can be obtained by forming a bigger structure with vanishingly dipole moment. In fact, the dipole moment of the T_2 -like structure is 3.8 Debyes

2.2 Formation of J2-like units

But what does it happen when more calcium ions are present? It seems reasonable to suppose that in this case, the possibility of larger numbers of bonds could overcome the energetic cost in terms of dipole-dipole interaction. This is indeed what our *ab-initio* simulations have shown. Following the same scheme employed above (i.e. HF calculations and DZV-d basis set) the most stable configuration that our calculations have found for two $P^{(-4)}$ units and four Ca^{++} ions is the one represented in Figure 3 (a). Comparing that configuration with the schematic representation of jennite crystal showed in Figure 3(b) it is easy to observe that the resulting structure actually corresponds to a single layer of a J_2 structure. Finally it is worth noting that the growth mechanism is in this case just bond-formations, since the formed piece of jennite exhibits a very large dipole moment (above 25 Debyes). Thus, it seems reasonable to think that ulterior dipole-dipole interactions between the J_2 units could yield still bigger structures. Ongoing research is currently in such a direction.

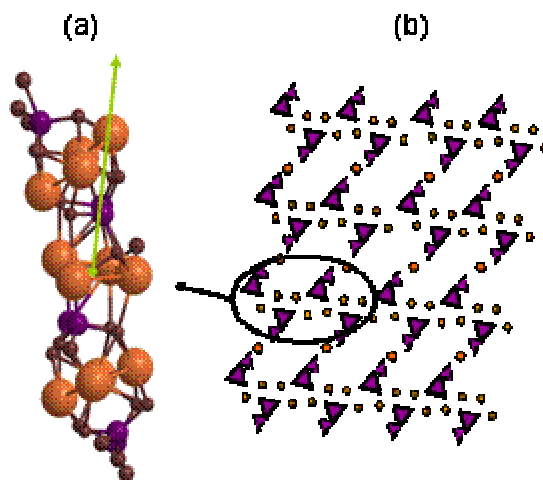


Figure 3. (a) Found relaxed geometry for the self-assembly of two $P^{(-4)}$ units and four calcium ions. To stress the large dipole moment of the so-formed structure, the dipole moments of the P units are indicated by arrows. (b) Schematic representation of a jennite crystal, where a piece as the one calculated in (a) is marked.

2.3 A preliminary Molecular Dynamics Study

To go further in the bottom-up approach, we have attempted to reproduce the formation of C-S-H gels by simulating the polymerisation of silicic acids ($\text{Si}(\text{OH})_4$) in presence of solvated Ca ions ($\text{Ca}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$). To this end we have randomly placed 157 $\text{Si}(\text{OH})_4$ molecules and 355 $\text{Ca}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ molecules into a cubic simulation cell. Later we have performed molecular dynamic simulations within the canonical ensemble (NVT) by means of the TREMOLO code [39].

The employed potential energy function to account for Si, O and H interactions is the one of Litton and Garofalini. The detailed potential functions and parameters are given in the literature [40]. To model the Si, O and Ca interactions we employ a variant of the Feuston and Garofalini potential model given by Su and Garofalini [41]. Additionally, we apply a screened Coulomb potential term $q_i \cdot q_j / r_{ij} \cdot \text{erfc}(r_{ij} / \beta_{ij})$ to model the repulsive interaction of Ca and H. Here, q_i denotes the ionic charge of particle i and r_{ij} denotes the distance between particle i and particle j , β_{ij} is a interaction-dependent parameter and erfc stands for the complementary error function. Here, we employ for the parameter β_{ij} a value of 2.31 Å for an atom pair Ca-H. The ionic charges for calcium ions and hydrogen we use are +2 and +1, respectively.

The NVT-simulations have been carried over 1500 ps at 1800 K. This high temperature was adopted to accelerate polymerisations and reduce drastically the computational time. Although the simulation temperature may seem to be unrealistically high, the thermal energy (KT) is only about 20% of the condensation energies involved in the formation of the siloxane bonds (Si-O-Si). Thus, the employment of such a high temperature to study the connectivity of the silicate chains is well justified. The number and types of siloxane bonds were computed to determine the connectivity of the silicate chains (namely, the Q_n distributions).

In Figure 4, we have represented the calculated Q_n distributions. It is remarkable that, contrary to the case of the polymerisation of pure silicic acids, negligible amounts of Q_3 and Q_4 sites are observed. This finding is in perfect agreement with the experimental evidence in cementitious systems, where linear forms are dominant. From the Q_n distributions we have also extracted the mean chain length (MCL) of the silicate chains by employing the equation [31] $\text{MCL} = 2(Q_1 + Q_2) / Q_1$. A value of $\text{MCL} = 2.5$ has been obtained, showing that most of the silicate chains are dimers. This fact is also in good concordance with the experiments [4,6].

