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# **Theoretical study about Calcium Silicate Hydrate (C-S-H) anisotropy growth**

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# 1. Abstract

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Calcium silicate hydrate (C-S-H) is the main phase in concrete. The size of the system, in the order of nanometres, and its non-ordered disposition are responsible of concrete's harden.

C-S-H particles have a limited size and very anisotropic shape. The atomic structure of C-S-H is known only for the bulk. In the current work an atomistic study of C-S-H growth in the different directions was performed.

C-S-H particles with different sizes were created and their energy was computed in molecular mechanics method through ReaxFF as force field and semi-empirical method through PM6 as Hamiltonian.

The results show anisotropy: the growth in x and y direction is preferable than in z direction. It shows anisotropy growth and confirms C-S-H particles' shape is as a pancake forming platelets. The size of computed particles is still in order of magnitude smaller, and thus it is not possible to have conclusions about the limited size of C-S-H particles.

## 2. Objective

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The objective of present project is the understanding of C-S-H growth. These particles are the main phase in concrete. There are several questions related with the growth of these particles to be solved.

- Explain theoretically the anisotropy growth which has been observed experimentally.
- Estimate and explain the limited size of these particles observed experimentally.
- Creation of a database of different sizes and shapes particles.

In order to solve these main questions it is necessary to study the system on atomistic level. It is necessary know the energy for different size structures to observe the gain in energy per atom increasing the size.

# 3. Introduction

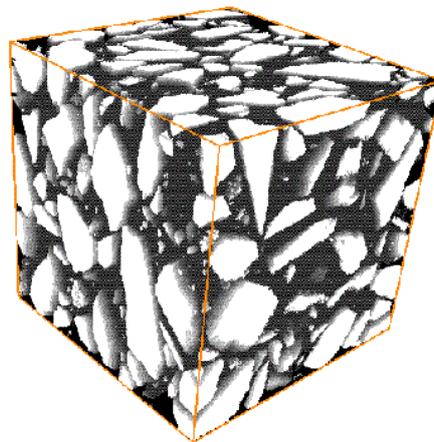
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In the present work we want to study the anisotropy growth and the optimal size in calcium silicate hydrate (C-S-H) particles which are the main phase in concrete. In this section, general concepts about cement chemistry are introduced.

Concrete is a mixture of aggregates which are sand and gravel or crushed stone and paste which is water and cement. It means that cement is an ingredient used to create concrete [1].

Concrete mechanical properties as hardness are the result of chemical and physical processes that take place between cement and water. In order to understand these properties and concrete's behaviour, it is important the knowledge of cement clinker and its reactions with water. Clinker is a nodular material which can be from 1mm to 25mm or more in diameter. Clinker has to be grinded and mixed with gypsum to obtain cement [2].

C-S-H particles are found in the size of tens nanometres in the nature [3-6]. Their non-ordered disposition and their small size cause the concrete's harden. This is because there is not a favourite direction along which concrete can be broken. C-S-H disposition in concrete appears in figure 1.



**Figure1.** C-S-H disposition in concrete

Recent studies about C-S-H nanoparticles are focused in their disposition and their size [3,5]. These are the most important properties because of they are the responsible of concrete's harden. Why C-S-H particles do not grow as a crystal or why they do not grow in an ordered way are the most frequent questions about C-S-H within scientific community. The answer to these questions is the key to understand concrete's properties and to improve them in the future.

## 3.1. Cement

Cement plays an important role in the construction, because it acts as glue between materials and when it dries up it is hardly linked with them. Cement is also very important as a concrete previous material.

From a chemical composition point of view, cement is classified inside inorganic materials as a ceramic compound. Different definitions about cement can be found.

One possible definition is: “Cement is a substance which fixes and hardens itself due to different chemical reactions when it is mixed with water” [7].

Another definition that is possible to find define it as: “Hydraulic conglomerates, it means, artificial materials of inorganic mineral nature, which eventually crushed and kneaded appropriately with water form pastes that harden because of hydration and hydrolysis reactions of its components, resulting in products hydrated mechanically stable and resistant both air and water” [8].

Portland cement is the most common used cement nowadays. Portland cement is formed by a mix of limestone and clay, which harden slowly and is really resistant. Portland cement was firstly developed from natural cements made in Britain in the middle of the 18th century [1,9-10]. Its name is derived from its similarity to Portland stone, a type of building stone quarried on the Isle of Portland in England. There are some other cement types as calcium aluminate cements, pozzolan-lime cements or slag-lime cements despite them are less used.

### 3.1.1. Cement preparation

Cement is prepared following the next steps [11]:

- a) Limestone, sand and clay are taken because of they contain the main elements (calcium, silicon, oxygen and aluminium) needed for cement preparation.
- b) Limestone rocks are crushed into small pieces.
- c) Small limestone pieces and the other materials are mixed.
- d) Raw materials are ground to a powder.
- e) Materials go to extremely hot rotating furnace to undergo a sintering process. Materials reach about 1400°C inside furnace which causes physical and chemical changes in them. Materials come out of the furnace as clinker.
- f) Clinker is cooled and grinded. A small amount of gypsum is after added. It is now the finished product, Portland cement.

### 3.1.2. Cement composition

Cement is mainly formed by four different types of compounds. These four mainly compounds can be observed in Table 1. It is often used in cement and concrete chemistry a special notation called Cement Chemist Notation (CCN) which is described in Appendix A.

**Table1.** Main compounds in Portland cement

Name	Chemical Formula	CCN
Tricalcium silicate	$3\text{CaO}\cdot\text{SiO}_2$	$\text{C}_3\text{S}$
Dicalcium silicate	$2\text{CaO}\cdot\text{SiO}_2$	$\text{C}_2\text{S}$
Tricalcium aluminate	$3\text{CaO}\cdot\text{Al}_2\text{O}_3$	$\text{C}_3\text{A}$
Tetracalcium Alumino-ferrite (Ferrite phase)	$4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$	$\text{C}_4\text{AF}$

### 3.1.3. Cement types

Several types of cement exist. Each type of cement is used depending on the conditions which this cement will be exposed and applications required for it. It can be observed in table 2 the five Portland cement types, its compositions and its applications [12].

**Table2.** Composition (%w/w) and application for the different Portland cement types

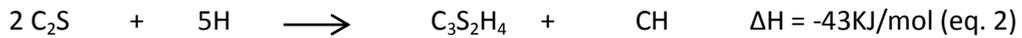
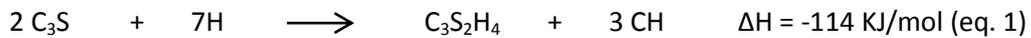
Type	Composition					Application
	$\text{C}_3\text{S}$	$\text{C}_2\text{S}$	$\text{C}_3\text{A}$	$\text{C}_4\text{AF}$	Others	
I	55	20	12	9	4	Ordinary cement. Sulphates sensitive. General building.
II	45	30	7	12	6	Moderate hydration heat. Sulphates sensitive. Antibacterial or hydrophobic cement.
III	65	10	12	8	5	Fast hardening. Emergency reparations, constructions in winter.
IV	25	50	5	13	7	Low hydration heat. Low hardening. Constructions which need a high concrete volume: dam
V	40	35	3	14	8	Sulphates resistance. Manholes, soils with sulphates presence.

In other compounds are included MgO, alkaline sulphates and free CaO. They are found in low concentrations in the different cement types as can be observed in table 2.

### 3.1.4. Cement hydration reactions

The chemical reactions describing the hydration of the cement compounds are complex. One approach to understanding them is the study of the hydration of the individual compounds separately. This approximation is not completely valid but at least is a good first approximation.

In this project, the interest resides in C-S-H particles then the only hydration reactions with interest for us are calcium silicate reactions. The hydration reactions of two calcium silicates are stoichiometrically very similar but the amount of formed calcium hydroxide and the measured hydration heats are considerably different [12]. It can be observed in equations 1 and 2.



Another important difference between  $\text{C}_3\text{S}$  and  $\text{C}_2\text{S}$  is that  $\text{C}_3\text{S}$  hydration is faster than  $\text{C}_2\text{S}$  because of  $\text{C}_2\text{S}$  is less reactive than  $\text{C}_3\text{S}$ .

The principal hydration product is a calcium silicate hydrate. The formula  $\text{C}_3\text{S}_2\text{H}_4$  is only approximate because of the composition of this hydrate is variable over a wide range. This family of hydrated compounds is known as C-S-H.

## 3.2. C-S-H phase

Calcium-silicate-hydrate (C-S-H) is the largest phase in concrete because of it comes from  $\text{C}_3\text{S}$  and  $\text{C}_2\text{S}$  which form the majority of cement as it can be observed in Table 2.

These particles have a known composition and atoms connectivity which allow represent them through a unit cell despite C-S-H phase is composed by nanoparticles in order of tens thousands atoms. C-S-H crystal structure is still under discussion because of there is not a decisive experimental technique which allows clarifying it. This experimental difficulty comes from nanometre size of the particles and a variable composition depending on the hydration. C-S-H is a compound of general formula  $\text{C}_x\text{S}_y\text{H}_z$  where calcium to silicon ratio (C/S) can vary in a wide range. However, the usual C/S ratio in hydrated cement is close to 1.7.

On the nanoscale, C-S-H is composed by particles of tens of nanometres or less in each direction [5]. It has also been observed the anisotropy in the growth in this material. The growth in x and y directions is much bigger than in z direction. For these reason, the particles use to show plate-like shapes [13].

### 3.2.1. C-S-H crystal structure

C-S-H crystal structure is formed by short silica chains linked by some calcium layers and some porous occupied by water molecule. The size of the chains is variable; the number of Si atoms in the chain might change between two to eleven. Ca atoms are disposed in layers between silica chains. Water molecules fill the empty space in the porous.

Despite C-S-H never grows to a crystal size, represent them as unit cells is a good first approximation. They grow until tens of nanometres it means that each of these particles

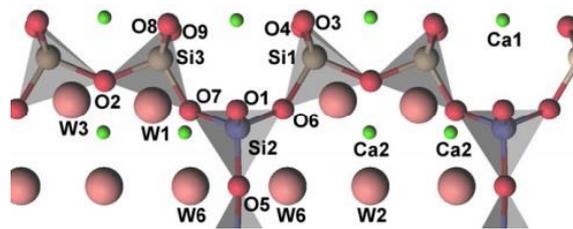
contain tens thousand atoms. It is extremely hard to build these particles without using any kind of periodicity and it is observed in some experimental techniques that C-S-H particles have some similarities to calcium silicates periodic minerals. For these reasons, the knowledge of C-S-H crystal structure is a first good approximation if we want to study them from an atomistic level. This structure can be the starting point to build after the different nanoparticles.

It had been discussed for a long time C-S-H structure for high C/S ratios, which are found in concrete. It was proposed that C-S-H in concrete could be a mix of tobermorite and jennite (both natural calcium silicate minerals). Tobermorite has a C/S ratio close to 0.8 while jennite has a C/S ratio equal to 1.5. However, synthetic C-S-H with high C/S ratios never shows XRD patterns of jennite and keeps diffraction compatible with a tobermorite-like structure [14].

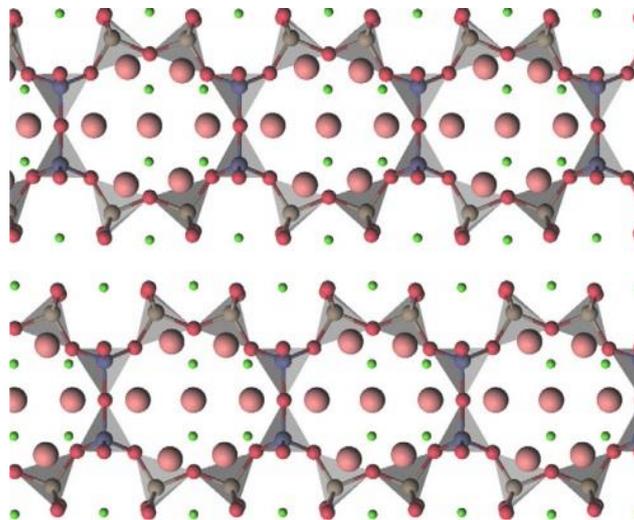
It has also been observed in  $^{29}\text{Si}$  NMR that in pure C-S-H at high C/S ratio, tertiary silica groups ( $\text{Q}_3$ ) do not exist and no conclusive evidence about monomeric ( $\text{Q}_0$ ) silica units have been found. Ratio between secondary and primary silica  $\text{Q}_2/\text{Q}_1$  is determined to be equal to 0.2 [15].

