Effect of Synthesis Parameters on Thermal Behaviour and Crystalline Structures of Calcium Silicate Minerals

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Abstract.

Calcium silicates are porous, large surface area ultra-light minerals, whose diversity comes from close Ca/Si ratios. Anhydrate calcium silicate (C-S) wollastonite and hydrate calcium silicates (C-S-H) xonotlite and tobermorite are common varieties. The structures whose economic production is limited are widely used as heat insulation and fire resistant especially in places that require special shaped passive fire protection (PFP) plate. In use as cement additive, in addition to its effects on the strength properties of concrete, it also creates serious effects especially on the hydration process. By using CaO as a calcium and silica fume as a silica sources, with different Ca/Si (0.83, 1.00) and water/solid (10, 15) ratios in synthesis suspensions, directly or after the 4 hour pre-reaction under different temperature (40 ^{o}C < T <80 ^{o}C) synthesis of calcium silicate structures were carried out at an autogenous pressure of 200 ^{o}C applying or non-applying filtration after the pre-reaction. The products obtained were dried at room temperature, in oven at 60 ^{o}C and -110 ^{o}C freeze-drying techniques. Higher mass loss was observed with synthesis at 80 ^{o}C pre-reaction temperature and tobermorite phase synthesis condition. The removal of structural water and –OH which took place above 250 oC was found more tobermorite phase synthesis feed ratio sample. Typical C-S-H crystal peaks were detected in X-ray diffraction patterns. The decomposition of calcium hydrosilicate crystals in 320-600 ^{o}C and phase transforms between 800-875 ^{o}C had been observed. The increase in success of xonotlite synthesis with pre-reaction temperatures was seen in X-ray diffraction peaks. The slight decreases in the descriptive peaks intensities were observed for samples synthesized at 40 and 80 ^{o}C pre-reaction temperatures and calcined at 300 ^{o}C, while even the most severe peak decreased significantly in samples calcined at 700 ^{o}C.

Keywords: xonotlite; tobermorite; thermal strength; mechanical strength; crystallinity

1. Introduction

While thermal insulation which is a necessity for building construction industry is generally covered by the petroleum derived plastic materials (EPS, XPS and polyurethane foam etc.), the fire insulation which is required by the industrial structures is provided either fibrous layered wool (glass wool, stone wool) or ceramic fiber type materials. Although plastic type thermal insulation materials have a low thermal conductivity, they have the disadvantage of being

dependent on oil and have disadvantages such as being flammable. Rockwool and similar inorganic materials with high fire resistance requires costly transport and construction operations due to their heavy weight. On the other hand light structures stand out as a cement additive. The importance of using light porous inert alternatives both as insulation and as cement additive material emerges [1, 2].

Calcium silicates (C-S) structures with high porosity, low density are used in heat insulation due to their light weight and high mechanical strength, while they are used as shaped materials for fire protection due to their high thermal resistance up to 1000 ^{o}C [3]. They are used in passive fire protection (PFP) as an additive material or specially shaped product to achieve the desired purpose [4]. In use as a cement additive, it creates positive effects on the hydration and hardening processes in addition to it affects the strength properties of concrete. In the hardening process of concrete, C-S-H forms a network with other compounds and contributes to hardening. In the cooling process, as the C-S-H and C-S formation increases, the strength of the concrete increases. As the result of the mineral admixtures are slow, the strength of the concrete containing pozzolonic material continues to last longer [5].

