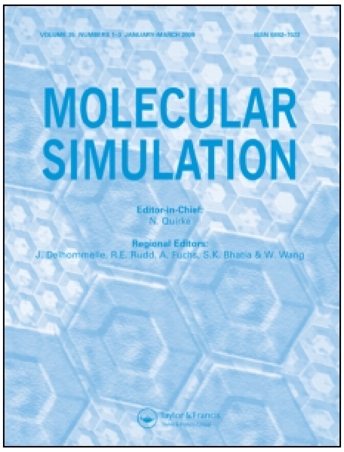

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Structural models of random packing of spheres extended to bricks: simulation of the nanoporous calcium silicate hydrates

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To cite this Article Morales-Flórez, Victor and Brunet, Fabrice(2009) 'Structural models of random packing of spheres extended to bricks: simulation of the nanoporous calcium silicate hydrates', Molecular Simulation, 35: 12, 1001 — 1006

To link to this Article: DOI: 10.1080/08927020903033117

URL: http://dx.doi.org/10.1080/08927020903033117

Molecular Simulation
Vol. 35, Nos. 12–13, October–November 2009, 1001–1006

Structural models of random packing of spheres extended to bricks: simulation of the nanoporous calcium silicate hydrates

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(*Received 20 January 2009; final version received 5 May 2009*)

Structure simulation algorithms of random packing of spheres and bricks have been developed. These algorithms were used to reproduce the nanostructure of the cementitious calcium silicate hydrates. The textural parameters (specific surface area, porosity, pore size, etc.) of a calcium silicate hydrates (C-S-H) sample, the main binding phase of hydrated cements, have been derived from N_2-physisorption experiments. At the same time, these parameters have been simulated by using a sphere-based structural model, where the spheres are randomly packed according to several hierarchical levels. The corresponding algorithm has been extended for managing cuboids instead of spheres. The C-S-H sample density is successfully predicted by considering the presence of water in pores defined by the sphere network within 10-nm-size globules and assuming a tobermorite-like skeleton. Simulations with bricks ($3 \times 2 \times 1.4\,\mathrm{nm}^3$) yield also textural parameters that are consistent with N_2-physisorption data, but with a globule radius (22 nm) twice as big as that obtained when using spheres.

Keywords: structure; nanoporous; hierarchical model; C-S-H; bricks

1. Introduction

Structural simulation by a porous medium has provided for decades a useful approach to reproducing and understanding nanostructured materials and for predicting their properties. Often, for the sake of simplicity, spheres are considered as elementary building units instead of particles with a more realistic geometry. This simplistic approach has even been ironised through the joke about the physicist rancher's friend who, for managing the cattle, considers the cows as spheres. Calcium silicate hydrates (C-S-H) represent an example of a nanoporous material for which the geometry of the elementary particles is believed to be closer to cuboids than to spheres. This was a major incentive to develop a C-S-H structural model based on randomly packed spheres, arranged in several hierarchical levels, and to extend the corresponding algorithm to elementary particles of cuboid geometry.

This hydrated silicate plays a binding role in cements. It is a quasi-mineral of variable composition, which has focussed the attention of the scientific community for decades [1,2]. Several features related to the C-S-H nanostructure are still poorly understood and still hardly discussed, such as the C-S-H-specific surface area, the pore size, or the size, shape and chemical composition of the elemental particles [3–8]. The central role of C-S-H on the properties of the hydrated cement characteristics as mechanical properties, diffusivity, reactivity due to weathering, durability of most of the constructions, etc. enhances and continuously renews the interest of this research [9].