### 3.2.1.1 Construction of the models

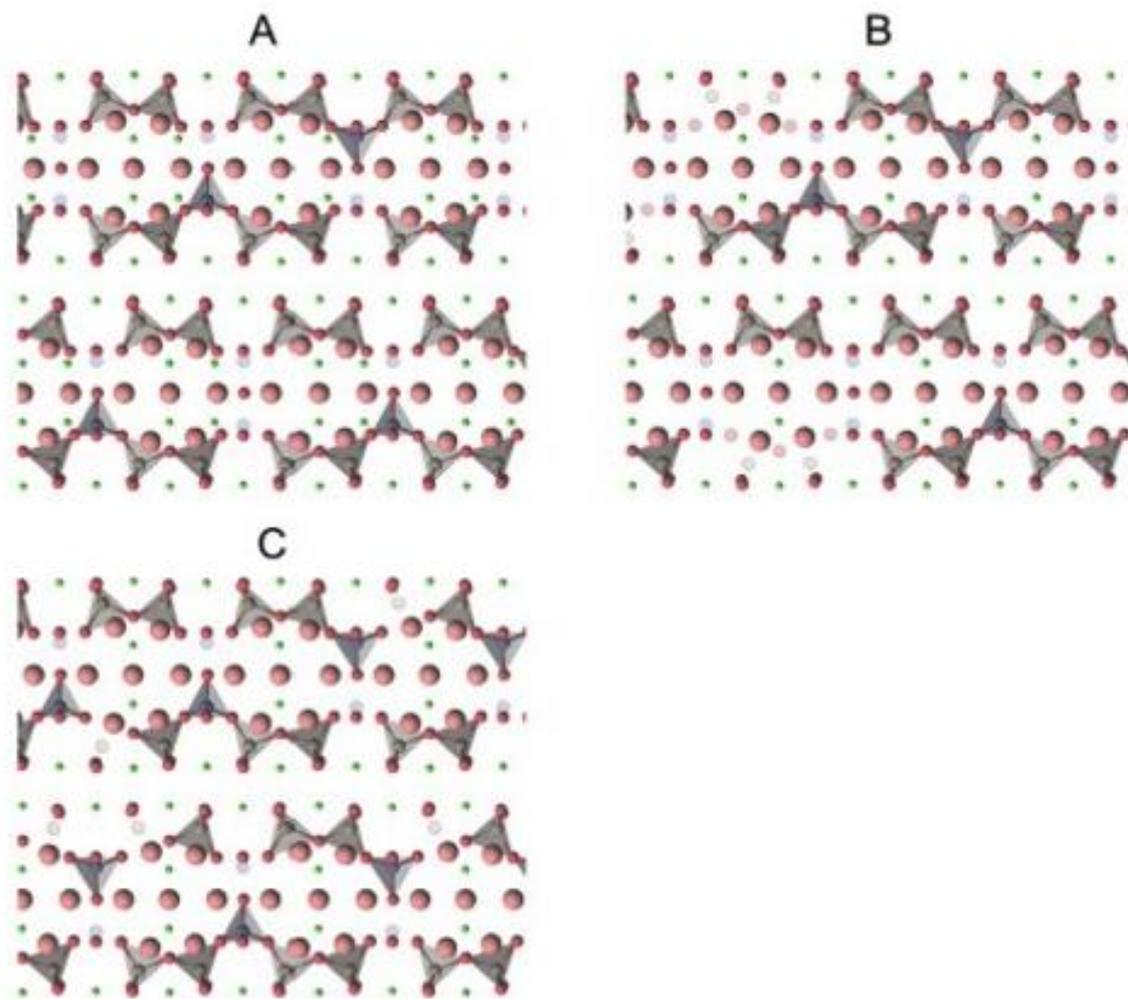
In some previous works different C-S-H crystallographic models for high C/S ratio were discussed and the most stable was accepted [16-17]. The models were created through a tobermorite 11 Å [18] structure introducing some modifications in order to obtain high calcium to silicon ratio. Initial tobermorite structure can be observed in figure 3.



**Figure2.** Atom labelling in models. W stands for a water molecule.



**Figure3.** Initial structure of ideal tobermorite 11 Å.



**Figure 4.** Structures corresponding to the three  $C_{1.67}SH_x$  models. A) corresponds model 1, B) model 2, C) model 3. Atoms removed from the original tobermorite appear as a translucent.

### 3.2.1.1.1. Model 1

Model 1 was created as a  $3 \times 4 \times 1$  supercell of tobermorite  $11 \text{ \AA}$ . Some modifications were done. Firstly, infinite silica chains of tobermorite were fragmented by randomly removing bridging Si (inverted tetrahedrons) Si2 sites according to labels in Figure 2. Then, Ca2 atoms (Fig.2) are added into the interlayers in order to adjust calcium to silicon ratio to 1.67 as it was expected.

Model 1 (Fig. 4A) is based on a calcium doped structure where each position of water coordinated has been duplicated. It is also mainly composed of dimers and pentamers of silicon oxides. But there is also chains of eight, eleven, fourteen... silicons because of Si2 were randomly removed.

#### **3.2.1.1.2. Model 2**

Model 2 (Fig. 4B) was created as a 3 x 5 x 1 supercell of tobermorite 11 Å. Modifications were introduced in order to create a Si defects similar than in jennite structure. Four consecutive silica atoms Si2-Si1-Si3-Si2 (Fig.2) were removed randomly in different parts of the supercell in order to create a distribution mainly of dimers and pentamer. Then, some calcium atoms had to be removed in order to keep the calcium to silicon ratio.

#### **3.2.1.1.3. Model 3**

Model 3 (Fig. 4C) was also created as a 3 x 5 x 1 supercell of tobermorite 11 Å. Modifications were introduced removing Si atoms randomly, no matter on the site of the removed atom. It creates some silica monomers ( $Q_0$ ), primary silica groups ( $Q_1$ ) and secondary silica groups ( $Q_2$ ). Some calcium atoms were also removed in order to keep the calcium to silicon ratio. Structures which contain more than 12% of silica monomers, 86% of primary silica groups or more than 14% of secondary silica groups were excluded.

### **3.2.1.2. Discussion**

These models were studied through force field methods and semi-empirical methods using for both periodic calculations. In force field methods, ReaxFF was used as force field while in semi-empirical methods PM6 was used as Hamiltonian.

For each model, different water concentration was possible. ReaxFF results showed that model 1 was the most stable for low water concentration followed by model 2 and 3. With increase of water content, the difference between model 1 and 2 became smaller and for H/S ratio close to 2, model 2 was most stable than model 1. The results obtained with PM6 Hamiltonian gave a preference for model 1 for all H/S ratios.

Model 1 showed the density closest to the experimental. Density values in ReaxFF results were lower than in PM6 results because of Si-O bonds are longer and H bonds are especially large in ReaxFF method.

For these reasons, accepted model was model 1. All the studies in the present work are done building different particles through this model 1.

#### **3.2.1.3. Unit cell**

C-S-H crystal structure comes from tobermorite crystal structure. Despite that after molecular dynamics cell parameters can have changed, C-S-H crystal is a monoclinic system as tobermorite 11 Å was. Parameter cells for each structure for different models are different but they are close to supercell values (Table 3).

Each model is not only formed by one structure, it is formed by a group of structures with the same composition. One structure cannot be representative for a model because C-S-H is a disordered material and the particles are not equal between them.

**Table3.** Unit cell parameters before optimization,  $\alpha$  and  $\gamma$  angles are 90.0 deg.

Cell parameter	Model 1	Model 2	Model 3
a/ Å	29.48	36.84	36.84
b/ Å	20.95	19.90	19.90
c/ Å	22.78	22.68	22.68
$\beta$ / deg	58.17	58.17	58.17

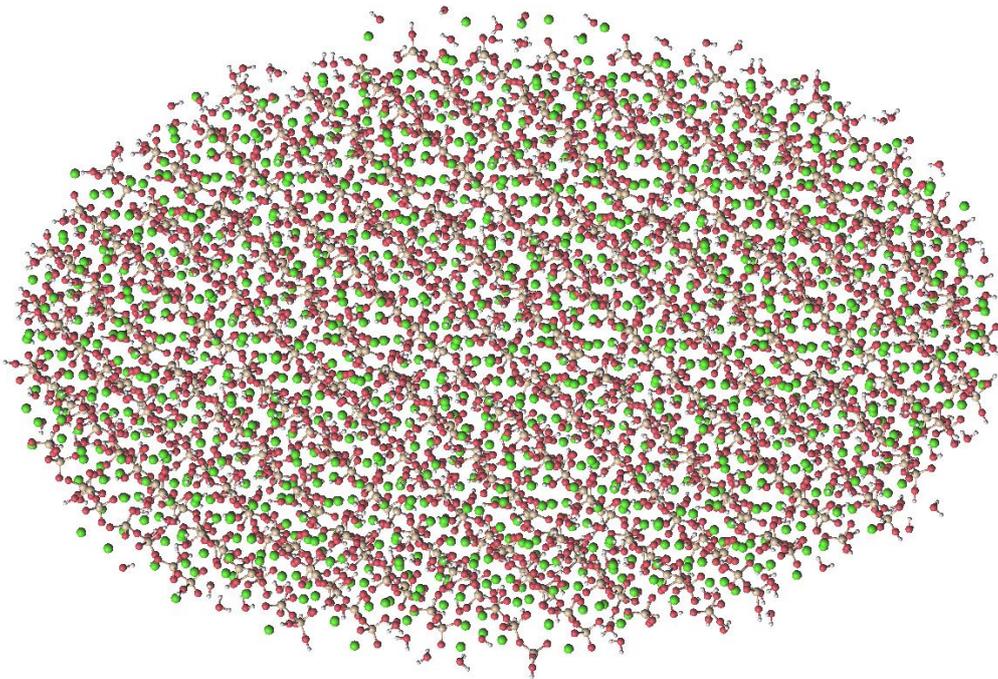
### 3.2.2. C-S-H nanoparticles

C-S-H phase does not form infinite crystals in the nature. It is found in concrete in form of nanoparticles with limited size. Based on the knowledge about C-S-H unit cells, it is possible to build the nanoparticles through these unit cells, based on the size and shape required for the particle. All the unit cells used come from model 1 for the reasons previously discussed.

Their disposition in concrete and their small size (Fig. 1) cause a high harden in concrete. It is really difficult to break concrete because it does not exist a direction along which these nanoparticles can be separated.

The main research lines about C-S-H in our days try to understand why C-S-H phase do not grow as crystals and which forces between them do not allow separating one to another. Atomistic level is necessary trying to answer the question about C-S-H growth which is the main objective in the current project.

The knowledge about size and shape of C-S-H nanoparticles is the key to understand concrete mechanical properties.



**Figure5.** C-S-H nanoparticle

# 4. Theoretical background

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In this chapter, it will be described the different calculations methods used. Some questions as which physical or chemical principles they use, which advantages and disadvantages implies using one or another or why they have been chosen in each case will be answered here.

Calculation methods are different ways for obtaining a value for the energy in the system. These methods can be quantum methods or classic methods depending on the physical and chemical principles to build them. It means that different methods use different accuracy levels. It causes that different methods allow obtaining different energy values, using much or less resources and assuming a bigger or lower error.

## 4.1. Force field methods

Force field methods might also be called molecular mechanics methods (MM). In force field methods, electronic energy is written as a parametric function of the nuclear coordinates. Electrons are not considered in force field methods. Atoms are the “building blocks” and the connectivity between atoms is needed for computing the energy with this method [19-20].

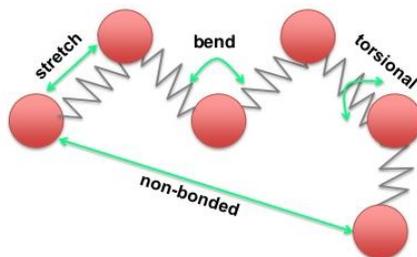
Molecules are described by a ‘ball and spring’ model in force field. Atoms have different sizes and softness and bonds have different lengths and stiffness.

### 4.1.1. The force field energy

The force field energy is the sum of different terms (eq. 3), each describing the energy required for distorting a molecule in a specific fashion (Fig. 6).

$$E_{FF} = E_{str} + E_{bend} + E_{tors} + E_{vdw} + E_{el} + E_{cross} \quad (\text{eq. 3})$$

$E_{str}$  is the energy function for stretching bond between two atoms,  $E_{bend}$  is the required energy for bending an angle,  $E_{tors}$  is the torsional energy for rotation around a bond,  $E_{vdw}$  and  $E_{el}$  describe the non-bonded energy and  $E_{cross}$  is a corrective term between the first three terms.



**Figure6.** Fundamental force field energy terms.

#### 4.1.1.1. The stretch energy

$E_{\text{str}}$  is the term for stretching a bond between two atom types: A and B. It is usually represented as a Taylor expansion around “natural” or equilibrium bond length  $R_0$  (eq.4).

$$E_{\text{str}}(R^{\text{AB}} - R_0^{\text{AB}}) = E(0) + \frac{dE}{dR} (R^{\text{AB}} - R_0^{\text{AB}}) + \frac{1}{2} \frac{d^2E}{dR^2} (R^{\text{AB}} - R_0^{\text{AB}})^2 + \frac{1}{6} \frac{d^3E}{dR^3} (R^{\text{AB}} - R_0^{\text{AB}})^3 + \dots \quad (\text{eq. 4})$$

The bigger the expansion order is, the larger spread of distance the energy value can be accepted. Independent term  $E(0)$  is defined as equal to zero because of it does not matter where zero point energy is, the importance resides in energy differences not in absolute values. First derivative term is equal to zero because of  $R_0^{\text{AB}}$  must be an energetically minimum. Other derivatives terms are constants and they usually appears as  $k_2^{\text{AB}}$ ,  $k_3^{\text{AB}}$  ...

#### 4.1.1.2. The bending energy

$E_{\text{bend}}$  is the term for bending an angle between three atoms. It is also represented as a Taylor expansion. It is usually terminated at second order, obtaining a harmonic expression (eq.5).

$$E_{\text{bend}}(\theta^{\text{ABC}} - \theta_0^{\text{ABC}}) = k^{\text{ABC}} (\theta^{\text{ABC}} - \theta_0^{\text{ABC}})^2 \quad (\text{eq. 5})$$

The second order expansion is usually sufficient in the chemically import region  $\sim 40\text{KJ/mol}$ .

#### 4.1.1.3. The torsional energy

$E_{\text{tors}}$  describes the energy function of dihedral angle. This energy corresponds with a rotation around B-C, where A-B-C-D atoms are connected. Torsional energy is often lower than bending and stretching energy. For this reason, large deviations from the minimum structure may occur and a Taylor expansion is not a good idea. Torsional energy has periodicity and it is written as a Fourier series (eq. 6).

$$E_{\text{tors}}(\omega) = \sum V_n \cos(n\omega) \quad (\text{eq.6})$$

The  $n$  describes different situations which might be presented around B-C bond rotation. The  $n=1$  term describes a rotation that is periodic by  $360^\circ$ , the  $n=2$  term is periodic by  $180^\circ$ , the  $n=3$  term is periodic by  $120^\circ$ ... The  $V_n$  constants determine the height of the barrier for rotation around B-C bond.

