Modeling of the Cement System and Clinker Phases using MOPAC and NWChem

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Cover: geometry optimization of jennite, see page 14

Abstract

The purpose of this study was to model compounds in the cement system with the software programs MOPAC and NWChem. The modeling was done by geometry optimization of chemical structures. The geometry optimization searched for the best heat of formation for the structure. The heat of formation was compared to literature and experimental data.

The main reactive components in cement; alite and belite, their reactants and reaction products were modeled. The hydration of calcium silicate was examined. Modification of jennite was used to simulate the polymerization reaction.

Almost all results did not differ more than 15 percent from reference data for the pure structures. For the dimers in water, dimer B had lower enthalpy than dimer A and is therefore more likely to appear in the polymerization reaction. Enthalpies of reactions were calculated by combining the enthalpies for pure phases in reactions. The reaction enthalpies corresponded poorer to the reference values than single pure phases. This is probably due to that several minor errors in the pure phases accumulate to larger errors in the reaction enthalpies.

The result of the modeling shows that MOPAC can be used as a tool in cement research and engineering. Software can be used to model and evaluate structures and reactions in the cement system. –

This work shows that MOPAC can produce acceptable results for modeling of pure structures. The main advantage of MOPAC over NWChem is that it is fast, due to the parametrization. But this is followed by several drawbacks; MOPAC needs a large structure, it does not have as good precision as NWChem and MOPAC cannot simulate hydrogen bonds particularly good.

Contents

1. Introduction

Portland cement has been around for 200 year now and different kinds of cement has been used since the romans. However, there is no complete understanding of the chemical reactions and physical processes occurring in Portland cement during hydration. Portland cement is made by heating a mixture of clay and limestone to a temperature of 1400°C. After heating the mixture, a clinker is obtained. The clinker optimally consists of 67 % CaO, 22 % SiO_2, 5 % Al_2O_3, 3 % Fe_2O_3 and 3 % other components. These compounds form the four common phases in concrete; 50 – 70 % alite, 15 -30 % belite, 5 - 10 % aluminate and 5 – 15 % ferrite. The clinker is mixed with gypsum and grinned to a fine powder. (Taylor, 1997)

Alite (Ca_3SiO_5) reacts with water to form a gel consisting of calcium, silica, oxygen and hydrogen of unknown proportions (C-S-H gel).The gel acts like glue, binding the grains in the concrete together. The gel is composed of SiO_4 monomer that polymerize to dimer, pentamer, octamer and some longer chains. The calcium oxygen chains are surrounded by calcium ions, water and hydroxide ions. The C-S-H is found to be amorphous but is often compared to the crystalline structures of jennite and tobermorite 14Å.

1.1. Aims

Because of the high complexity of the cement system, computer aided modeling can be of significant use. Thus, the aim of this project is to model clinker and hydration products and their transient species. The modeling is done by geometry optimizing structures in using the programs MOPAC and NWChem. The results are to be compared to existing databases and experimental data when these are available. Reactions for alite and belite are of primary interest.

1.2. Reactions

There are several reactions in the cement system where many are characterized but some are not fully understood, such as formation of the C-S-H gel. It is worth noting that there are more reactions known then are described in this rapport. This study focus mainly of the formation of alite and belite and their reactions to form C-S-H.

1.2.1. Clinker Reactions

During clinker production three main reactions occurs. First the calcium carbonate is thermally decomposed into lime and carbon dioxide. This reaction is called the calcination reaction and can be seen in reaction R1. The lime produced in the calcination reaction reacts further with silica to form belite, as in reaction R2. If silica is present in excess and the temperature is increase to 1400°C, belite will react with silicate to form alite as in reaction R3.

$CaCO_3 \rightarrow CaO + CO_2$ $\quad \Delta H_r^{\ominus} = 187$ kJ/mol (Taylor, 1997) $\hspace{2cm}$ (R1)

$3CaO + SiO_2 \rightarrow Ca_3(SiO_4)O$ $\quad\quad \Delta H_r^{\ominus} = -495$ kJ/mol (Taylor, 1997) $\hspace{1cm}$ (R2)

$2CaO + SiO_2 \rightarrow Ca_2SiO_4$ $\hspace{6cm}$ (R3)

1.2.2. Hydration Reactions

Belite and alite hydrate to almost the same products but at different times in the hardening process of the concrete. Alite gives the early strength and after about a year and forward the hydration product of belite is the main strength giving compound in concrete. The reactions for hydration of alite and belite can be seen in reaction R4 and R5.

$Ca_3(SiO_4)O + H_2O \rightarrow$ C-S-H $+ Ca(OH)_2$
      (R4)

$Ca_2SiO_4 + H_2O \rightarrow$ C-S-H $+ Ca(OH)_2$ (R5)
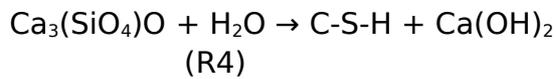
Hydration can be seen as a multi stage reaction where the clinker species are first dissolved. Portlandite crystalizes as the solution is getting saturated with calcium. Then silicate tetrahedrons have been shown to polymerize to short chains in adjacent to calcium ions and hydroxide ions to form C-S-H. The multi stage reaction can be seen in reaction R6. Po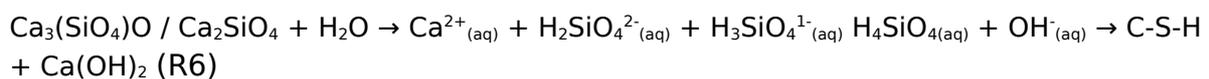lymerization forms dimers, pentamers and octamers at 25°C, the chain length increase with time. Higher polymers are formed at temperatures over 65°C. (Hirljac, Wu and Young, 1983)

$Ca_3(SiO_4)O / Ca_2SiO_4 + H_2O \rightarrow Ca^{2+}_{(aq)} + H_2SiO_4^{2-}_{(aq)} + H_3SiO_4^{1-}_{(aq)} H_4SiO_{4(aq)} + OH^-_{(aq)} \rightarrow$ C-S-H $+ Ca(OH)_2$ (R6)

1.3. Jennite and Tobermorite

Jennite and tobermorite 14Å has been widely discussed and accepted as similar to C-S-H in general terms, except for some obvious differences. C-S-H is an amorphous structure, jennite and tobermorite are crystalline. The ratio between calcium and silicon in C-S-H is approximately   1.75, whereas jennite has 1.5 and tobermorite has 0.83. Jennite and tobermorite has very long chains whereas C-S-H appears to have chain lengths from 2 to 5 and higher depending on age and temperature. With many arguments concerning whether tobermorite or jennite is more similar to C-S-H, several different models have been presented. (Taylor, 1993) (Taylor, 1986) (Richardson, 2008) (Nonat, 2004)

1.3.1. Taylor's Model (1986)

Taylor presented a model based on that the structure of C-S-H is a mix of both jennite and tobermorite in layers where the structures have high degree of imperfection. The jennite and tobermorite structures were thought to be imperfect by exclusion of every third silicate tetrahedral (the bridging tetrahedral). (Taylor, 1986)

1.3.2. Jennite

(Bonaccorsi, Merlino and Taylor, 2004) determined the structure of jennite. Silicate tetrahedrons are linked together by sharing an oxygen atom to form a chain along the b axis of the unit cell. The chain consists of a repetition of three tetrahedrons where two are paired together along the length of the chain and the third is located offset from the chain and bridge the pairs to another pair, this repeating structure is called dreierkette or wollastonite-type. Between the silicate chains there are rows of calcium ions, hydroxide ions and water molecules. This structure can be seen in figure 1.

2
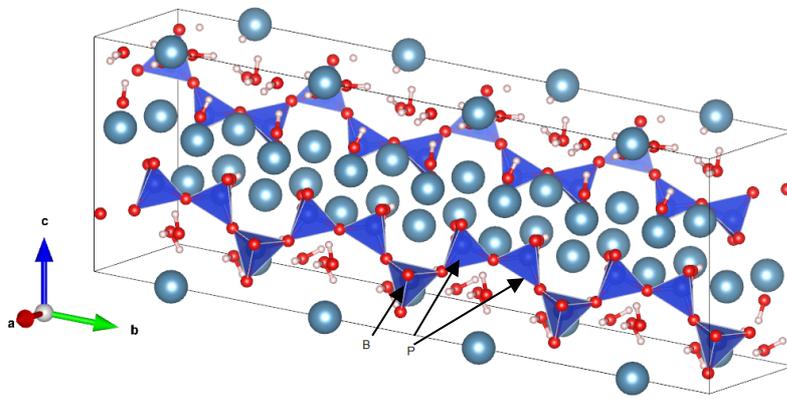
Figure 1. In the figure the structure of jennite can be seen and the dreierkette chain of silicate tetrahedron. The bridging tetrahedral is marked by B and the paired tetrahedron with P.

1.3.3. Tobermorite 14Å

Tobermorite can be separated into different phases which differ in the spacing between the calcium layers. The length of the spacing correlates to the degree of hydration where 9Å is the least hydrated and 14Å the most. Tobermorite 14Å, also known as plombierite, has a similar dreierkette structure of the silicate chain as in jennite but the chains are packed differently. Tobermorite 14Å also contains less calcium then jennite. The hydroxides are not located between the silicate chains and the calcium ions like in jennite but are instead incorporated in the silicate tetrahedral chains on the bridging tetrahedral. (Bonaccorsi, Merlino and Kampf, 2005) This structure of tobermorite 14Å can be seen in figure 2 and a comparison with jennite can be seen in figure 3.

Figure 2. The figure shows the structure of tobermorite 14Å, the dreierkette chains are clearly lustrated and the length of the spacing is illustrated.

Figure 3. The figure shows how jennite and tobermorite are packed differently. The figure to the left is jennite and tobermorite is the figure to the left.

3

2. Theory

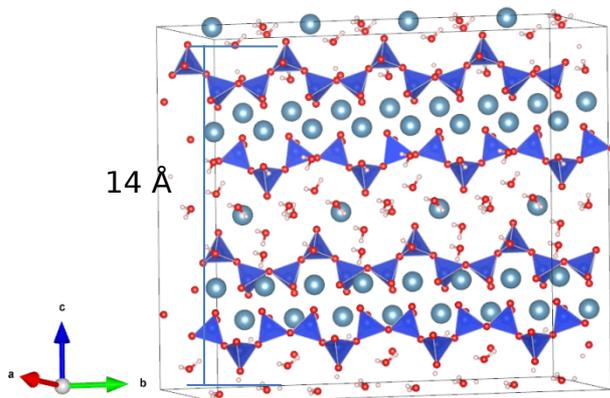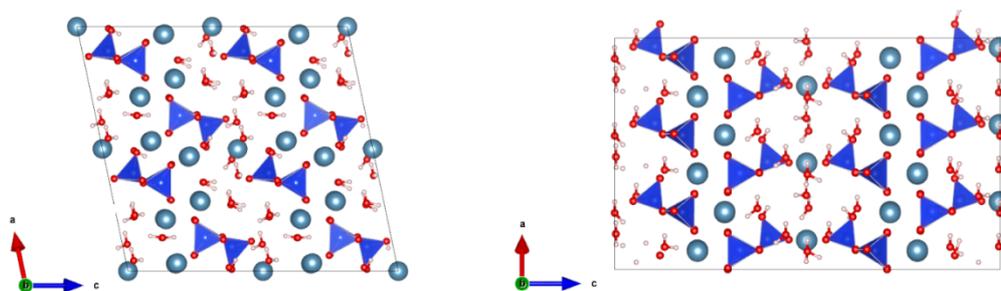In this work two software programs were used to model structures. These modeling programs use different ways of simulating reality. Two chemical visualization and editing programs were used to build and edit structures. A fifth program, a graphical user interphase was used to run MOPAC and NWChem in.