Calcium silicate minerals, whose diversity depends on close Ca/Si ratios, exist in anhydrate (C-S) and hydrate (C-S-H) forms. The most common forms are wollastonite (Ca/Si: 1.00) and tobermorite (Ca/Si: 0.83) group minerals [6]. The wollastonite group which has the anhydrate form wollastonite 1Å ($CaSiO_3$) and the hydrate form xonotlite ($Ca_6Si_6O_{17}(OH)_2$) are widely used in the industry. With different length/diameter ratios, wollastonite can replace the short fiber mineral filler and other synthetic crystals with its needle structure support [7]. Xonotlite which has lower specific gravity than wollastonite, has high surface area, thermal resistance, low specific gravity, low thermal conductivity properties.
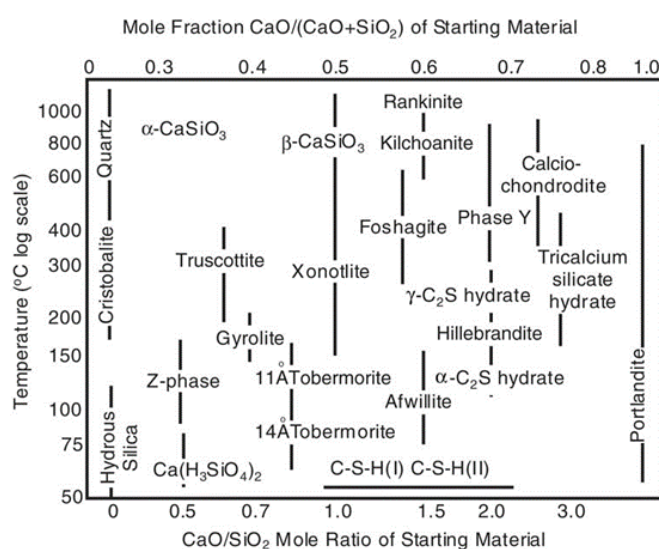

Figure 1. Variations of calcium silicate phases with feed ratio and synthesis temperature [8].

Synthetic C-S structures are preferred both their uniform structure and elimination of dangerous impurities. The final product diversity in calcium silicate synthesis is highly dependent on the molar ratios (Ca/Si) and temperature of the starting materials. In the graph

below, calcium silicate hydrate phases which may occur according to synthesis conditions are given in different CaO/SiO_2 and $CaO/CaO + SiO_2$ molar ratios from 50 ºC to 1000 ºC (Figure 1). Those with high potential for isolation are aqueous calcium silicate (C-S-H) xonotlite and tobermorite. Xonotlite can be synthesized at low temperature, so energy cost is low. It is preferred as an insulating material and especially in PFP board production [2].

2. Experimental

In the synthesis studies, CaO (Sciencelab, $\geq$ 99% CaO) and silica fume (Sigma, $\geq$ 99% SiO_2, 0.2-0.3μm) were used as calcium and silicon sources, respectively. The Ca/Si ratio in starting synthesis solution was kept either tobermorite (0.83) or xonotlite (1.00) feed conditions and water/solid (w/s) was changed as 10 and 15. The resulting suspensions were subjected to pre-reaction at different temperatures (40, 60 and 80 ºC) for 4 hours, after then the synthesis was completed at temperatures 200 °C in autoclave for 8 hours either applying or non-applying the vacuum filtration after pre-reaction. The synthesized products were dried at room temperature (15 days), 60 ºC oven (72 hours) or freeze-dryer (2 and 3 h at -110 ºC) and subsequently calcined at either 300 ºC or 700 ºC

Perkin Elmer Pyris 1 thermogravimetric analyzer was used to determine the thermal behavior in the air environment at a flow rate of 60 ml/min with a heating rate of 5 ºC/min within the range of room to 1000 ºC. X-ray diffraction patterns were taken for 2Ɵ values between Bragg angles of 5º and 60º using "CuKα" beam source with a wavelength of 0.15418 nm at a scanning speed of 1º/min using GNR APD 2000 PRO (40kV-30mA) device.

