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3 **Structural models of random packing of spheres extended to bricks.**

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5 **Simulation of the nanoporous Calcium-Silicate-Hydrates.**

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3 ABSTRACT
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7 Structure simulation algorithms of random packing of spheres and bricks have been
8 developed. These algorithms were used to reproduce the nanostructure of the
9 cementitious calcium-silicate-hydrates. The textural parameters (specific surface area,
10 porosity, pore size, etc.) of a C-S-H sample, the main binding phase of **hydrated**
11 cements, have been derived from N₂-physisorption experiments. In the same time,
12 these parameters have been simulated by using a sphere-based structural model
13 where the spheres are randomly packed according to several hierarchical levels. The
14 corresponding algorithm has been extended for managing cuboids instead of
15 spheres. The C-S-H sample density is successfully predicted by considering the
16 presence of water in pores defined by the sphere network within 10 nm-size globules
17 and assuming a tobermorite-like skeleton. Simulations with bricks (3x2x1.4 nm³) yield
18 also textural parameters which are consistent with N₂-physisorption data but with a
19 globule size (22 nm) twice as big as that obtained when using spheres.
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40 KEYWORDS
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42 structure, nanoporous, hierarchical model, C-S-H, bricks.
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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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3 hierarchical levels. They are formed by linking silica tetrahedra chains in the so-called
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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 $(\text{CaO})_{1.7}(\text{SiO}_2)(\text{H}_2\text{O})_{1.8}$.

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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
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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
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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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30 Each new brick is characterized by six coordinates generated randomly. The eight
31 corners of this new brick along with the eight corners of the nearest brick are
32 consecutively transformed, first, to the universal system, and then to the reference
33 system of the other brick. This way, any given point (x, y, z) will fall inside the brick
34 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.
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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**

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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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3
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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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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