2.1. MOPAC

MOPAC is a semi empirical modeling program for quantum chemistry. In MOPAC chemical structures and molecules can be inserted or drawn in the program. MOPAC can solve various chemical properties in different ways. In this work MOPAC was used to find enthalpies of structures using geometry optimization. (Stewart, 2015)

2.1.1. Hartree-Fock formalism

The Hartree-Fock formalism is a method to solve the wave function and energy for stationary states in quantum many-body systems. The Hartree-Fock equation is an approximation of the Schrödinger equation which is solved with the behavior that electrons move because of an electrostatic field induced by all electrons together and external forces. It is calculated iteratively to converge.

2.1.2. Neglect of Diatomic Differential Overlap

NDDO is a formalism written by John A Pople. It is used in several empiric models, one of which is MOPAC. NDDO uses integrals for repulsion between charges from different centers with the assumption that the two orbitals do not overlap (Dewar and Thiel, 1977).

NDDO replaces the matrix for overlapping orbitals S with the unit matrix, thus, Hartree-Fock secular equation; $|H - ES| = 0$ is replaced with $|H - E| = 0.$ (Dewar and Thiel, 1977).

2.1.3. PM6

PM6 (Parametrization Method 6) is a modification of the NDDO by using experimental data and ab inito data using the Hartree-Fock formalism to achieve a better parametrization for molecules. The parametrization was made by using parameters such as; heat of formation, geometries, dipole moments and ionization potential but also other kinds of reference data and combinations of data to form rules for parametrization (Stewart, 2007).

2.1.4. PM7

PM7 is a further development and re-parametrization of PM6. It uses more and better data to achieve better estimations for heat of formation. PM7 was tested for crystal structures and heat of formation of solid compounds (Stewart, 2012). MOPAC searches for the structure with the lowest enthalpy through geometry optimization.

2.2. NWChem

NWChem is a program for quantum chemistry and molecular dynamics. NWChem uses DFT (Density Functional Theory). DFT is a functional that uses the electron density of the many body system for calculations. Instead of calculation the wave function for every electron in the structure with n atoms which gives the number of variables n x 3, the electron density is a function with only three variables. In this way the Schrödinger equation for the density of a single electron can be used. The total energy of the system can be calculated with the electron density of the system. NWChem is based only on theoretical models unlike MOPAC. DFT gives more reliable results compared to MOPAC but takes considerably longer time. (Newton.ex.ac.uk, 2015) (Sholl & Steckel, 2009)

2.3. Avogadro

Avogadro is software for visualization, drawing and modification of chemical structures in 3D. It is compatible with many other computational chemistry and molecular modeling software such as MOPAC and NWChem. Avogadro can make extensions to those programs, for example if a structure in built in Avogadro a *.mop file* can be created instantly to be run in MOPAC. (Hanwell et al., 2012) (Hanwell, Hutchison and Vandermeersch, 2015)   The only problem with the current version is the super cell builder which enlarges unit cells does not work. Therefore Vesta is used to create larger cells. Avogadro cannot write *.cif file* which would have been useful.

2.4. Vesta

Vesta is a visualization program for chemistry. In Vesta chemical structures can be created and modified. But the coordinates must be given for the atoms, the atoms cannot be drawn manually as in Avogadro. Vesta was in this work only used to enlarge the unit cell. Vesta cannot read *.xyz files* in angstroms, so these Cartesian coordinates needs to be in fractional even though there is no unit cell. But Vesta can write in many other file formats such as *.cif*. (Momma and Izumi, 2011)

2.5. Gabedit

Gabedit is graphical user interface for several modeling and chemical computer programs. Gabedit makes it easier to create input files and to interpret output files. Gabedit can visualize optimization convergence and structures from MOPAC and NWChem. This gives insight for the user to what happens in MOPAC geometry optimization. Gabedit can also be used to draw molecules and chemical structures. (Allouche, 2010)

3. Method

The different compounds involved in the production of cement and the hydration species were modeled in MOPAC to give heat of formation for the geometry optimized species. Lime, calcite, carbon dioxide, quartz, alite, belite, jennite and tobermorite 14 Å was modeled in pure phases in solid state.

Dissolution of species was modeled by inserting the species into a cube containing water molecules. Lime, $Ca^{2+} \bullet H_2SiO_4^{2-}$ and $2Ca^{2+} \bullet H_2SiO_7^{4-}$ was modeled in this manner.

Jennite was modified to resemble C-S-H phases at different polymerization levels and calcium/silicon rations. This was done by removing some of the bridging tetrahedral in the dreierkette structure, in accordance to Taylor´s Model.

3.1. Keyword used in MOPAC

There are many commands that can be used in MOPAC. This is an explanation for those used for this work. With all these keyword the programmer tells the program which method to use, restrictions for the method, state of the structure, physical parameters, etc. All keywords can be found on MOPAC´s website. (Stewart, 2015)

3.1.1. PM7

This command tells MOPAC to use the PM7 method for geometry optimization and heat of formation calculations. When generation *a .mop file* with Avogadro, PM6 is default this is why this should be changed for solid structures.

3.1.2. CHARGE=0

CHARGE=0 describes that the total charge of the structure is zero. This value is set according to the structure. In this work it is always zero.

3.1.3. Singlet

This command restricts the spin state of combined two ½ spin particles to a spin state of zero.

3.1.4. AUX

Command AUX gives a graphical file in which changes in the structure can be observed. The AUX file can be opened in Gabedit and Avogadro.

3.1.5. GNORM=n.n

GNORM=n.n is a criteria for geometry optimization; n.n can be set to any positive number. When the convergent gradient (GRAD) is lower than GNORM the optimization is finalized. A lower value gives a more accurate calculation but takes longer time.

3.1.6. RECALC=n

When using RECALC the Hessian matrix is numerically recalculated after n optimization cycles. This takes very long time for large structures but may solve convergence problems.

3.1.7. EF

For large structures L-BFGS is the default optimization routine, it is fast for large structures but not as accurate as EF. EF is a geometry optimizing routine using Eigenvector Following which is a slow and computer power heavy but accurate routine. EF will often make the structure converge when L-BFGS do not, this is why EF can be recommended for structures which has difficulties to converge.

3.1.8. LET

The LET command just means "let me do this", the program will ignore some safety checks and run the optimization. Recommended when encountering safety issues that can be ignored.

3.1.9. DDMIN=n.n

This command can be used in combination with EF. It is very useful for structures which are very near the optimal geometry. DDMIN sets the smallest trust radius for EF, this is the smallest distance an atom can be moved in one cycle. For optimization of near optimized structures DDMIN=0 can be used to get a stabile optimization.

3.1.10. EPS=78.39 RSOLV=1.3

The combination of EPS=78.39 and RSOLV=1.3 simulates an electrostatic background similar to that of a water system. These commands with these values are used when modeling in water environment. Other electrostatic backgrounds can also be simulated by different values of EPS and RSOLV.

3.2. Different file formats

Different file format contain information that can be different even if the substance described in the files are the same. There are standards but all programs cannot read all file formats. This can creates some problems when multiple programs are used.

3.2.1. .cif

Crystallographic Information File is a standard file format for information of crystal structures. It describes the symmetry, unit cell, atom positions with fractional occupations. The coordinate are described as fractional parameters of the unit cell. .cif files can easily be edited in text editors. (Hall, Allen and Brown, 1991) Example can be seen in appendix I.

3.2.2. .xyz

The *.xyz file* describes the structure only as Cartesian coordinates with angstrom as units. The first row in the file is the amount of atoms in the structure. The second row is the compound name, this is optional and can be kept blank. The rest of the rows are the atoms in the structure with their Cartesian coordinates. Example can be seen in appendix II.

3.2.3. .mop

The *.mop* is an input file to MOPAC. It contains command for the program and the structure of the chemical system. The commands are presented on a single row at the top of the file and on the second row the title can be written. The third row is often kept empty in this work and the atoms are presented with one atom per row. The structure is presented as Cartesian coordinates in angstrom.

The number 1 is located after every coordinate of all the atoms that are going to be geometry optimized. Translation vectors are on the last rows in the file after the atoms if the system is a solid. Their coordinates are based on the first atom in the file, the coordinate for the first Tv is where the atom would be in a unit cell placed next to the first unit cell along the x-axis. The coordinate for the second Tv is where the atom would be in a unit cell placed next to the first unit cell along the y-axis. The coordinate for the third Tv is where the atom would be in a unit cell placed next to the first unit cell along the z-axis. Example can be seen in appendix III.

3.2.4. .out

In the *.out file* the results of MOPAC can be found and also what has been done and general information about the structure. Depending on what has been specified in the commands for MOPAC other information such as bonds can be seen in the *.out* file. An example of an *.out* file can be seen in appendix IV.

3.3. *Methodology* from raw file to MOPAC output

To get a structure from American Mineralogist Crystal Structure Database to MOPAC can be a winding and tricky path. Therefore a working routine was established. A flowchart of the routine with the different programs and file formats can be seen in figure 4.

1. Cif file for many crystalline substances can be downloaded from American Mineralogist Crystal Structure Database. (Downs & Hall -Wallace, 2003)

2. Avogadro and Vesta can only read coordinates for individual atoms. Molecules like water or hydroxide can be written with single coordinates in the *.cif* file. Therefore the coordinates of the molecules need to be replaced with coordinates for the individual atoms to make it readable for Avogadro and Vesta.

3. Molecules like water were marked by changing them into easy to find atoms. For example, water molecules which are written as Wat can be changed into an atom which does not exist otherwise in the structure such as F for Fluorine.
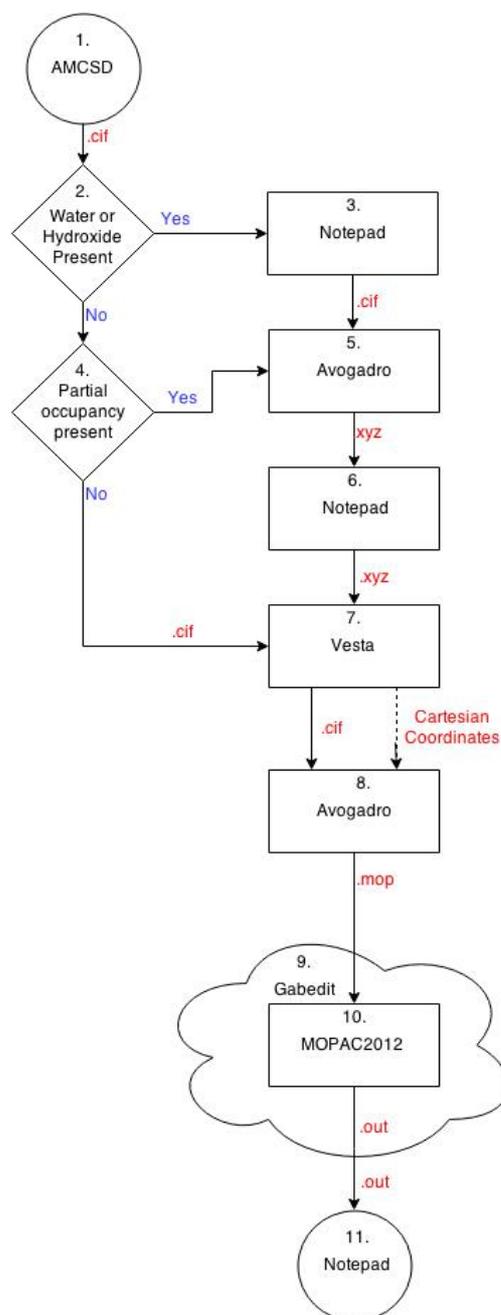

Figure 4. The figure illustrates a flowchart of the routine used for the preparation and execution of the computations from the AMCSD database.

4. If the structure contains partial occupancy atoms, some of them must be removed to obtain the correct charge and stoichiometry of the structure.

5. The marked water molecules were changed with Avogadro to oxygen bounded to two hydrogen atoms each. The partial occupancies were corrected. Because Avogadro cannot save .cif file the structure was usually saved as *.xyz file*.

6. Because Vesta cannot read Cartesian coordinates in angstroms, the Cartesian coordinates were changed into fractional Cartesian coordinates.