#### 4.1.1.4. The Van der Waals energy

$E_{\text{vdw}}$  is the Van der Waals energy describing the repulsion or attraction between atoms that are not directly connected. This is the interaction between electron clouds. At large interatomic distances it is zero and it becomes very repulsive for short distances. At intermediate distances, there is a slight attraction because of induced dipole-dipole interactions or London forces.

It is often represented by Lennard-Jonnes potential where  $\epsilon$  is the depth of the minimum or geometric mean of atomic ‘softness’ and  $R_0$  the minimum energy distance (eq.7).

$$E_{\text{vdw}}(R) = \epsilon \left[ \left( \frac{R_0}{R} \right)^{12} - 2 \left( \frac{R_0}{R} \right)^6 \right] \quad (\text{eq.7})$$

#### 4.1.1.5. The electrostatic energy

The other part of the non-bonded energy is because of a redistribution of electrons which create positive and negative charges in the different atoms. Atoms can be considered as punctual interactions and their interactions are computed by Coulomb potential (eq. 8). The bonds might be considered as dipoles and their interactions are computed in another way (eq.9).

$$E_{el}(R^{AB}) = \frac{Q^A Q^B}{\epsilon R^{AB}} \quad (\text{eq. 8})$$

$$E_{el}(R^{AB}) = \frac{\mu^A \mu^B}{\epsilon (R^{AB})^3} (\cos \chi - 3 \cos \alpha_A \cos \alpha_B) \quad (\text{eq. 9})$$

#### 4.1.1.6. Cross terms

This term is created in order to avoid an accumulation of errors. For example, it happens when one bond must be a bit longer or shorter than  $R_0$  then the optimal value for the angle is not the same as it was.

Cross term is created in order to correct the total energy value and there are stretching-stretching corrections, stretching-bending, bending-bending....

### 4.1.2. Advantages and disadvantages

The main advantages of force field methods are the speed with which calculations are run and the big systems that can be afforded through these methods.

The disadvantage resides in the need of good parameters. The lack of good parameters is the main problem and it causes bad results. As it is obvious, these methods have the low accuracy because of electrons are not considered in them.

#### 4.1.3. Types

It exist a lot of different force fields depending on which system must be studied one or other is a better option. In Table 4, some of them have been picked up and compared.

**Table4.** Comparison of common force fields

Force field	Atom types	$E_{str}/E_{bend}$	$E_{el}/E_{cross}$	Molecules
AMBER	41	P2/ P2	Charge/ none	Proteins, nucleic acids
CHARMM	29	P2/ P2	Charge/ none	Proteins
GROMOS	97	P2/ P2	Charge/ none	Proteins, nucleic acids,
MM3	153	P4/ P6	Dipole or charge/ sb,bb,st	General (all elements)
ReaxFF <sub>SiO</sub>	9	Exponential	Charge/ none	Silicon oxides

The force field used in the present work has been ReaxFF<sub>SiO</sub> because of it is created specifically for silicon oxides. They are found in C-S-H particles. A fundamental difference between ReaxFF and other force fields is that it does not need connectivity assignments for the chemical bonds. The total energy is calculated as a sum of bond and Van der Waals energy [21].

#### 4.1.4. Molecular dynamics

Generally, the properties are calculated for static systems. The general criterion in optimizations is to find a minimum. However, there are systems, often big systems, where it is not a good idea only searching for a minimum because they have several local minimums. In these systems, it is a good idea doing a molecular dynamics which allows finding different minimums in a structure [19].

Molecular dynamics allow arrive to different structures solving Newton's second equation in differential form (eq. 10). If the system has enough Temperature and dynamics is applied for enough time, different minimums in the structure will be picked up.

$$-\frac{dV}{dr} = \frac{d^2r}{dt^2} \text{ (eq.10)}$$

The Temperature is computed in the criterion to accept or decline a new structure. If the system is localized in a local minimum and temperature is not large enough the system never will escape to this minimum because all the new structures will be discarded for increasing the energy.

In the current project, it is not applied a normal molecular dynamics. The objective is not finding a lot of different minimums and making an average of them. We want just relaxing a little the structure and find a global minimum. The molecular dynamics is done to a low temperature and for a short time.

## 4.2. Semi-empirical methods

A brief introduction about mean field methods has to be done before starting with semi-empirical methods because of semi-empirical methods are derived from the Hartree-Fock model by neglecting some of its integrals [19-20].

Hartree-Fock model (HF) is an "ab initio" calculations, it means that its solutions are generated just by solving time-independent non relativistic Schrödinger equation (eq. 11) without references to experimental data.

$$\mathbf{H}\psi = E\psi \text{ (eq. 11)}$$

Hamiltonian is composed by kinetic and potential energies of the nuclei and electrons. Born-Oppenheimer approximation considers nucleuses are quiet in comparison with electrons. It allows neglecting kinetic energy of nucleus because they are thousand times heavier than

electrons. It also allows us writing potential energy between nucleuses as a constant because it is assumed that they are quiet.

HF methods assume that the interaction between one electron and all others can be replaced by the interaction between one electron and the charge density caused by all the others. It simplifies the Hamiltonian (eq. 12) and allows solving it because now the energy of each electron only depends on its own coordinates.

$$\nabla^2 \psi_{1s}(r) - \frac{Ze^2}{r} \psi_{1s}(r) - \left( \sum_{i=2} \frac{e^2 \psi_i^2(r)}{r} \right) \psi_{1s}(r) + \left( \sum_{i=2} \frac{e^2 \psi_i^*(r) \psi_{1s}(r)}{r} \right) \psi_i(r) = \hat{f} \psi_{1s}(r) \text{ (eq.12)}$$

The first and the second term are one-electron operator. They are first electron kinetic energy and first electron-nucleus potential energy, respectively. The third and fourth terms are two electron operators that compute the potential energy of between the first electron and the mean field generated by the other electrons.

In the wave function, it is used the LCAO Approximation (Linear Combination of Atomic Orbitals). Molecular orbitals are represented as linear combination of atomic orbitals.

Each term in Fock matrix is built through the interaction between two molecular orbitals under Hamiltonian influence (eq.13).

$$f_{ij} = \langle \psi_i | \hat{f} | \psi_j \rangle \text{ (eq.13)}$$

A lot of integrals must be solved. They are classified depending on the molecular orbitals which are involved and the number of centres which appear in the integral.

When i is equal to j then the integral to solve is one-electron integral.

$$a_k a_l \langle \chi^k | \hat{h} | \chi^l \rangle = a_k a_l \left( \int \chi^k \nabla^2 \chi^l dr + \int \chi^k (\hat{V}^A + \hat{V}^B + \hat{V}^C + \dots) \chi^l dr \right) \text{ (eq. 14)}$$

$$a_k b_l \langle \chi^k | \hat{h} | \chi^l \rangle = a_k b_l \left( \int \chi^k \nabla^2 \chi^l dr + \int \chi^k (\hat{V}^A + \hat{V}^B + \hat{V}^C + \dots) \chi^l dr \right) \text{ (eq. 15)}$$

Equation 14 and 15 are terms within one of diagonal Fock matrix's term. In equation 14, one-centre integrals and two-centre integrals appear while in equation 15, two- and three-center integrals appear. This number of integrals increases up to square increasing the number of atoms.

When i is different to j then to integral to solve is two-electron integral. This number of integrals increases up to four increasing the number of atoms.

$$a_k a_l a_m a_n \int \frac{\chi^k(r_1) \chi^l(r_1) \chi^m(r_2) \chi^n(r_2)}{r_{12}} dr_1 dr_2 \text{ one-center integrals (eq.16)}$$

$$a_k b_l a_m b_n \int \frac{\chi^k(r_1) \chi^l(r_1) \chi^m(r_2) \chi^n(r_2)}{r_{12}} dr_1 dr_2 \text{ two-center integrals (eq.17)}$$

$$a_k b_l b_m c_n \int \frac{\chi^k(r_1) \chi^l(r_1) \chi^m(r_2) \chi^n(r_2)}{r_{12}} dr_1 dr_2 \text{ three-center integrals (eq.18)}$$

$$a_k b_l c_m d_n \int \frac{\chi^k(r_1) \chi^l(r_1) \chi^m(r_2) \chi^n(r_2)}{r_{12}} dr_1 dr_2 \text{ four-center integrals (eq.19)}$$

Semi-empirical methods are not “ab initio” methods due to not all these integrals are solved. One-electron integrals are solved if it is one-centre integral and are neglected if the integral is between two centres. Two-electron integrals can be neglected or can be parameterized through empirical results.

The basis set is a minimal basis set, only valence orbitals are considered. All three- and four-centre integrals are neglected.

## 4.2.1. Types

It exist different types of semi-empirical methods depending on the integrals that are parameterized instead of solved.

### 4.2.1.1. Neglect of Diatomic Differential Overlap (NDDO).

NDDO is the most complex group within semi-empirical methods. It exist more than one parameter for couple of atoms in two-electron between two centres integrals. It also exist one parameter for each atom in the two-electron one-centre integrals. It exist one parameter for each couple of orbital type.

$$(ss|ss) = \gamma^{sp} \quad (pp|pp) = \gamma^{pp} \dots \quad (s^A s^A | s^B s^B) = \gamma_{ss}^{AB} \quad (s^A s^A | p^B p^B) = \gamma_{sp}^{AB} \dots$$

NDDO is still widely used, while INDO and CNDO are obsolete.

In the present work semi-empirical method used has been PM6 which is one of NDDO type.

PM6 has parameters for 70 different atoms. A large amount of species was used to build the parameters of PM6 Hamiltonian. PM6 is the new version of PM5 and PM4 semi-empirical methods and there is a lower error on its calculations [22].

## 4.2. Comparison between PM6 and ReaxFF

PM6 is a Hamiltonian, it is included within semi-empirical methods and ReaxFF is a force field. The difference between PM6 and ReaxFF resides in their respective accuracies. Their accuracies depend on the number of calculations that have to be done in each method. At the same time, this number of calculations causes a bigger or lower computational time. In the Table 5 appears a comparison in the time used by ReaxFF and PM6 for different cylinder sizes and shapes which will be explained in detail in the following chapters.

ReaxFF is much faster than PM6 (Table 5). It can be observed that the difference is really important. The number of converged structures in ReaxFF is much bigger than in PM6.

**Table5.** Comparison in the time used by ReaxFF and PM6 for different sizes.

SIZE		COMPOSITION				METHOD	
Radius	Height	Si	Ca	O	H	ReaxFF	PM6
5	11.5	8	12	43	30	8sec	7min
10	11.5	34	54	176	108	46sec	4h 15min 53sec
15	11.5	71	124	370	208	1min 53sec	-
80	11.5	2072	3534	10503	5650	1h 13min	-
5	23	17	28	90	56	18sec	31min 13sec
45	23	1338	2241	6715	3596	49min12sec	-
50	23	1652	2769	8280	4414	1h 02min	-
5	34.5	26	39	139	96	30sec	2h 20min
45	34.5	1994	3309	9899	5204	1h 26min 51sec	-
5	46	34	48	176	120	34sec	5h
35	46	1640	2716	8198	4404	1h 20min	-
30	57.5	1482	2462	7451	4050	1h 05min	-

### 4.3. Other possible methods

It would be interesting doing the calculations in these systems with a more accurate method as DFT. The problem resides in the computation time and computational limitations as memory that DFT demands.

DFT is even more accurate than semi-empirical method. While in semi-empirical methods some Hartree-Fock integrals are neglected and some of them are parameterised, in DFT methods all HF integrals are computed and more terms are included to add the correlation energy. For these reasons, DFT usual calculations are not affordable yet for this kind of systems [19].

However, it has been implemented recently a new method for using DFT that can be applied in big systems as C-S-H particles. This method divides the system in several smaller parts. Each of these parts is computed by DFT and its influence is included to the Hamiltonian of the other parts as a sum of punctual charges that represent its electronic density. Each part change for the influence of the others to arrive to a convergence.

This method is still in development because it is not clear how to divide the particles. It is thought that each of these smaller parts should be electro-neutral but it is not developed yet. It will be done in the future.

# 5. Methods

---

It will be discussed in this chapter, the used methods in order to obtain the results, why they have been chosen and how they work in order to simplify the understanding of the work.

It is necessary a code that build different cylinders from the bulk in order to prove the growth properties on these particles.

## 5.1. Construction of C-S-H particles

C-S-H particles are built from the unit cells created in previous works [16]. It has been discussed previously that the most stable model is model 1. All the unit cells used to generate the different particles are from Model 1.

It has been explained previously that the main objective in the present work was to determine the ideal size for C-S-H particles and their anisotropy growth. C-S-H nanoparticles' shape in experimental works looks as plates which can be geometrically represented by cylinders. It is also chosen cylinders as geometrical shape because C-S-H in the bulk is a layered material in z-direction. If we choose sphere as the shape of the particles these layers would be destroyed. The cut in x and y directions can be done without limitations and radius might have any value. But, in z direction, the cut has to be done taking care in the layers and the height only might have specific values.

For these reasons, cylinders are taken as chemical system in this project. These cylinders are built through a code.

The code needs the radius and height for the cylinder that will be built and the origin of coordinates in the unit cell for the expected cylinder. It is also needed the geometry of the unit cell that will be used, including its translation vectors.

Cylinders are built based on given dimensions. This cylinder is created in mathematical criteria without taking care in which bonds are being cut or which is the system charge. For these reasons, some charge and connectivity rules must be applied.

These rules can be applied in some different ways. Rules in our code have been built through chemical sense but it is not the only way of doing it. It is also possible to apply these rules through an energetically criteria. It would be possible through a small potential comparing the energy for the system removing/adding one atom in different parts of the system. In this code, it has been chosen a chemical criterion because of it was easier and the program run faster.