3. Results and Discussion

Thermal analysis was conducted to interpret the synthesis mechanism and determine the calcination temperature of calcium silicates according to the phase transitions. The TGA and DTA behaviors of the samples obtained under tobermorite and xonotlite feed conditions under pre-reaction conditions with a water/solid ratio of 15 at 60 and 80 ºC are given in Figures 2 and 3, respectively. The removal of moisture which was little for samples synthesized by tobermorite synthesis feed ratio, with a mass loss of about 6% up to 150 °C represents an endothermic reaction in the DTA curve in the range of 35-80 °C. The mass loss between 150-250 ºC which was caused by inter-layer water remained constant after a 1% mass loss up to 170 ºC under under tobermorite phase synthesis conditions, while this mass loss showed an endothermic peak range of 150-170 ºC in the DTA curve. After 150 ºC, higher mass loss was observed with synthesis at 80 ºC pre-reaction condition. The mass loss, which stand stationary up to 250 °C, became clear evident. Samples synthesized by 80 ºC and 60 ºC pre-reaction conditions exhibited similar mass loss behavior up to 180 ºC and 330 ºC, respectively. The mass loss after 250 ºC was due to the removal of the structural water and -OH, and the DTA curve gave an endothermic peak at 260 ºC. For tobermorite phase synthesis feed ratio, mass losses up to 300 ºC were higher than that of xonotlite due to the excess -OH and H_2O groups in the structure. Samples with pre-reacted synthesis conditions of 60 ºC showed less mass loss up to 350 ºC compared to the sample at the other temperature, after this temperature the mass loss became apparent. The peak range (250-300 ºC) exhibited the same thermal behavior under tobermorite and xonotlite synthesis conditions with the presence of endothermic reaction. After

400 ^{o}C, the mass loss of the samples synthesized at 60 ^{o}C pre-reaction temperature decreased again. It is known that CaOH dehydration occurs in the range of 420-540 ^{o}C. The mass loss observed in low preheated synthesis under tobermorite synthesis conditions can be interpreted as the presence of significant CaOH impurity in the structure. After 700 ^{o}C, the mass loss was reduced except for the samples in 80 ^{o}C pre-reactions. The exothermic reaction in the wide peak range between 800-850 ^{o}C represents the transition to wollastonite 1 Å phase [7, 9, 10]. Between 800-850 ^{o}C, exothermic peaks caused by water loss from structural hydroxyls. In this temperature range, the loss of mass remained approximately constant for the synthesis rate where the Ca/Si representing xonotlite was 1.00, while in tobermorite synthesis conditions it was observed that the loss of water was higher with a small difference as expected from the structural formula derived from bound H_2O or -OH.
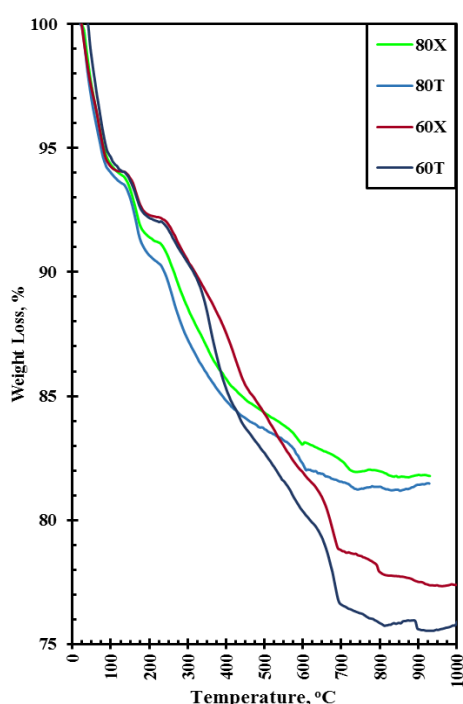

Figure 2. Termograms of calcium silicate samples synthesized at different pre-reaction temperatures under different feed ratios (w/s: 15; 80 and 60 ^{o}C denote pre-reaction temperatures; X and T denote conditions of xonotlite and tobermorite synthesis feed ratios, respectively)
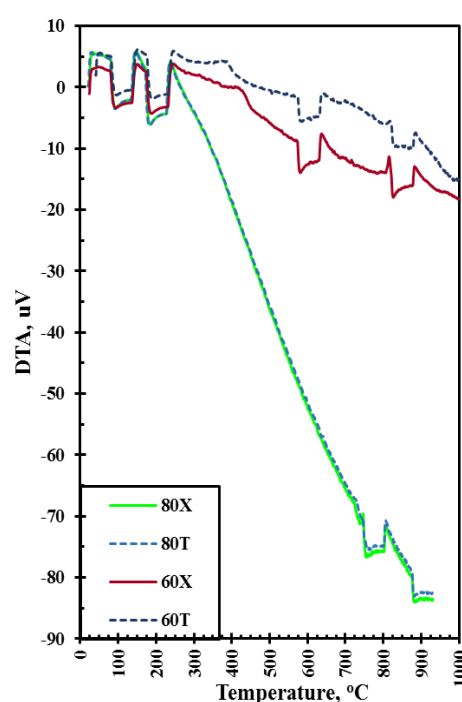
Figure 3. DTA curves of calcium silicate samples synthesized at different pre-reaction temperatures of under different feed ratios (w/s = 15; 80 and 60 oC denote pre-reaction temperatures; X and T denote conditions of xonotlite and tobermorite synthesis feed ratios, respectively)