7. If the structure was in a *.xyz file,* the original unit cell needs to be given to Vesta by inserting the cell parameters manually. Then the unit cell was multiplied to create a unit cell which can accommodate a sphere with a diameter of minimum 8 angstroms. Because an atomic orbital in the centre of the cell needs to have a distance to the atomic orbital on the edge of the cell so they have a negligible overlap. The structure was saved as a .cif file or the Cartesian coordinates for the larger unit cell were copied from Vesta and inserted into Avogadro.

8. Avogadro was used in this step to create a *.mop file* that can be run in MOPAC. Translation vectors were also added to solids.

9. Gabedit is a graphical user interface in which MOPAC is run from. Commands for MOPAC can be given here. If no other keyword are specified in results the keywords; AUX CHARGE=0 Singlet PM7 GNORM=10 was used in this study.

10. MOPAC runs a geometry optimization with the given commands and an *.out* file is generated.

11. The results of the geometry optimization can be viewed with both Gabedit and Notepad. In Gabedit the structure can be seen and the convergence can be seen in a graph.

12. The heat of formation was divided by the number of smallest unit and then listed in results.

4. Results

4.1. Geometry optimization using PM7 in MOPAC

All structures were downloaded from American Mineralogist Crystal Structure Database and the amcsd codes are given for each structure in corresponding text. Avogadro and Vesta were used to modify and prepare the structures for PM7 calculations in MOPAC. Gabedit was used as a graphical user interphase for MOPAC.

4.1.1. Pure Phases

The pure phases were modeled separately to obtain heat of formation for different phases. The heat of formation can be seen in the equation in the text for all phases and also summarized in table 1.

4.1.1.1. Lime CaO

The structure with amcsd code: 0008276 was used as a basis for Lime. The structure was enlarged from A = B = C = 4.815 Å to A = B = C = 19.26 Å to accommodate the required size of a sphere of 8 Å in diameter. Translation vectors were added with Avogadro.

Geometry optimization was successfully run on the system containing 256 oxygen atoms and 256 calcium atoms. After 91 cycles the iteration was finished and resulted in a total heat of formation for the entire system of -134481.5 kJ/mol.

4.1.1.2. Calcite $CaCO_3$

The structure with amcsd code: 0000098 was used as a basis for calcite. The cell was enlarged from;

| A = 4.9900 Å | B = 4.9900 Å | C = 17.0615 Å |

α = 90°   β = 90°   γ = 120°

To a cell with parameters;

| A = 19.96 Å | B = 19.96 Å | C = 17.0615 Å |

Geometry optimization with MOPAC was run for the structure containing 96 carbon, 96 calcium and 288 oxygen atoms. After 1068 iteration cycles, the optimization was terminated manually for the reason that it did not converge. After a long period of a stabile gradient the system became very instable with very high gradients this can be seen in figure 5. A value at the stabile region was taken as a converged value. The gradient after the 249th cycle was as low as 13.27 this was considered to be the best value of the optimization and therefore its heat of formation was adopted as the systems heat of formation at -128341.397 kJ/mol.
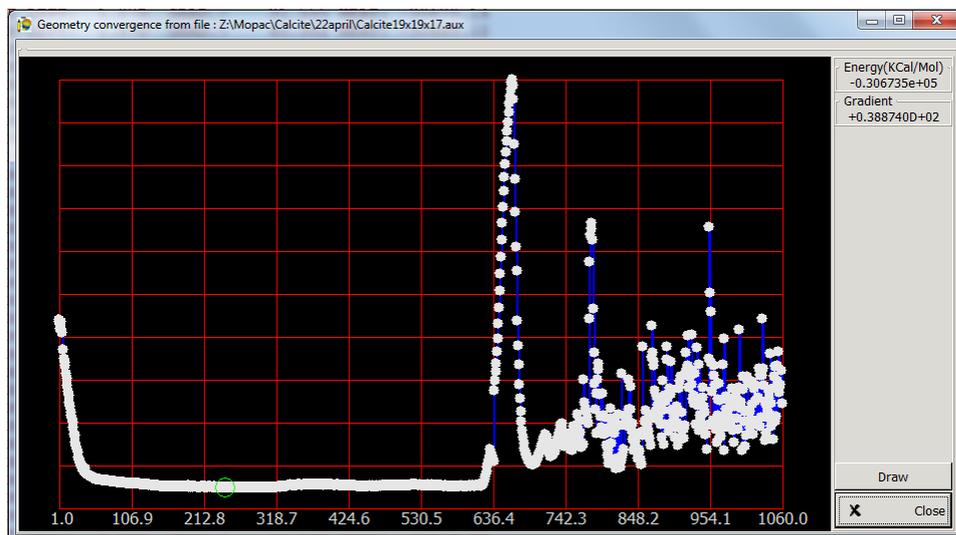
Figure 5. Geometry convergence for Calcite.

The reference value for heat of formation for calcite is -1207 kJ/mol. The calculated value is only 10 % off, even though it did not converge. This indicates that a non-converging value can be acceptable under the condition that it is in the right range. It was also observed that at the very start of the optimization the heat of formation was calculated to be -1207kJ/mol that gives strong indications that calcite is being used as a reference value in the program.

4.1.1.3. Carbon dioxide CO_2

Carbon dioxide was constructed directly in Gabedit using its drawing tool as it is not a solid. It was made as a single CO_2 molecule and was geometry optimized. For this simple system, optimization tock only 13 cycles to reach a gradient of 0.291. At this point a heat of formation of -353.6 kJ/mol was achieved.

4.1.1.4. Quartz SiO_2

The crystal structure of quartz was downloaded with amcsd code: 0008971. The *.cif file* was modified in Vesta, by lengthening all sides with a factor 3 to a cell with parameters;

A = 14.94 Å   B = 14.94 Å   C = 16.38 Å
α = 90°   β = 90°   γ = 120°

The structure containing 81 silicon and 162 oxygen atoms was run in MOPAC through Gabedit.
After 121 cycles the optimization had converged for the gradient of 8.525. This resulted in a heat of formation of -72373.758 kJ/mol, for the entire structure.

4.1.1.5. Alite $Ca_3(SiO_4)O$

The mineral form of alite, hatrurite was downloaded as a *.cif-file* with amcsd code: 0014729. Six out of the nine oxygen atoms with 1/3 occupancy was removed to achieve a neutral charge. The selection of 1/3 occupation oxygen atoms can be seen in figure 6.
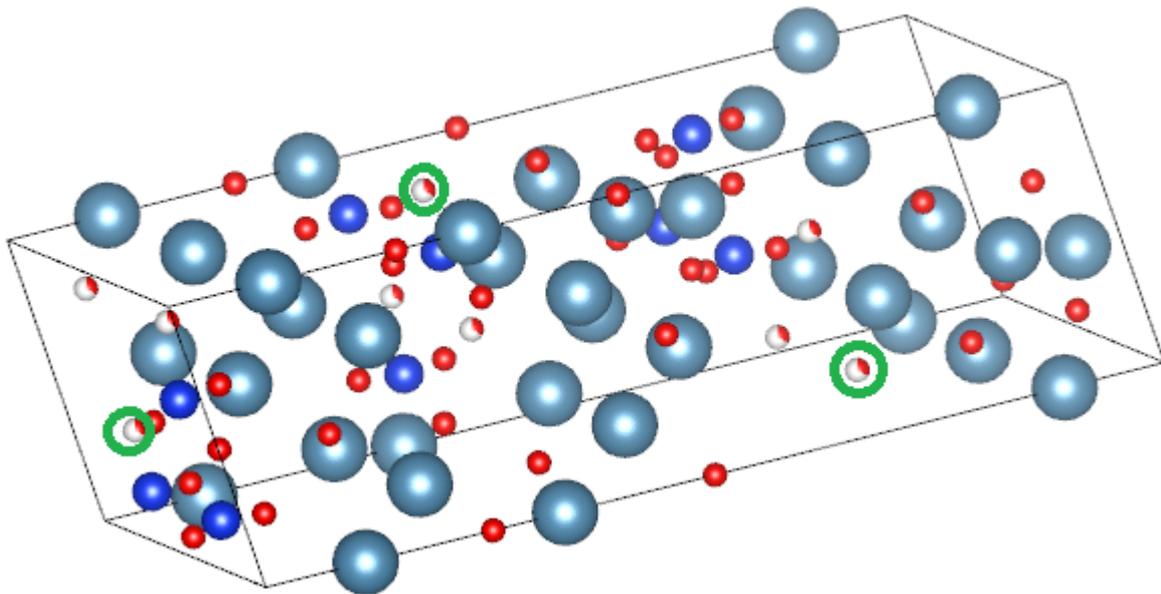
Figure 6. The figure shows the selection of 1/3 occupying oxygen atoms, the white and red are the 1/3 occupying oxygen atoms, those surrounded by green circles was the once that were kept in the structure. The blue atoms are silicon and the blue/grey are calcium. The figure is illustrated with Vesta.

The unit cell was extended by A x 3 and B x 3 to be able to be run in MOPAC.
From cell parameters;

A = 7.078 Å   B = 7.078 Å   C= 24.94 Å
α = 90°   β = 90°   γ = 120°
to a cell with parameters;
A = 21.1234 Å   B = 21.234 Å   C= 24.94 Å
α = 90°   β = 90°   γ = 120°

Geometry optimization with MOPAC was run for the structure containing 243 calcium, 81 silicon and 405 oxygen atoms. After 833 cycles the gradient was down at 8.458 which gave a heat of formation of -211493.48 kJ/mol for the structure.

4.1.1.6.   Belite Ca_2SiO_4

The mineral form of belite, larnite was downloaded as a *.cif-file* with amcsd code: 0012179. The unit cell was enlarged by a factor 2 of all sides to form a cell with parameters:

A = 16.5123 Å   B = 13.5244 Å   C= 18.6562 Å
α = 90°   β = 94.172°   γ = 90°

Geometry optimization was run for the structure containing 96 calcium, 48 silicon and 192 oxygen atoms. After 337 cycles the gradient was down at 7.322 which gave a heat of formation of
-104898.39 kJ/mol for the structure.

4.1.1.7.   Jennite - $Ca_9Si_6O_{18}(OH)_6 \bullet 8H_2O$

The structure of jennite was downloaded from American Mineralogist Chrystal Structure Database with amcsd code: 0012177. In this structure water and hydroxide was present as single coordinates which were replaced by individual atoms.

The unit cell with parameters;

A = 10.576 Å   B = 7.265 Å   C= 10.931 Å

α = 101.3° β = 96.98001°   γ = 109.65°

was multiplied by two to all sides to give a large enough cell for MOPAC, this results in a new cell with parameters:

A = 21.152 Å   B = 14.53 Å   C= 21.862 Å

α = 101.3° β = 96.98001°   γ = 109.65°

Geometry optimization was done for the system containing 72 calcium, 48 silicon, 256 oxygen and 176 hydrogen atoms. A heat of formation of -113107.09 kJ/mol was achieved for the whole system after 812 cycles with GRAD = 9.252.

4.1.1.8. Jennite revised - $Ca_9Si_6O_{18}(OH)_6 \cdot 8H_2O$

It was observed that after enlargement of the unit cell and the conversion between different file formats, some hydrogen and oxygen atoms were located by themselves without any bond. The hydrogen atoms had been separated from their water molecules that were located on the other side of the unit cell. The hydrogen atoms were moved back to the other side of the cell to form water molecules where they belonged. The oxygen atoms were relocated to the other side of the unit cell to where oxygen atoms were missing in the silicon-oxygen chain. The structure can be seen in figure 7. These modifications were made in Avogadro on the same *.cif file* used for the enlarged jennite in previous section. This should not be a problem as it is a periodic system.

