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► **To cite this version:**

Victor Morales-Florez, Fabrice Brunet. Structural models of random packing of spheres extended to bricks. Simulation of the nanoporous Calcium-Silicate-Hydrates.. *Molecular Simulation*, 2009, 35 (12-13), pp.1001-1006. 10.1080/08927020903033117 . hal-00530455

HAL Id: hal-00530455

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Submitted on 29 Oct 2010

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Structural models of random packing of spheres extended to bricks. Simulation of the nanoporous Calcium-Silicate-Hydrates.

Journal:	<i>Molecular Simulation/Journal of Experimental Nanoscience</i>
Manuscript ID:	GMOS-2009-0016.R2
Journal:	Molecular Simulation
Date Submitted by the Author:	23-Apr-2009
Complete List of Authors:	Morales-Florez, Victor; Ecole normale superieure - CNRS, Terre-Atmosphère-Océan Brunet, Fabrice; Ecole normale superieure - CNRS, Terre-Atmosphère-Océan
Keywords:	Structure, Nanoporous, Hierarchical model, C-S-H, Bricks

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10 Victor Morales-Flórez*, Fabrice Brunet

11 NOTE: Paper for the J. A. Mejías Memorial Issue.

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ABSTRACT

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 C-S-H sample, the main binding phase of **hydrated** cements, have been derived from N₂-physisorption experiments. In 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 (3x2x1.4 nm³) yield also textural parameters which are consistent with N₂-physisorption data but with a globule size (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, since decades, a useful approach to reproduce and understand 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 ironized 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^{3,4,5,6,7,8}. 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 research⁹.

Nevertheless, there is a general agreement on the description of C-S-H phase as a nanoporous medium formed by random packing of particles¹⁰. These particles have nanometric sizes, and they arrange according to clusters ordered in several

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2
3 hierarchical levels. They are formed by linking silica tetrahedra chains in the so-called
4
5 *dreierketten* structure, bounded to calcium atoms layers and enclosing water
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7 molecules. The chemical composition of the particles can vary widely depending on
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9 the synthesis process. It has been found by chemical analysis coupled to
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11 transmission electron microscopy that the Ca/Si ratio of C-S-H nanoparticles can vary
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13 locally from 0.7 to 2.3¹¹. Likewise, the structural data obtained from different types of
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15 C-S-H can be very different depending on the characterization means (SAXS, SANS,
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17 N₂ physisorption, etc.). Moreover, very different particle shapes, porosities and
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19 densities were found in C-S-H phases, the heterogeneity in C-S-H properties has
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21 been reduced by classifying them into two types ⁷ which co-exist in **hydrated**
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23 cements. Actually, this description in two groups is not free of discussion^{12,13}. For
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25 example, the stoichiometry of C-S-H formed between clinker grains of cements has
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27 recently been established³ to be $(\text{CaO})_{1.7}(\text{SiO}_2)(\text{H}_2\text{O})_{1.8}$.

28
29 This composition, and especially the SiO₂/H₂O ratio (~1.8) does not match that of
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31 tobermorite, Ca₅Si₆O₁₆(OH)₂·4H₂O (SiO₂/H₂O ~ 0.8), to which C-S-H are usually
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33 compared. Likewise, the mean calcium to silicon ratio (Ca/Si) in C-S-H of common
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35 cements is roughly twice that of tobermorite. Since the model by Feldman and
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37 Sereda¹⁴, several structural models have been proposed to account for elemental
38
39 particle formation in C-S-H ^{15,16} and for the final nanometric structure³. Hence,
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41 different particle shapes as irregular grains³, spheres^{7,17} as well as lamellae-like¹⁸ or
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43 brick-like particles⁸ have been ~~assumed or~~ suggested. Whatever their shape, these
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45 nanoparticles are randomly packed and this packing is organized according to
46
47 several hierarchical levels^{19,20,21}.

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

C-S-H sample was synthesized according to the coprecipitation method proposed by Sugiyama²² which consists in adding, under stirring, a solution of Na_2SiO_3 to a filtered CaO-saturated solution. CaO was obtained by decarbonation of CaCO_3 (Merck, 99%) at 1100°C for 24 hours whereas a Na_2SiO_3 solution (Merck, 1l = 1.35 kg) was diluted to the desired concentration. The C-S-H sample was synthesized 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 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 24h in order to remove adsorbed water and other volatile contaminants. Physisorption experiment was carried out at 77K in a Sorptomatic automatic device (FISONS Instruments). 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 to slightly different systems. Therefore, for each set, from 5 to 10 different replicas were built and characterized. 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 for simulate nanoporous structures^{24,25} was used. This algorithm works as follows: it places an elemental particle in the space and randomly surrounds it by other similar particles at a previously defined contact distance d . Then, each of the new placed particle is surrounded with similar particles, always taking care on avoiding 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. Deeper description of the algorithm and the techniques used for characterization can be found in references 24 and 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 N₂ physisorption, a single test particle with a finite size of 0.227 nm, i.e. equals 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 as skeleton density ρ_{sk} , that is, 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):

$$V_p = \rho^{-1} - \rho_{sk}^{-1} \quad [1]$$

$$P = \rho V_p \quad [2]$$

3.2 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 regarding to a universal axis. The main geometrical parameters that characterize 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.

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

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24 When dealing with cuboids, the distance between neighbour bricks centres only
25 cannot be used as an overlapping criterion. Therefore the overlapping test procedure
26 was implemented as follows:
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31 Each new brick is characterized by six coordinates generated randomly. The eight
32 corners of this new brick along with the eight corners of the nearest brick are
33 consecutively transformed, first, to the universal system, and then to the reference
34 system of the other brick. This way, any given point (x, y, z) will fall inside the brick
35 only and only if all the following conditions are satisfied:
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$$42 \quad |x| < a/2$$

$$43 \quad |y| < b/2$$

$$44 \quad |z| < c/2$$

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50 a, b, c being the three edge lengths of the bricks. If these conditions are met, the new
51 brick is added to the structure. Obviously, it is a first approach of the problem since
52 not all the possible overlapping configurations are covered with this algorithm.
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3 The applications previously generated to retrieve the texture parameters of porous
4 structures made of spheres, were extended to handle cuboids. Typical C-S-H
5 structural models built with this algorithm contain several thousands of particles.
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10 11 12 13 14 **4. Results**

15 16 17 18 19 *4.1 Real system*

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21 The physisorption isotherm is plotted in Figure 1. This curve is typical for meso- or
22 microporous materials (type IV) with hysteresis loops which indicate a structure
23 formed by assemblages of rigidly joint particles²⁶. Hysteresis loop shows a very
24 regular pore shape and size distribution. The PSD obtained by the BJH method²⁷ is
25 extremely sharp centred on a pore radius of 2 nm as can be seen on Figure 2.
26 Specific surface area S_{BET} was obtained by the BET method²⁸ whereas porosity P
27 was obtained through Eqs. 1 and 2. All experimental values are displayed in Table 1.
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40 41 *4.2 Simulated structures with spheres*