### 5.1.1. Dimensions

First of all is built a 'supercell' from which the final cylinders will be built. This 'supercell' is built as a combination of unit cells.

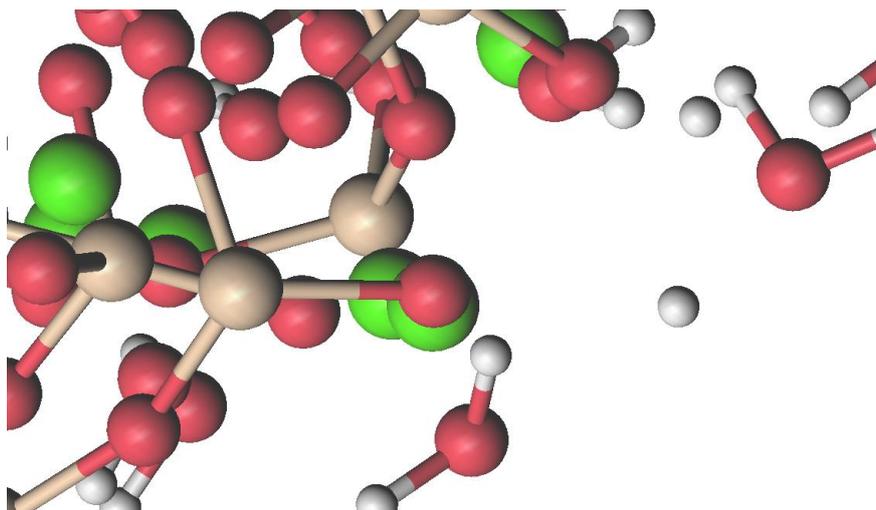
The number of unit cells, which have to be disposed along each direction, is established in the following way. The length of each translation vector is computed and the largest translation vector is selected. Next, the radius value is multiplied for three. This value is divided by the length of the largest translation vector and the value is approximated to the closest integer. The obtained value is called  $i_1$  and if it was 0 then it is established as 1, it is the expansion of unit cells that the code will do along x and y axes in both positive and negative directions. (Example: if  $i_1=2$ , the 'supercell' will have five unit cells length in both x and y axes).

Similar procedure is done in z direction, the height value is multiplied for two and the value is divided by the length of the largest translation vector and the value is approximated. The obtained value is called  $i_2$  and has the same limitations and properties as  $i_1$ .

After the 'supercell' is created, the first cylinder has the geometry to be built. Through this 'supercell' geometry, taking the origin, radius and height the cylinder is built.

### 5.1.2. Connectivity rules

The cylinder is now built but some covalent bonds have been cut and some atoms have lost all their connectivity (Fig.7). For these reasons, several rules must be applied in order to preserve atoms connectivity.



**Figure7.** Si trivalent and non-bonded H before can be observed before applying connectivity rules.

A chemical criterion has been applied to create the code. Silicon and hydrogen atoms are always connected to the same number of oxygen atoms forming covalent bonds. Rules have been created so that all silicon atoms in the system have four oxygen neighbours and all hydrogen atoms one oxygen neighbour. Oxygen can be connected to silicon, hydrogen and calcium forming covalent or ionic bonds. The number of possibilities complicates rules establishment for oxygen, but different rules have been applied so that oxygen has at least two neighbours. Applying rules for calcium is even more difficult because calcium is only connected to oxygen forming ionic bond. Each calcium atom has not the same number of oxygen neighbours in the unit cell and it is not possible to establish easily a rule. The created rule says that all calcium atoms must be connected with at least one oxygen atoms.

The rules used in the code can be observed entirely in Appendix B.1. All rules are applied twice in order to avoid that a rule could spoil another one.

### **5.1.3. Charge rules**

Created cylinders have to be electro-neutral as C-S-H nanoparticles are in nature. Some rules have to be added after the connectivity rules in order to obtain a non-charged system.

It is established a charge of +4 for Si, +2 for Ca, +1 for H and -2 for O. Based on this charges, the total charge for the system is computed. Three different situations can happen, the system might be positively charged, the system might be negatively charged or the system might be neutral.

If the system is not neutral the rules in Appendix B.2 are applied.

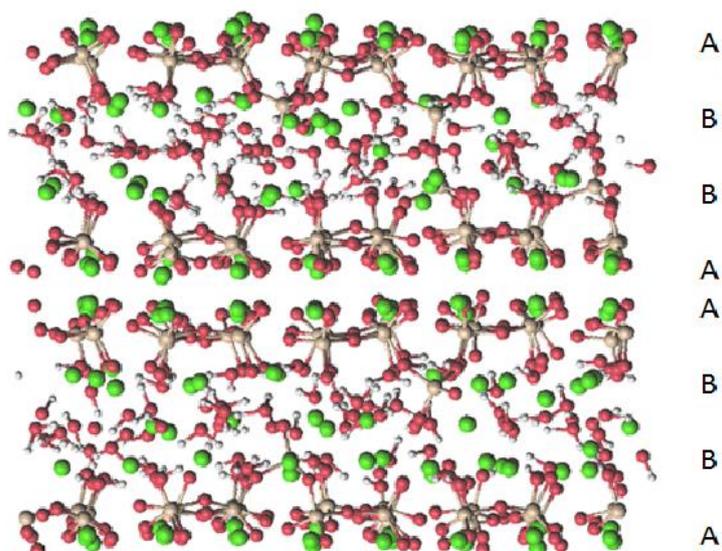
### **5.1.4. Database**

It has been created a big database with a large number of different particles. There are almost five hundreds of different structures with different sizes and different shapes. The radius of these cylinders changes from 5 to 80 Å and the height changes from 11.5 to 80 Å.

## **5.2. C-S-H surfaces**

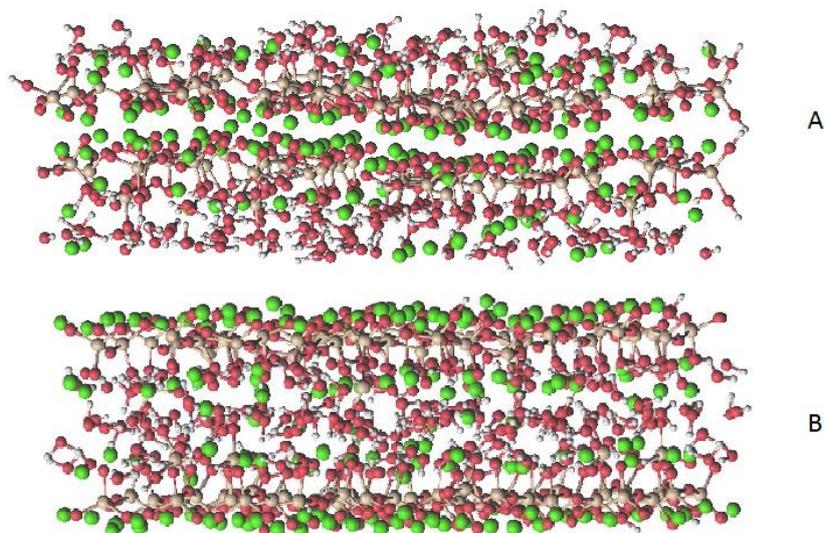
C-S-H particles are composed by Ca, Si, O and H atoms. Si and H are both bonded to O forming covalent bonds while Ca forms ionic bonds with O. Ca forms in the structure several layers in z direction. The growth around these layers is studied in this part of the project.

In the structure, two different kinds of Ca layers can be distinguished according to their different environments. Layers kinds A have empty space between them while layers kinds B have water molecules between them. It can be observed in the figure 8.



**Figure8.** C-S-H view through yz plane

The sequence in these Ca layers is not an alternative sequence. It is presented a sequence type ABBAABBA... In this part of the project is studied if it is better a structure type ABBA or BAAB (Fig9.A and Fig9.B) which are the two only possible structures formed without breaking covalent interlay bonds.



**Figure9.** C-S-H surfaces: A) Structure BAAB, B) Structure ABBA.

In order to prove which of these sequences is more stable several cylinders are created with the code. These cylinders have four different radius values (10, 12.5, 15 and 17.5) Å and two different heights (11.5 and 23) Å which correspond to half of the cell and all cell length in z direction respectively. They are created from optimized unit cells with different water contents. Different cylinders of each group (same radius and same height) are created modifying their origins in unit cells. Four different families are obtained according to origin in z direction (different Ca layers sequence).

Each of these families has a group of cylinders with structure type ABBA for one height value and a group with structure type BAAB for the other height value as it can be observed in Table6.

**Table6.** Four different families according to z-origin and its layers sequence

Family	Z-Origin	Height 11.5 A	Height 23 A
Structure 0	11.5	BAAB	ABBA ABBA
Structure 1	17.25	ABBA	BAAB BAAB
Structure 2	0.0	BAAB	ABBA ABBA
Structure 3	5.75	ABBA	BAAB BAAB

Calculations are done in two different environments for the particles. On one hand, calculations are done in the vacuum. On another hand, the cylinders are solvated with a large amount of water molecules. Another objective in this part is to observe if there is an important difference between calculations done in vacuum and calculations done with the solvation model. Cylinders built by code are used as initial geometries in the LAMMPS calculations for vacuum environment; ReaxFF is used as force field.

Structures obtained after the optimization in vacuum are used as the initial structures in the solvation model. In order to add this large amount of water molecules, Packmol package is used. It is chosen a tolerance distance between atoms of 2 Å. A large amount of water molecules (3500) are added in a cubic box with 50 Å as side. The amount of water added is calculated in order to obtain a system with density between 0.85-1 g/cm<sup>3</sup> depending on the cylinder size in the box. After Packmol package is executed, solvated cylinders are obtained and they are optimized in LAMMPS.

In some previous works, it has been demonstrated that semi-empirical calculations offers a results closer to the experimental than molecular mechanics calculations. For this reason, the smallest groups of cylinders are also run in PM6. The results in PM6 calculations should confirm the same tendency observed in ReaxFF results.

### 5.3. C-S-H in water environment

C-S-H grow in the nature in an aqueous environment because of C-S-H are formed from hydrated reaction of C<sub>2</sub>S and C<sub>3</sub>S.

Despite C-S-H grow in an aqueous environment; calculations with an aqueous environment are more expensive computationally than calculations in vacuum. For this reason, different structures are created and they are run in different environments.

Calculations are run in MOPAC using semi-empirical methods with PM6 as Hamiltonian. They are run in MOPAC because it offers a better accuracy but can only be affordable for these small systems.

Firstly, small molecules are created in order to prove that aqueous environment is less energetic than vacuum environment. After, some structures are created with different radiuses and different heights in order to study if water environment is always less energetic in the same proportion; it would mean that vacuum calculations can be used. Despite vacuum calculations do not give the most accurate energy, the observed tendency would be the same and vacuum calculations might be used.

Aqueous environment is created in three different ways.

- A) Explicit water: water molecules are explicitly added to the structure with Packmol package. The same amount of water is added for all the structures.
- B) COSMO: an external potential is added out of the structure simulating the water influence.
- C) Mix: is a mix between COSMO and explicit water. Explicit water is added and the external potential too.

## 5.4. C-S-H growth

The growth of these different cylinders is done by blocks; it means that the growth is not done in the way of adding more atoms to an initial structure. Cylinders with different sizes are taken and their energy per atom is computed and plotted. It is done in this way for several reasons. Firstly, because it is not known the building block in C-S-H, it is not obvious how these particles can grow. Secondly, because the created intermediates are unstable due to it is not known the building block for C-S-H. Finally, because the growth that C-S-H particles have in an aqueous environment is completely different than the growth that could be studied in the vacuum due to the particles movement is completely different.

After observing the results about C-S-H surfaces and observing that there is not difference between surface types ABBA and BAAB (see Chapter 6.1), it does not matter in which surfaces the cylinders are built, any z origin can be taken taking care of not destroying any Ca layer.

Different sizes cylinders are created. Radiuses are 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75 and 80 Å. Heights depends on which unit cell is selected in each case but approximately are 11.5, 23, 34.5, 46 and 57.5 Å. Not all these combinations are available, combinations with highest radiuses and highest heights are not possible due to the number of atoms of the system would be too big to run any calculation with it.

All the cylinders are run in LAMMPS with molecular mechanics methods and the smallest cylinders are also run in MOPAC.

## 5.5. Calculations details

MOPAC and LAMMPS programs are used to create the input files. These programs generate the requirements to run calculations with semi-empirical methods and molecular mechanics methods. The details in these programs are the following.

### 5.5.1. LAMMPS set up

There are different steps in LAMMPS calculations. ReaxFF is always the force field used, others force fields have not been tried in the current project.

- 1) Energy minimization of the non-silicates. All atoms except Si atoms are optimized.
- 2) Low Temperature Molecular Dynamics. Dynamics is done in a low temperature ( $T=0.1\text{K}$ ) and for a short time ( $t=50\text{fs}$ ).
- 3) Energy minimization with no frozen atom. All atoms are optimized.
- 4) Low Temperature Molecular Dynamics with no frozen atoms.
- 5) Energy minimization with no frozen atoms.

Dynamics are done for a short time and a low temperature because the interest resides in relaxing a little the structure and finding a global minimum not in finding the different minimums (stable geometries) that each structure have.

### 5.5.2. MOPAC set up

MOPAC calculations are run using PM6 as Hamiltonian.

All atoms are optimized except Si atoms which remain frozen.

PULAY method is used as converger to obtain SCF.

The keyword  $T=4.nnD$  is used in order to avoid that job stop without finishing the optimization.

PL is required in order to control the steps during the process and PRTCHAR is used in order to know the atomistic charge in the system.

# 6. Results

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In this chapter, the results are commented. The different studies that have been realised had been commented in Chapter 5. They are about C-S-H surfaces, C-S-H environment and C-S-H growth. The first two studies have been done to know more conditions for the third study which is the main part in the project.