A geometry optimization was run for the structure with revised hydrogen but not oxygen atoms. The optimization was done with the same key words and settings as with unmodified jennite in previous section. After 599 cycles GRAD was 9.984 which meet the requirement. A heat of formation of
-112893.93 kJ/mol was obtained for the system.
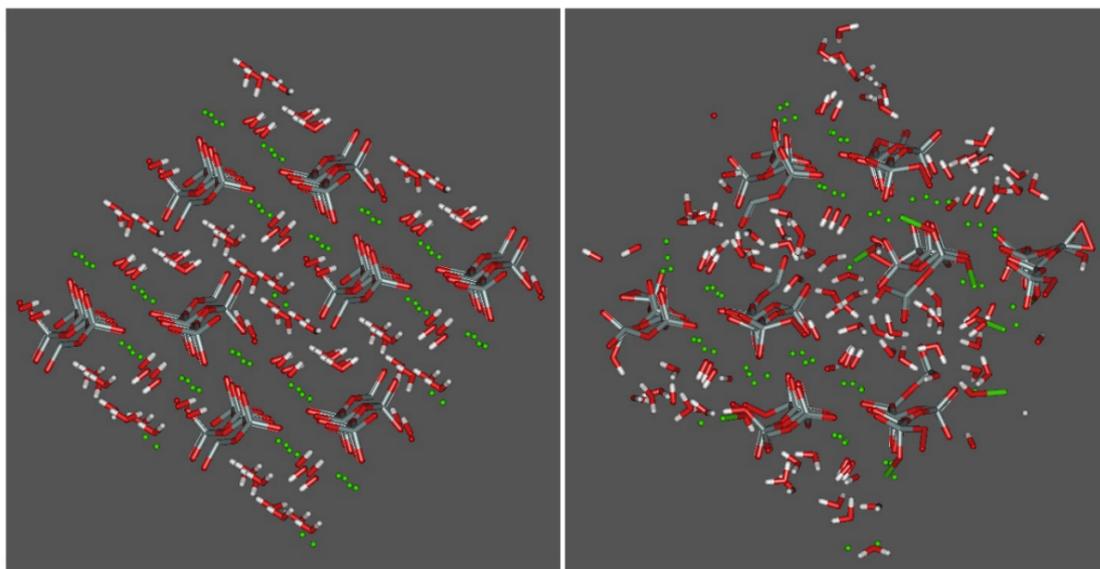
Figure 7. The figure shows the geometry optimization for jennite were the alone hydrogen atoms have been moved but not the oxygen atoms. Observe the triangular binding between one silicon and two oxygen atoms. These triangular bindings encouraged the rearrangement of alone oxygen atoms. The left figure is prior to geometry optimization and the right is after.

A geometry optimization was made for the structure in which both hydrogen and oxygen atoms had been moved. The modified *.cif file* was as in the hydrogen

case also based on the *.cif file* from enlarged unmodified jennite and was also run with the same keywords and settings. In this case it took only 354 cycles to reach a GRAD at 9.62. A heat of formation of -114117.64 kJ/mol was obtained for the entire system. The structure before and after optimization can be seen in figure 8.

This enthalpy is lower than the unmodified jennite, but not significantly. This can indicate that small errors do little damage to the entire system. But as it can be seen by the numbers of cycles the modified takes less than half the cycles and this saves time, so much time can be saved by checking and correcting each structure before running any program.
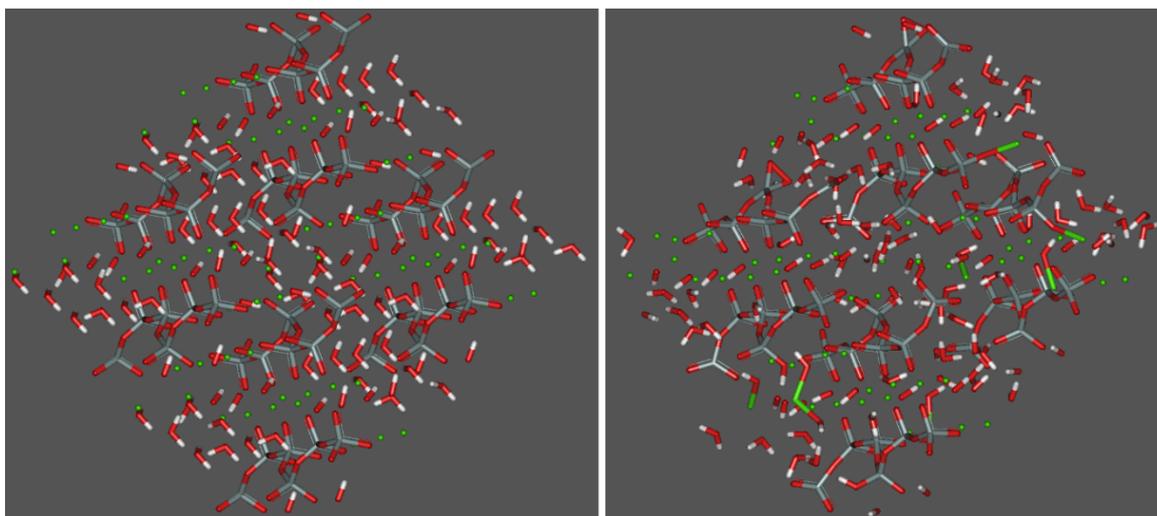
Figure 8. The figure illustrate the geometry optimization of jennite without alone hydrogen and oxygen atoms. The image to the left is before optimization and the on to the right is after. As could be seen on figure 7 the same kind of silicon-oxygen-oxygen triangle can be observed. Two of these triangles can be observed and if only this had been the case the charge of the system would have changed but this is countered by one calcium binding to two hydroxide groups and two calcium binding to one hydroxide group each to keep the zero charge on the system.

4.1.1.9. Tobermorite 14Å $Ca_5Si_6O_{16}(OH)_2 \cdot 7H_2O$

The structure of plombierite was downloaded with amcsd database code 0014073. As is contains water and hydroxide which were written as single coordinates for the molecules, the molecules were replaced by individual atoms.

The original unit cell with lattice parameters:
A = 6.735 Å   B = 7.425 Å   C= 27.987 Å
$\alpha = 90°$ $\beta = 90°$ $\gamma = 123.25°$
was enlarged by multiplying A and B by two to give a larger unit cell with parameters;
A = 13.47 Å   B = 14.85 Å   C= 27.987 Å

After 145 cycles of optimization, MOPAC was automatically terminated because of the GRAD value was very high at 99999.999. The lowest heat of formation for the structure was therefore used and was -80388.15 kJ/mol for the entire structure.

4.1.1.10. Portlandite $Ca(OH)_2$

Portlandite was downloaded with amcsd database code: 0000117 as a *.cif file*. The unit cell was enlarged by multiplying A and with 5 and C by 3, this gives a

unit cell with lattice parameters:

A = 17.9625 Å   B = 17.9625 Å   C= 14.715 Å

α = 90°   β = 90°   γ = 120°

MOPAC was run on the system containing 75 calcium, 150 oxygen and 150 hydrogen atoms. After 1361 optimization cycles MOPAC was terminated because of the structure did not converge. The lowest heat of formation achieved was -68117.93 kJ/mol.

4.1.1.10.1.   Portlandite EF calculation

The *.mop file* from previous section was run in MOPAC again but with command row; AUX CHARGE=0 SINGLET PM7 GNORM=10 RECALC=50 EF LET DDMIN=0.0. This commands changes the routine to give a more exact calculation and makes it easier for the system to converge. RECALC=50 instructs the routine to recalculate every position numerically after every fiftieth cycle. This results in a very time consuming modeling, but the system converges. After 240 optimization cycles the system converged with a GRAD of 9.574 thus the optimization was finished. A heat of formation of -68223.52 kJ/mol was obtained for the system.

4.1.2. Water and Dissolution of Species

Dissolution of lime and calcium silicate was tested to find heat of dissolutions and to observe how they behaved in a water environment. The test subjects were inserted in a theoretical cube of water.

4.1.2.1.   Water with Translation Vectors

First a water system needed to be modeled. To make it simple a calculated cube was filled with water molecules and was modeled as a solid system with translation vectors.

ρ = 0.997773 g/mol at 25°C

M_{H2O} = 18.016 g/mol

$$\frac{\rho}{M} = \frac{n}{cm^3} = 0.55382604 \ mol/cm^3 \tag{E1}$$

Equation E1 converts density to moles per cubic centimeter.

$$\frac{\rho}{M} \times N_A = 3.33521896 \times 10^{22} \ H_2O/cm^3 \tag{E2}$$

Equation E2 calculates moles per cubic centimeter to water molecules per cubic centimeter.

$$3.33521896 \times 10^{22} \ H_2O/cm^3 = 0.03335219 \ H_2O/Å^3 \tag{E3}$$

Equation E3 calculates water molecules per cubic centimeter to water molecules per cubic angstrom.

$$\frac{1}{0.03335219 \ H_2O/Å^3} = 29.98303895 \ Å^3/H_2O \tag{E4}$$

Equation E4 gives the volume one water molecule occupies to have a density of 0.997773 g/mol.

$$\sqrt[3]{29.98303895 \text{ Å}^3 / H_2O} = 3.106646819 \text{ Å} \qquad\qquad (E5)$$

Equation E5 gives the side lengths of a cube that contains one water molecule.

A unit cell with parameters:
A = 3.10665 Å   B = 3.10665 Å   C= 3.10665 Å
α = 90°   β = 90°   γ = 90°
was created in Avogadro and one oxygen atom with fractional Cartesian coordinates; 0.5 0.5 0.5 was added. Avogadro's automatic hydrogen function was used to add two hydrogen atoms to the oxygen to create one water molecule.

The cell was enlarged by multiplying all side by five to create a new unit cell containing 125 water molecules with lattice parameters:
A = 15.5332409 Å   B = 15.5332409 Å   C= 15.5332409 Å
α = 90°   β = 90°   γ = 90°
Avogadro was used to add translation vectors was and to generate a .mop file.

Geometry optimization was run for the cube and was automatically terminated after 1831 cycles when the GRAD value was extremely large, thus the structure did not converge. But a lowest value for GRAD was obtained after 877 cycles at 11.647. The best heat of formation was -40737.77 kJ/mol for the entire system.

4.1.2.2.   Water without Translation Vectors
Water was also modeled as a more liquid structure without translation vectors. The same *.mop file* was used with the same commands but without translation vectors. After 264 geometry optimizing cycles the GRAD reached 9.854 which gave a heat of formation of -38256.35 kJ/mol for the whole system.

4.1.2.3.   Dissolution of CaO in Water
The structure which was created in previous section 4.1.2.1. containing 125 water molecules was used as a basis for this experiment. In Avogadro a water molecule was deleted. One calcium atom and one oxygen atom was added. A *.mop* file was created for the system. The *.mop* file was opened in Gabedit and the command row was changed to AUX EPS=78.39 RSOLV=1.3 CHARGE=0 Singlet PM7 GNORM=2.

After 3118 cycles MOPAC was automatically terminate when the heat of formation was stationary over many cycles. The lowest heat of formation was -39592.35 kJ/mol for the entire structure.

4.1.2.4.   Silica Monomer in Water
The structure created in previous section 4.1.2.1, containing 125 water molecules was used as a basis for this experiment. The water molecule in the middle of the cube was replaced by a silicon atom bonded to two hydroxide groups and two oxygen atoms. One calcium ion was placed adjacent to the two oxygen atoms which in this case had one negative charge each. The arrangement can be seen in figure 9. This was done in Avogadro and a *.mop file* was create for this system.
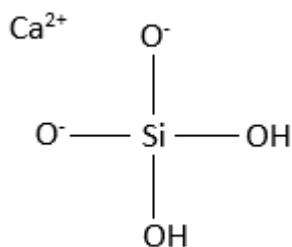
Figure 9.Describes how the atoms were arranged in the water cluster.