Nevertheless, there is a general agreement on the description of the C-S-H phase as a nanoporous medium formed by random packing of particles [10]. These particles have nanometric sizes, and they arrange according to clusters ordered in several hierarchical levels. They are formed by linking silica tetrahedra chains in the so-called *dreierketten* structure, bound to calcium atoms layers and enclosing water molecules. The chemical composition of the particles can vary widely depending on the synthesis process. It has been found by chemical analysis coupled to transmission electron microscopy that the Ca/Si ratio of C-S-H nanoparticles can vary locally from 0.7 to 2.3 [11]. Likewise, the structural data obtained from different types of C-S-H can be very different depending on the characterisation means (SAXS, SANS, N_2 physisorption, etc.). Moreover, very different particle shapes, porosities and densities were found in C-S-H phases, the heterogeneity in C-S-H properties has been reduced by classifying them into two types [7], which coexist in hydrated cements. Actually, this description in two groups is not free from discussion [12,13]. For example, the stoichiometry of C-S-H formed between clinker grains of cements has recently been established [3] to be $(CaO)_{1.7}(SiO_2)(H_2O)_{1.8}$.

This composition, and especially the SiO_2/H_2O ratio (~ 1.8), does not match that of tobermorite, $Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$ ($SiO_2/H_2O \sim 0.8$), to which C-S-H are

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ISSN 0892-7022 print/ISSN 1029-0435 online

DOI: 10.1080/08927020903033117
http://www.informaworld.com

usually compared. Likewise, the mean calcium to silicon ratio (Ca/Si) in C-S-H of common cements is roughly twice that of tobermorite. Since the model by Feldman and Sereda [14], several structural models have been proposed to account for elemental particle formation in C-S-H [15,16] and for the final nanometric structure [3]. Hence, different particle shapes as irregular grains [3], spheres [7,17] as well as lamellae-like [18] or brick-like particles [8] have been suggested. Whatever their shape, these nanoparticles are randomly packed and this packing is organised according to several hierarchical levels [19–21].

Following Jennings [8], who proposed that the shape of the structural elements of C-S-H is a cuboid, instead of spheres, we introduce here a computational algorithm to account for C-S-H nanostructure based on spheres and cuboids.

2. Experimental

A C-S-H sample was synthesised according to the coprecipitation method proposed by Sugiyama [22], which consists of adding, under stirring, a solution of Na_2SiO_3 to a filtered CaO-saturated solution. CaO was obtained by decarbonation of $CaCO_3$ (Merck, Darmstadt, Germany; 99%) at 1100°C for 24 h, whereas a Na_2SiO_3 solution (Merck, $1 l = 1.35$ kg) was diluted to the desired concentration. The C-S-H sample was synthesised in a solution with a Ca/Si ratio of 1, yielding a pH of around 11.9. This solution was aged for up to 21 days in sealed recipients at ambient temperature. Finally, the supernatant was removed and the residual solid product was dried at ambient conditions in the presence of silica gel in a CO_2-free atmosphere.

Prior to N_2 physisorption experiments, dried sample was milled and put into a furnace box at 100°C under vacuum for 24 h in order to remove adsorbed water and other volatile contaminants. A physisorption experiment was carried out at 77 K in a Sorptomatic automatic device (Fisons Instruments, San Carlos, CA, USA). The bulk density ρ measurement was possible by measuring both weight and volume of a piece with a well-defined geometry (Table 1).

The simulation work was undertaken in FORTRAN 95, compiled under the developing environment Plato3 Integrated Developing Environment by Silverfrost, Ltd [23] in a DELL laptop provided of an Intel 1.83 GHz. The simulation of conventional systems typically took from minutes to days. Due to the random nature of this algorithm, two identical sets of parameters of simulation yield slightly different systems. Therefore, for each set, between 5 and 10 different replicas were built and characterised. The actual value of any simulation result for each model is taken as the mean value.