The thermal behavior of the samples showed that the removal of moisture and inter-layer water up to 250 ^{o}C, after which the bound water and –OH removal started, and became apparent after 300 ^{o}C. It was seen that solid phase transformation occurs after 700 ^{o}C. In order to evaluate the effect of structure formation, synthesis and extensive characterization studies were carried out by selecting calcination temperature as 300 ^{o}C and 700 ^{o}C.

Typical C-S-H crystal peaks were detected in X-ray diffraction patterns (Figure 4 and 5). It has been reported in the literature that the typical peak of the C-S-H mineral obtained under different synthesis conditions yields the most severe peak (I/I$_o$: 100) at 20-35° [11-13]. The

ascending peak in 2Ө range of 30-32º represents the amorphous phase in the C-S-H structure [8, 14]. In this study, peak behavior in peak range of 2Ө: ~28-30º was observed in all XRD outputs with expanding peak in the same range. The success of xonotlite synthesis was observed to increase with an increase in pre-reaction temperature.

Figure 4. X-ray diffraction patterns of samples synthesized at different pre-reaction temperatures of under different feed ratios and different w/s ratios (80 and 60 ºC denote pre-reaction temperatures; X and T denote conditions of xonotlite and tobermorite synthesis feed ratios, respectively)
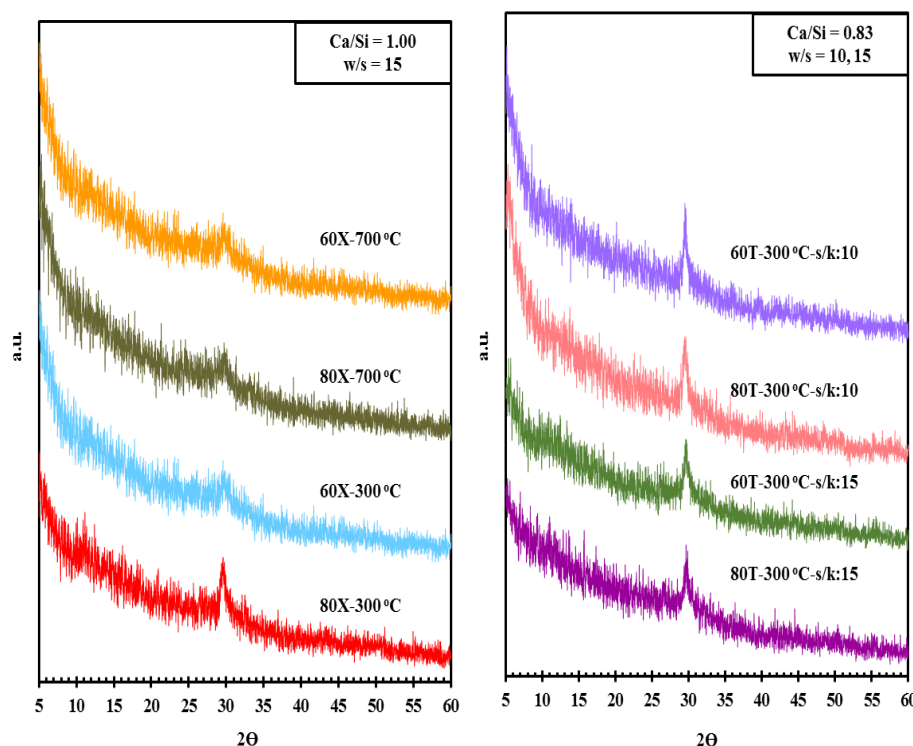
The highest peak (I/I_o: 100) defined in the literature for the tobermorite (Ca/Si: 0.83) phase is given as 2Ө: 6-10º [10, 15]. It is known that hkl planes exhibiting layered structure in crystal structures as seen SBA, MCM, clay are in 2Ө≤10 regions [16, 17]. Grangeon et al. (2013) described 2Ө: ~ 6º, 16º and 29.5º peaks as 002, 101 and 110 plane reflections, respectively [18]. The peak (2Ө: ~ 6) of (002) plane reflection observed in the study was evaluated as the reflection of the layered structure of tobermorite (Figure 4). In the study conducted for w/s: 15, I/I_o: 100 peaks were clearly observed around 2Ө: ~ 6º in all samples, while I/I_o: 65 and I/I_o: 45 peaks were occurred at 2Ө: ~ 25º and ~ 29.75 Bragg 's angles, respectively (Figure 5).