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43 The structural simulation was carried out by using first spheres as elementary units
44 and was then extended to bricks. A special attention was paid to the role of water. As
45 it has been established^{3,7}, water can be trapped inside the elemental pieces of the C-
46 S-H structure. The globules that form the structure can be described on the basis of a
47 tobermorite-like skeleton²⁹ where the empty space (*intraglobular pores*) is filled with
48 molecular water. This type of water is not evaporable by the *d-drying* method, as it is
49 not adsorbed on the surface of the particles. Two structural models for the C-S-H
50 sample were considered: the “dry” case where the intraglobular pores are empty
51 (called *DryModel* hereafter) or saturated (called *HydModel*).
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3 Hence, the sample skeleton has been considered as an assembly of rigidly joined
4 particles randomly packed to form nanometric globules, these globules being
5 randomly packed themselves to form the complete structure with two structural
6 levels. If the intraglobular pores are filled with water (*HydModel*), the N₂ physisorption
7 experiments are only able to resolve the structure at the coarser structural level since
8 at the globule scale the surface is not available due the presence of the intraglobular
9 water.
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11 The density of the elemental globules (2.35 g/cm³) in the *HydModel* was calculated
12 from the experimental values of porosity obtained by N₂ physisorption and from the
13 bulk density (according to Eq. 1). After building several structural models by tuning
14 the different variables of the algorithm, the one that matches the texture parameters
15 of the sample (Table 1) has an elemental globule size of 10 nm.
16
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18 For the *DryModel*, where the structure density is unknown, the size of the elemental
19 spheres was set to 1.2 nm, as it has been reported⁷. The intraglobular pore space is
20 then defined as the space available in the random packing of elemental spheres of
21 1.2 nm size (at first aggregation level). By building models with a globule size of 10
22 nm (matching *HydModel*'s result), an intraglobular porosity of 7% is found. If now, this
23 porosity is filled with water (1 g/cm³), an skeleton density of 2.45 g/cm³ is required to
24 obtain the hydrated globule density of 2.35 g/cm³ derived (see above). This value of
25 density for the dry skeleton of the globules is actually consistent with that of
26 tobermorite (2.43 g/cm³). The corresponding simulated texture values are listed in
27 table 1. One snapshot³⁰ of the simulation box of system *DryModel* is shown in Figure
28 3. The experimental and simulated PSD are compared in figure 2. Simulated curve
29 for system *HydModel* shows a wider PSD than the experimental one, but its
30 maximum it is located at exactly the same typical pore radius of 2.0 nm. On the other
31 hand, PSD corresponding to system *DryModel* reveals the existence of an even
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2 wider pore distribution also centred around 2.0 nm, but the most important population
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4 of pores is found at smaller size of around 0.6 nm.
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9 10 4.3 The bricks model

11 The sphere algorithm which successfully reproduced the properties of nanoporous C-
12 S-H structures, has been extended to bricks (*BrickModel*). The brick size and density
13 were calculated with the help of the previous simulation results. The *BrickModel* was
14 built with nanobricks of $3 \times 2 \times 1.4 \text{ nm}^3$. The lengths of 1.4 and 3 nm, were chosen from
15 already published data¹¹. The size of the third edge was set to 2 nm in order to have
16 analogous structural elements, with a gyration radius close to the size of the
17 elemental sphere previously used. The density of these bricks is taken as 2.45 g/cm^3
18 (see above). This structural model leads to globules of $22.2 \pm 0.1 \text{ nm}$ radii (Table 1),
19 the building parameters are found in table 2. In addition, a snapshot of *BrickModel*
20 can be seen on figure 5.
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38 5. Discussion

39 The construction of hierarchical structural models based on geometrical
40 considerations can provide a major support to the C-S-H structural models described
41 in the literature, as they have not been computationally built and characterized up to
42 now. The predictive potential of this type of structural model is tested here against
43 N₂-physisorption data (textural data):
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51 The *HydModel* fits well the textural values obtained experimentally, as shown in table
52 1. Especially, typical sizes of these structures have been successfully reproduced.
53 For example, it can be seen that *HydModel* matches perfectly the globule size
54 reported by Jennings⁷.
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3 The *DryModel* yields a skeleton with a density very close to that of tobermorite. This
4 confirms the assumption that, due to the presence of water, the intraglobular pore
5 surface is not reactive to physisorption experiments.
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9 The PSD in *HydModel* is not as sharp as obtained from N₂-physisorption
10 experiments, what let us think that elemental globules could be far away from the
11 spherical shape.
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15 The simulated model constructed with *nanobricks* as elementary particle can also
16 reproduce the textural parameters of the sample. A globule diameter of around 45 nm
17 is found in agreement with the values reported by Bentz⁹.
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24 25 26 **6. Conclusions**

27
28 The structural models presented here (either spheres or bricks) which are based on
29 geometrical considerations reproduce the C-S-H structural features in the range of a
30 few nanometres. **The major conclusion of this paper is that the hierarchical structural
31 models that were reported previously are geometrically possible and they are
32 coherent with some of the experimental microstructural data also published.**
33
34 Moreover, they confirm that *intraglobular* water is located in an intraglobular
35 nanoporosity with pore sizes below 1 nm. Therefore, all these results prove that it is
36 geometrically possible to explain these textures values in terms of spheres or bricks.
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54 55 **Acknowledgements**

56
57 V. M-F would like to thank to J.A. Toledo-Fernandez and I. Garcia-Lodeiro by their
58 wise advices on the synthesis of the samples. This work was funded by the European
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2 Union by a Marie Curie action within the GRASP project MRTN-CT-2006-035868.

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4 We would like to acknowledge the Sol-Gel laboratory of the University of Cadiz

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6
7 (Spain) for their kind help on the N₂ physisorption experiments.
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Table 1

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

Table 1.- Texture values of the C-S-H sample obtained by N₂ physisorption and values of the structural models. HydModel emulates texture of calcium-silica with intraglobular water, whereas DryModel represents the solid skeleton without intraglobular water. BrickModel simulate the dry structure with bricks instead of spheres as the elemental particle. (-) No data available.

Table 2

Parameters of the simulated systems	
HydModel	1 level, $R_0=10$ nm, $d_1=0.83$. Elemental particle density= 2.35 g/cm ³
DryModel	2 levels, $R_0=1.2$ nm, $d_1=0.72$, $d_2=0.83$, Elemental particle density= 2.45 g/cm ³
BrickModel	2 levels, $3 \times 2 \times 1.4$ nm ³ , $d_1=0.5$, $d_2=0.5$, Elemental particle density= 2.45 g/cm ³

Table 2.- Parameters considered for building each simulated structure.