## 6.1. C-S-H surfaces

It has been explained in Chapter 5.2, which are the different surfaces that C-S-H can form in its growth. There, it has also been explained how the calculations have been realised. Two different types of methods have been used. The calculations have been realised in MOPAC with PM6 as Hamiltonian and vacuum as environment. The calculations realised in LAMMPS with ReaxFF as a force field have been done in two different environments: explicit water (added by Packmol) and vacuum.

The interest in this part of the work resides in the energy differences between cylinders with the same shape and size.

### 6.1.1. ReaxFF study of C-S-H surfaces

In this section, the calculations have been realised in two different environments due to that C-S-H environment in nature is aqueous but vacuum calculations are easier to realise and faster.

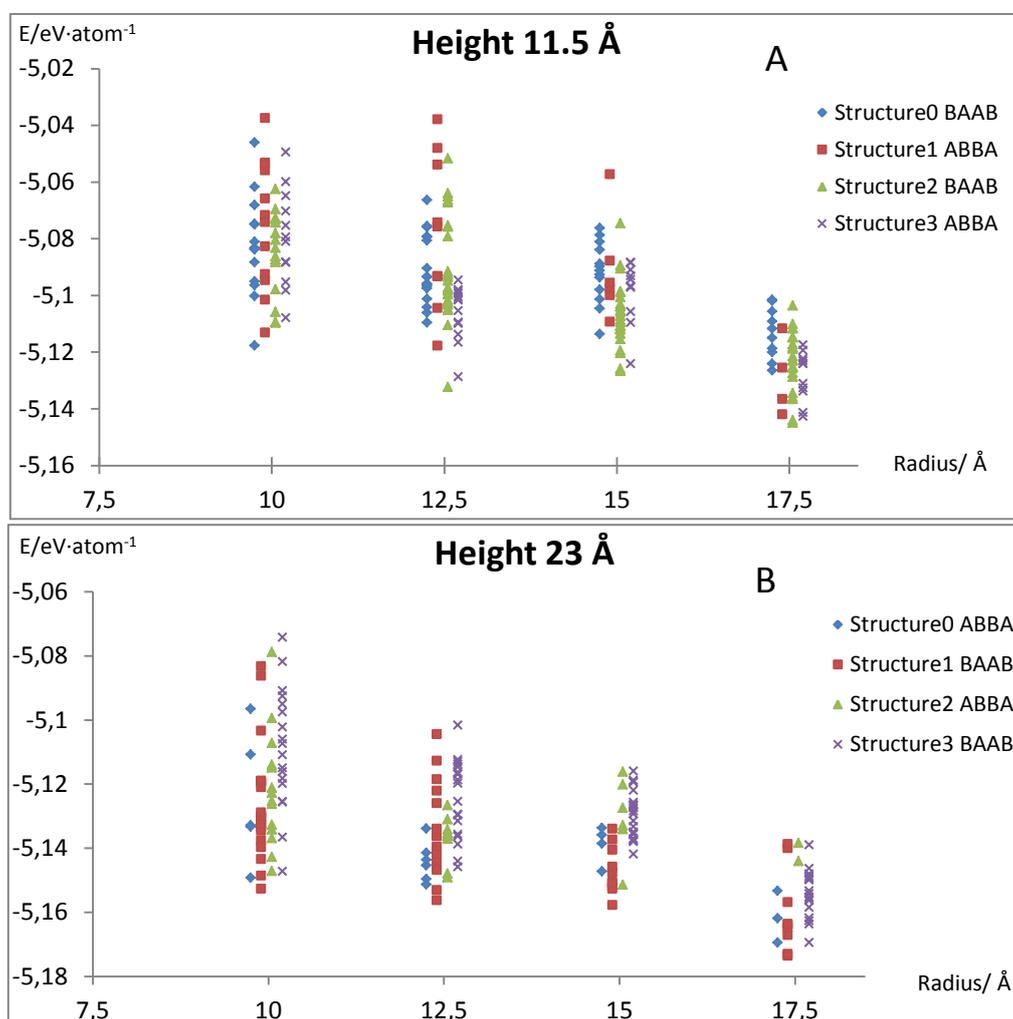
#### 6.1.1.1. Results in vacuum of C-S-H surfaces

There are different cylinders with different sizes (different radiuses and heights). The plots (Fig.10A and Fig.10B) are done for different heights. It means that with the same height different radiuses are represented in x-axes.

It does not matter in this section, in which way the plots are created. What is wanted to answer here is if there is any difference between different surfaces. For trying to answer this question, it has to be observed if there is any difference between the families of cylinders in the same group (same radius and height).

In order to plot the energy per atom, a theoretical composition is established based on Si atom that are in average in each cylinder size. The number of Ca atoms is computed based on C/S relation and the number of H atoms is computed through a relation H/S of 1.67 too. The difference between theoretical composition and real composition is computed and some Si, Ca and H atoms have to be added or

removed. Si atoms are added/removed as  $\text{Si}(\text{OH})_4$  molecule, Ca atoms as  $\text{Ca}(\text{OH})_2$  molecule and H atoms as  $\text{H}_2\text{O}$ . After, the corrected energy is divided by the number of theoretical atoms.



**Figure10.** LAMMPS vacuum results. A) Height 11.5 Å, B) Height 23Å

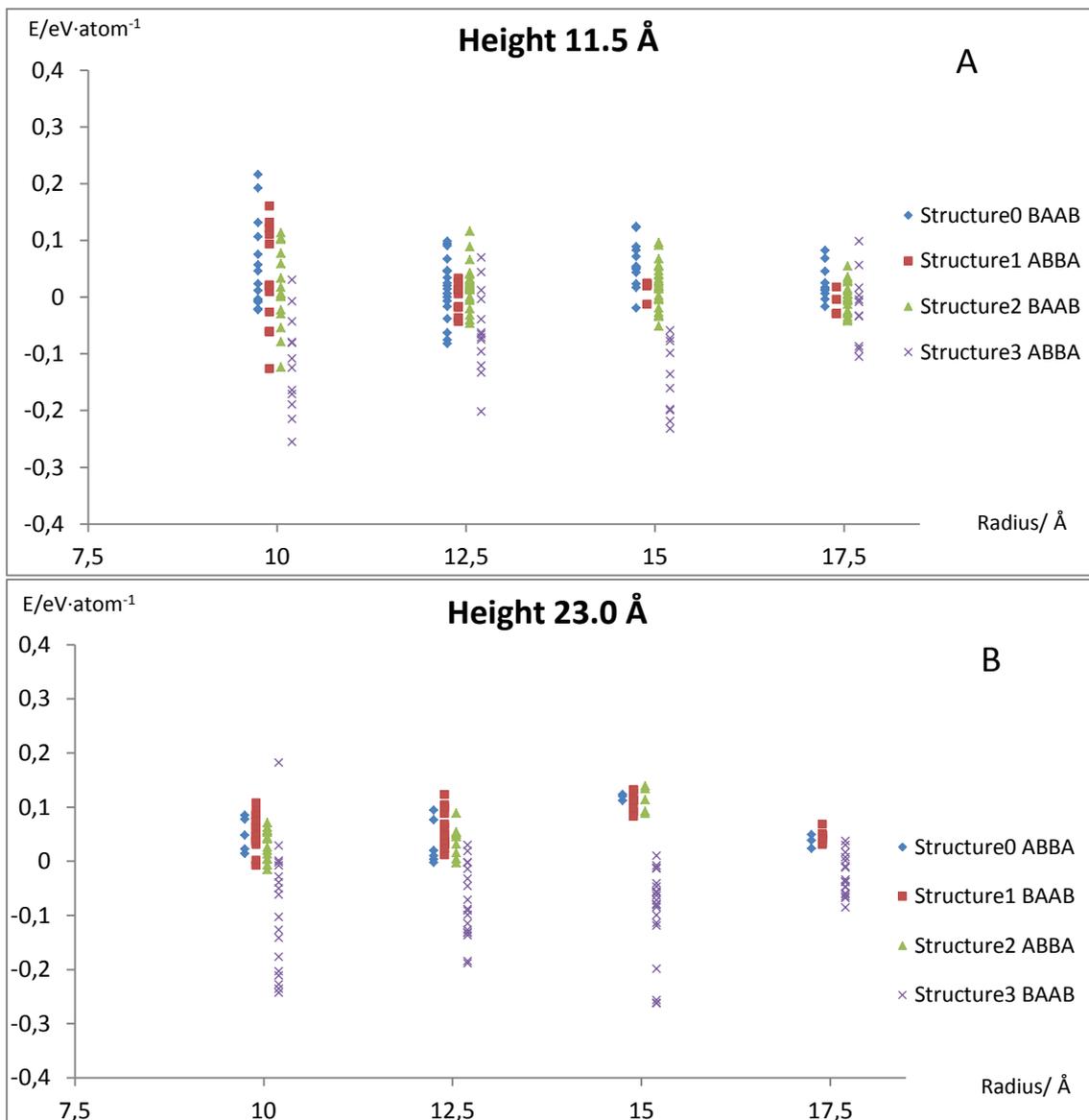
There is not a clear difference between structures type ABBA and structures type BAAB as can be observed in the graphs (Fig.10).

### 6.1.1.2 Results in aqueous environment of C-S-H surfaces

The optimized cylinders in vacuum are surrounded for a large amount of water molecule. The structure surrounded for water is calculated with the requirements in LAMMPS in chapter 5.5.1.

Energy is corrected in the same way as it was corrected in the vacuum. After all these corrections, the energy of the water molecule is multiplied by the number of water added and that energy is subtracted to the vacuum corrected energy. This corrected energy is divided by the number of theoretical atoms.

The results are normalised within each group (same radius and same height), the normalisation is done in order to plot all the results around zero. The average in each group is equal to zero. The normalisation is done because it is not important the tendency between groups. The interest resides in the difference between structures in the same group.



**Figure11.** LAMMPS aqueous environment results. A) Height 11.5 Å, B) Height 23Å

There is not any important difference between structures ABBA or BAAB (Fig.11A and Fig.11B).

### 6.1.2. PM6 study of C-S-H surfaces

The results obtained in LAMMPS have to be confirmed in MOPAC. For this reason, the small groups of cylinders are calculated in MOPAC because of it has been proved that semi-empirical methods offer a better result than molecular mechanics methods.

The same corrections in the energy as in LAMMPS have been done. Si(OH)<sub>4</sub>, Ca(OH)<sub>2</sub> and H<sub>2</sub>O energies have been computed in MOPAC and these molecules have been used to correct the energy for the different cylinders compositions in order to compare them.

In MOPAC results no difference between ABBA cylinders and BAAB can be appreciate neither (Fig. 12)

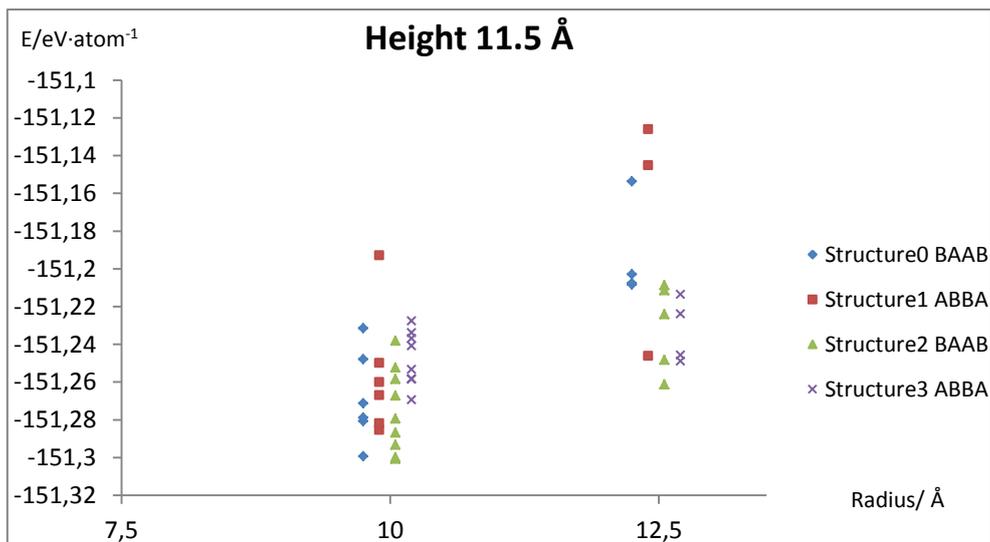


Figure12. MOPAC vacuum results

## 6.2. C-S-H in water environment

It has been observed in the previous section that there was not a change in tendencies changing the environment within the same group of cylinders. A lower energy per atom in the system in aqueous environment has been observed.

It is necessary to know if the aqueous influence is constant increasing the size. If it is proved then calculations can be realised in vacuum environment. Water correction would be a constant value in energy per atom, without take care in the number of atoms in the system.

Different cylinders are created in two different groups. In one group, all the cylinders have the same height and the radius is changed. In the other group, all the cylinders have the same radius and the height is changed. It is wanted to prove that water influence can be treated as a constant independently on the surface of the cylinder (tower or pancake).

