Synthesis of nano-structured Calcium silicate hydrate

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ABSTRACT

Calcium Silicate Hydrates (C-S-H) is the main product of hydrated Portland cements. A better understanding of its kinetics, growth mechanism and atomic structure will provide us with knowledge in assessing the new alternative material for substitution in cementitious material on more scientific basis rather than trial and error. Further to its role in cement, synthetic C-S-H has promising applications in fields such as drug delivery and oil spill adsorption owing to its high specific surface area. Also these C-S-H can be loaded with phase change material (PCM), which serves as excellent packaging material for sensitive products.[1][2]

The aim of this project is to synthesis C-S-H via precipitation route at Ca/Si ratio varying from 0.7 to 2. All the physical parameters such as pH, Ca^{2+} ion concentration, reactant addition are monitored. Reaction times between 1 and 24 hrs, producing a solid precipitate of C-S-H. The solid is separated, washed and filtered over the 200nm filter.[3] The collected solid and the aqueous phase has been characterized by XRD, TGA, ICP, SEM-TEM, BET and ^{29}Si NMR. It is the first time anyone could produce such a high Ca/Si ratio in a synthetic system. Also, on comparison of experimental results with thermodynamics modeling software (i.e.) Gibbs energy minimization software (GEMS) a good match is found when the formation of $Ca(OH)_2$ is prohibited in the simulations. The particles have a foil-like morphology with thickness of 5-10nm and diameters of 100-200nm, they are heavily agglomerated (microns) but have surface areas in the order of 50-200 m^2/g

Keywords: *Calcium silicate hydrates, precipitation, thermodynamic modelling*

1 INTRODUCTION

The main product of the hydration of Portland cement is a nearly amorphous material, Calcium Silicate Hydrate (C-S-H) that forms up to about 50-60% by volume of the paste. Cement shorthand nomenclature is used throughout this report, where C=CaO, S=SiO_2, A=Al_2O_3, H=H_2O. The hyphens in C-S-H indicate indefinite stoichiometry and the hydrate is sometimes referred to as "C-S-H gel".[1,2]

In the last few decades, many new aspects of the C-S-H have been revealed with the advancements in the analytical techniques and application of new methods such as nuclear magnetic resonance (NMR) spectroscopy. Recent experiments are able to give some information about its atomic structure, hence; the atomic structure of C-S-H gel is partially resolved.[2,4,5] However, experiments have revealed that C-S-H gel has a layered structure, at short length scales (1 to 5) nanometers and the layers stack to form compact domains in which the distance between individual C-S-H layers is of the order of a few nanometers, i.e. the same order as the interlayer distance in a Tobermorite or Jennite crystals. At larger length scales (5 to 100) nanometers, these ordered stacks form three-dimensional structures called C-S-H particles. Transmission Electron Microscopy (TEM) revealed that the actual C-S-H particle is disk shape and has a thickness of 5 nanometers with the long axis in the 60 nm range.[6–9] During hydration these C-S-H particles grow and perhaps aggregate to form low-density and high-density C-S-H gel at the micron length scale. The amorphous nature of C-S-H makes it very difficult to measure the amount of "bound" and "unbound" water in C-S-H gel and thus, makes the quantitative measurements (such as surface area) extremely challenging. Also, other compounds such as Calcium Hydroxide ($Ca(OH)_2$) coexist with the C-S-H gel. Hence, it is very difficult to separate $Ca(OH)_2$ from C-S-H gel. In addition, since C-S-H has no fixed stoichiometry, the chemical composition of C-S-H gel can change from point to point within a cement paste and hence, C-S-H gel is often defined by its average molar ratio of CaO to SiO_2 (Ca/Si) ratio.[1,10,11]

During precipitation new particles are created by nucleation events. The rate of nucleation plays an important role in controlling the final particle size distribution; however, this step is the most poorly understood. The nucleation process can be broken down into three main categories: (1) primary homogeneous, (2) primary heterogeneous and (3) secondary nucleation. Homogeneous nucleation occurs in the absence of a solid interface; heterogeneous nucleation occurs in the presence of a solid interface of a foreign seed and secondary nucleation occurs in the presence of a solute-particle interface. The mechanisms that govern primary and secondary nucleation are different and thus result in very different rate

expressions. Therefore, the relative importance of each nucleation process varies with each specific precipitation reaction. Among several possibilities of synthesizing C-S-H, two of the most often encountered is:

   Direct precipitation: For the direct precipitation approach different reactants may be used i.e. solutions may be made from silica and $Ca(OH)_2$ or by using sodium silicate and calcium nitrate solutions. The results from both methods have been used to augment the thermodynamic modeling for C-S-H. This methods often result in large quantities of product but accompanied with the drawbacks that often the supersaturations used are far higher than those found in hydrating cement, by a factor 100 to 10000. The C-S-H gel produced has been well characterized chemically but physical characterization (particle size, size distribution, particle morphology, specific surface area) has not been reported. With more investigation on concentration in mother liquor allied with thermodynamic modeling, can help to approach supersaturations found in cementitious systems.[18,20]

For thermodynamic modelling the GEM-Selektor(GEMS) is a Gibbs Energy Minimization program package for interactive thermodynamic modeling of heterogeneous aquatic (geo)chemical systems will be used. It is a useful tool in not only predicting the state of the experiment, but with validation with our system can be used to design future experiment with known/predicted conditions.

2   MATERIALS AND METHODS

2.1   Synthesis and development of semi-crystalline calcium silicate

C-S-H synthesis is done by the double precipitation of calcium salts $(Ca(NO_3).4H_2O)$ with silicate (e.g. $Na_2SiO_3.5H_2O$) in solution phase. Further, the C-S-H precipitate is washed with water-ethanol mixture to remove unwanted ionic species in the precipitate. The overall experimental setup and condition is show in the Figure 1. We kept the Ca to Si ratio constant at 2 and precipitation were carried out in two ways namely - *Dropwise* and *Micromixer*. In the Micromixer method , we introduce NaOH in a reaction vessel and Calcium nitrate and Sodium silicate are introduced into the reactor after micromixing, whereas in the Drop wise method NaOH is present in the reaction vessel along with Sodium silicate and Calcium carbonate is introduced in the vessel in a drop wise manner at a fixed rate. The chemical concentration used were 0.2 mol/L for calcium nitrate and 0.1 mol/L for sodium silicate. Solutions in both cases were prepared by mixing with ultra pure water previously boiled to 110°C to remove the CO_2. The gel obtained after precipitation was washed as mentioned before and filtered and stored in air tight containers. The pH value of the solution was adjusted to about 13.3 using sodium hydroxide (NaOH) appropriate concentration.
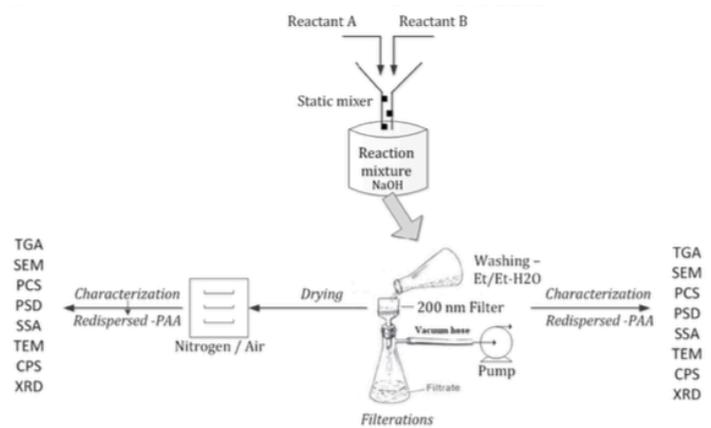