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3 Figure captions
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7 Figure 1.- Physisorption isotherm of N₂ at 77K for the C-S-H sample.
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10 Figure 2.- Normalized Pore Size Distributions of the synthesized C-S-H and structural
11 models HydModel and DryModel.
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13
14 Figure 3.- Snapshot of DryModel. The sphere radius is 1.2 nm and simulation box is
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16 26.4 nm edge.
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19 Figure 4.- Snapshot of system BrickModel. Each brick is 3x2x1.4 nm³ size.
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Figure 1

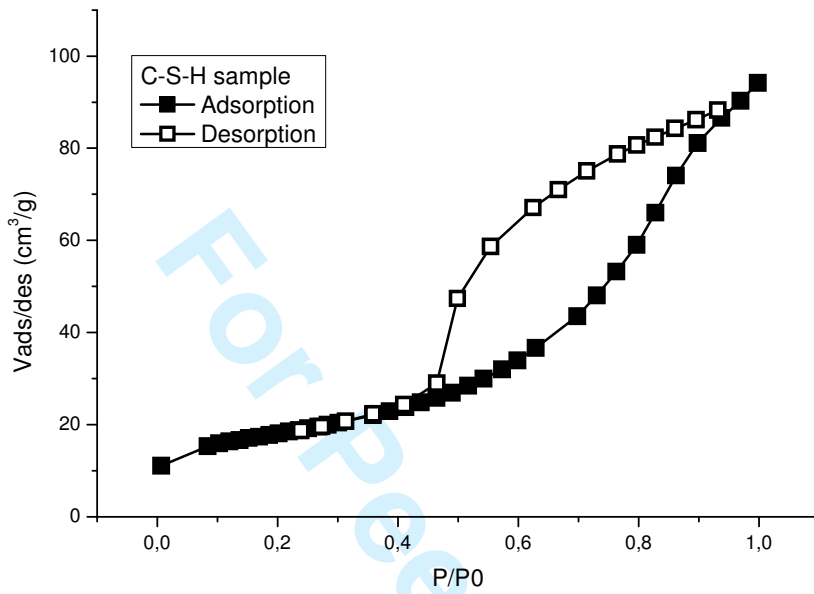


Figure 2

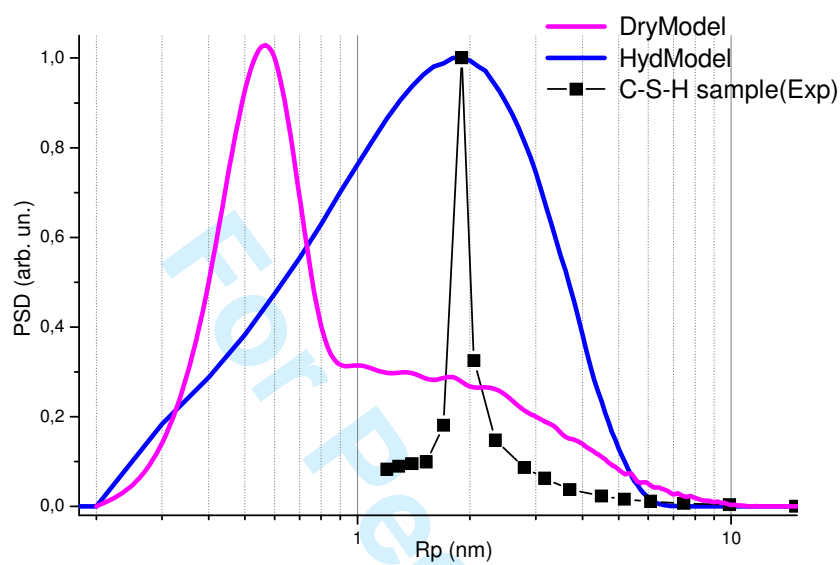
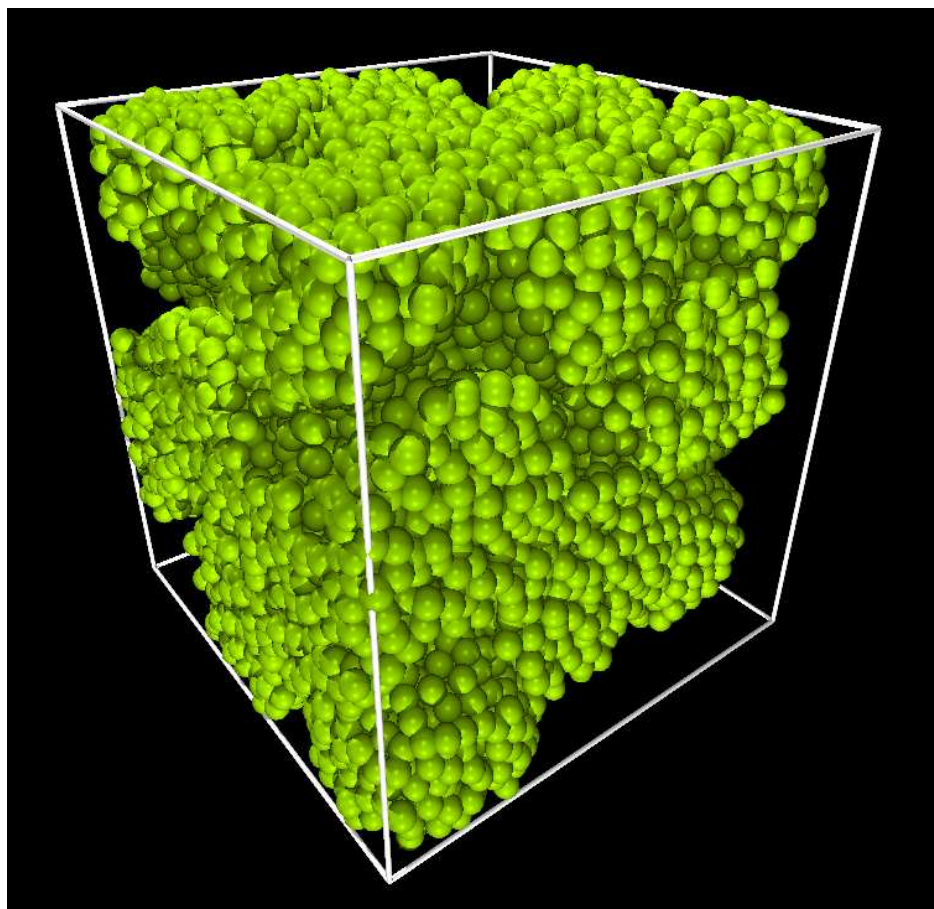