The *.mop file* was opened in Gabedit and the command row was changed to AUX EPS=78.39 RSOLV=1.3 CHARGE=0 Singlet PM7 GNORM=5. After 704 cycles MOPAC was done when GRAD was as low as 4.31. The best obtained heat of formation was -40701.36 kJ/mol for the entire system. The structure before and after optimization can be seen in figure 10.
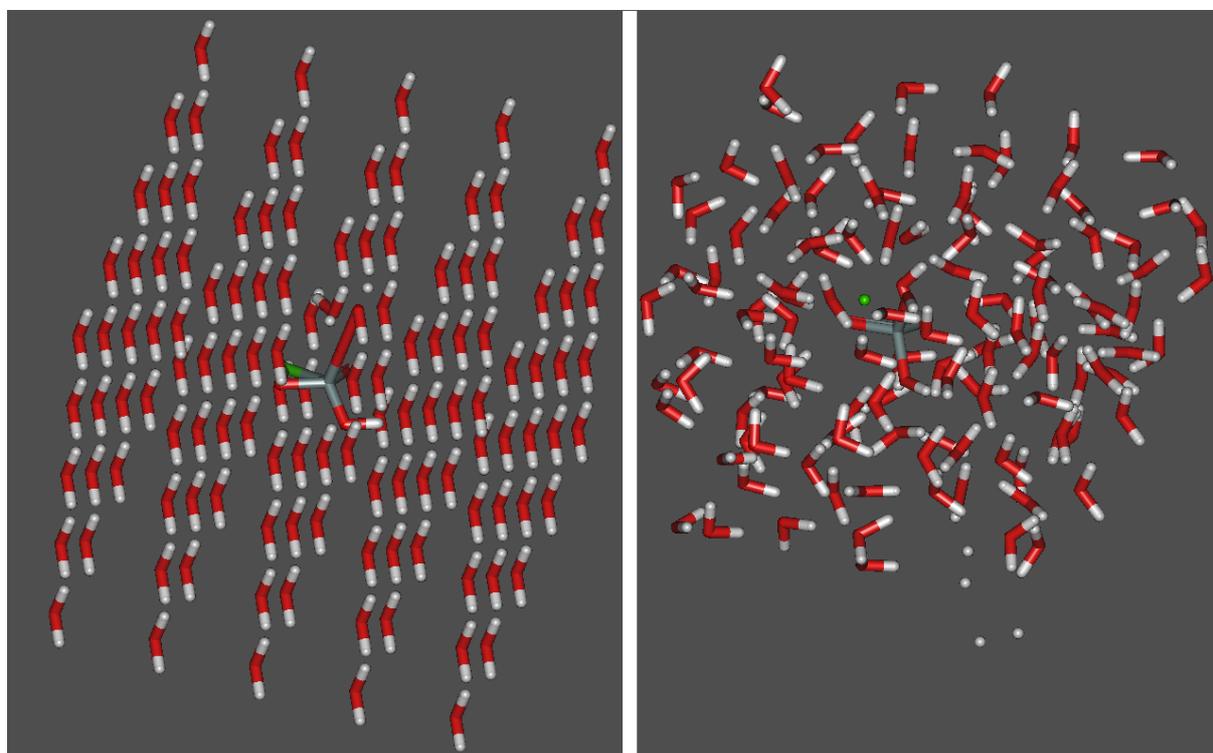
Figure 10. The figure illustrates how the geometry changed in the geometry optimizing. The structure to the left is the original structure and the structure to the right is the geometry optimized structure. Note the hydrogen atoms in the lower right corner of the right structure that have lost their oxygen atoms., This is just a graphical error, the oxygen are there but they are not visible.

4.1.2.5.   Silica Dimer in Water Alternative A

The *.cif file* that was created in previous section 4.1.2.1. containing 125 water molecules was used as a basis for this experiment. Four water molecules in the middle of the cube was removed to give place for a silicate dimer. Two silicon atoms both bound to one oxygen atom was place in the middle of the cell. Two oxygen atoms and one hydroxide group was added to both silicon atoms. Two calcium ions were placed adjacent to the charged oxygen atoms. The arrangement is illustrated in figure 11.
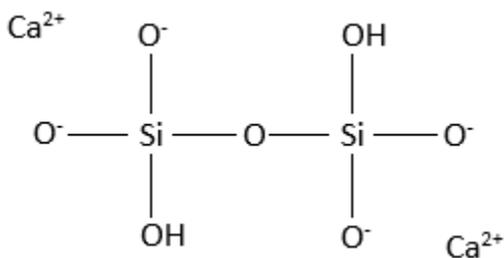
Figure 11. The figure shows how the atoms were arranged in the water cluster.

The *.mop file* was opened in Gabedit and the command row was changed to AUX EPS=78.39 RSOLV=1.3 CHARGE=0 Singlet PM7 GNORM=5. After 752 cycles MOPAC was done when GRAD was as low as 4.985. The best heat of formation was -41008.81kJ/mol for the entire system. The structure before and after optimization can be seen in figure 12.
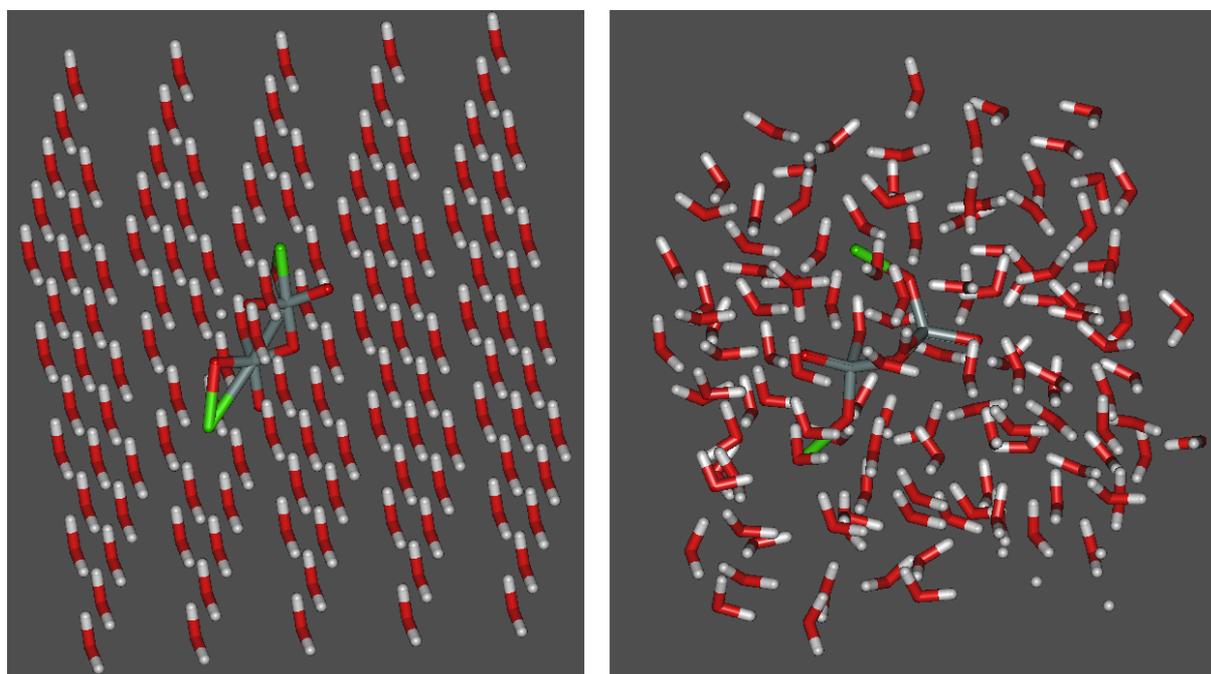
Figure 12. The figure shows the geometry optimization of silica dimer in water, the structure to the left is the start structure and the structure to the right is the final structure. Note the hydrogen atoms that have lost their oxygen atoms in the lower right corner in the final structure it is just a graphical error.

4.1.2.6.   Silica Dimer in Water Alternative B

The same procedure as for section 4.1.2.5 was used but the positioning of the calcium ions and the hydroxide groups was altered to act more similar the structure in tobermorite. The structure can be seen in figure 13. The structure was modeled in the cases with 118 or 121 water atoms. With the difference in enthalpy for different water content the enthalpy of only the dimer can be calculated. MOPAC calculated the enthalpy for the entire system to -41122.84 kJ/mol for dimer with 121 water molecules and -39964.31 kJ/mol for dimer with 118 water molecules.
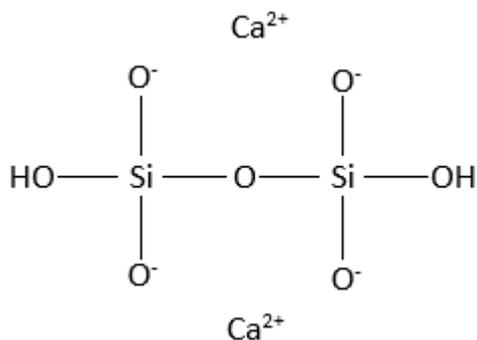
Figure 13. The figure illustrates how the atoms were arranged in the center of the water cube.

Form the enthalpies with different amount of water molecules, the enthalpy of adding one water molecule in a cube of water with one dimer in it was calculated with the following equation E6.

$$\frac{-41122.84-(-39964.31)}{3} = -386.18 \; kJ/mol \, water \, molecule \tag{E6}$$

4.1.2.7. Comparison of Silica Dimers and Monomer

With the enthalpies for the dimers A and B a comparison shows that dimer B has lower enthalpy then dimer A. If dimer A would rearrange to dimer B 114 kJ heat would be evolved per dimer. This indicate that dimer B is the more likely dimer to exist.

The reaction where two monomers react to one dimer is a more difficult calculation because it involves a large compensation for excess of water. The monomers were modeled with 124 water molecules and the dimer with 121, therefore one cube with only water and three water molecules was added in the calculation. The three extra water molecules was used with the enthalpies calculated in section 4.1.2.6 with equation E6 as water dissolved in a cube of water containing one dimer. The reaction is described in reaction R7.

2 x (Monomers + 124 water) → (Dimer B + 121 water) + 3 H_2O + 125 H_2O

(R7)

Hess's Law was used to calculate the enthalpy of the reaction.

$$\Delta H_r^\ominus = \Sigma(\Delta H_f^\ominus \; products) - \Sigma(\Delta H_f^\ominus \; reactants)$$

$\Delta H_r^\ominus$ = (-41122.84 ⁻ 38256.35 + 3 x -386.18) – (2 x -40701.36) = 865.02 kJ/mol

(E7)

Equation E7 results in a positive heat of formation which means that this reaction is endothermic and would need energy to happen.

4.1.3. Modification of Jennite

As jennite reach the closest heat of formation to C-S-H, compared to tobermorite. Jennite was chose as basis for modification to model C-S-H. The jennite structure was modified to resemble different stages in the hydration process by cutting the

dreierkette chains in the jennite structure to obtain silicate dimers and pentamers.

4.1.3.1. Modified Jennite Alternative 1, Dimers

The .cif file from section 4.1.1.8. was used. Every bridging silicate tetrahedral was replaced by a water molecule to obtain dimers in the structure. The water molecule was inserted to fill the void to prevent the structure to rearrange too much and to keep the unit cell with the same parameters. The structure can be seen in figure 14. In this modification the calcium/silicon ratio is increased from 1.5 to 2.25.
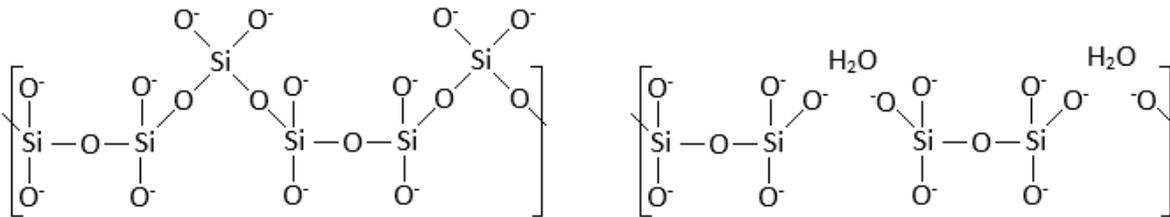
Figure 14. The figure shows how the structure was modified. The left structure is the unmodified and the structure to the right is the modified. As can be seen by the figure the charges on the bridging tetrahedral is moved inwards to the chain.