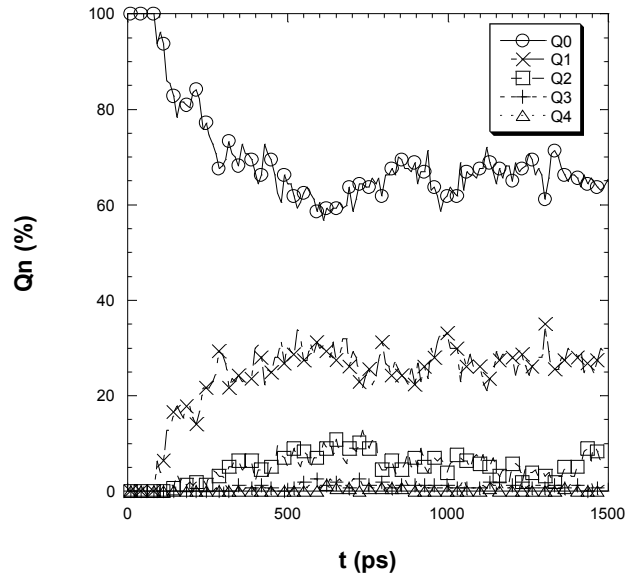


Figure 4. Time evolution of the Qn peaks.

REFERENCES

- [1] Ramachandran, V. S., Beaudoin, J. J. Handbook of Analytical Techniques in Concrete. (William Andrew Publishing, New York, 2001).
- [2] Taylor H. F.; Proposed structure for calcium silicate hydrate gel. J. Am. Ceram. Soc. **69** (6) (1986) 464-467.
- [3] Richardson I. G. and Groves G. W.; *Cement and Concrete Research* 22 (1992) 1001-1010.
- [4] Cong X. and Kirkpatrick R. J.; *Adv. Cem. Based Mater.* **3** (1996) 144-146
- [5] Nonat A. and Lecoq X. *The structure, stoichiometry and properties of C-S-H prepared by C₃S hydration under controlled conditions. Nuclear Magnetic resonance Spectroscopy of Cement-Based Materials*, Springer, Berlin (1998) 197-207.
- [6] Chen J. J., Thomas J. T, Taylor H. F. W., and Jennings H. M.; *Cement and Concrete Research* **34** (2004) 1499-1519.

- [7] Jönsson B., Nonat A., Labbez C., Cabane B. and Wennerström H.; *Langmuir* **21** (2005), 9211-9221.
- [8] Pellenq R. J.-M., Caillol J. M., and Delville A.; *J. Phys. Chem. B* **101** (1997) 8584-8584.
- [9] Delville A. and Pellenq R. J. –M.; *Molecular Simulation* **24**, (2000) 1-24.
- [10] Derjaguin B. and Landau L. D; *Acta Physicochim. URSS* ,**14**, (1941) 635; Verwey, E. J. W. And J.T.G. Overbeek; *Theory of the Stability of Lyophobic Colloids*; Elsevier: New York, 1958.
- [11] Gmira A., Zabat M., Pellenq R.J.-M. and Van Damme H.; *Materials and structures/Concrete Science and Engineering*, **37** (2004) 3-14.
- [12] Faucon P. et al.; *J. Phys. Chem B* **103** (1999) 7796-7802.
- [13] Kalinitchev A. and Kirkpatrick R.J.; *Chem. Mater.* **14** (2002) 3539-3549
- [14] Brough, A. R., Dobson, C. M., Richardson, I. G., Groves, G. W., *Journal of Materials Science* 29, 3926-3940 (1994).
- [15] Richardson I. G.; *Cement and Concrete Research* **34** (2004) 1733-1777.
- [16] A.Gmira, M.Zabat, R.J.-M.Pellenq and H.Van Damme, *Concrete Science and Engineering*, 37, 3-14 (2004).
- [17] J.L.Laugesen in “Nanotechnology in Construction” Symposium Proceedings, P.J.M.Bartos Editor, RSC Pub, (2004).
- [18] C.Plassard, E.Lesniewska, I.Pochard, A.Nonat, *Ultramicroscopy*, 100, 331-338 (2004).
- [19] S.W.Cho, C.C.Yang, R.Huang, *J.Marine Sci. Tech.*, 10, 8-13, (2002).
- [20] L.P.Martin, E.A.Lindgren, M.Rosen and H.Sidhu, *Mater. Sci. Eng.*, 279, 87-94 (2000).
- [21] A.Bourniz, D.Sorrentino, C.Vernet and F.C.Tenoudji, in “Hydration and Setting“ A.Nonat, Editor, Rilem Pub SARL (2000).
- [22] P. Acker. Swelling, shrinkage and creep: a mechanical approach to cement hydration, *Materials and Structures / Concrete Science and Engineering*, Vol. 37, 237-243 (2004).