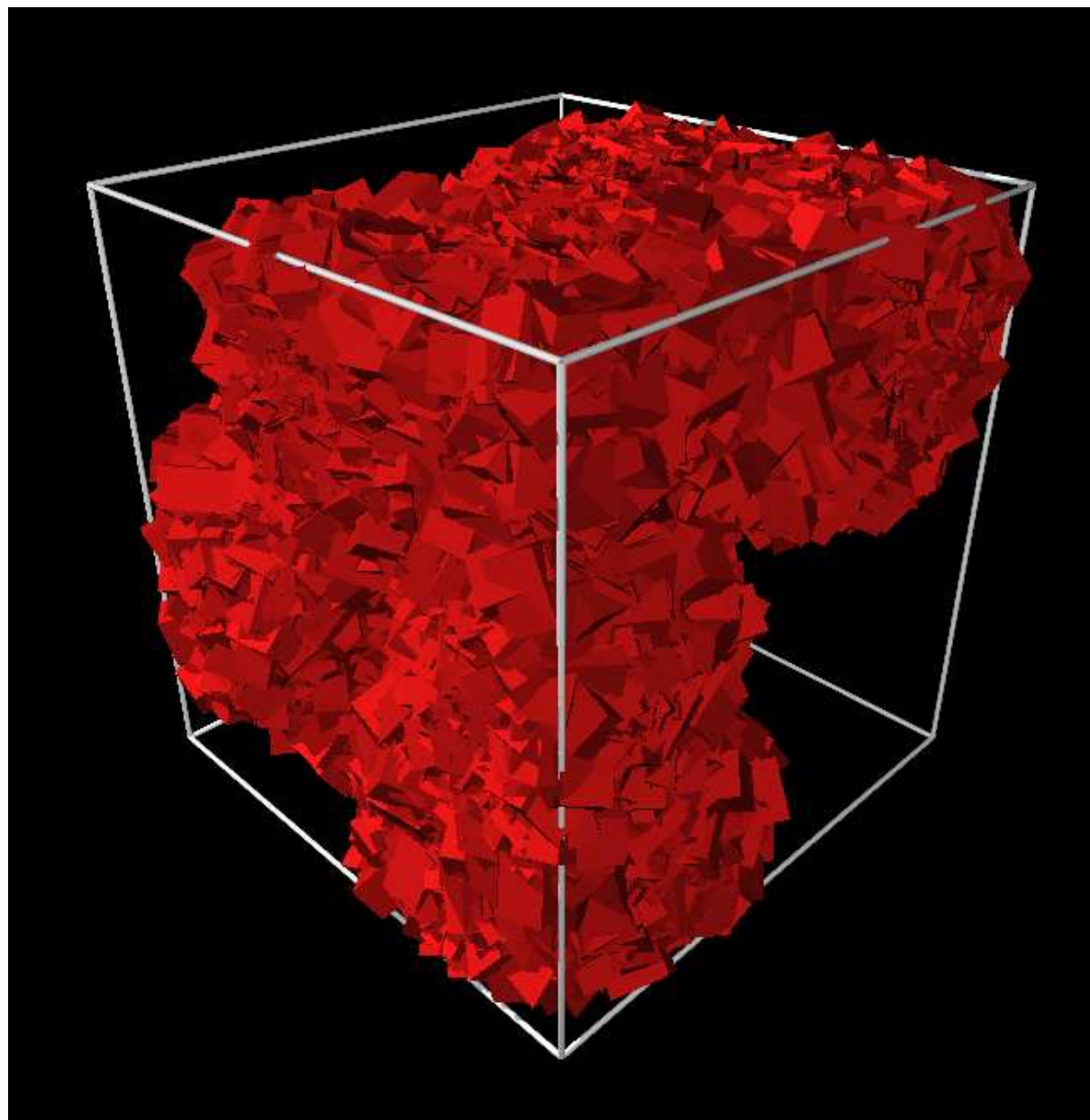
Figure 3



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Figure 4



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³⁰ Snapshots were rendered with POVRay software (www.povray.org, last visit on 11/2008).

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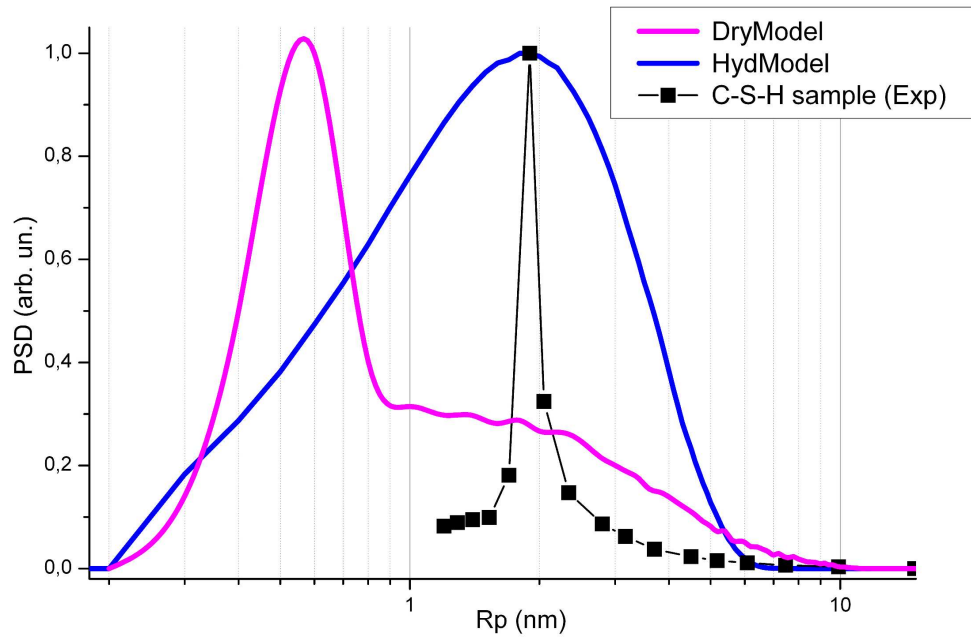


Figure 2.- Normalized Pore Size Distributions of the synthesized C-S-H and structural models HydModel and DryModel.
191x134mm (600 x 600 DPI)