It was observed that the intensity of reflections of samples with Ca/Si: 0.83 decreased after calcination with 300 ºC. Although there was no big difference in calcined samples at 300 ºC, the peak intensities decreased as pre-reaction temperature increased for the calination temperature of 700 ºC. Due to the improvement in the crytalline properties with an increase of pre-reaction temperature, the syntheses were carried out at 60 and 80 ºC with the ratio of s/k: 10. According to X-ray diffraction patterns, peak intensities of s/k: 10 for tobermorite phase were found to be relatively high compared to syntheses with s/k: 15 (Figure 4).
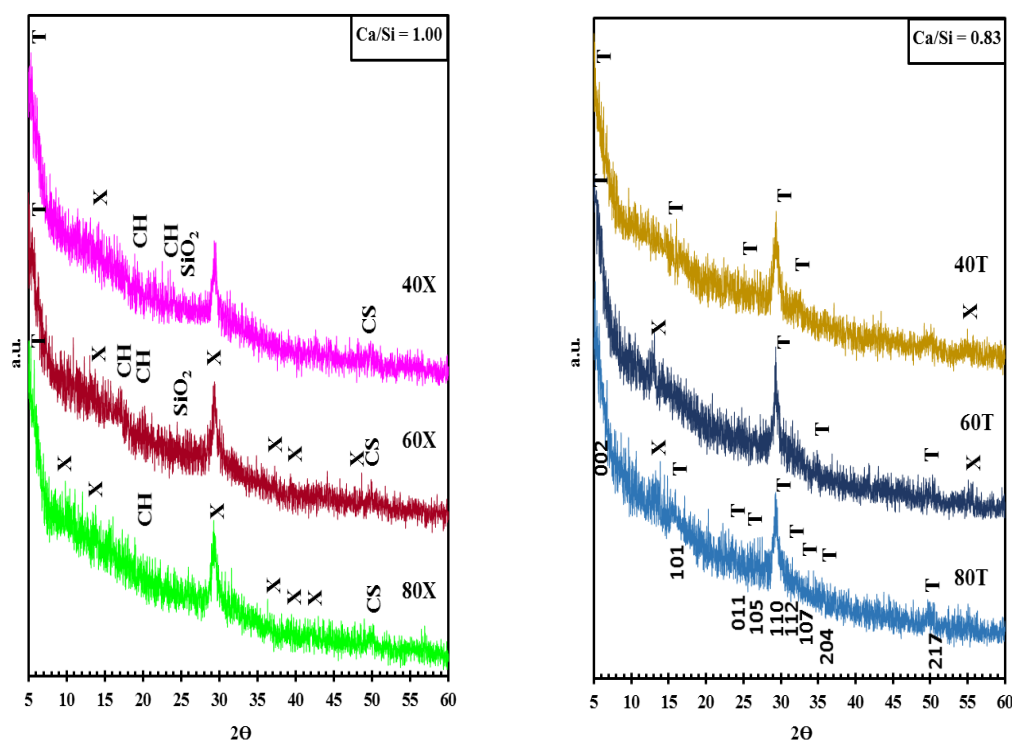
Figure 5. X-ray diffraction patterns of samples synthesized at different pre-reaction temperatures of under different feed ratios (w/s = 15; 80, 60 and 40 °C denote pre-reaction temperatures; X and T denote conditions of xonotlite and tobermorite synthesis feed ratios, respectively)

It has been reported in the literature that I/I_o: 100, 65 and 45 reflect planes of (002), (001), (110) [15, 18]. For the Ca/Si: 0.83 ratio, the (112) reflection (2Ө: ~ 31°) became slightly apparent. The peak I/I_o: 13 defined as plane reflection (107) was observed at an angle of 2Ө: 32°. In the sample synthesized with a ratio of Ca/Si: 0.83, the reflections of 6.31°, 29.5°, 16.1°, which are more pronounced, indicated the clarity of the tobermorite phase in the final product. In tobermolite synthesis conditions, peak density was found to be highest at 60 °C and relatively lower at 80 °C and 40 °C (Figure 5).