Figure 01: Micromixer method

3   RESULTS AND DISCUSSION

3.1   Concentration, Super saturation and Final ratio

In micromiser case, the super saturation value is order of 10^5 shown in figure 02, whereas in the case of the Dropwise method the super saturation is a function of time which changes with the addition of Calcium nitrate as shown in figure 07. Although due to formation of precipitate and consumption of solutes, the calculated Super saturation is the maximum super saturation possible, the actual super saturation will be always lower than calculated super saturation. ICP measurement shown in figure 4.9 the Ca/Si ratio obtained is close to input ratio (i.e.) 2.
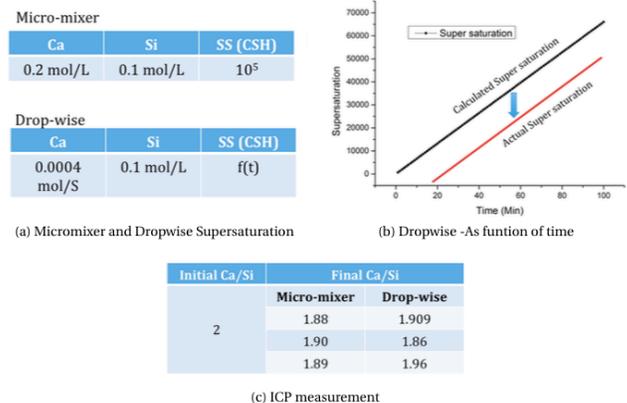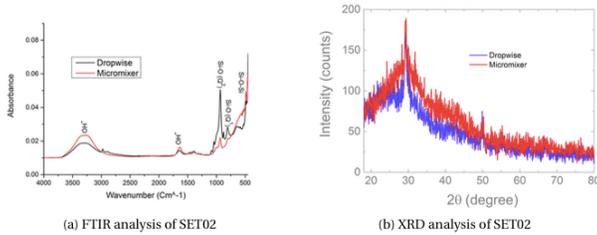

Micro-mixer

Ca	Si	SS (CSH)
0.2 mol/L	0.1 mol/L	10^5

Drop-wise

Ca	Si	SS (CSH)
0.0004 mol/S	0.1 mol/L	f(t)

(a) Micromixer and Dropwise Supersaturation

(b) Dropwise -As funtion of time

Initial Ca/Si	Final Ca/Si	
	Micro-mixer	Drop-wise
2	1.88	1.909
	1.90	1.86
	1.89	1.96

(c) ICP measurement

Figure 02 Concentration and Ca/Si ratios

3.2 Chemical and structural analysis

FTIR analyses were performed on the sample and we can clearly see in figure 8(a) the peak of Q1, Q2 and Si-O-Si bonding of C-S-H in the sample. The presence of some Aragonite was seen in the case of the Dropwise method,

where as no portlandite was detected in any of the samples. Figure 03 shows no additional peaks of presence of portlandite at the expected wavenumber of 3600 (cm^{-1}). During XRD analysis we can clearly observe the two crystalline peaks of convectional C-S-H reported in the literature occurring at 30 & 55 (degrees 2q) (Figure 3(b), whereas no peaks for portlandite or calcium carbonate are observed, for both the Dropwise and Micro mixing methods.

(a) FTIR analysis of SET02   (b) XRD analysis of SET02

Figure 03: FTIR & XRD analysis

TGA analysis was performed on dried (6 hrs. & 10 hrs. in nitrogen) and non-dried samples. We see higher water losses in Micromixer case, before drying (Figure 4(a)). Figure 04(b) shows the two graphs for the sample from dropwise and micromixer method after dyring for 6 and 10hrs respectively. The TGA analysis shows that we do not posses portlandite greater than 1% of the total solid formation in any of the samples. The . Micromixer sample shows two extra dweight losses (200-300°C and 600-800°C) in the curve which has been attibuted to a secondary "gel" phase seen in TEM analysis, which is believed to be formed at early state of reaction in the micromixer from which the foil like structures (see below) which dominate the morphology are formed as at these high pHs (13.3).


(a) TGA of non-dried sample   (b) TGA of dried sample in N2
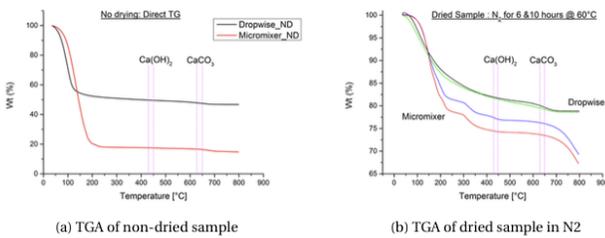
Figure 04: TGA analysis

3.3 Morphological analysis

TEM analysis shows *nanofoils* like morphology which are more homogenous in the Dropwise method (Figure 5(b)) when compared to the Micromixer method (Figure 5(a)where we have a secondary phase in the background that seems to be more of globular gel like phase which we believe is formed immediately after the rapid mixing of the reactant in the micromixer where supersaturations are extremely high (10^5). The Dropwise method shows very

homogenous sheet formation as shown in figure 6 where SEM imaging confirms the formation of the *nanofoils*.