3. Simulated structures

For creating the structural models for the C-S-H, the Cluster Model, an algorithm already designed to simulate nanoporous structures [24,25] was used. This algorithm works as follows: it places an elemental particle in the space and randomly surrounds it with other similar particles at a previously defined contact distance d. Then, each of the newly placed particles is surrounded with similar particles, always taking care to avoid overlap (avoiding more overlapping than allowed by the given contact distance d) with the already placed ones. This process can be repeated as many times as needed with each new particle. In this way, a one-level random packing cluster of particles is built. Then, the size of this cluster is measured and it is randomly packed with identical clusters in a similar manner, forming a two-level random system. This new two-level system can then be measured as well, and randomly packed with itself, and so on. Different elemental particle sizes, number of levels, number of surrounding particles, contact distances, etc. yield different texture values; consequently, these parameters have to be tuned in order to obtain a structure of given properties.

When working with spheres as elemental particles, the reduced unit is taken as the diameter of the sphere whereas, when dealing with cuboids, it is the length of their space diagonal. Except if indicated explicitly, reduced units will be used throughout this study. For obtaining specific surface area, porosity, specific porous volume, pore size distribution (PSD), etc. Monte Carlo algorithms and geometrical calculi were implemented. A deeper description of the algorithm and the techniques used for characterisation can be found in references [24,25].

When analysing nanostructures by simulated gas adsorption experiments, the finite volume of the adsorbed molecule is a relevant parameter. So, for reproducing the experimental values obtained by N_2 physisorption, a single

Table 1. Texture values of the C-S-H sample obtained by N_2 physisorption and values of the structural models.

System	Density (g/cm^3)	Porosity (%)	S_{BET} (m^2/g)	V_p (cm^3/g)	R_p (nm)	Globule radius (nm)
C-S-H sample	1.77	25	63	0.139	2	–
HydModel	1.75 ± 0.02	23.90 ± 0.01	62 ± 0.9	0.137 ± 0.004	2	10
DryModel	1.53 ± 0.09	35 ± 4	260 ± 10	0.24 ± 0.04	0.6	10
BrickModel	1.61 ± 0.08	33 ± 3	230 ± 10	0.21 ± 0.03	–	22.2 ± 0.1

HydModel emulates texture of calcium silica with intraglobular water, whereas *DryModel* represents the solid skeleton without intraglobular water. *BrickModel* simulates the dry structure with bricks instead of spheres as the elemental particle. (–) No data available.

test particle with a finite size of 0.227 nm, i.e. equal to the size of the nitrogen molecule, was used. In the case of bulk density ρ and porosity P measurements, a mathematical point was used as test particle. Other parameters such as skeleton density ρ_{sk}, i.e. the density of the solid skeleton that forms the porous structure, or specific porous volume V_{p} were calculated by simple relationships (Equations (1) and (2)):

$$V_{\mathrm{p}} = \rho^{-1} - \rho_{\mathrm{sk}}^{-1}, \quad (1)$$

$$P = \rho V_{\mathrm{p}}. \quad (2)$$

3.1 Extension to non-spherical particles

Up to now, the Cluster Model was designed to use spheres as elementary particles. Here, the algorithm has been extended to the use of cuboids, namely, brick-like parallelepipeds with six rectangular faces. In this framework, each elemental particle is considered to be a bulk brick of a given density, where each of the three edge lengths a, b, c can be defined independently. This extended algorithm works in a similar fashion as for spheres, but in addition to the random location of each brick, a random orientation is also defined. Thus, for each brick, a set of six parameters is needed: the three spatial coordinates of the brick centre and three angular coordinates (Euler's angles), which determine its rotation with regard to a universal axis. The main geometrical parameters that characterise these brick-cluster models are the three edge lengths a, b, c of the elemental brick, the contact distance between them and between higher hierarchical levels, the number of shells of bricks in each hierarchical level and the number of levels.

The algorithm starts by placing one brick centred at the coordinate origin with three perpendicular basis axes normal to its faces. This way, the universal reference system is defined. From now on, random positions and orientations will be defined for any new brick regarding this reference. As shown in the following, it might also be convenient to define a local basis for each brick considering the origin of this basis at the centre of the brick and rotated regarding to the brick's Euler's angles. In order to prevent the occurrence of bricks disconnected from the rest of the structure, every new brick will have to overlap with, at least, one which has already been placed.