The most severe peak observed at 2Ө: 28.92° is defined as I/I_o: 100 peak for xonotlite synthesis condition (Ca/Si: 1.00) was lower than the one for tobermorite synthesis condition. Hsiang et al. (2015) reported that an increase in pre-reaction temperature increase mean chain length [19]. Unlike tobermorite, the highest peak at 80 °C was exhibited in accordance with the literature, while small decreases were observed regularly at 60 and 40 °C. For xonotlite I/I_o: 50 peaks are given at 31.61° and I/I_o: 40 peaks are given at 33.19°. In the synthesis studies carried out in the literature, it is seen that peaks are exhibited at this angle and its vicinity. In the present study, the first peak was observed with a low intensity at 40 °C and 80 °C at an angle of 2°: ~ 32° and for a pre-reaction temperature of 60 °C it was not observed.

It was observed that peak intensities were decreased slightly in samples which were synthesized at 40 and 80 °C pre-reaction temperatures and calcined at 300 °C, while even the most severe peak decreased significantly in samples calcined at 700 °C. The peak intensities of the samples synthesized under Ca/Si: 0.83, that is tobermorite synthesis conditions, have

been proved to be higher than the peak intensities of samples synthesized under xonotlite synthesis conditions of Ca/Si: 1.00. In comparison with the I/I_o: 100 peaks, xonotlite has been found to pass into a more fragile calcium silicate structure, 11Å tobermorite, with a decrease in Ca/Si ratio. In this case, it can be interpreted that the silicon content in the structure is high. The decrease in Ca/Si ratio did not cause a significant difference in 2Ѳ value of sharp peak. In other words, the increase in the pre-reaction temperature led to a small increase in the peak intensity of xonotlite raw material and to a small decrease in tobermorite. The presence of xonotlite and tobermorite reflections in the structure at both ratios can be interpreted as the presence of xonotlite-tobermorite mixture in all samples. The sharp reflection of [002] plane reflection found around 2Ѳ: ~6º representing tobermorite, also observed in conditions of Ca/Si: 1.00 at 40 and 60 ºC pre-reaction temperature represents tobermorite impurity in xonotlite phase. It is known that silicon materials in the literature are exhibited in the range of 2Ѳ: 20-30º in the studies of silicon materials (Figure 4).

4. Conclusions

In this study, calcium silicates (C-S) which can be used as additives, fillers or specially shaped products in thermal insulation due to their mechanical and microstructural properties were investigated. The synthesis of tobermorite (Ca/Si: 0.83) and xonolite (Ca/Si: 1.00) C-S-H minerals was carried out successfully. Phase transformations at 300 ºC and 700 ºC were determined by thermal TGA/DTA curves. It was determined that mass loss up to 600 ºC in TGA outputs was caused by both -OH removal and CaOH degradation which may occur in the structure detected in XRD patterns. In XRD graphs, I/I_o: 100 peak of C-S-H minerals was observed in all samples, while other plane reflections were not very clear. Compared to the I/I_o: 100 peaks, it was found that xonotlit was passed to 11Å tobermorite structure which is a more fragile calcium silicate structure with the decrease of Ca/Si ratio. It has been proved that the peak intensities of the samples synthesized under tobermorite synthesis conditions are higher than the peak intensities of samples synthesized under xonotlite synthesis conditions.

References

[1] Picker, A., Nicoleau, L., Nonat, A., Labbez, C., and Cölfen, H. (2014). *Identification of binding peptides on calcium silicate hydrate: A novel view on cement additives.* Advanced Materials, 26(7), pp. 1135-1140.