In the geometry optimization the structure did not converge and the structure rearranged in an unexpected manner, illustrated in figure 15. The charged oxygen reacted with the water molecules. This resulted in a heat of formation of -104834.29 kJ/mol for the entire structure containing; 72 calcium, 32 silicon, 240 oxygen and 208 hydrogen atoms.
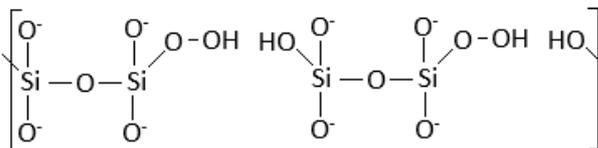
Figure 15. The figure illustrates how the structure rearranged during the geometry optimization.

4.1.3.2. Modified Jennite Alternative 2, Dimers

To prevent the oxygen to react with water a different approach was used to remove the bridging silicate tetrahedral. The silicon atom was deleted and one hydrogen was added to the four oxygen atoms which had been bound to the silicon,seen in figure 16. In this case the charges were kept at the same places.
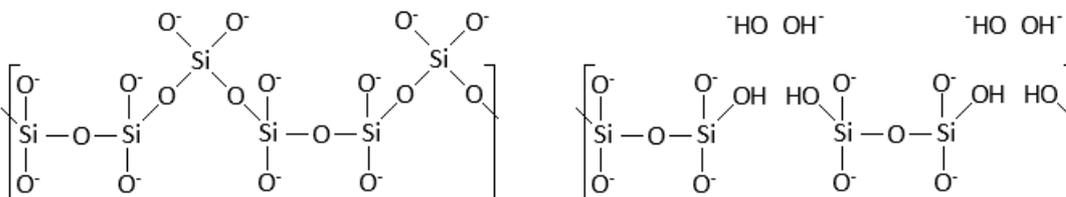
Figure 16. The figure shows how the modification was made. The left structure is the unmodified and the structure to the right is the modified. As can be seen in the figure the charges on the bridging tetrahedral is not moved.

 This structure was more stable compared to the first modification alternative. The structure was largely unchanged during the geometry optimization. A final

heat of formation of -101386.17 kJ/mol was achieved for the entire structure containing 72 calcium, 32 silicon, 256 oxygen and 240 hydrogen atoms.

4.1.3.3.   Modified Jennite Alternative 2, Pentamers

Jennite was modified as in previous section but instead of removing every bridging tetrahedral only every other bridging silicate tetrahedral was removed to obtain pentamer chains in a semi-dreierkette, this can be seen in figure 17. In this structure a calcium/silicon ratio of 1.8 was achieved.
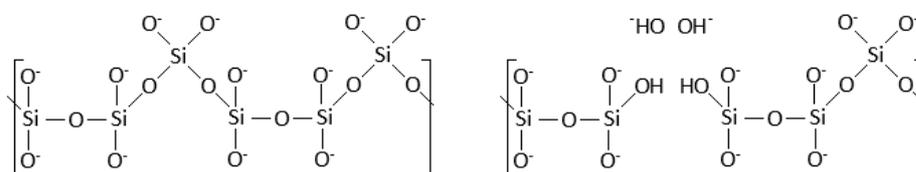
Figure 17. The figure illustrates how the jennite was modified. The left structure is the structure of the dreierkette silicate structure of jennite and the right structure is the modified jennite structure.

The geometry optimization did not converge but a heat of formation of -113510.5 kJ/mol was obtained for the structure containing; 72 calcium, 40 silicon, 256 oxygen and 208 hydrogen atoms.

Table 1. All MOPAC modeling results are listed in the table and compared to literature. The MOPAC enthalpies marked with green are converged structures with good results, the yellow marked are non-converged structures with acceptable values. Reference values with orange text are values that are calculated from literature.

Compound	MOPAC $\Delta H_f^{\ominus}$	(Aylward & Findlay, 2007)	(Lothenbach et al., 2008)	Calculated From Taylor	deviation from Ref
	kJ/mol	kJ/mol	kJ/mol	kJ/mol	%
Calcite ($CaCO_3$)	-1336.89	-1207	-1207		-10.8
Lime (CaO)	-525	-635			17.3
CO_2(g)	-353.6	-394			10.3
Quartz (SiO_2)	-893.5	-911	-903		1.9
Hatrurite (Alite C_3S)	-2611		-2931	**-2599**	10.9
Larnite (Belite C_2S)	-2185.4		-2308		5.3
Jennite $Ca_9Si_6O_{18}(OH)_6$ x $8H_2O$	-14138.4		**-16338**		13.5
Jennite revised $Ca_9Si_6O_{18}(OH)_6$ x $8H_2O$	-14264.7		**-16338**		12.7
Tobermorite 14Å $Ca_5Si_6O_{16}(OH)_2$ x $7H_2O$	-10048.52		**-11496**		12.6
Portlandite ($Ca(OH)_2$)	-909.65	-986	-985		7.7

H_2O(l)	-306.05	-286	-237.15		-7.0
H_2O(s) with translation vectors	-325.9				
Ca^{2+} + $2OH^-$ + 123 H_2O	-39592.35				
Silica monomer ($CaSiO_4H_2$ x 124 H_2O)	-40701.36				
Silica Dimer alt.A ($Ca_2SiO_7H_2$ x 121 H_2O)	-41008.81				
Silica Dimer alt.B ($Ca_2SiO_7H_2$ x 121 H_2O)	-41122.84				

C-S-H (1,7CaO x SiO2 x 2,617 H$_2$O) x6				**-17340**	
Modified Jennite Alt1 Dimer (Ca$_9$Si$_4$O$_{14}$(OH)$_6$ x 10H$_2$O)	-13104.3				
Modified Jennite Alt2 Dimer (Ca$_9$Si$_4$O$_{14}$H$_4$(OH)$_{10}$ x 8H$_2$0)	-12673.3				
Modified Jennite Alt2 Pentamer (Ca$_9$Si$_5$O$_{16}$H$_2$(OH)$_8$ x 8H$_2$O)	-14188.8				

4.2. Enthalpy of Reactions

The reaction enthalpy was calculated using the enthalpies obtained in MOPAC and Hess´ Law. Enthalpy of reaction for calcination was also calculated with values from NWChem.

4.2.1. Heat of reaction for hydration of Lime

The heat of formation of the components in the reaction was modeled by using MOPAC.

Heat of formation for H$_2$O and CaO were modeled separately and calculated to -306.05 kJ/mol and

-525 kJ/mol respectively. Ca$^{2+}_{(aq)}$ + 2OH$^-_{(aq)}$ + 123 H$_2$O$_{(l)}$ was on the other hand modeled as a whole system by building a system containing one Ca atom adjacent to one O atom in the center of a cube filled with 124 water molecules as described in reaction R8.

124 H$_2$0$_{(l)}$ + CaO$_{(s)}$ → Ca$^{2+}_{(aq)}$ + 2OH$^-_{(aq)}$ + 123 H$_2$O$_{(l)}$

(R8)
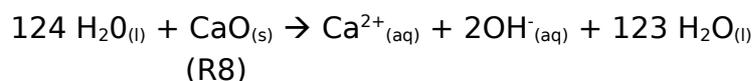
Hess's Law was used to calculate the enthalpy of reaction R8. Equation E8 describes the calculation.

$\Delta H_r^\ominus$ = (-39592.35) – (-525,318 + 124 x -306.05) = -1116.83 kJ/mol

(E8)

4.2.2. Calcination Reaction Using MOPAC results

Values of heat of formation for calcite, lime and carbon dioxide was used to calculate the enthalpy of reaction, for the reaction; $CaCO_3 \rightarrow CaO + CO_2$. The calculation can be seen in equation E9.

$\Delta H_r^\ominus$ = (-525 + -353.6) – (-1336.89) = 458 kJ/mol

(E9)

4.2.3. Calcination Reaction Using NWChem Results

The species involved in the calcination reaction was modeled in NWChem as reference software. In this software the result is presented as total energy in Hartree. The results of modeling of the three species can be seen below in table 2.

Table 2. The table list the Calcination compounds and the total energy modeled by NWChem.

	total energy (E_h)	total energy (kJ/mol)
CaCO3	-54.79	-143900
CaO	-17.01	-44660
CO2	-37.67	-98900

Hess's law was applied to calculate a change in energy for the reaction. The calculation can be seen in equation E10.

$$\Delta H_r^\theta = (-37.67 - 17.01) - (-54.79) = 0.10775\ E_h = 282.9\ \text{kJ/mol}$$

(E10)

The change in total energy is equal to the enthalpy change. NWChem preforms it calculations at zero kelvin whilst MOPAC calculates for 25°C, this can lead to some differences.

4.2.4. Reaction to form Alite

Heat of formation values for lime, quartz and alite obtained in MOPAC was used in Hess's Law to calculate an enthalpy for reaction R3. The calculation can be seen in equation E11.

$$3CaO + SiO_2 \rightarrow Ca_2(SiO_4)O$$

(R3)

$$\Delta H_r^\theta = (-2611) - \big(3 \times -525 + (-893,5)\big) = -142.5\ \text{kJ/mol}$$

(E11)

4.2.5. Reaction to form Belite

Heat of formation values for lime, quartz and alite obtained in MOPAC was used in Hess's Law to calculate an enthalpy for reaction R2. The calculation can be seen in equation E12.

$$2CaO + SiO_2 \rightarrow Ca_2SiO_4$$

(R2)

$$\Delta H_r^\theta = (-2185,4) - \big(2 \times -525 + (-893,5)\big) = -241.9\ \text{kJ/mol}$$

(E12)

Table 3. The table lists reactions calculated with values from MOPAC and NWChem compared to literature.

	This work	(Taylor, 1997)	Calculated with values from (Lothenbach et al., 2008) and (Aylward & Findlay, 2007)	(Shi, Zhao and Li, 2002)
	kJ/mol	kJ/mol	kJ/mol	kJ/mol
Hydration of Lime	-1116.8			-65.4
Calcination MOPAC	458	187	178	
Calcination NWChem	282.9	187	178	
Reaction to Alite	-142.5	-495	-123	
Reaction to Belite	-241.9	-126	-135	

5. Discussion

The pure unmodified phases were modeled with acceptable results compared to literature as can be seen in table 1. This confirms that MOPAC can model solid structures that are similar to those on which data MOPAC is approximated with. Some of the structures did not converge with L-BFGS but when changed to EF the structures converged easier. When using EF instead of L-BFGS the heat of formation did not change notably from an unconverged L-BFGS optimization to a converged EF optimization for the same structure. This shows that the L-BFGS method works even if the structure does not converge to a required level.

In the case of jennite it was found that some error in the structure does not influence the enthalpy significantly. But fixing the errors made the enthalpy more similar to that in the literature. Fixing the error also helped the geometry to converge.

For the dissolution of species the dimer B was calculated to have a lower enthalpy then dimer A. This can be because of how the calcium ions affect the bond angle freedom of the dimer, it can be that dimer B makes it possible for the silicon-oxygen bonds in the dimer to have a more optimal angle and length compared to dimer A. The fact that tobermorite and jennite has this structure further strengthens the theory that C-S-H is similar to jennite and tobermorite 14Å, it also strengthens the polymerization theory. The systems containing water should be modeled in NWChem because MOPAC cannot model hydrogen bonds particularly good.

The reaction from monomer to dimer B was calculated to be highly endothermic, this is likely not true. In the compensation of water there can be several minor errors that build up to a larger error, the choice of enthalpy of water to use in compensation is of great importance as it affects everything in the structure and the compensation water is half the system. To explore this reaction further, the monomer and dimer should be modeled at different water contents.

Jennite was modified in two different ways. With modification alternative one, the structure rearranged in a peculiar way, to form a Si-O-O-H structure at the ends of the dimers. This was the result of the modification that changed the position of the charges inwards to the chain structure.