When dealing with cuboids, the distance between neighbouring brick centres only cannot be used as an overlapping criterion. Therefore, the overlapping test procedure was implemented as follows.

Each new brick is characterised by six coordinates generated randomly. The eight corners of this new brick along with the eight corners of the nearest brick are consecutively transformed, first, to the universal system, and then to the reference system of the other brick. This way, any given point (x, y, z) will fall inside the brick only and only if all the following conditions are satisfied:

$$|x| < a/2,$$

$$|y| < b/2,$$

$$|z| < c/2,$$

a, b, c being the three edge lengths of the bricks. If these conditions are met, the new brick is added to the structure. Obviously, it is a first approach of the problem since not all the possible overlapping configurations are covered with this algorithm.

The applications previously generated to retrieve the texture parameters of porous structures made of spheres were extended to handle cuboids. Typical C-S-H structural models built with this algorithm contain several thousands of particles.

4. Results

4.1 Real system

The physisorption isotherm is plotted in Figure 1. This curve is typical for meso- or microporous materials (type IV) with hysteresis loops, which indicate a structure formed by assemblages of rigidly joint particles [26]. The hysteresis loop shows a very regular pore shape and size distribution. The PSD obtained by the Barrett–Joiner–Halenda method [27] is extremely sharp centred on a pore radius of 2 nm as can be seen in Figure 2. Specific surface area S_{BET} was obtained by the Brunauer–Emmett–Teller (BET) method [28], whereas porosity P was obtained through Equations (1) and (2). All experimental values are displayed in Table 1.

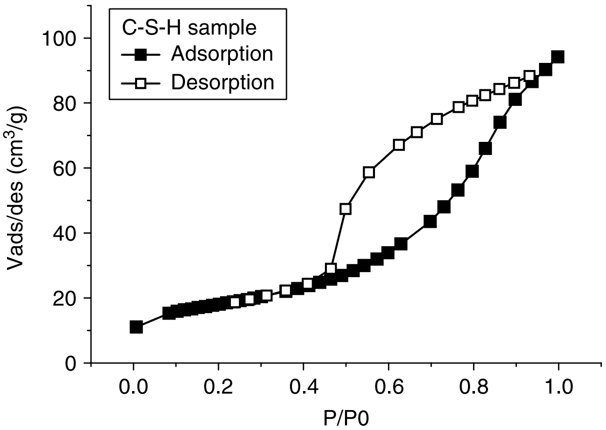

Figure 1. Physisorption isotherm of N_2 at 77 K for the C-S-H sample.

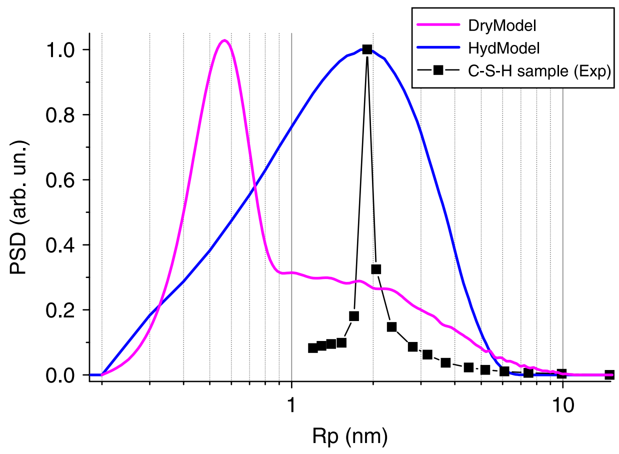

Figure 2. Normalised PSDs of the synthetic C-S-H and structural models *HydModel* and *DryModel*.