[2] Hall, M. R. (2010). *Materials for Energy Efficiency and Thermal Comfort in Buildings Germany:* Woodhead Publishing, pp. 193-228.

[3] Ingham, J. P. (2012). *Geomaterials under the microscope London:* Academic Press, pp. 121-127.

[4] Carabba, L., Emrys Scarponi, G., Tugnoli, A., Chiara Bignozzi, M., and Moricone, R. (2018). *Investigation of lightweight geopolymer mortars as fireproofing coatings*.

[5] Erdoğdu, Ş. and Kurbetçi, Ş. *Betonun performansına sağladıkları etkinlik açısından kimyasal ve mineral katkı maddeleri.*

[6] Richardson, I. G. (2008). *The calcium silicate hydrates. Cement and concrete research*, 38(2), pp. 137-158.

[7] Wu, H., Yang, J., Ma, H., and Wang, M. (2013). *Preparation of acicular wollastonite using hydrothermal and calcining methods.* Integrated Ferroelectrics, 146(1), pp. 144-153.

[8] Meller, N., Hall, C., and Phipps, J. S. (2005). *A new phase diagram for the CaOAl2O3SiO2H2O hydroceramic system at 200° C.* Materials Research Bulletin, 40(5), pp. 715-723.

[9] Gordienko, P. S., Mikhailov, M. M., Banerjee, S., Sharma, Y. C., Yarusova, S. B., Zhevtun, I., Vlasov, V., Shabalin, I., and Sushkov, Y. V. (2017). *Effect of annealing conditions on the structure, phase and granulometry composition, and reflectance spectra and their changes on irradiation for calcium silicate powders.* Materials Chemistry and Physics, 197, pp. 266-271.

[10] Galvánková, L., Másilko, J., Solný, T., and Štěpánková, E. (2016). T*obermorite synthesis under hydrothermal conditions. Procedia Engineering,* 151, pp. 100-107.

[11] Singh, S. P. and Karmakar, B. (2011). Mechanochemical synthesis of nano calcium silicate particles at room temperature. New journal of glass and ceramics, 1(2), pp. 49-52.

[12] Diamond, S., Dolch, W., and White, J. L. (1964). *Studies on tobermorite-like calcium silicate hydrates.* Highway Research Record, pp. 62

[13] Kapeluszna, E., Kotwica, Ł., Różycka, A., and Gołek, Ł. (2017). *Incorporation of Al in CASH gels with various Ca/Si and Al/Si ratio: Microstructural and structural characteristics with DTA/TG, XRD, FTIR and TEM analysis.* Construction and Building Materials, 155(643-653.

[14] Sasaki, K., Masuda, T., Ishida, H., and Mitsuda, T. (1996). S*tructural degradation of tobermorite during vibratory milling.* Journal of the American Ceramic Society, 79(6), pp. 1569-1574.

[15] İnternet: Tobermorite Mineral Data http://webmineral.com/data/Tobermorite.shtml#.XS0N_Oszapo, Access date: 16.07.2019

[16] Zhao, D., Huo, Q., Feng, J., Chmelka, B. F., and Stucky, G. D. (1998). *Nonionic triblock and star diblock copolymer and oligomeric surfactant syntheses of highly ordered, hydrothermally stable, mesoporous silica structures.* Journal of the American Chemical Society, 120(24), pp. 6024-6036.

[17] Øye, G., Sjöblom, J., and Stöcker, M. (2001). *Synthesis, characterization and potential applications of new materials in the mesoporous range.* Advances in Colloid and Interface Science, 89, pp.439-466.

[18] Grangeon, S., Claret, F., Lerouge, C., Warmont, F., Sato, T., Anraku, S., Numako, C., Linard, Y., and Lanson, B. (2013). *On the nature of structural disorder in calcium silicate hydrates with a calcium/silicon ratio similar to tobermorite.* Cement and Concrete Research, 52, pp. 31-37.

[19] Hsiang, H.-I., Chen, W.-S., and Huang, W.-C. (2016). *Pre-reaction temperature effect on C–S–H colloidal properties and xonotlite formation via steam assisted crystallization.* Materials and Structures, 49(3), pp. 905-915.