(a) TEM Image of Micromixer   (b) TEM Image of Dropwise
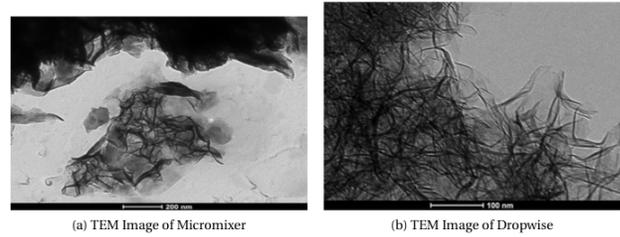
**Figure 5: Nanofoils formation**
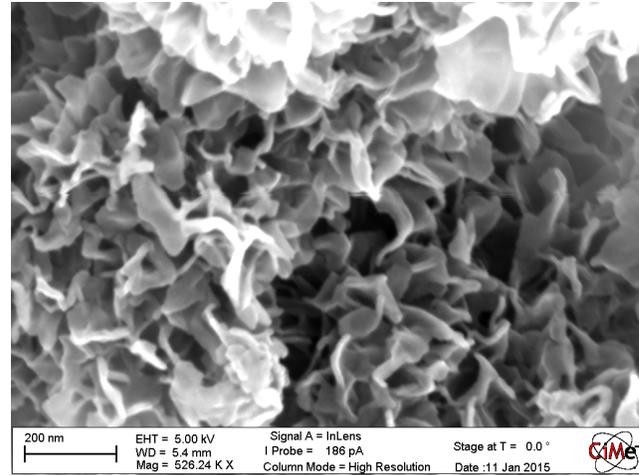
Figure 6: SEM image

It was difficult to quantify the Ca/Si ratio using EDX, when performed directly on the sample. Although the ratio remain consistent over the regions tested. For more accurate quantification (corresponding to ICP results) sample can be further embedded into resin and slide flat surface can be analyzed under EDX

3.4 Comparison with thermodynamic modeling

With GEMS we predict the formation of portlandite at 0.25 mol/L concentration of NaOH at about 12.3 pH value, whereas we do not see (<1%) of portlandite formation in our sample (pH 13.3). Under these conditions the C/S ratio for the C-S-h was predicted to be 1.6, significantly below the value of 2 seen in our experiments. The GEMS software was forced inhibit the formation of portlandite and under these conditions and we arrive at a very close agreement between the experimental and calculated values as shown in figure 7. In the process of shutting off the Portladite formation, we observe no change in the pH or any unexpected change of the species in solution. Please note that, the red small square shows our experimental point in each graph.

(a) Ca/Si ratio in aqueous & Solid state

(b) pH & formation of Portlandite

(c) No Formation of portlandite

(d) pH variation
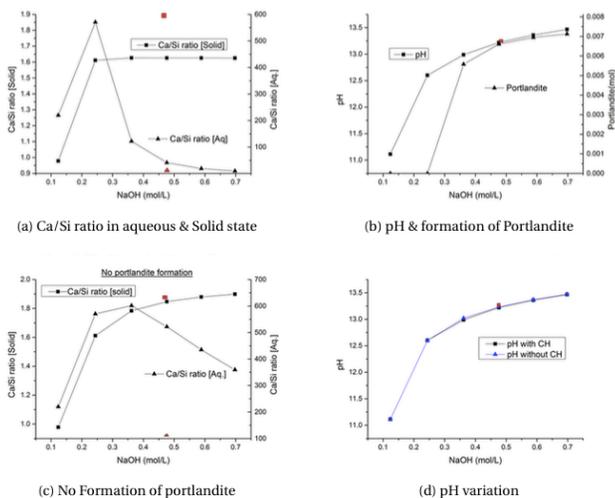
Figure 07: Comparison with of experiment and thermodynamic modelling using GEMS – experimental points are red symbols in each of the figures

4   CONCLUSIONS

The synthetic precipitation synthesis route produces homogeneous phases, with a plate-like or nanosheet morphology. For the first time in the a higher Ca/Si ratio was prepared in a synthetic system, this was achievd by controlling the pH of the system with NaOH in well controlled enviroment. The formation of portlandite is inhibited in our experimental system . Mixing did not play a significant role considering the high concentration and supersaturation, although some residual globular gel particles were observed suggesting a two-step formation of C-S-H in the Micromixing method. The dropwise precipitation showed the homogeneous formation of Nanofoils for our chemical system and concentrations. GEMS showed good correspondence for our system when the precipitation of portlandite was inhibited and hence can be useful for designing future experiments planned to investigate different C/S ratios.. Further chemical characterization is underway to help us to clearly identify the degree of homogeneity at different levels and further investigation of the kinetics of the growth of the high C/S ratios nanofoils is planned.