4.2 Simulated structures with spheres

The structural simulation was carried out by using first spheres as elementary units and was then extended to bricks. Special attention was paid to the role of water. As it has been established [3,7], water can be trapped inside the elemental pieces of the C-S-H structure. The globules that form the structure can be described on the basis of a tobermorite-like skeleton [29], where the empty space (*intraglobular pores*) is filled with molecular water. This type of water is not evaporable by the *d-drying* method, as it is not adsorbed on the surface of the particles. Two structural models for the C-S-H sample were considered: the 'dry' case, where the intraglobular pores are empty (called *DryModel* hereafter) or 'saturated' (called *HydModel*) (Table 2).

Hence, the sample skeleton has been considered as an assembly of rigidly joined particles randomly packed to form nanometric globules, these globules being randomly packed themselves to form the complete structure with two structural levels. If the intraglobular pores are filled with water (*HydModel*), the N_2 physisorption experiments are only able to resolve the structure at the coarser structural level since at the globule scale, the surface is not available due the presence of the intraglobular water.

Table 2. Parameters considered for building each simulated structure.

	Parameters of the simulated systems
HydModel	One level, $R_0 = 10\,\mathrm{nm}$, $d_1 = 0.83$. Elemental particle density $= 2.35\,\mathrm{g/cm^3}$
DryModel	Two levels, $R_0 = 1.2\,\mathrm{nm}$, $d_1 = 0.72$, $d_2 = 0.83$. Elemental particle density $= 2.45\,\mathrm{g/cm^3}$
BrickModel	Two levels, $3 \times 2 \times 1.4\,\mathrm{nm^3}$, $d_1 = 0.5$, $d_2 = 0.5$. Elemental particle density $= 2.45\,\mathrm{g/cm^3}$

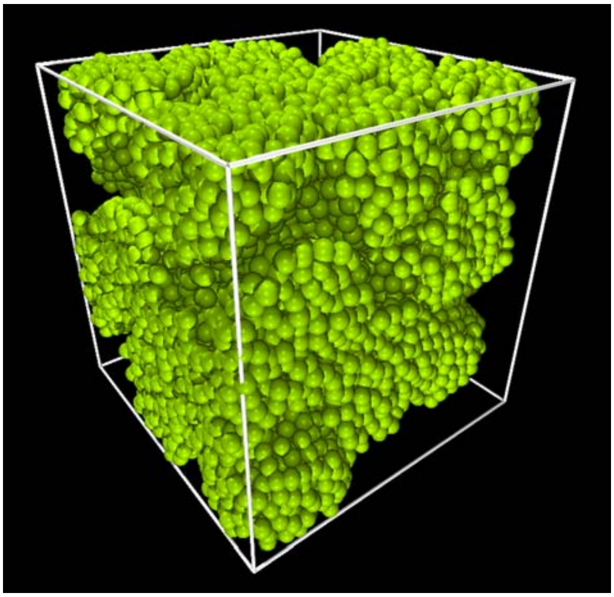

Figure 3. Snapshot of *DryModel*. The sphere radius is 1.2 nm and simulation box is 26.4 nm edge.

The density of the elemental globules ($2.35\,\mathrm{g/cm^3}$) in the *HydModel* was calculated from the experimental values of porosity obtained by N_2 physisorption and from the bulk density (according to Equation (1)). After building several structural models by tuning the different variables of the algorithm, the one that matches the texture parameters of the sample (Table 1) has an elemental globule radius of 10 nm.