Alternative two for the modification of jennite was a response to the first alternative to keep the charges at the same positions as in unmodified jennite. This modification gave a better structural geometry but a higher enthalpy then the first alternative. This modification alternative was used to form both dimers and pentamers but this alternative needs hydrogen atoms to be placed on the oxygen atoms that were bound to the silicon atoms that were removed. These hydrogens make the reaction formula unbalanced. A third alternative could be to place a calcium ion between the dimers as in figure 18, instead of terminating them with hydrogen.
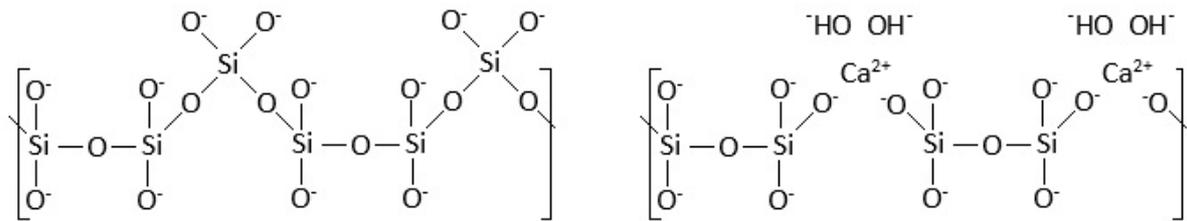
Figure 18. The figure illustrates how the dreierkette structure in jennite can be modified to obtain shorter chains and higher Ca/Si ratio. The structure to the left is the unmodified and the structure to the right is the modified.

The reactions that were calculated with values from MOPAC and NWChem can be seen in table 3. There it can be observed that the hydration of lime is very different compared to reference data. This can be because of the unrealistically modeling of water in a cube or the modeling of lime in water. The calcination reaction, the reaction to form alite and the reaction to form belite are in the correct range but differ somewhat from values in literature, this can be due to the enthalpy error of lime which is in all those reactions.

The calcination reaction was calculated with both MOPAC and NWChem, the results can be compared and it can be observed that the results from NWChem are nearer to the reference values compared to that of MOPAC. This is probable due to that NWChem uses a more sophisticated method. The drawback of NWChem is that it takes considerably longer rime to run.

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6. Conclusion

MOPAC and NWChem were used to model clinker and hydration products and their transient species. The modeling was done mainly with geometry optimization using MOPAC and some species were modeled in NWChem. The results of geometry optimization, in form of heat of formation were compared to literature values and were found to be acceptable. This proved that relatively simple software can be used to model structures and reactions in the cement system. This can be important to the future of cement research as it is a complex composition of reactions and compounds that are difficult to distinguish from each other. Modeling can therefore be a tool for a large array of people from academic researchers to cement engineers. However, if the input file is incorrect the output file is going to be incorrect, this is why the operator needs knowledge of the system being studied in both chemical and computational details. As modeling requires minimal laboratory work it saves chemicals and minimizes exposer for the laboratory worker. But modeling cannot entirely replace actual laboratory experiments as modeling results needs to be compared to actual experimental data.

7. Further Studies

Further studies could investigate modification of jennite and tobermorite with the third alternative presented in the discussion. Different strategies of removing the bridging tetrahedral for both jennite and tobermorite should be examined. The extent of removal of the bridging tetrahedral should be studied for different effects.

The systems containing water should be modeled in NWChem because MOPAC cannot model hydrogen bonds particularly good. Dissolutions of alite and belite can also be modeled in further studies.

The water simulating cube should be replaced by a more accurate substitute or a continual system with translation vectors. The waster bulk should the large enough so that the water molecules in the outer part of the bulk are not affected by what is in the middle of the bulk. The water molecules in the outer bulk should ideally have the same energy as pure water.

8. Acknowledgements

I would like to thank my supervisor Rikard Ylmén who introduced me to and exciting and challenging thesis. His help with the software was greatly appreciated.

I would also like to show my appreciation to all those who tried to listen to me when I have explained what I have done all this time.

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Appendix I: Tips & Tricks

In *.cif* files water molecules can sometimes be written simply as Wat, but Avogadro and Vesta can only read atoms so the water molecules appears as black atoms. If the black dots are difficult to distinguish from other atoms then Wat in the *.cif* file can be changed to a more distinguishable atom by opening the .cif file in notepad and replace Wat with a better atom which is then made to a water molecule in Avogadro.

The same as water goes for OH⁻ which are written as O-H in .cif, but this is even trickier because they appear as oxygen atoms. Change O-H to something else such as I for iodide which is nice and green to be replaced with OH in Avogadro.

Avogadro cannot write .cif files and Vesta cannot read *.xyz* files containing coordinates in angstrom. But if a structure is saved as a *.xyz* file in Avogadro and the Cartesian coordinates are changed to fractional with notepad then the file can be opened in Vesta and if a unit cell is added with Vesta then Vesta can save the structure as a *.cif* file.

When translations vectors are added in Avogadro, the first atom can be copied to the last three rows in the Cartesian editor. The three atoms are then renamed to something easy to identify, for example Ti. In fractional coordinates the coordinates are changed by addition 1 to the x coordinate for the first Ti atom, 1 to the y coordinate for the second Ti atom and 1 to the z coordinate for the third Ti atom. The Ti are later in Gabedit changed to Tv.

For example if the first atom in the Cartesian coordinate system has the coordinates in fractional;
```
Ca 0.057 0.114 0.215
```
the Ti are written with the fractional Cartesian coordinates:
```
Ti 1.057 0.114 0.215
Ti 0.057 1.114 0.215
Ti 0.057 0.114 1.215
```

Appendix II: Example of the content in a .cif file

```
data_global
_chemical_name_mineral 'Calcite'
loop_
_publ_author_name
'Graf D L'
_journal_name_full 'American Mineralogist'
_journal_volume 46
_journal_year 1961
_journal_page_first 1283
_journal_page_last 1316
_publ_section_title
;
 Crystallographic tables for the rhombohedral carbonates
;
_database_code_amcsd 0000098
_chemical_formula_sum 'Ca C O3'
_cell_length_a 4.9900
_cell_length_b 4.9900
_cell_length_c 17.0615
_cell_angle_alpha 90
_cell_angle_beta 90
_cell_angle_gamma 120
_cell_volume 367.916
_exptl_crystal_density_diffrn      2.710
_symmetry_space_group_name_H-M 'R -3 c'
loop_
_space_group_symop_operation_xyz
  'x,y,z'
  '2/3+x,1/3+y,1/3+z'
  '1/3+x,2/3+y,2/3+z'
  'x,x-y,1/2+z'
  '2/3+x,1/3+x-y,5/6+z'
  '1/3+x,2/3+x-y,1/6+z'
  'y,x,1/2-z'
  '2/3+y,1/3+x,5/6-z'
  '1/3+y,2/3+x,1/6-z'
  '-x+y,y,1/2+z'
  '2/3-x+y,1/3+y,5/6+z'
  '1/3-x+y,2/3+y,1/6+z'
  '-x,-x+y,1/2-z'
  '2/3-x,1/3-x+y,5/6-z'
  '1/3-x,2/3-x+y,1/6-z'
  '-y,-x,1/2+z'
  '2/3-y,1/3-x,5/6+z'
  '1/3-y,2/3-x,1/6+z'
  'x-y,-y,1/2-z'
  '2/3+x-y,1/3-y,5/6-z'
  '1/3+x-y,2/3-y,1/6-z'
  'y,-x+y,-z'
  '2/3+y,1/3-x+y,1/3-z'
  '1/3+y,2/3-x+y,2/3-z'
  '-x+y,-x,z'
  '2/3-x+y,1/3-x,1/3+z'
  '1/3-x+y,2/3-x,2/3+z'
  '-x,-y,-z'
  '2/3-x,1/3-y,1/3-z'
  '1/3-x,2/3-y,2/3-z'
  '-y,x-y,z'
```

'2/3-y,1/3+x-y,1/3+z'
 '1/3-y,2/3+x-y,2/3+z'
 'x-y,x,-z'
 '2/3+x-y,1/3+x,1/3-z'
 '1/3+x-y,2/3+x,2/3-z'
loop_
_atom_site_label
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
Ca   0.00000   0.00000   0.00000
C   0.00000   0.00000   0.25000
O   0.25780   0.00000   0.25000

Appendix III: Example of the content in a .xyz file

```
30
Calcite
Ca       0.00000       0.00000       0.00000
C       -0.00000      -0.00000       4.26538
O        1.28642      -0.00000       4.26538
Ca      -0.00000      -0.00000       8.53075
Ca       2.49500       1.44049       5.68717
Ca       2.49500       1.44049      14.21792
Ca      -0.00000       2.88098      11.37433
Ca      -0.00000       2.88098       2.84358
C       -0.00000      -0.00000      12.79613
C        2.49500       1.44049       9.95254
C        2.49500       1.44049       1.42179
C       -0.00000       2.88098      15.63971
C       -0.00000       2.88098       7.10896
O       -0.64321       1.11407       4.26538
O        1.85179       3.20739       4.26538
O        3.70358      -0.00000      12.79613
O       -1.85179       3.20739      12.79613
O        0.64321       1.11407      12.79613
O        3.78142       1.44049       9.95254
O        1.85179       2.55456       9.95254
O        1.85179       0.32641       9.95254
O        1.20858       1.44049       1.42179
O        3.13821       0.32641       1.42179
O        3.13821       2.55456       1.42179
O        1.28642       2.88098      15.63971
O       -0.64321       3.99505      15.63971
O       -0.64321       1.76690      15.63971
O       -1.28642       2.88098       7.10896
O        0.64321       1.76690       7.10896
O        0.64321       3.99505       7.10896
```

Appendix IV: Example of an input file for MOPAC

AUX   CHARGE=0   SINGLET   PM7   GNORM=10

Calcite

Ca	0.00000	1	0.00000	1	0.00000	1
C	-0.00000	1	-0.00000	1	4.26538	1
O	1.28642	1	-0.00000	1	4.26538	1
Ca	-0.00000	1	-0.00000	1	8.53075	1
Ca	2.49500	1	1.44049	1	5.68717	1
Ca	2.49500	1	1.44049	1	14.21792	1
Ca	-0.00000	1	2.88098	1	11.37433	1
Ca	-0.00000	1	2.88098	1	2.84358	1
C	-0.00000	1	-0.00000	1	12.79613	1
C	2.49500	1	1.44049	1	9.95254	1
C	2.49500	1	1.44049	1	1.42179	1
C	-0.00000	1	2.88098	1	15.63971	1
C	-0.00000	1	2.88098	1	7.10896	1
O	-0.64321	1	1.11407	1	4.26538	1
O	1.85179	1	3.20739	1	4.26538	1
O	3.70358	1	-0.00000	1	12.79613	1
O	-1.85179	1	3.20739	1	12.79613	1
O	0.64321	1	1.11407	1	12.79613	1
O	3.78142	1	1.44049	1	9.95254	1
O	1.85179	1	2.55456	1	9.95254	1
O	1.85179	1	0.32641	1	9.95254	1
O	1.20858	1	1.44049	1	1.42179	1
O	3.13821	1	0.32641	1	1.42179	1
O	3.13821	1	2.55456	1	1.42179	1
O	1.28642	1	2.88098	1	15.63971	1
O	-0.64321	1	3.99505	1	15.63971	1
O	-0.64321	1	1.76690	1	15.63971	1
O	-1.28642	1	2.88098	1	7.10896	1
O	0.64321	1	1.76690	1	7.10896	1
O	0.64321	1	3.99505	1	7.10896	1
Tv	4.9899997711		0.0000000000		0.0000000000	
Tv	0.0000000000		4.3214664213		0.0000000000	
Tv	0.0000000000		0.0000000000		17.0615005493	