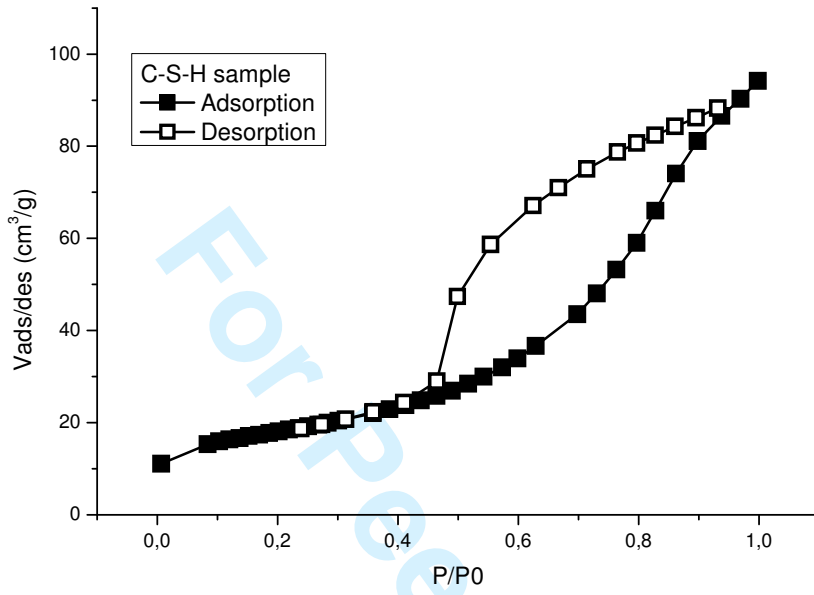


Figure 2

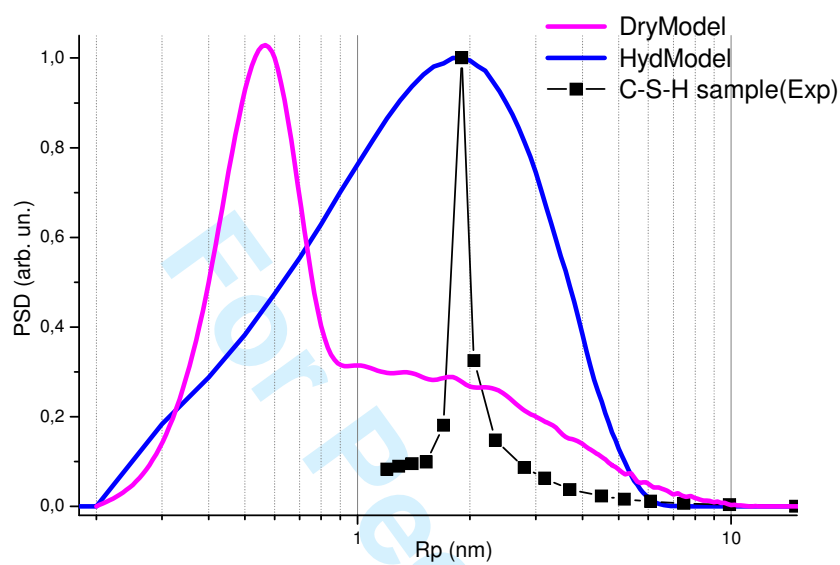
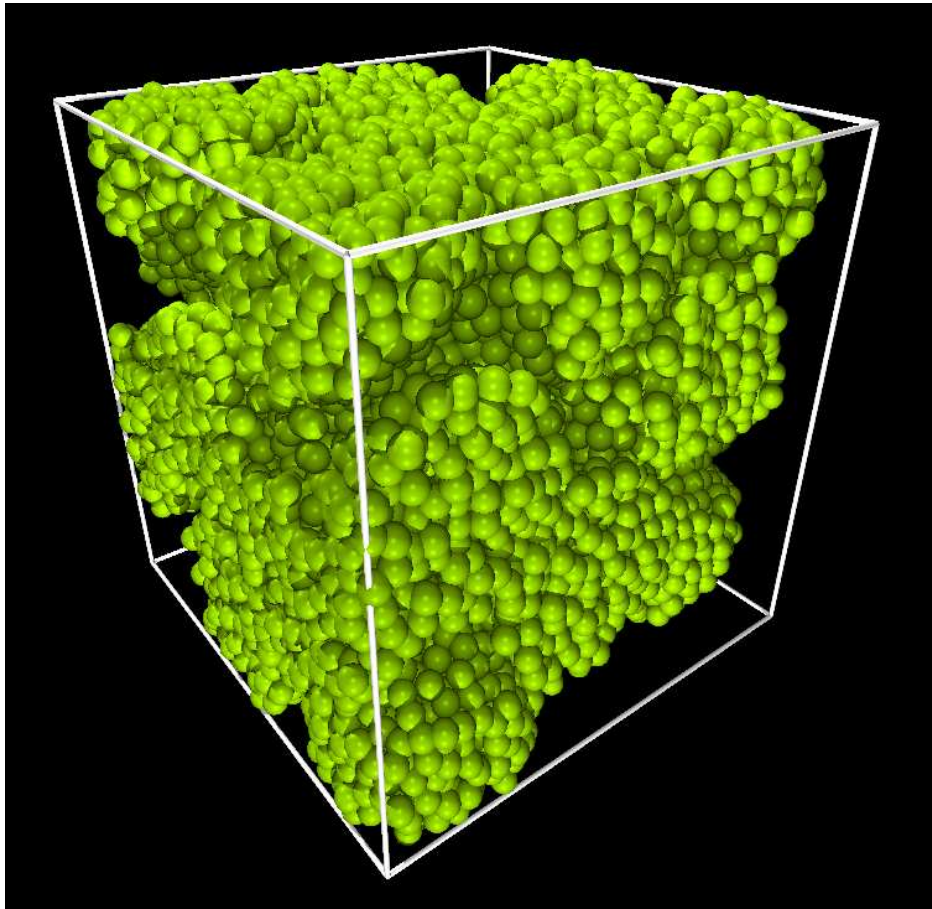
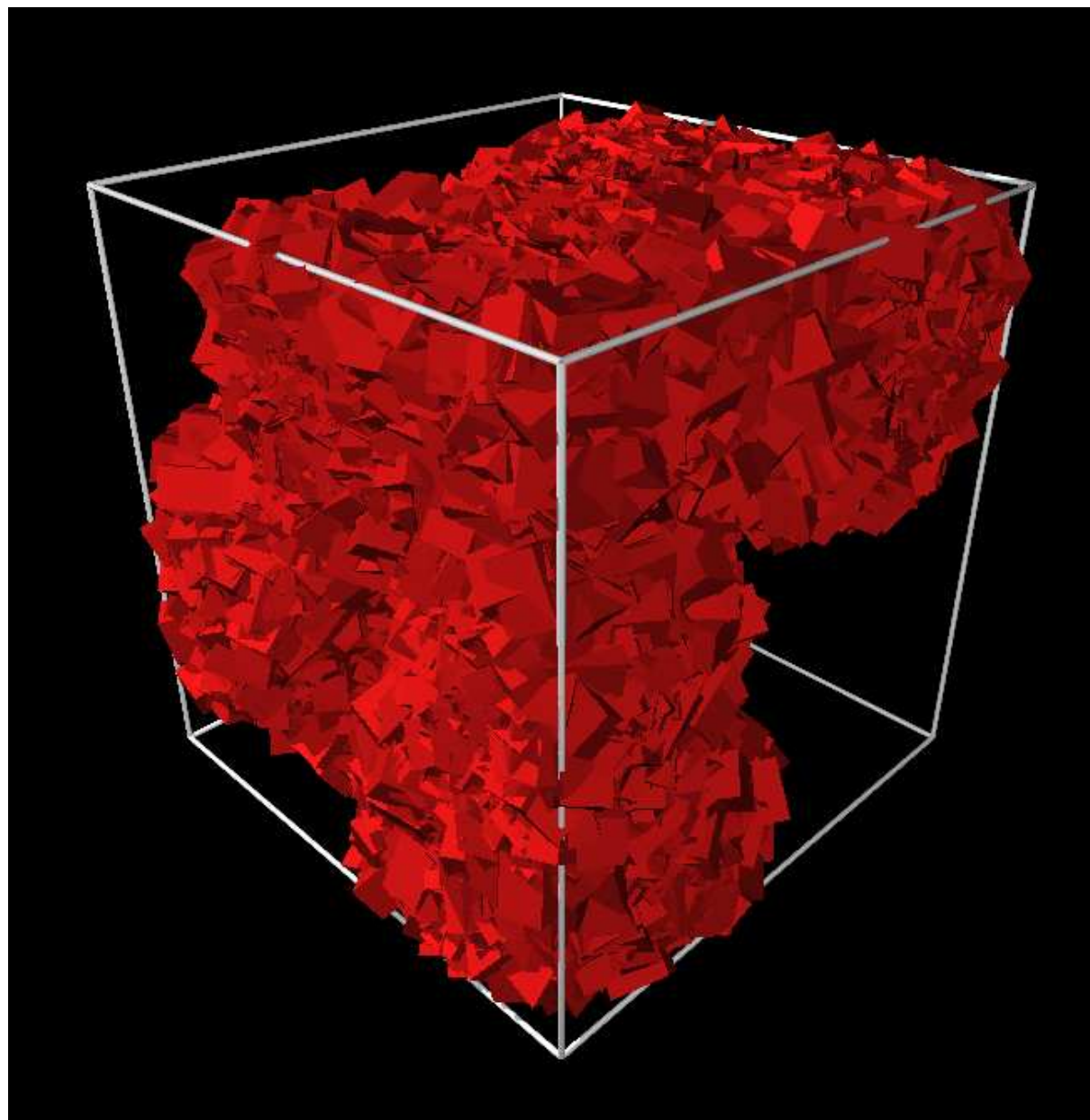