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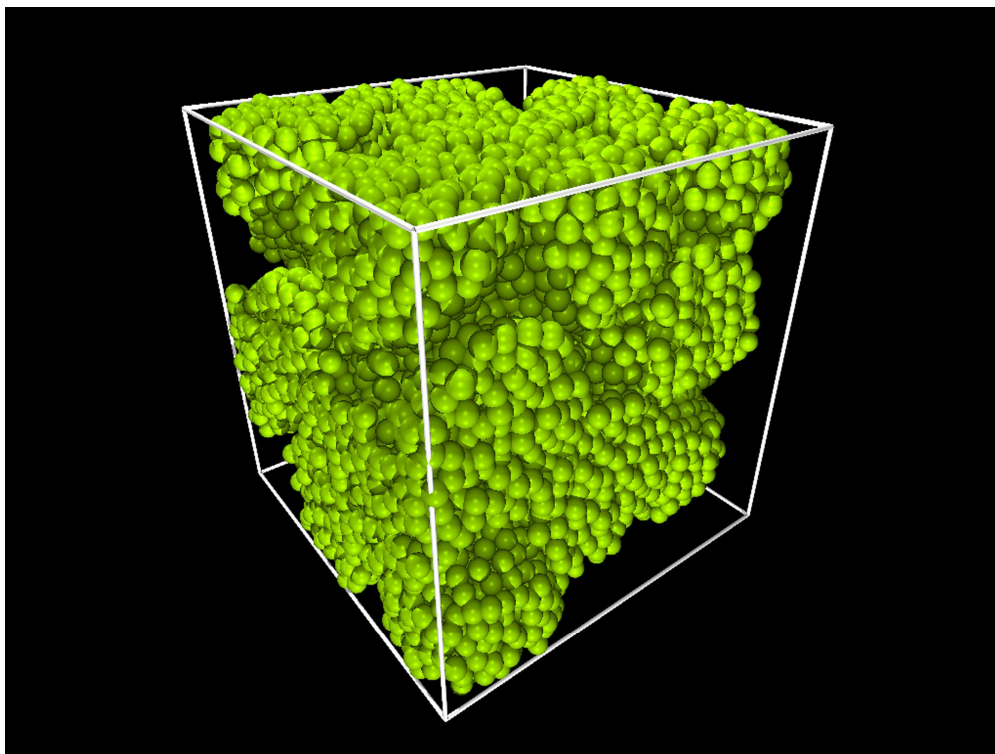


Figure 3.- Snapshot of DryModel. The sphere radius is 1.2 nm and simulation box is 26.4 nm edge.
361x270mm (200 x 200 DPI)

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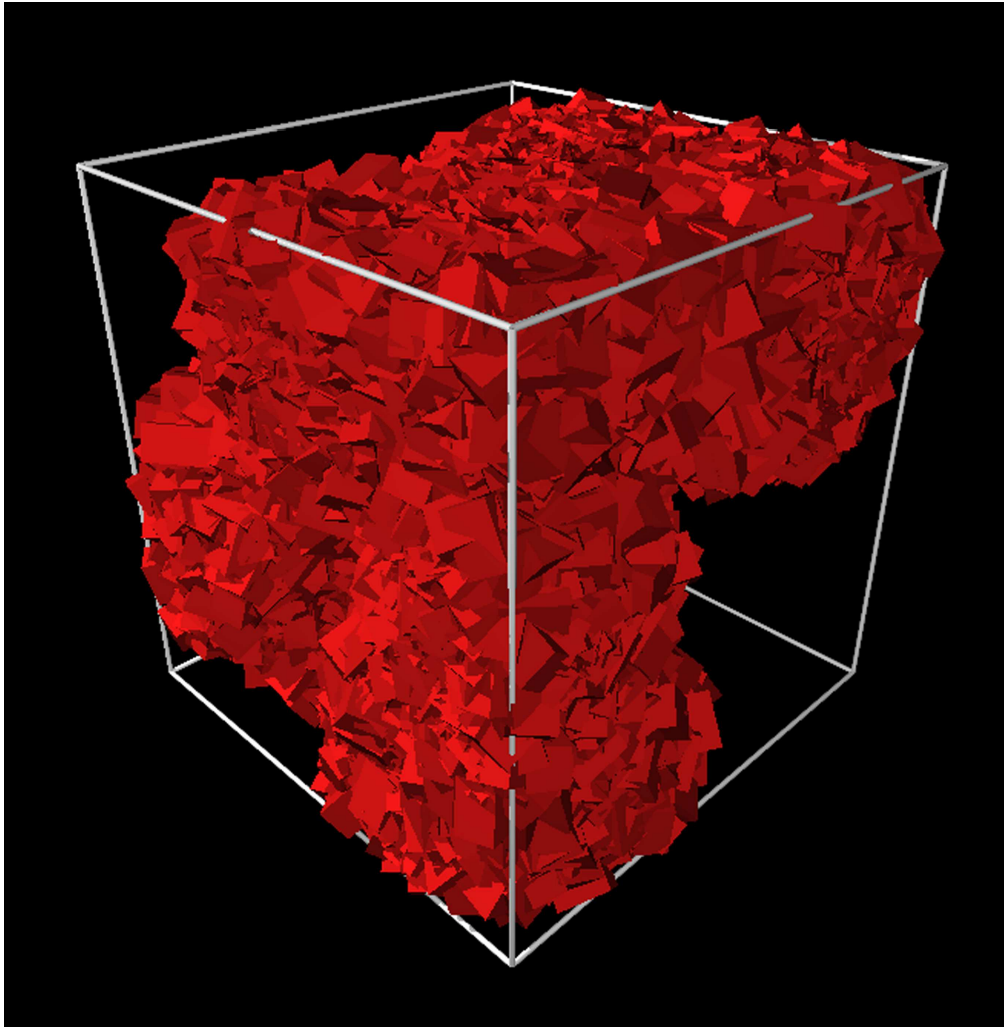


Figure 4.- Snapshot of system BrickModel. Each brick is $3 \times 2 \times 1.4 \text{ nm}^3$ size.
230x235mm (300 x 300 DPI)