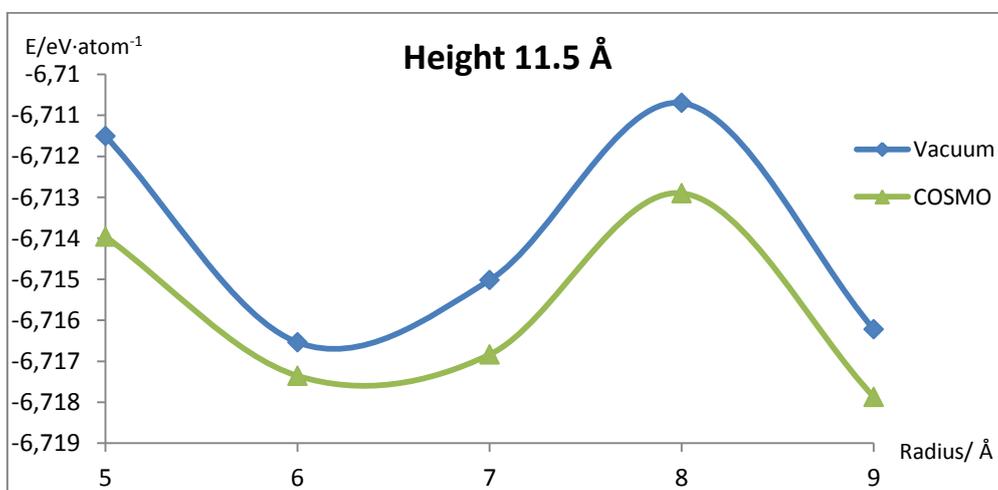


Figure13. MOPAC results comparison for platelets structures between vacuum and COSMO.

All calculations are realised in MOPAC with the requirements explained in section 4.2. Semi-empirical methods show results closer to the experimental than molecular mechanics methods.

Unfortunately, not all calculations have converged in MOPAC. There are not enough results in structures with tower shape (same radius) to plot it. Explicit water results can neither be plotted because selected amount of water was the same, box dimensions too but cylinder size increases. For this reason, in explicit water calculations, the interactions increase when the cylinder size increase and the tendency cannot be compared with vacuum and COSMO models.

Finally, it is wanted to tell that fluctuations are not important in this section because of only one cylinder of each size have been taken and the error bar in small cylinders is really high.

Aqueous effect can be considered as a constant (Fig. 13) and tendencies observed in calculations done in vacuum are expected to be equal than tendencies in aqueous environment.

### 6.3. C-S-H growth

Different cylinder sizes are created through the acquired knowledge about C-S-H surfaces. It does not matter C-S-H surface, for this reason z-origin is fixed and cylinders have an alternative surface increasing the height.

There are two different ways of observing the anisotropy growth. On one hand, plotting the energy per atom versus radius and energy per atom versus height and obtain different tendencies. On the other hand, compare the energy between two particles with the same composition and different shape.

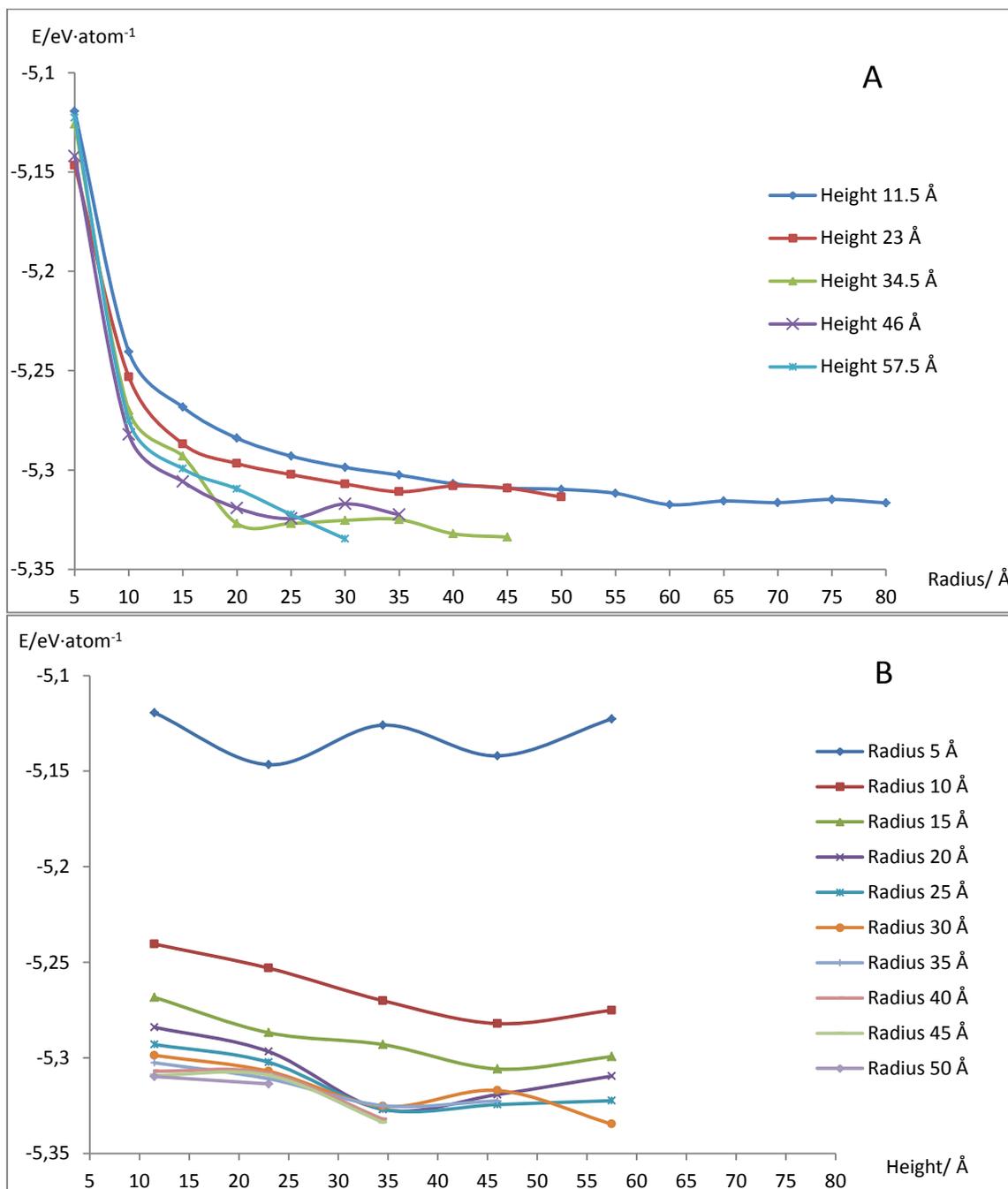
All the cylinders have been obtained through the model with lower water content, the general formula is  $C_{1.67}SH_{1.4}$ . All the corrections are done thinking in this theoretical composition.

First of all the density of the cylinder is computed for each unit cell. The number of atoms is constant and the volume can be calculated as mix product between the three translation vectors of each unit cell. An average between the volumes is done and after the number of atoms is divided by the volume obtaining a density measured in atoms/ $\text{\AA}^3$ . Based on this value, the theoretical composition and the cylinder dimension, it is possible to compute the theoretical composition that each cylinder should have. The difference between theoretical composition and real composition is corrected adding or removing atoms in form of molecules.  $Si(OH)_4$ ,  $Ca(OH)_2$  and  $H_2O$  are used as molecules. The obtained energy value is corrected multiplying the number of each molecule for its energy.

When the energy has been computed, the outlier points are removed through the quartiles. First quartile ( $Q_1$ ) and third quartile ( $Q_3$ ) are calculated in each group and the interquartile (IQR) is computed as  $Q_3 - Q_1$ . Then, the lower fence is computed as  $Q_1 - 1.5 \cdot (IQR)$  and the upper fence as  $Q_3 + 1.5 \cdot (IQR)$ . All the values which are not within these limits are removed [23].

### 6.3.1. ReaxFF study of C-S-H growth

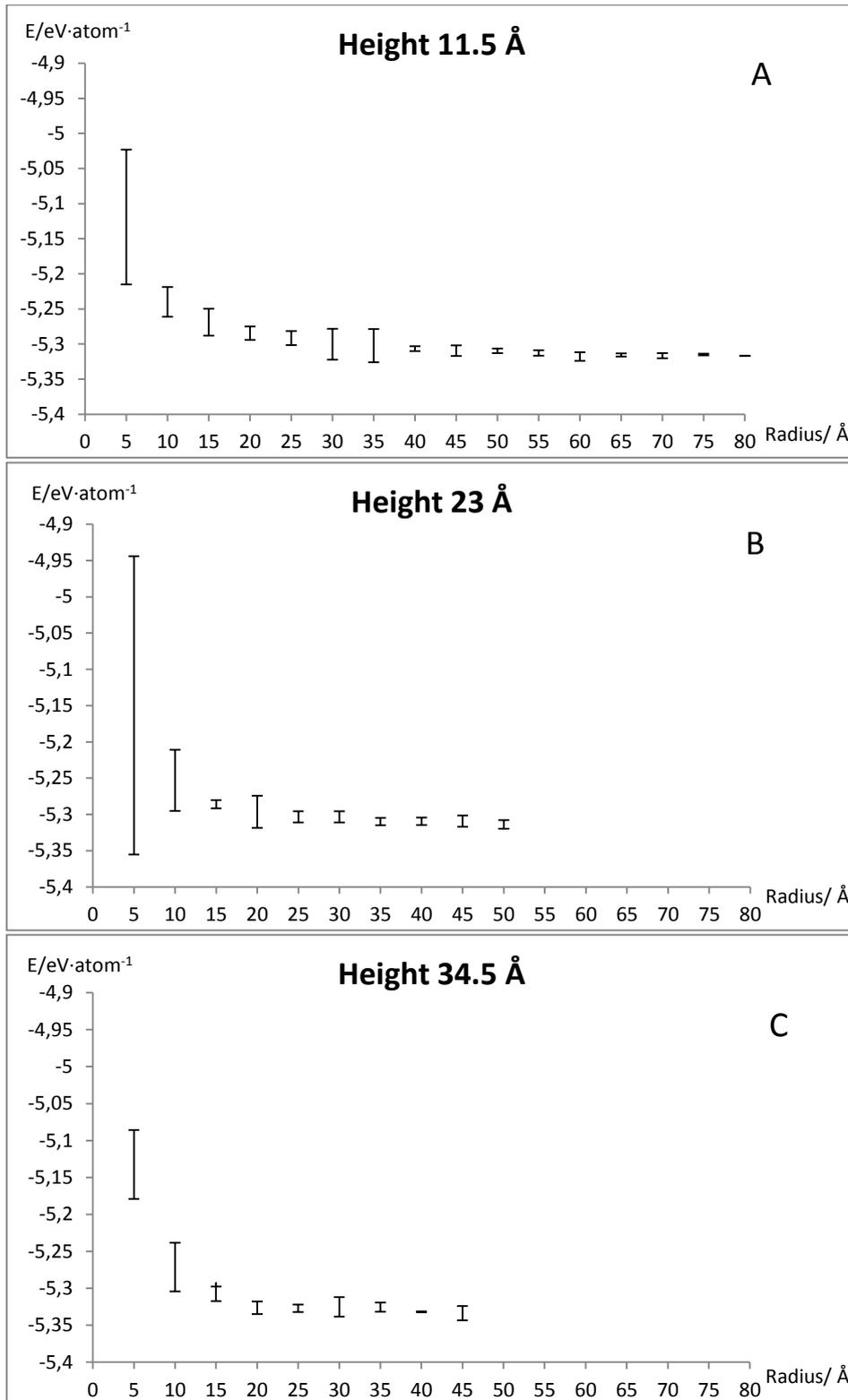
In LAMMPS, larger cylinders can be calculated. It can be observed, that there is not a gain in energy increasing the height, growing in z-direction but a clear gain in energy can be observed increasing the radius, growing in x and y directions (Fig.14a and Fig.14b).

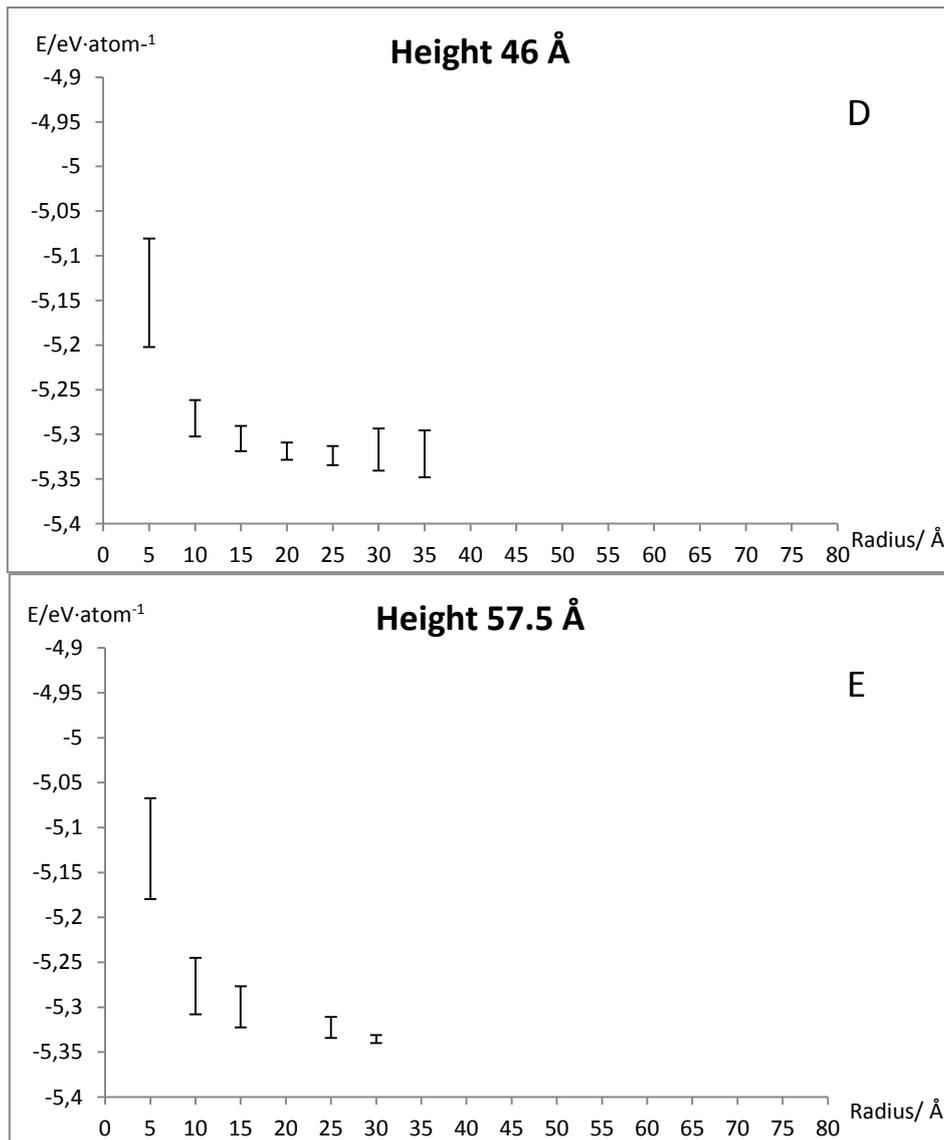


**Figure14.** Mean values of A) Energy per atom versus radius for different heights of C-S-H particles; B) Energy per atom versus height for different radiuses of C-S-H particles