Figure 3



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Figure 4



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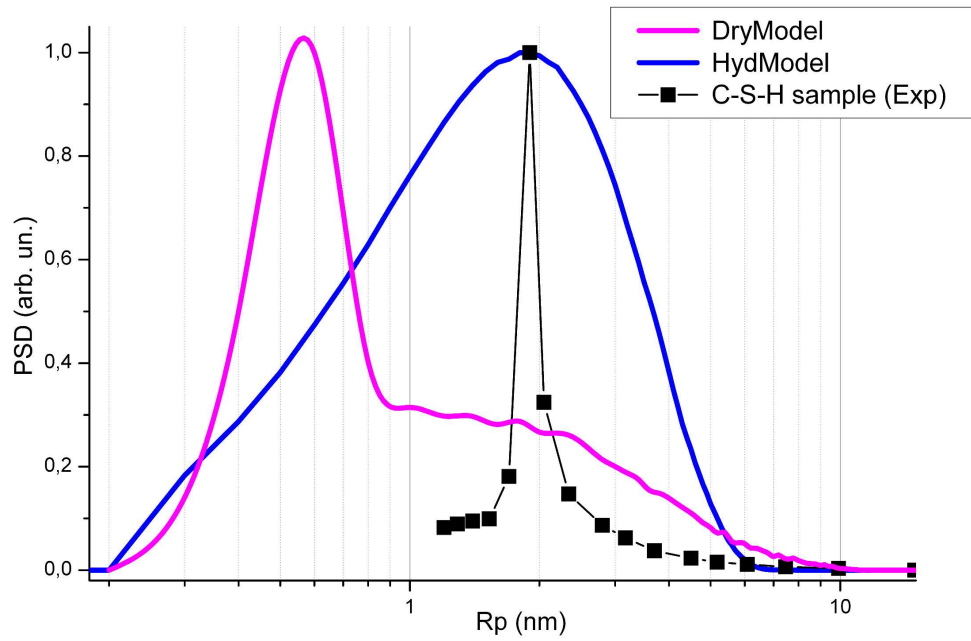