For the *DryModel*, where the structure density is unknown, the size of the elemental spheres was set to 1.2 nm, as has been reported [7]. The intraglobular pore space is then defined as the space available in the random packing of elemental spheres of 1.2 nm size (at first aggregation level). By building models with a globule size of 10 nm (matching *HydModel* result), an intraglobular porosity of 7% is found. If now this porosity is filled with water ($1\,\mathrm{g/cm^3}$), a skeleton density of $2.45\,\mathrm{g/cm^3}$ is required to obtain the hydrated globule density of $2.35\,\mathrm{g/cm^3}$ derived (see above). This value of density for the dry skeleton of the globules is actually consistent with that of tobermorite ($2.43\,\mathrm{g/cm^3}$). The corresponding simulated texture values are listed in Table 1. One snapshot [30] of the simulation box of system *DryModel* is shown in Figure 3. The experimental and simulated PSD are compared in Figure 2. Simulated curve for system *HydModel* shows a wider PSD than the experimental one, but its maximum is located at exactly the same typical pore radius of 2.0 nm. On the other hand, PSD corresponding to system *DryModel* reveals the existence of an even wider pore distribution also centred around 2.0 nm, but the most important population of pores is found at smaller size of around 0.6 nm.

4.3 The bricks model

The sphere algorithm, which successfully reproduced the properties of nanoporous C-S-H structures, has been extended to bricks (*BrickModel*). The brick size and density were calculated with the help of the previous simulation results. The *BrickModel* was built with nanobricks of $3 \times 2 \times 1.4\,\mathrm{nm}^3$. The lengths of 1.4 and 3 nm were chosen from already published data [11]. The size of the third edge was set to 2 nm in order to have analogous structural elements, with a gyration radius close to the size of the elemental sphere previously used. The density of these bricks is taken as $2.45\,\mathrm{g/cm}^3$ (see above). This structural model leads to globules with a radius of 22.2 ± 0.1 nm (Table 1); the building parameters are found in Table 2. In addition, a snapshot of *BrickModel* can be seen in Figure 4.

5. Discussion

The construction of hierarchical structural models based on geometrical considerations can provide a major support to the C-S-H structural models described in the literature, as they have not been computationally built and characterised up to now. The predictive potential of this type of structural model is tested here against N_2-physisorption data (textural data):

The *HydModel* fits well the textural values obtained experimentally, as shown in Table 1. Especially, typical sizes of these structures have been successfully reproduced. For example, it can be seen that *HydModel* matches perfectly the globule size reported by Jennings [7].

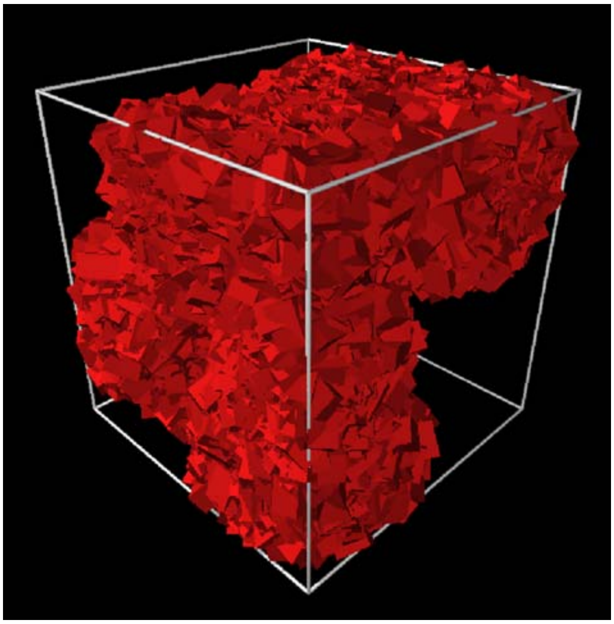

Figure 4. Snapshot of system *BrickModel*. Each brick is $3 \times 2 \times 1.4\,\mathrm{nm}^3$ in size.

The *DryModel* yields a skeleton with a density very close to that of tobermorite. This confirms the assumption that, due to the presence of water, the intraglobular pore surface is not reactive to physisorption experiments.

The PSD in *HydModel* is not as sharp as obtained from N_2-physisorption experiments, which makes us think that elemental globules could be far away from the spherical shape.