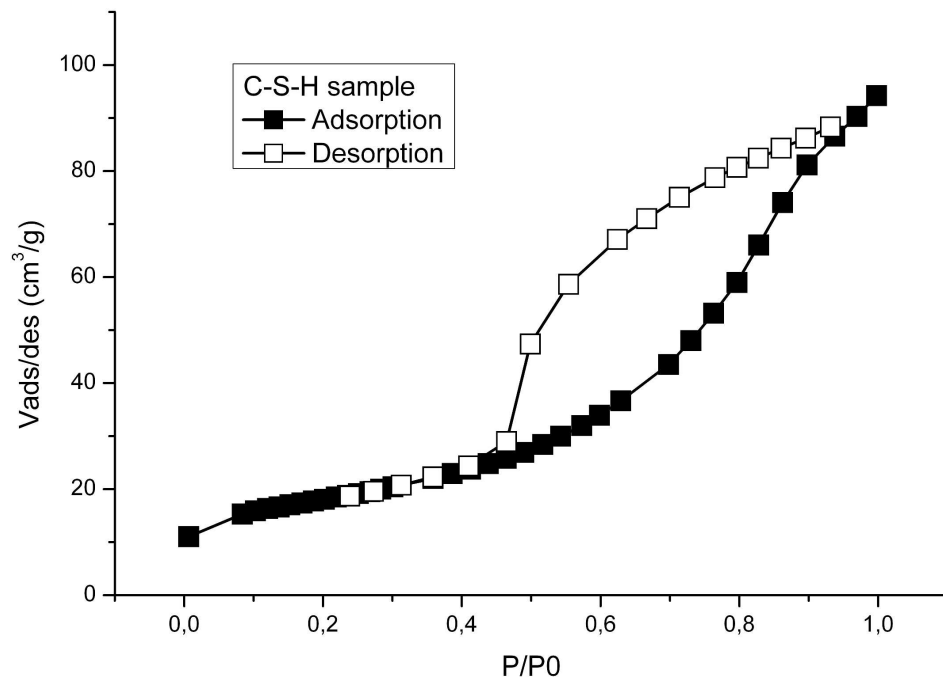


Figure 1.- Physorption isotherm of N₂ at 77K for the C-S-H sample.
191x134mm (600 x 600 DPI)

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5 **Referee 1**
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7 **1) The most intriguing thing to me has to do with the sizes of the basic particles for**
8 **the DryModel (1.2nm) and their packing factor (93%) to give globules 10nm sized . I**
9 **think that the authors should explain the feasibility of such high packing factors.**
10 **Are they realistic? What do they mean?**
11

12 This value was obtained by packing spheres of 1.2 nm size and 2.45 g/cm³ to form a globule of 10
13 nm size and 2.35 g/cm³, considering that the pore space among the spheres is filled with water.
14 Watching the little difference between the sphere density and the globule density, it is clear that no
15 high porosity could be expected. In fact, these high packing factors can only be found inside the
16 globules, as the bulk sample packing factor will also take into account packing factors of upper
17 hierarchical levels, yielding this way to realistic porosities of C-S-H's. When drying the solid
18 structures, collapsing of small pores (higher pressures) could yield to the smaller hierarchical level to
19 shrink from a more "natural" random packing of spheres with porosities around 20-50% to the
20 collapsed system as obtained. Moreover, in real systems some degree of polydispersity could exist so
21 this also can increase packing factor. It should be taken into account that we are dealing with soft
22 spheres, so overlapping is allowed and higher packing factors can be obtained. We have recently
23 obtained supercritically dried CSH in order to understand the influence of the drying process on the
24 structure of CSH.
25
26

27
28 **2) When speaking about the chosen 3x2x1.4 nm³ nanobricks, the authors say that the**
29 **number 2 was set so to fit with the size of the elemental sphere previously used.**
30 **However, according to Table 2 the sizes for the elementary spheres were 20 nm**
31 **(R=10nm) (HydModel) and 2.4 nm (R0=1.2nm)...Why did the author employ 2 instead of**
32 **2.4, for instance?**
33

34 Some different sets of side lengths were proven (e.g. 3x2x1 as the first and simplest case, 3x2x1.1,
35 and finally 3x2x1.4. The aim was not to match just only one of the sides with the size of the spheres,
36 as this will yield a very different volume and mass differences on the elemental structures. In fact, the
37 chosen set of sides for the bricks has gyration radii between 2.2 and 3.2 (depending on the relative
38 axis), very close to the size of the elemental sphere. To leave this clearer in the text, we propose
39 changing this sentence (Line 9, page 11)
40

41 *"The size of the third edge was set to 2 nm in order to fit the brick size to that of the elemental*
42 *sphere previously used"*
43

44 ... by the following one:

45
46 *"The size of the third edge was set to 2 nm in order to have analogous structural elements, with a*
47 *gyration radius close to the size of the elemental sphere previously used".*
48

49 **3) A very interesting Figure is the Fig.2. However I have observed that the PSD data for the**
50 **cuboids is not displayed. I consider that it should be shown. In fact, the authors think that**
51 **the sharp PSD obtained from N₂-physisorption experiments points to not spherical**
52 **geometries...**
53

54
55 We totally agree with the necessity of the PSD for the brick geometry. The computational complexity
56 of this new task together with the large computational resources that are needed make it unaffordable
57 at the moment. Just as a reference, PSD for small spherical models take from some days up to some
58 weeks, so probably the calculi of this PSD will need large computational facilities.
59
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4 **4) Minor thing: The authors employ some times "cements" where they should say**
5 **"cement-based materials or cementitious materials": C-S-H is not present in cements**
6 **but in hydrated cements...**
7

8 We agree. We have included "hydrated" before the word "cement" in several cases along the text.
9

10
11 **5) Minor thing: The authors say that the author of Ref.8 says that the basic**
12 **elementary particles of C-S-H are cuboids instead of spheres. I consider that the**
13 **authors should smooth a bit such a statement, since Ref. says that a plate-like**
14 **morphology would fit better with the layered atomic structure of C-S-H gel.**
15

16 In line 21, page 4 we stated:
17

18 *"Hence, different particle shapes as irregular grains³, spheres⁷, as well as lamellae-like or brick-like*
19 *particles⁸ have been assumed or suggested."*
20

21
22 And in line 24, page 4:
23

24 *"Following Jennings 8, who stated that the shape of the structural elements of C-S-H are cuboids,*
25 *instead of spheres"*
26

27 The author of ref 8 says:
28

29 *"The cornerstone of the model is a description of the globules (used here to mean small brick like*
30 *particles)" (in the abstract), or "it is acknowledged that they are not spherical and they have an internal*
31 *sheet like structure, perhaps layered bricks should be used" (page 275, 2nd paragraph of point 1).*
32
33

34 We propose smoothing the wording of lines 21 and 24, page 4 by the following:
35

36 *"Hence, different particle shapes as irregular grains³, spheres⁷, as well as lamellae-like or brick-like*
37 *particles⁸ have been suggested."*
38

39 *"Following Jennings 8, who proposed that the structural elements of C-S-H are cuboids instead of*
40 *spheres"*
41
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46 **Referee: 2**
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48
49 **1) The packing algorithms are not clear enough. They are also not clear enough in refs. 24**
50 **and 25. There is simply not enough detail to replicate the simulation and independently**
51 **verify any of the reported research. Given that there may be some importance to the**
52 **authors' findings this is a serious shortcoming. For example, the reader is not told of the**
53 **size of the individual packed regions used for the higher scale packing etc.**
54