Appendix V: Example of an .out file from MOPAC

```
**************************************************************
**********
 ** Site#: 21813        For non-commercial use only    Version
15.077W 64BITS**

**************************************************************
**********
 ** Cite this work as:
**
  **
**
 ** (a) MOPAC2012, James J. P. Stewart, Stewart Computational
Chemistry,       **
 **  Version 15.077W web: HTTP://OpenMOPAC.net        Days
remaining: 324    **
 **
**
  **                              AND
**
  **
**
 ** (b) Maia, J.D.C., et al., J. Chem. Theory Comput. 2012, 8, 3072-
3081.     **
 **               DOI: 10.1021/ct3004645.
**


**************************************************************
**********
  **
**
  **                             MOPAC2012
**
  **
**

**************************************************************
**********


                    PM7 CALCULATION RESULTS



**************************************************************
**********
 *   CALCULATION DONE:                       Tue Apr 28
08:27:02 2015  *
 *   PM7        - The PM7 Hamiltonian to be used
 *   SINGLET    - SPIN STATE DEFINED AS A SINGLET
 *
 *
 *
 *             CHARGE ON SYSTEM =      0
 *
 *
```

```
   *
   *  T=              - A TIME OF 172800.0 SECONDS REQUESTED
   *  DUMP=N          - RESTART FILE WRITTEN EVERY  7200.000 SECONDS
   *  GNORM=          - EXIT WHEN GRADIENT NORM DROPS BELOW  10.00
   *  AUX             - OUTPUT AUXILIARY INFORMATION


**************************************************************
**********
 AUX    CHARGE=0 SINGLET   PM7   GNORM=10


        ATOM    CHEMICAL        X              Y              Z
       NUMBER   SYMBOL      (ANGSTROMS)    (ANGSTROMS)    (ANGSTROMS)

         1        Si        2.34603000  *   0.00000000  *   0.00000000
   *
         2        Si        2.34603000  *   0.00000000  *   5.45995000
   *
         3        Si        2.34603000  *   0.00000000  *  10.92005000
   *
         4        Si       -0.14395000  *   4.31276000  *   0.00000000
   .
   .
   .
   *
       241        O         3.88067000  *  11.79078000  *   4.81244000
   *
       242        O         3.88067000  *  11.79078000  *  10.27239000
   *
       243        O         3.88067000  *  11.79078000  *  15.73250000
   *
       244        Tv       17.28602820  *   0.00000000  *   0.00000000
   *
       245        Tv        2.34602820  *  12.93841953  *   0.00000000
   *
       246        Tv        2.34602820  *   0.00000000  *  16.38000000
   *


                 THE SYSTEM IS A SOLID


              UNIT CELL TRANSLATION VECTORS


                  X              Y              Z
        T1 = 17.2860282      0.0000000      0.0000000
        T2 =  2.3460282     12.9384195      0.0000000
        T3 =  2.3460282      0.0000000     16.3800000


           CARTESIAN COORDINATES

     NO.       ATOM       X        Y        Z

       1        Si      2.3460   0.0000   0.0000
       2        Si      2.3460   0.0000   5.4600
       3        Si      2.3460   0.0000  10.9200
       4        Si     -0.1440   4.3128   0.0000
   .
```

.
.
```
   241         O        3.8807   11.7908    4.8124
   242         O        3.8807   11.7908   10.2724
   243         O        3.8807   11.7908   15.7325
```

==================== shared-memory parallel CPU Section ======================
      **
**
      **   MOPAC calculations will run in shared-memory parallel CPUs **
      **
**
      **   Number of Threads =   4
**
      **
**
      **
**
      **   For information on this work, see:
**
      **
**
      **   Maia, J.D.C., et al., J. Chem. Theory Comput. 2012, 8, 3072-3081.   **
      **   DOI: 10.1021/ct3004645.
**
      **
**
      ==================== shared-memory parallel CPU Section ======================

          Empirical Formula: O162 Si81 =   243 atoms

 SINGLET STATE CALCULATION

      RHF CALCULATION, NO. OF DOUBLY OCCUPIED LEVELS =   648

      Geometry optimization using EF

          DIAGONAL MATRIX USED AS START HESSIAN

 CYCLE: 1 TIME: 336.176 TIME LEFT: 2.00D GRAD.: 1434.389 HEAT: -11734.99

```
 CYCLE:     2 TIME:  39.170 TIME LEFT:  2.00D  GRAD.:  1177.468
HEAT: -12012.99
 CYCLE:     3 TIME:  39.266 TIME LEFT:  2.00D  GRAD.:   902.607
HEAT: -12329.23
.
.
.

CYCLE:   119 TIME:  48.410 TIME LEFT:  1.92D  GRAD.:    13.681
HEAT: -17297.37
 CYCLE:   120 TIME:  48.879 TIME LEFT:  1.91D  GRAD.:    13.737
HEAT: -17297.73
 CYCLE:   121 TIME: 186.750 TIME LEFT:  1.91D  GRAD.:     8.525
HEAT: -17297.74

     GRADIENT =  8.52480  IS LESS THAN CUTOFF = 10.00000
```


 AUX   CHARGE=0 SINGLET PM7   GNORM=10

```
     GEOMETRY OPTIMISED USING EIGENVECTOR FOLLOWING (EF).
     SCF FIELD WAS ACHIEVED
```

                      PM7 CALCULATION
                                        MOPAC2012
(Version: 15.077W)
                                        Tue Apr 28
10:33:09 2015
                                        No. of days
left = 324

```
       FINAL HEAT OF FORMATION =     -17297.74326 KCAL/MOL =
-72373.75780 KJ/MOL
       H.o.F. per unit cell    =      -213.55239 KCAL, for  81
unit cells


       TOTAL ENERGY            =     -56531.44506 EV
       ELECTRONIC ENERGY       = -252444853.51793 EV
       CORE-CORE REPULSION     =  252388322.07288 EV

       GRADIENT NORM           =         8.52480
       IONIZATION POTENTIAL    =         8.852609 EV
       HOMO LUMO ENERGIES (EV) =        -8.853  0.640
       NO. OF FILLED LEVELS    =        648
       MOLECULAR WEIGHT        =       4866.828

       MOLECULAR DIMENSIONS (Angstroms)
```

```
         Atom        Atom      Distance
         O   225   Si   19   25.53517
          O   214   Si   28   17.36989
         Si   19    O   225    0.23876

      VOLUME OF UNIT CELL        3130.381 CUBIC ANGSTROMS
      DENSITY                       2.582 GRAMS/CC
      Pressure required to constrain translation vectors
      Tv( 244)  Pressure:  -0.00 GPa
      Tv( 245)  Pressure:  -0.03 GPa
      Tv( 246)  Pressure:   0.09 GPa


      SCF CALCULATIONS          =         149

      WALL-CLOCK TIME           = 2 HOURS  6 MINUTES AND  7.485
SECONDS
      COMPUTATION TIME          = 3 HOURS 30 MINUTES AND 20.169
SECONDS



       FINAL  POINT  AND  DERIVATIVES

    PARAMETER      ATOM    TYPE            VALUE        GRADIENT
        1         1 Si    CARTESIAN X    2.451279      0.415793
KCAL/ANGSTROM
        2         1 Si    CARTESIAN Y    0.100208      0.140766
KCAL/ANGSTROM
    .
    .
    .
KCAL/ANGSTROM
      734       245 Tv    CARTESIAN Y   12.758872      1.371351
KCAL/ANGSTROM
      735       245 Tv    CARTESIAN Z    0.019717      2.087716
KCAL/ANGSTROM
      736       246 Tv    CARTESIAN X    0.165736     -0.104501
KCAL/ANGSTROM
      737       246 Tv    CARTESIAN Y    0.077101      0.550848
KCAL/ANGSTROM
      738       246 Tv    CARTESIAN Z   16.604446     -2.335397
KCAL/ANGSTROM



     ATOM   CHEMICAL        X                Y                Z
    NUMBER   SYMBOL     (ANGSTROMS)     (ANGSTROMS)      (ANGSTROMS)


      1       Si       2.45127882  *   0.10020805  *  -0.13113588
 *
      2       Si       2.45875342  *   0.13097937  *   5.46497150
 *
      3       Si       2.60837992  *   0.09931768  *  10.97443046
 *
      4       Si      -0.00304254  *   4.34233099  *  -0.05338418
    .
```

```
  .
  .
  *
   241        O          3.98537062  *  12.03851542  *   4.57222900
  *
   242        O          4.16707878  *  11.97117828  *  10.08496615
  *
   243        O          4.21239550  *  12.02782257  *  15.57661405
  *
   244        Tv        14.74618963  *  -0.14814206  *  -0.12863573
  *
   245        Tv         2.48700763  *  12.75887172  *   0.01971670
  *
   246        Tv         0.16573646  *   0.07710078  *  16.60444630
  *


                        CARTESIAN COORDINATES

     1   Si        2.451278817       0.100208048      -0.131135881
     2   Si        2.458753419       0.130979372       5.464971497
     3   Si        2.608379922       0.099317682      10.974430459
  .
  .
  .
241   O        3.985370619      12.038515417       4.572228997
 242   O        4.167078781      11.971178276      10.084966147
 243   O        4.212395497      12.027822568      15.576614049


         Empirical Formula: O162 Si81  =   243 atoms




                        EIGENVALUES
 -31.60626 -30.74073 -30.73047 -30.70779 -30.70598 -30.56906
-30.56063 -30.44650
 -30.43517 -30.40682 -30.39636 -30.39142 -30.36864 -30.35574
-30.34752 -30.31350
 -30.27657 -30.25820 -30.24860 -30.23956 -30.19979 -30.11417
-30.10201 -30.08462
 -30.07619 -30.00970 -30.00280 -29.92796 -29.92475 -29.91667 -
 .
 .
 .

  29.40660  29.40813  29.41324  29.41849  29.42643  29.42797
29.43191  29.43434
  29.43994  29.44319  29.44581  29.46547  29.46976  29.47168
29.47788  29.48174
  29.48604  29.49588  29.50027  29.50254  29.50756  29.51088
29.51995  29.52374
  29.52797  29.53812  29.54056  29.54318  29.54950  29.55550
29.55765  29.56078
  29.56889  29.58194  29.58746  29.59570  29.60147  29.60404
29.61230  29.61856
  29.65290
```

41

NET ATOMIC CHARGES AND DIPOLE CONTRIBUTIONS

ATOM NO.	TYPE	CHARGE	No. of ELECS.	s-Pop	p-Pop	d-Pop
1	Si	0.912427	3.0876	0.60232	1.97726	0.50800
2	Si	0.906433	3.0936	0.60250	1.98101	0.51005
3	Si	0.910647	3.0894	0.60288	1.97871	0.50777
4	Si	0.910385	3.0896	0.60248	1.97839	0.50874
5	Si	0.907566	3.0924	0.60276	1.98056	0.50912
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239	O	-0.451712	6.4517	1.56360	4.88811	
240	O	-0.508331	6.5083	1.57095	4.93738	
241	O	-0.454526	6.4545	1.56741	4.88712	
242	O	-0.455275	6.4553	1.56136	4.89392	
243	O	-0.448994	6.4490	1.55810	4.89089	

ATOMIC ORBITAL ELECTRON POPULATIONS

Atom	s	px	py	pz	x^2-y^2	xz	z^2	yz	xy
1 Si	0.60232	0.64417	0.66489	0.66820	0.08180	0.11576	0.08614	0.11366	0.11062
2 Si	0.60250	0.64752	0.66679	0.66670	0.08346	0.11620	0.08564	0.11175	0.11300
3 Si	0.60288	0.64459	0.66668	0.66744	0.08192	0.11548	0.08594	0.11351	0.11091
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79 Si	0.61319	0.67821	0.68838	0.68378	0.10094	0.11732	0.08721	0.10505	0.09418
80 Si	0.60242	0.66238	0.65025	0.66651	0.10462	0.11406	0.08584	0.11463	0.09014
81 Si	0.60365	0.65792	0.64775	0.66837	0.10539	0.11518	0.08630	0.11351	0.08522
82 O	1.56376	1.69500	1.58176	1.61994					
83 O	1.55930	1.68960	1.57440	1.62557					
84 O	1.56041	1.69224	1.56996	1.63334					
85 O	1.56403	1.68790	1.57623	1.62802					
86 O	1.56252	1.69417	1.57095	1.62873					
87 O	1.55869	1.69532	1.57935	1.61938					
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241 O	1.56741	1.67678	1.58471	1.62562					

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242  O   1.56136   1.67922   1.58502   1.62968
243  O   1.55810   1.68180   1.58135   1.62775
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             JOB ENDED NORMALLY

TOTAL JOB TIME: 7569.33 SECONDS

== MOPAC DONE ==