It can be observed more clear in the following graphs where is plotted the energy per atom versus radius taking height as a constant (Fig.15) and others where is plotted energy per

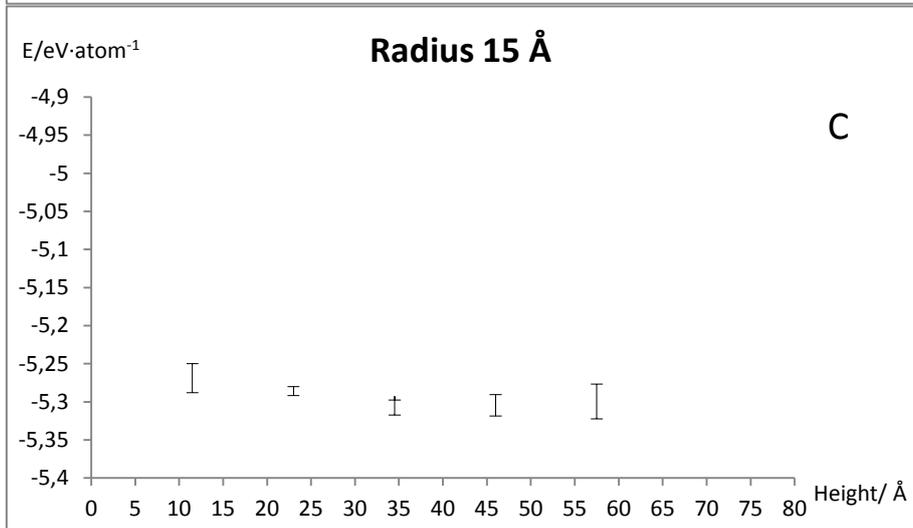
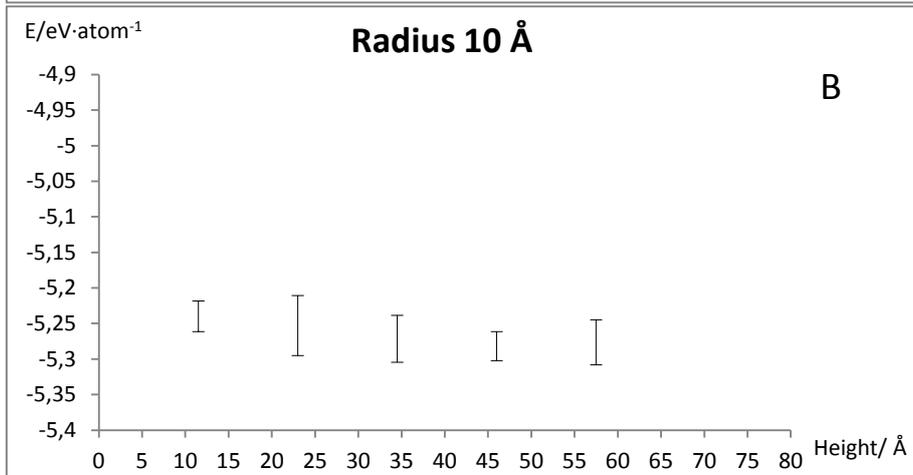
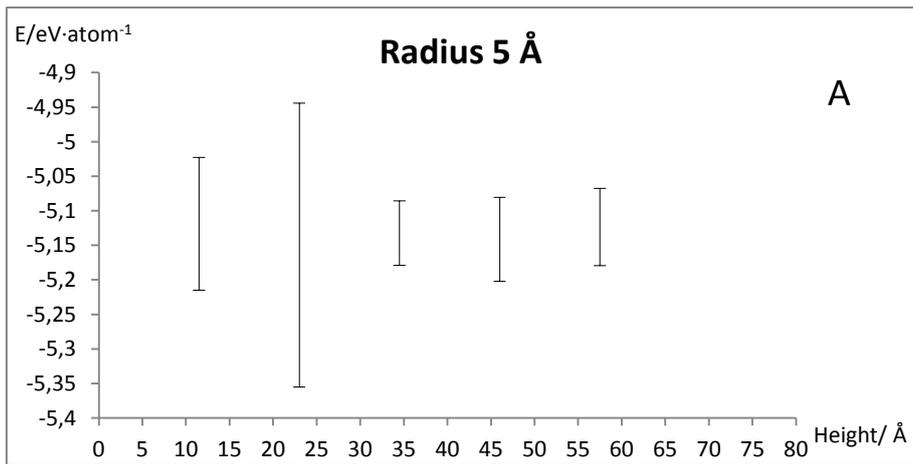
volume versus height taking radius as a constant (Fig.16). In these graphs, it is represented the error bar limited for the upper fence ( $Q3+1.5\cdot IQR$ ) and the lower fence ( $Q1-1.5\cdot IQR$ ). It is plotted the same scale in all the graphs for doing easier the visual comparison between them.

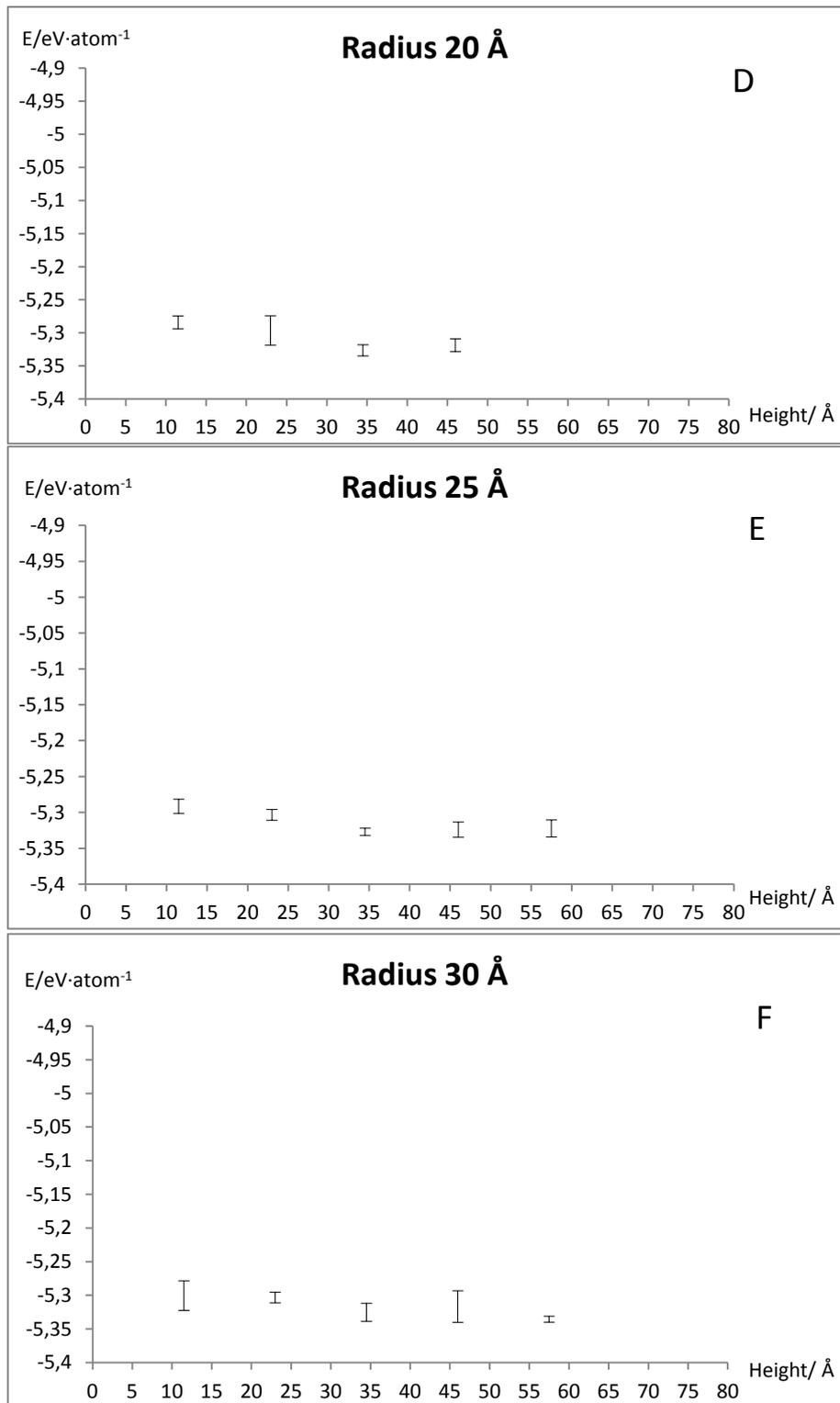




**Figure15.** Plot energy per atom versus radius for different heights; A) Height 11.5 Å, B) Height 23 Å, C) Height 34.5 Å, D) Height 46 Å, E) Height 57.5 Å.

There is an important decrease in energy per atom when the radius increases at small radiuses (Fig.15). When the radius increases the slope decreases, despite the slope is always going down.





**Figure16.** Plot energy per atom versus heights for different radiuses; A) Radius 5 Å, B) Radius 10 Å, C) Radius 15 Å, D) Radius 20 Å, E) Radius 25 Å, F) Radius 30 Å.

There is a general gain in energy, increasing the height (Fig.16) but it is not observed in all the graphics and between all the different heights.

It also can be conclude again that there is not an important difference between surface ABBA and BAAB surface.

It is also observed that a growth in the radius (growth in x and directions) gives a lower energy than the growth in height (growth along z direction).

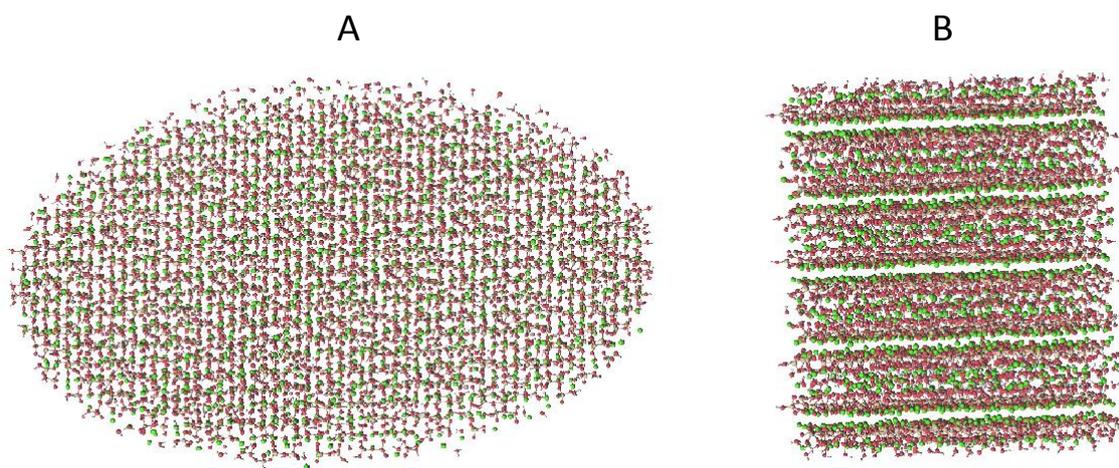
However, the optimal size cannot be computed, it is observed a decrease in energy increasing the radius but it is not observed a minimum in energy. Entropic factor gain in importance when the radius increases and taking care in this term would give the optimal size for the system. Unfortunately, it is not easy to compute this entropic factor and energy cannot be corrected.

Another way for observing the anisotropy growth is observing if there is a preference between a pancake shape or a tower shape (Fig.17a and Fig.17b). It has to be compared, two structures with similar composition in the two different shapes. The energy of  $\text{Si}(\text{OH})_4$ ,  $\text{Ca}(\text{OH})_2$  and  $\text{H}_2\text{O}$  is added in order to compare structures with identical composition. Different structures with different composition have been taken (Table 7).

**Table7.** Comparison of structures like tower and structures like pancake

Shape	Composition	Size/Å	$\Delta E(E_T - E_P)/\text{eV}$
Tower	$\text{Ca}_{1014}\text{Si}_{1658}\text{O}_{4988}\text{H}_{2604}$	R25-H57,5	251
Pancake	$\text{Ca}_{1013}\text{Si}_{1668}\text{O}_{4961}\text{H}_{2534}$	R55-H11,5	
Tower	$\text{Ca}_{830}\text{Si}_{1381}\text{O}_{4184}\text{H}_{2286}$	R50-H11,5	145
Pancake	$\text{Ca}_{835}\text{Si}_{1377}\text{O}_{4098}\text{H}_{2102}$	R25-H46,8	

The structure with pancake shape is more stable than structure with tower shape (Table 7).