55 We consider that the information about the main ideas of the algorithm is enough. In comparison with
56 other simulation works it is not short at all. This is an old algorithm that it just have modified to
57 manage cuboids. In this regard, when it was introduced on previous publications, no claim of more
58 detail was ever received, and consequently it has no sense to have it here. In addition, But, if more
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3 information is still required, we will consider the inclusion of a flux diagram. And, of course,
4 FORTRAN90 source code of all the used software is available for the referee to judge it.
5
6

7 **2) Another shortcoming is that the density of the packed particles is computed for both wet**
8 **and dry conditions, apparently using the assumption that the globule or brick has a density**
9 **of 2.34 g/cm³. It is totally unclear why this number is used and what it exactly means (for**
10 **example does this density include a monolayer of water on the surface of the globules).**
11 **This number is used to compute the size of the globules or bricks but no details are given.**
12

13 We understand that the set of chained experimental/simulation results could easily yield to confusion.
14 The value of the density of 2.35 is used first for the structural models based on spheres. In this
15 regard, we explained (Line 8, page 10):
16

17 *"The density of the elemental globules (2.35 g/cm³) in the HydModel was calculated from the*
18 *experimental values of porosity obtained by N₂ physisorption and from the bulk density (according to*
19 *Eq. 1)"*
20

21
22 This is not an assumption but an experimental derived result, from both density measurements and
23 N₂ physisorption results. Bulk density is measured as explained in Line 16, page 5 from a little piece
24 of 0.13 cm³ and with 0,2298 g of mass. To remark this value, we included the words "Table 1" at the
25 end of that line. So, the globule density of 2.35 g/cm³ is considered as the density of the globules,
26 that is the smaller structural elements that can be seen by the N₂ molecules, whether the globules
27 have a monolayer of water or not. This is part of the discussion of the simulation work. So, we don't
28 agree with the statement "it is totally unclear why this number is used". This density value is used as
29 an experimental input on the simulation work. It is true that no details are given in the wording (Line
30 10, Page 10):
31

32 *"An elemental globule size of 10 nm was obtained by matching the structural model to the texture*
33 *parameters of the sample (Table 1)."*
34

35 So, for the sake of clarity on how the simulation works, we swap this sentence by the following:
36

37 *"After building several structural models by tuning the different variables of the algorithm, the one*
38 *that matches the texture parameters of the sample (Table 1) has an elemental globule size of 10 nm".*
39

40
41
42 **2. bis) This requires values for surface area and there seems to be no justification for using**
43 **BET without any information about sample preparation.**
44

45 The value of surface area is used as a target parameter. That is, the structural parameters are tuned
46 and features as specific surface area are measured continuously for all the models that were tested,
47 up to find one system with the target features. Concise sample preparation for N₂ physisorption
48 measurements is explained in section 2.
49

50
51 **2. tris) I think this type of model should explore the consequences of using different**
52 **densities. Indeed the sensitivity of all variables should be explored.**
53

54 We agree with the potentialities of this simulation procedure. Exploring different densities, the effect
55 of elemental particle size, packing degree etc. are considered for future work. In fact, Pore Size
56 Distribution for bricks systems and simulation of small angle scattering are being currently developed.
57

58 There are huge differences on the bulk parameters on using different structural parameters. For
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3 example, elemental particle size is critical for specific surface area or pore size. Overlapping distance
4 is critical on pore size, specific surface or porosity. Number of hierarchical levels is critical on porosity
5 or PSD ...and so on. We understand that for fully understand how this algorithm works all these
6 details (why are two levels used? what happens if size of particles is changed? what is the influence of
7 each used structural parameter? ...) and we thank this interest shown by the referee. We will be very
8 glad in keep on talking deeper about the details with the referee but we consider this survey not to be
9 necessary in this work, but on one work exclusively focused on the model without any experimental
10 validation. We will consider this for future publications.

11 **2. quat) According to ref 3 the density of globule is 2.6 g/cm³, why is this not used?**

12
13
14 Density of globules is one of the few experimental values that we could obtain in our laboratory. So,
15 we preferred to use our own value than others, as we will work on the rest of the work with these our
16 samples. But, as we have stated before, it will be interesting make use of these models for exploring
17 the influence of the different parameters on the large dispersion that can be found in the experimental
18 data of CSH, as now the influence of the different values can be explored computationally, so
19 theoretical hypothesis can be checked out.
20
21

22 **3) The major conclusion seems to be that the modeling proves the validity of a multi-level 23 structural description of C-S-H. After several times reading the paper I still do not 24 understand the details of the proof. How do the results change if the multi-level structural 25 model is not used, or the size of the structural units is changed?**

26
27
28 The major conclusion of this paper is that the hierarchical structural models that were reported
29 previously (more precisely, the pseudo-bricks models recently published in ref 8) are geometrically
30 possible and coherent with the experimental microstructural data published. It is absolutely not to set
31 any major conclusion about the nature of the nanostructure of C-S-H, topic that it has been (and it is
32 being) discussed a lot. However, our result is not trivial or insignificant, as geometrical coherence and
33 validation is essential for any model: for example, it is geometrically impossible building structures of
34 random packings of silica spheres of 10 nm radius with specific surfaces of 150 m²/g.
35 So, the fact is, building computationally these models (with these algorithms) is the support to the
36 idealized, invented, thought models. This is briefly stated in the conclusions section. We propose
37 swapping this line (Line 14, page 12):
38
39

40 *"They confirm the relevance of the multi-level structural description of C-S-H's."*

41
42 For the following phrasing:

43
44 *"The major conclusion of this paper is that the hierarchical structural models that were reported
45 previously are geometrically possible and they are coherent with some of the experimental
46 microstructural data also published".*
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3 Reply to referee #3:
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7 First of all, we would like to acknowledge the warning on the use of the BJH model in
8 non-cylindrical pore geometries. Also, we sincerely thank the given references on the
9 discussion about pore geometries and the applicability of the BJH model.
10

11 In general, this discussion relies mainly on the following idea: obviously, the pores
12 among random packing of the spheres cannot be considered as cylinders, so what
13 can be deduced from the results of this cylindrical approximation about this system?
14