- [23] G.Constantinides,F -J.Ulm, Cement and Concrete Research, 34, 67-80, (2004).
- [24] F.-J. Ulm, G.Constantinidis and F.H.Heukamp. Is concrete a poromechanical material?- A multiscale investigation of poroelastic properties. Materials and Structures / Concrete Science Engineering, Vol. 37, pp 43-58 (2004).
- [25] O.Bernard, F.-J.Ulm and E.Lemarchand. A multiscale microimechanics-hydration model from the early-age elastic properties of cement-based materials. Cement and Concrete Research 33, 1293-1309 (2003)
- [26] H. Manzano, J.S. Dolado, A. Guerrero and A. Ayuela. Mechanical properties of cementitious crystalline calcium-silicate-hydrates: comparison with C-S-H gels. Submitted to Physica Status Solidii A.
- [27] A.Gmira "Étude texturale et thermodynamique d'hydrates modèles du ciment", Thesis, University of Orléans, France, (2003).
- [28] J.D.Gale and N.J.Henson, JCS Faraday Trans., 90, 3175 (1994).
- [29] H.M.Jennings in "Nanotechnology in Construction" 2nd Symposium Proceeding; Edited by Peter JM Bartos, Yolanda de Miguel and Antonio Porro, ISBN: 2-912143-87-X (2006).
- [30] T.Mori and K.Tanaka, Acta Metallurgica 21 (5), 1605-1609 (1973)
- [31]I. G. Richardson; The nature of C-S-H in hardened cements. Cement and Concrete Research 29 (1999) 1131-1147
- [32]I. G. Richardson and G.W. Groves. The incorporation of minor ad trace elements into calcium silicate hydrate (C-S-H) gel in hardened cement pastes. Cement and Concrete Research 23 (1993) 131-138
- [33]I.G. Richardson et al. Location of aluminium in substituted calcium silicate hydrate (C-S-H) gels as determined by 29 Si and 27 Al NMR and EELS. J. Am. Ceram. Soc. 76 (1993) 2285-2288
- [34] M.D. Andersen et al.. Characterisation of white Portland cement hydration and the C-S-H structure in the presence of sodium aluminates by 27 Al and 29 Si NMR spectroscopy. Cement and Concrete Research 43 (2004) 857-868

[35] M. D. Andersen et al.; Incorporation of Aluminium in the Calcium Silicate Hydrate (C-S-H) of Hydrated Portland Cements: A High-Field 27 Al and 29 Si MAS NMR investigation. *Inorganic Chemistry* 42 (2003) 2280-2287.

[36] H. Manzano, A. Ayuela and J.S. Dolado. On the formation of cementitious C-S-H nanoparticles. Accepted in *The Journal of Computer-Aided Materials Design*.

[37] Richardson I. G.; *Cement and Concrete Research* 34 (2004) 1733-1777.

[38] GAMESS – General Atomic and Molecular Electronic Structure System. Schmidt M.W, Baldrige K.K., Boatz J.A, Elbert S.T, Gordon M.S., Jensen J.J., Koseki S., Matsunaga N., Nguyen K.A., Su ., Windus T.L., Dupuis M., Montgomery J.A.. *J.Comput.Chem.* **14**, (1993) 1347-1363.

[39] M. Griebel, S. Knapek, G. Zumbusch and A. Caglar; *Numerische Simulation in der Moleküldynamik; Numerik, Algorithmen, Parallelisierung, Anwendungen*, Springer, Berlin, Heidelberg, 2003. See also the web page <http://www.ins.uni-bonn.de/info/md>.

[40] D. A. Litton and S. H. Garofalini; Modeling of hydrophilic wafer bonding by molecular dynamics simulations; *J. Appl. Phys.*, Vol. 89, No. 11, 1 June 2001

[41] X. Su and S. H. Garofalini; Role of Nitrogen on the Atomistic Structure of the Intergranular Film in Silicon Nitride: A Molecular Dynamics Study; *J. Matls. Res.* 19 (2004) 3679-3678