Figure 2.- Normalized Pore Size Distributions of the synthesized C-S-H and structural models HydModel and DryModel.
191x134mm (600 x 600 DPI)

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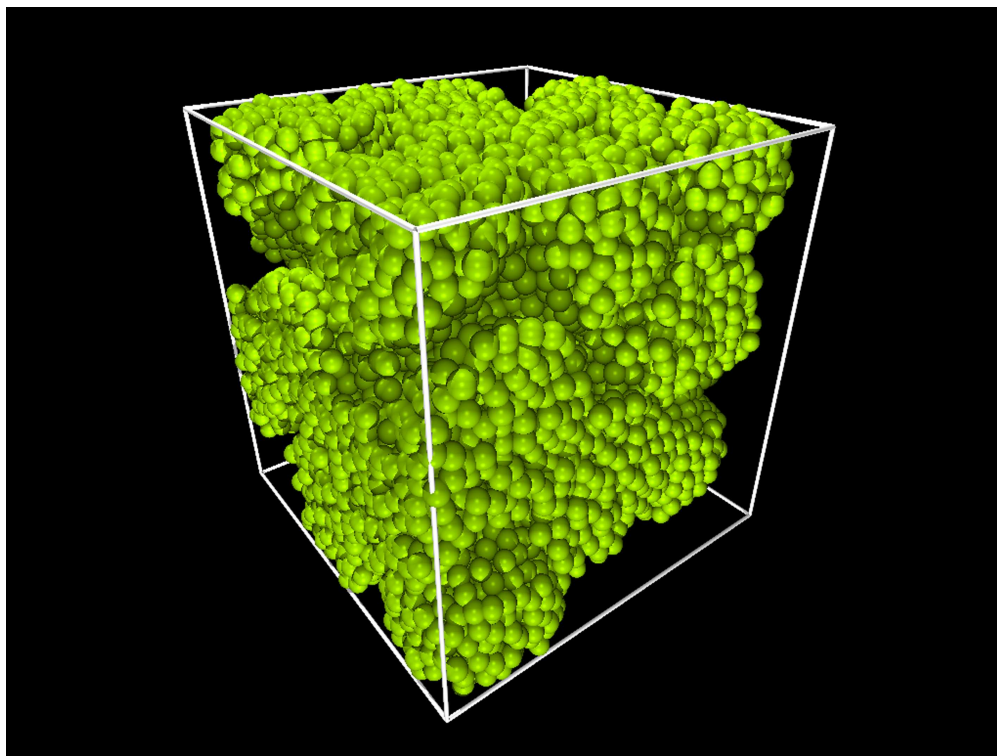


Figure 3.- Snapshot of DryModel. The sphere radius is 1.2 nm and simulation box is 26.4 nm edge.
361x270mm (200 x 200 DPI)