The simulated model constructed with *nanobricks* as elementary particle can also reproduce the textural parameters of the sample. A globule diameter of around 45 nm is found in agreement with the values reported by Bentz [9].

6. Conclusions

The structural models presented here (either spheres or bricks), which are based on geometrical considerations, reproduce the C-S-H structural features in the range of a few nanometres. The major conclusion of this paper is that the hierarchical structural models that were reported previously are geometrically possible and they are consistent with some of the experimental microstructural data also published. Moreover, they confirm that *intraglobular* water is located in an intraglobular nanoporosity with pore sizes below 1 nm. Therefore, all these results prove that it is geometrically possible to explain these textures' values in terms of spheres or bricks.

Acknowledgements

V.M.-F would like to thank to J.A. Toledo-Fernandez and I. Garcia-Lodeiro by their wise advices on the synthesis of the samples. This work was funded by the European Union by a Marie Curie action within the GRASP project MRTN-CT-2006-035868. We would like to acknowledge the Sol–Gel Laboratory of the University of Cadiz (Spain) for their kind help on the N_2 physisorption experiments.

Note

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References

[1] H.F.W. Taylor, *Cement Chemistry*, Thomas Telford Publishing, London, 1997.
[2] E.E. Bodor, J. Skalny, S. Brunauer, J. Hagymassy, Jr, and M. Yudenfreund, *Pore structures of hydrated calcium silicates and Portland cements by nitrogen adsorption*, J. Colloid Interf. Sci. 34(4) (1970), pp. 560–570.
[3] A.J. Allen, J.J. Thomas, and M. Jennings, *Composition and density of nanoscale calcium-silicate-hydrate in cement*, Nat. Mater. 6 (2007), pp. 311–316.
[4] C.A. Garcia-Gonzalez, A. Hidalgo, C. Andrade, M.C. Alonso, J. Fraile, A.M. Lopez-Periago, and C. Domingo, *Modification of composition and microstructure of Portland cement pastes as a result*

of natural and supercritical carbonation procedures, Ind. Eng. Chem. Res. 45 (2006), pp. 4985–4992.

[5] F. Merlin, H. Lombois, S. Joly, N. Lequeux, J.L. Halary, and H. Van Damme, *Cement-polymer and clay-polymer nano- and meso-composites: spotting the difference*, J. Mater. Chem. 12 (2002), pp. 3308–3315.

[6] A. Ayuela, J.S. Dolado, I. Campillo, Y.R. de Miguel, E. Erkiza, D. Sanchez-Portal, A. Rubio, and A. Porro, *Silicate chain formation in the nanostructure of cement-based materials*, J. Chem. Phys. 127 (2007), 164710.

[7] H.M. Jennings, *A model for the microstructure of calcium silicate hydrate in cement paste*, Cement Concr. Res. 30 (2000), pp. 101–116.

[8] H.M. Jennings, *Refinements to colloid model of C-S-H in cement: CM-II*, Cement Concr. Res. 38 (2008), pp. 275–289.

[9] See for example GRASP project, available at http://www.grasp-co2.eu, or COSMOS I and II projects, available at www.eureka.be/cosmos (accessed on November 2008).

[10] D.P. Bentz, D.A. Quenard, V. Baroghel-Bouny, E.J. Garboczi, and H.M. Jennings, *Modelling drying shrinkage of cement paste and mortar. Part 1. Structural models from nanometres to milimetres*, Mater. Struct. 28 (1995), pp. 450–458.

[11] I.G. Richardson, *Tobermorite/jennite- and tobermorite/calcium hydroxide-based models for the structure of C-S-H: applicability to hardened pastes of tricalcium silicate, β-dicalcium silicate, Portland cement, and blends of Portland cement with blast-furnace slag, metakaolin, or silica fume*, Cement Concr. Res. 34 (2004), pp. 1733–1777.