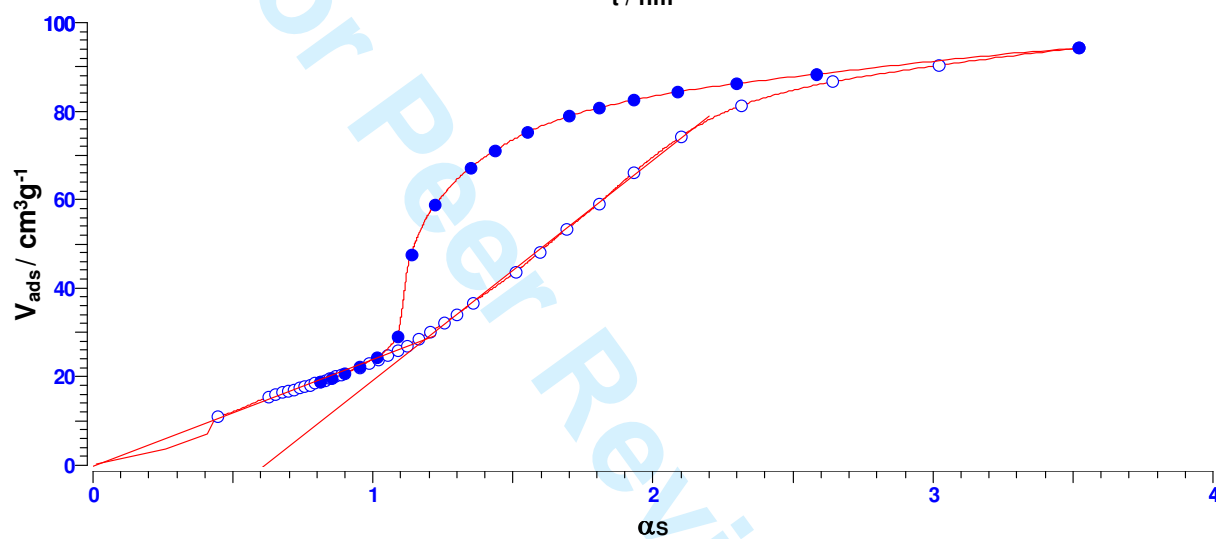
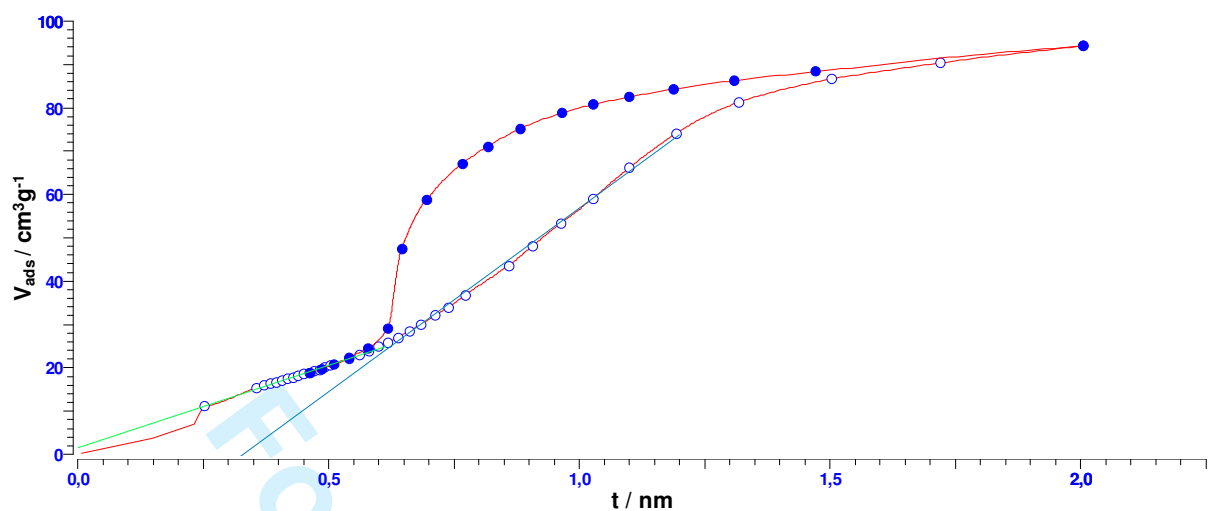
15
16 The BJH approximation has been used successfully in non-cylindrical pores, as those
17 made by spheres packings, giving reliable and contrasted data. See for example the
18 following papers comparing electron microscopy and BJH method results:
19

- 20
21 1.- Francisco Lorenzano-Porrás, Peter W. Carr, Alon V. McCormick,
22 "Relationship between Pore Structure and Diffusion Tortuosity of ZrO₂
23 colloidal Aggregates", *Journal of Colloid and Interface Science*, 164 (1), 1-
24 8, (1994).
25
26 2.- Yu-Guo Guo, Yong-Sheng Hu and Joachim Maier "Synthesis of
27 hierarchically mesoporous anatase spheres and their application in lithium
28 batteries", *Chem. Commun.*, 2783 - 2785, (2006) DOI: 10.1039/b605090e.
29
30 3.- Yamada Y, Nakamura T, Ishi M, Yano K, "Reversible control of light
31 reflection of a colloidal crystal film fabricated from monodisperse
32 mesoporous silica spheres" *LANGMUIR* 22 (6) 2444-2446, 2006. show a
33 good comparative between spheres packing and BJH pore size results.
34
35

36 Results from computer simulation performed by Gelb and Gubbings (Lev D. Gelb and
37 K. E. Gubbins, "Pore Size Distribution in Porous Glasses: A Computer Simulation
38 Study" *Langmuir* 15, 305-308, 1999) are also very eloquent. They simulated the
39 isotherm curve on a random sphere packing. This isotherm is analysed by the
40 common techniques as BET or BJH and their results compared with those obtained
41 from geometrical characterization (Monte Carlo). This study reveals a rather good
42 fitting between geometrical ("exact") results and those derived from the BJH analysis.
43
44

45
46 Regarding to the microporosity of the structural models, the Monte Carlo algorithm
47 can measure "mathematically" the space between two spheres in contact, only
48 limited by the size of the test point. So microporosity will always be found. This result
49 cannot be found on the studied real system at all.
50

51
52 The t-plot and alpha-s plot of our sample were calculated with de Boer's reference
53 curve, (taken from B.C. Lippens, B.G. Linsen, J.H. de Boer, *J. Catalysis* 3(1964) 32).
54 No downward deviation can be found. They do not show neither the morphology of
55 the microporous materials (e.g. M. Kruk et al., *Chem. Mater.* 13, 3169-3182, (2001),
56 or Jaroniec et al. *Langmuir* 15, 5410-13 (1999)), nor that obtained on a structure with
57 a "globally positive curvature" (Gomes, Blacher and Pirard, *Langmuir* 21 (5) 1703-
58 1705, 2005). Actually, the alpha-s curve is quite similar to mesoporous MCM-41 (6.0)
59 published by Kruk et al. (*Langmuir* 13 (23) 6267-73 (1997)).
60



In fact, as discussed in the paper, the microporosity of C-S-H, if any, would be blind for N_2 physisorption experiments, due to the presence of intraglobular water. So taken these facts into account, the use of the BJH method is justified and its results could be used as a reliable input for the simulation work. Moreover, due to the simulation nature of this work and the journal, microscopic observations of this one and similar samples will be considered for a complete physical and chemical characterization.