REFERENCES

1. Macphee, D. E., Luke, K., Glasser, F. P. & Lachowski, E. E. Solubility and Aging of Calcium Silicate Hydrates in Alkaline Solutions at 25°C. *J. Am. Ceram. Soc.* **72,** 646–654 (1989).
2. Escalante-Garcia, J. I., Mendoza, G. & Sharp, J. H. Indirect determination of the Ca/Si ratio of the C-S-H gel in Portland cements. *Cem. Concr. Res.* **29,** 1999–2003 (1999).
3. Chen, J. J. The Nanostructure of Calcium Silicate Hydrate. (Northwestern University, Evanston Illinois US, 2003).
4. Wu, J., Zhu, Y.-J. & Chen, F. Ultrathin Calcium Silicate Hydrate Nanosheets with Large Specific Surface Areas: Synthesis, Crystallization, Layered Self-Assembly and Applications as Excellent Adsorbents for Drug, Protein, and Metal Ions. *Small* **9,** 2911–2925 (2013).
5. Mehrali, M. *et al.* Facile synthesis of calcium silicate hydrate using sodium dodecyl sulfate as a surfactant assisted by ultrasonic irradiation. *Ultrason. Sonochem.* **21,** 735–742 (2014).
6. Beaudoin, J. J., Dramé, H., Raki, L. & Alizadeh, R. Formation and characterization of calcium silicate hydrate–hexadecyltrimethylammonium nanostructure. *J. Mater. Res.* **23,** 2804–2815 (2008).
7. Allen, A. J., Thomas, J. J. & Jennings, H. M. Composition and density of nanoscale calcium-silicate-hydrate in cement. *Nat Mater* **6,** 311–316 (2007).
8. Fung, B. M., Khitrin, A. K. & Ermolaev, K. An improved broadband decoupling sequence for liquid crystals and solids. *J. Magn. Reson. San Diego Calif 1997* **142,** 97–101 (2000).
9. Muller, A. C. A., Scrivener, K. L., Gajewicz, A. M. & McDonald, P. J. Densification of C–S–H Measured by 1H NMR Relaxometry. *J. Phys. Chem. C* **117,** 403–412 (2013).
10. Jennings, H. M. Aqueous Solubility Relationships for Two Types of Calcium Silicate Hydrate. *J. Am. Ceram. Soc.* **69,** 614–618 (1986).
11. Brown, P. W. The System Na2O-CaO-SiO2-H2O. *J. Am. Ceram. Soc.* **73,** 3457–3461 (1990).
12. Harris, A. ., Manning, M. ., Tearle, W. . & Tweed, C. . Testing of models of the dissolution of cements—leaching of synthetic CSH gels. *Cem. Concr. Res.* **32,** 731–746 (2002).
13. L'Hôpital, E. Aluminium and alkali uptake in calcium silicate hydrates (C-S-H). (Ecole Polytechnique Fédérale de Lausanne, 2014). at <http://infoscience.epfl.ch/record/203121>
14. Cong, X. & Kirkpatrick, R. J. 17O MAS NMR Investigation of the Structure of Calcium Silicate Hydrate Gel. *J. Am. Ceram. Soc.* **79,** 1585–1592 (1996).
15. Kirkpatrick, R. J., Yarger, J. L., McMillan, P. F., Ping, Y. & Cong, X. Raman spectroscopy of C-S-H, tobermorite, and jennite. *Adv. Cem. Based Mater.* **5,** 93–99 (1997).
16. Cong, X. & Kirkpatrick, R. J. 29Si MAS NMR study of the structure of calcium silicate hydrate. *Adv. Cem. Based Mater.* **3,** 144–156 (1996).
17. Scrivener, K. L. & Nonat, A. Hydration of cementitious materials, present and future. *Cem. Concr. Res.* **41,** 651–665 (2011).