[12] I. Odler, *Discussion of the paper 'A model for the microstructure of calcium silicate hydrate in cement pastes' by H.M. Jennings*, Cement Concr. Res. 30 (2000), pp. 1337–1338.

[13] H.M. Jennings, *Reply to the discussion of the paper by Ivan Odler 'A model for the microstructure of calcium silicate hydrate in cement paste'*, Cement Concr. Res. 30 (2000), pp. 1339–1341.

[14] R.F. Feldman and P.J. Sereda, *A new model for hydrated Portland cement and its practical implications*, Eng. J. 53(8/9) (1970), pp. 53–59.

[15] I.G. Richardson, *The calcium silicate hydrates*, Cement Concr. Res. 38 (2008), pp. 137–158.

[16] J.S. Dolado, M. Griebel, and J. Hamaekers, *A molecular dynamics study of cementitious calcium silicate hydrate (C-S-H) gels*, J. Am. Ceram. Soc. 90(12) (2007), pp. 3938–3942.

[17] F.J. Ulm, G. Constantinides, and F.H. Heukamp, *Is concrete a poromechanics material? – A multiscale investigation of poroelastic properties*, Mater. Struct. 37 (2004), pp. 43–58.

[18] A. Nonat, *The structure and stoichiometry of C-S-H*, Cement Concr. Res. 34 (2004), pp. 1521–1528.

[19] D.P. Bentz, E.J. Garboczi, H.M. Jennings, and D.A. Quennard, *Multi-scale digital-image-based modelling of cement-based materials*, Mat. Res. Soc. Symp. Proc. 370 (1995), pp. 33–41.

[20] H.M. Jennings, J.J. Thomas, J.S. Gevrenov, G. Constantinides, and F.J. Ulm, *A multi-technique investigation of the nanoporosity of cement paste*, Cement Concr. Res. 37 (2007), pp. 329–336.

[21] R. Vocka, C. Galle, M. Dubois, and P. Lovera, *Mercury intrusion porosimetry and hierarchical structure of cement pastes. Theory and experiment*, Cement Concr. Res. 30 (2000), pp. 521–527.

[22] D. Sugiyama and T. Fujita, *A thermodynamic model of dissolution and precipitation of calcium silicate hydrates*, Cement Concr. Res. 36 (2006), pp. 227–237.

[23] Plato 3 V 3.5, *Integrated developing environment, Silverfrost Ltd*, software available at http://www.silverfrost.com/16/plato3.aspx (accessed on November 2008).

[24] V. Morales-Florez, N. de la Rosa-Fox, M. Pinero, and L. Esquivias, *The cluster model: a simulation of the aerogel structure as a hierarchically-ordered arrangement of randomly packed spheres*, J. Sol–Gel Sci. Technol. 35 (2005), pp. 203–210.

[25] J.A. Anta and V. Morales-Florez, *Combined effect of energetic and spatial disorder on the trap-limited electron diffusion coefficient of metal-oxide nanostructures*, J. Phys. Chem. B 112(27) (2008), pp. 10287–10293.

[26] M. Kruk and M. Jaroniec, *Gas adsorption characterization of ordered organic–inorganic nanocomposite materials*, Chem. Mater. 13 (2001), pp. 3169–3183.

[27] E.P. Barret, L.G. Joyner, and P.P. Halenda, *The Determination of pore volume and area distributions in porous substances. I. Computations from nitrogen Isotherms*, J. Am. Chem. Soc. 73 (1951), pp. 373–380.

[28] S. Brunauer, P.H. Emmet, and E. Teller, *Adsorption of gases in multimolecular layers*, J. Am. Chem. Soc. 60 (1938), p. 309–319.

[29] H. Manzano, A. Ayuela, and J.S. Dolado, *On the formation of cementitius C-S-H nanoparticles*, J. Comp.-Aided Mater. Des. 14 (2007), pp. 45–51.

[30] Snapshots were rendered with POVRay software; software available at www.povray.org (accessed on November 2008).