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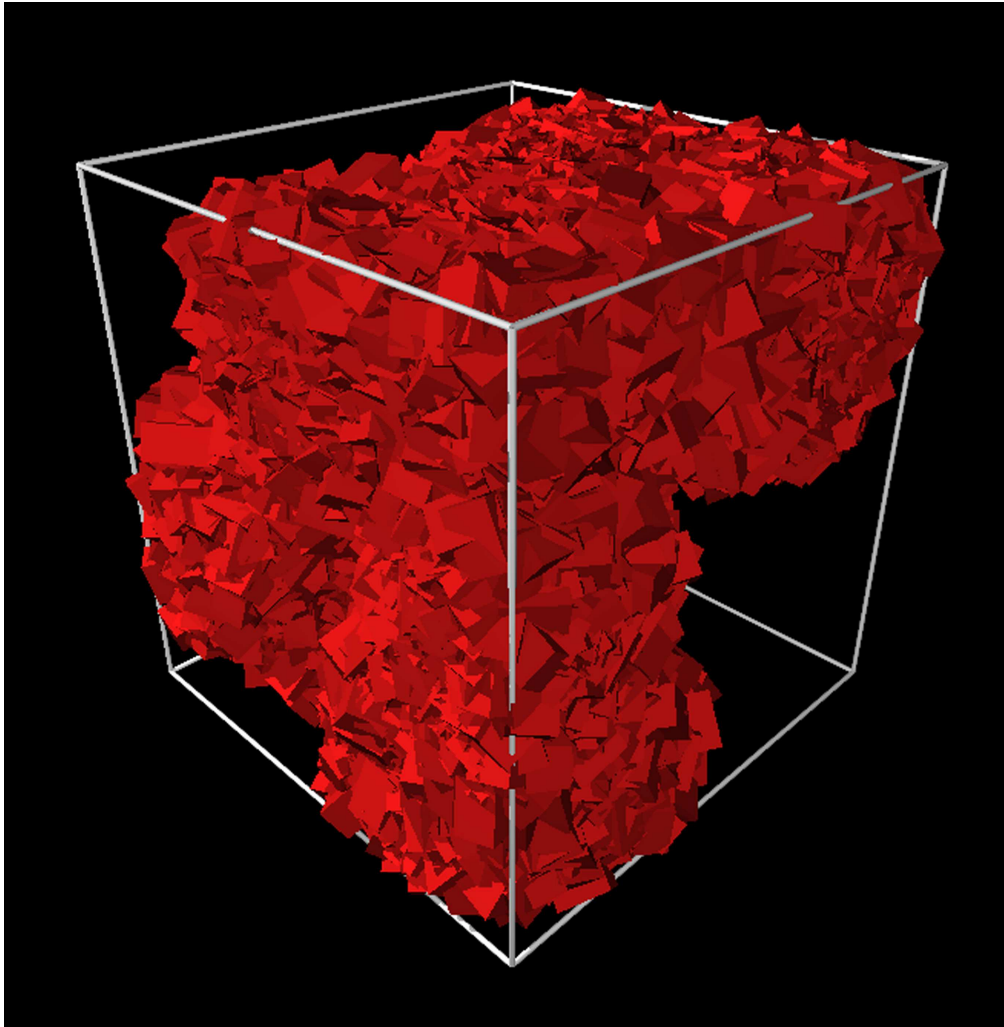


Figure 4.- Snapshot of system BrickModel. Each brick is 3x2x1.4 nm³ size.
230x235mm (300 x 300 DPI)



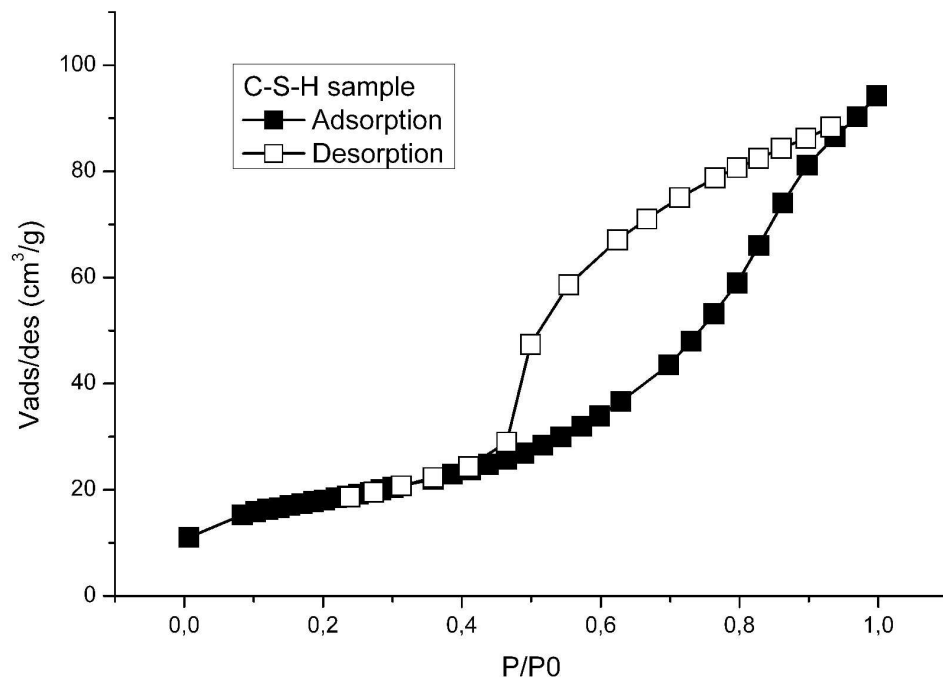


Figure 1.- Physorption isotherm of N₂ at 77K for the C-S-H sample.
272x191mm (631 x 631 DPI)