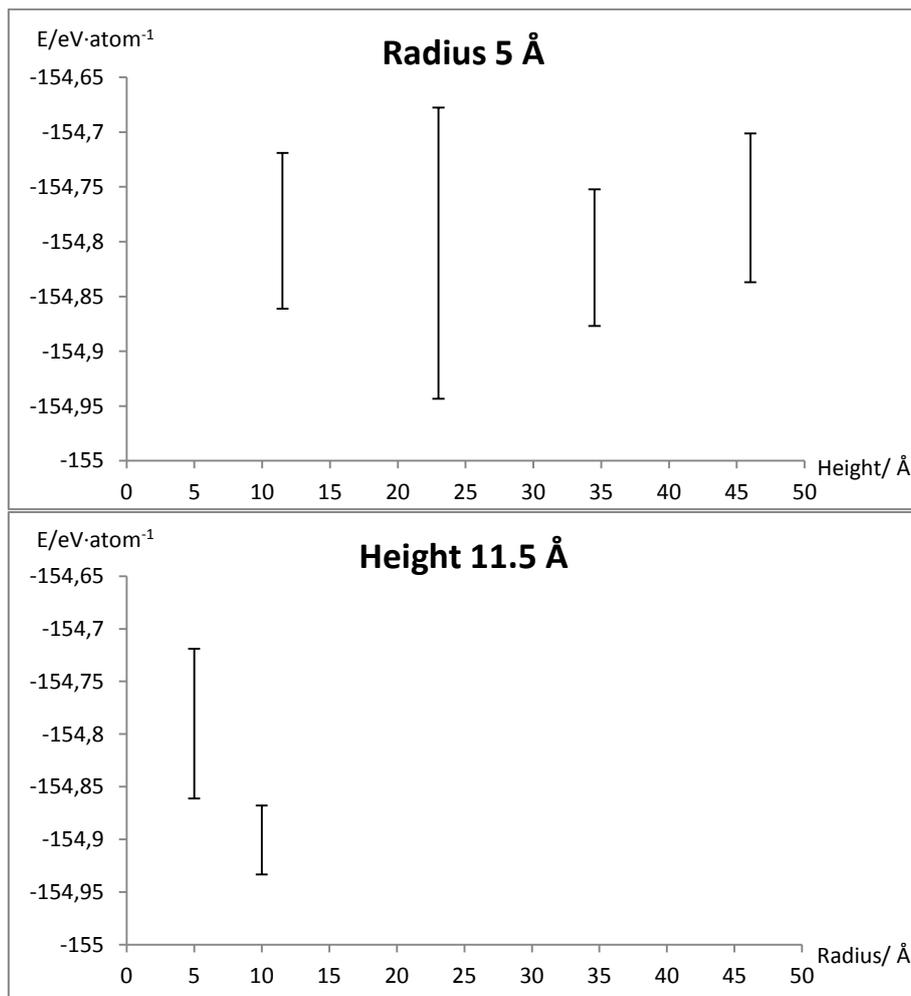


**Figure17.** Structures with almost the same composition and different shapes; A) Pancake; B) Tower.

### 6.3.2. PM6 study of C-S-H growth

It is not affordable doing the calculations for all cylinder sizes through PM6 because the computational cost is too high. The small amount of calculations converged in PM6 does not allow observing any tendency in these calculations. However, PM6 calculations are used in order to confirm ReaxFF observed tendencies.

There are only five groups of cylinders that are converged in PM6. They are disposed in two different graphs (Fig. 18).



**Figure18.** PM6 results: a) Constant radius for different heights; b) Constant heights for different radius

It is observed the same tendencies in PM6 results than in ReaxFF (Fig.18a) and (Fig. 16a), (Fig.18b) and (Fig.15a).

The results are the same but total energy is different because the point of zero energy depends on the method. The importance comparing two different methods resides in the energy differences, not in the total energy.

## 7. Conclusions

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In this project, it has been observed that the growth in C-S-H particles decrease the energy per atom in the system, gaining in stability. In the bibliography, it is talked to a size of tens of nanometres in each direction, the larger cylinder that has been calculated had 16 nm of diameter and no minimum has been observed.

C-S-H nanoparticles are more stable in pancake shape than in tower shape. It proves, that there is a bigger gain in energy for them in a growth along x and y directions than in z direction. It proves that exist anisotropy in C-SH growth and z direction is less preferable. The anisotropy is also proved through the graphs because in the graphs where energy per atom is plotted versus radius, it is always observed a gain in energy increasing the radius (growth in x and y directions) while in the graphs where energy is plotted versus height, no clear tendency can be observed.

The non-finding optimal structure through a minimum can happen because of entropic factor which increase with the size have not been include or maybe it does not exist a local minimum for a particular size and in nature these particles have a size of nanometres because it gives a higher gain in energy the growth in small sizes than in bigger ones.

It has been developed a code capable to build C-S-H nanoparticles in different sizes and different shapes. This code is capable to build structures of tens thousand atoms. It has also been created a database of almost five hundred different structures with different shapes and different sizes.

This project is partially included in the Abstract "Multiscale Modelling of C-S-H from the force field to the Quantum Chemistry" by Valera Veryazov, Goran Kovačević, Marc Alias, Liviu Ungur that has been accepted for the presentation at Multiscale Modelling of Materials and Molecules 2016, 7-9/06 2016, Uppsala, Sweden.

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# Appendix A. Notation

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Cement language uses a special notation called Cement Chemist Notation (CCN). CCN notation is used in order to simplify the formulas of oxide compounds which form cement. It is a shorthand way of writing the chemical formulas for cement compounds. Symbols which receive each oxide can be observed in Table A1.

**TableA1.** Name, chemical formula and CCN of main cement oxides.

<b>Name</b>	<b>Chemical Formula</b>	<b>CCN</b>
Calcium oxide or lime	CaO	C
Silicon oxide or silica	SiO <sub>2</sub>	S
Aluminium oxide or alumina	Al <sub>2</sub> O <sub>3</sub>	A
Iron oxide or rust	Fe <sub>2</sub> O <sub>3</sub>	F
Titanium dioxide	TiO <sub>2</sub>	T
Magnesium oxide	MgO	M
Potassium oxide	K <sub>2</sub> O	K
Sodium oxide	Na <sub>2</sub> O	N
Water	H <sub>2</sub> O	H
Carbon dioxide	CO <sub>2</sub>	$\bar{C}$
Sulphur trioxide	SO <sub>3</sub>	$\bar{S}$
Phosphorous hemi-pentoxide	P <sub>2</sub> O <sub>5</sub>	P

# Appendix B. Code rules

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## B.1. Connectivity rules

The cylinder is built but some covalent bonds have been cut and some atoms have lost all their connectivity. For these reasons, several rules must be applied in order to protect atoms connectivity.

### B.1.1 H rules.

Each H has to be connected to one O. If the code finds a different situation, a rule has to be implemented in order to keep its right connectivity.

#### B.1.1.1. H has no neighbours.

If the program finds any H atom, it has to look for any oxygen inside the cylinder in a distance from H equal or smaller than rho ( $\rho=1.1 \text{ \AA}$ ). If there is not any O, H has to be removed.

### B.1.2. O rules.

Each O has to be connected at least to two different atoms. These atoms can be Si, H or Ca. O form covalent bonds with H and Si while form ionic bonds with Ca. The maximum covalent bonds that O can form are two while there is not an obvious maximum of ionic bonds.

#### B.1.2.1. O has only one H neighbour.

If the program finds any O atom which is connected with one H inside the cylinder and another H outside the cylinder, then H that was outside the cylinder has to be included in the cylinder.

#### B.1.2.2. O has only one Si neighbour

If there is any oxygen atom which is connected to one Si atom inside the cylinder then the program has to find for its Ca neighbours. If the oxygen atom is not connected to any inside Ca atom then H neighbours have to be searched. If O is neither not connected to any H atom then an H has to be added. It has to be situated in a rho\_real distance ( $\rho_{\text{real}} = 1.0 \text{ \AA}$ ) and it has to form a SiOH angle of  $180^\circ$ .

#### B.1.2.3. O has 0 H neighbours.

If oxygen has not neighbours two different cases must be studied. It has to be observed if this O in the unit cell formed a water molecule or a hydroxyl group. Despite it is distinguished between these different cases, the procedure is the same. The program has to find for O connectivity in both cases.

If O is connected with two H atoms which are outside of cylinder, then these H have to be included in the cylinder. It means that O formed water in unit cell and is also forming water molecule in cylinder.

If O is connected with only one H which is situated outside the cylinder then this H has to be included in the cylinder. It means that O formed a hydroxyl group in unit cell and is forming now a hydroxyl group in cylinder.

#### **B.1.2.4. O has 0 Si neighbours**

The program has to find for all O atoms. It has to search for any Si atom in a distance equal or smaller than  $r_{sio}$  ( $r_{sio}=2.0$  A). If the program does not find any Si inside the cylinder and find some Si outside, then O atom has to be removed.

#### **B.1.2.5. OH groups not connected to any Ca**

The program has to find for any O atom connected to an H atom, forming a hydroxyl group. It is computed the number of Ca and Si neighbours that this oxygen have in a lower distance than  $r_{cao}$  ( $r_{cao}=2.85$  A) and  $r_{sio}$  ( $r_{sio}=2.0$  A), respectively. If oxygen atom is not connected to any Si and Ca atom inside the cylinder and is connected to at least one outside Ca atom, then hydroxyl group is removed.

### **B.1.3. Si rules**

Each Si has to be connected to four O atoms. Some rules have to be implemented in order to keep its connectivity.

#### **B.1.3.1. Si has three different neighbours**

For all Si atoms in the cylinder, the program has to find all oxygen in a distance lower than  $r_{sio}$  ( $r_{sio} = 2.0A$ ). If there are three oxygen atoms inside the cylinder and one oxygen atom outside the cylinder then this oxygen has to be added to the cylinder. If this oxygen is also connected to another Si atom inside the cylinder then it has a correct connectivity and it means it is a bridging O. Unless it is connected to another Si atom then an H atom has to be added. This H is added to a position in order to have a  $\rho_{real}$  distance ( $\rho_{real} = 1.0A$ ) and SiOH angle  $180^\circ$ .

#### **B.1.3.2. Si has two different neighbours**

For all Si atoms in the cylinder, the program has to find all oxygen in a distance lower than  $r_{sio}$ . If there are two oxygen atoms inside the cylinder and two oxygen atoms outside then these two oxygen atoms have to be included to the cylinder. Then, the same procedure explained in the other rule has to be applied for each of these oxygen atoms.

#### **B.1.3.3. Si has one neighbour**

For all Si atoms in the cylinder, it has to be found oxygen atoms in a lower distance than  $r_{sio}$ . If there is one oxygen atom inside the cylinder and three oxygen atoms outside then these three

oxygen have to be included in the cylinder. Finally, the explained procedure for detecting O bridging or non-connected oxygen has to be applied.

#### **B.1.3.4. Si has not neighbours**

It has to be found the connectivity for each Si atom in the cylinder. The connectivity is computed searching for oxygen atoms in a distance lower or equal to 2.0 Å from Si atom. If there is not any oxygen atom inside the cylinder and four oxygen atoms outside then these four oxygen atoms have to be added to the cylinder. Then, it is applied the same procedure in order to keep a good connectivity for these oxygen atoms.

### **B.1.4. Sanity check**

In order to confirm that all rules have been well applied a sanity check is established at the end of all these rules. H and Si atoms connectivity are reviewed while Ca and O atoms are not because of the large number of different connectivity situations that Ca and O atoms can present in the structure.

#### **B.1.4.1. Si atom review**

The program has to review if all Si atoms are connected to four O atoms inside the cylinder; if it is not true then the cylinder geometry file will not be created.

#### **B.1.4.2. H atom review**

The program has to review if all H atoms are connected to one O atom inside the cylinder; if it does not happen then the program stops and the geometry file is not generated.

## **B.2. Charge rules**

Created cylinders have to be electro-neutral as CSH nanoparticles are in nature. In order to keep the electro-neutrality, some different rules are added. It can be distinguished as two very different situations. These are positive charge and negative charge. It is established a charge of +4 for Si, +2 for Ca, +1 for H and -2 for O in order to compute it and make it equal to zero.

### **B.2.1. Positively charged**

When the charge is positive then two different cases have to be distinguished. If it is odd then a hydroxyl has to be removed in order to transform the charge value to an even value. When the value is even, Ca atoms can be removed until arriving to a neutral system.

In order to remove a hydroxyl group, the program has to find for an hydroxyl group not connected to Si, if the hydroxyl group found is not connected to a Si atom it can be removed.

When it has happened, the system is now positive charged with an even value. Then, some Ca atoms have to be removed. It is computed the distance between Ca and cylinder origin, the Ca

atom which is situated to a higher distance to the centre is removed, this condition is applied until the charge of the system is equal to zero.

### **B.2.2. Negatively charged**

When the charge is negative, it is possible to solve the problem in two different ways. On one hand, it is possible to remove hydroxyl groups and on another hand, it is possible to remove alone oxygen atoms. Remove alone oxygen atoms is a better solution because of in the unit cell there are not alone oxygen single atoms.

If it is wanted to arrive to the neutrality removing alone oxygen atoms, before starting the charge in absolute value has to be even. For this reason, the code has to search for any hydroxyl group not connected to Si atom and remove it. Then the charge is even and it is possible to start removing alone oxygen atoms. All O atoms which are not connected to any H atom neither Si atom are selected. This of them which is farer to the Z axis is removed. The procedure is repeated until the charge is equal 0 or there is not any O alone atom.

If the charge is still negative then some hydroxyl groups must be removed. The program has to find any O atom connected to an H atom and not connected to a Si atom and then O atom and H atom are removed. The procedure has to be repeated until the charge is equal to zero.

### **B.2.3. Charge checking**

After all these rules about the charge a sanity check is applied. Charge for the cylinder should be neutral. For this reason, charge is computed again. If the obtained value is not equal to zero then the program is stopped without create the geometry file.