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The influence of starting materials' solubility on tobermorite structure formation under the hydrothermal conditions

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Abstract. Overall, the tobermorite mineral crystallises under the hydrothermal conditions from the CaO-SiO₂-H₂O system. The system of calcium hydrosilicates species is extremely complex and many factors play an important role. The solubility of starting materials belongs to one of the most important factors. Dissolution rates of SiO₂ source are significantly affected by their particle size distribution. Also the starting cation's concentration in the aqueous solution affects the yield of the hydrothermal reaction. The main aim of this contribution is to study the influence of water-to-solid ratio on tobermorite crystallization. The effect of particle size of various sources of SiO₂ was also studied. The cost effective Ca and Si sources was primarily favoured. The C/S ratio of the experiments was set to 0.83. All syntheses were performed at 180 °C in laboratory steel autoclaves. The prepared powdered samples were characterized in order to determine the phase composition by using of X-Ray diffractometry. The thermal behaviour of prepared samples was studied by TG-DTA analyser. Morphology and particle size of synthesized powdered products was studied by scanning electron microscopy.

1. Introduction

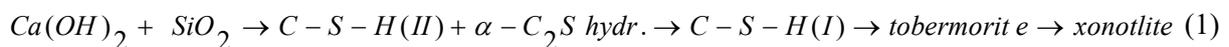
Tobermorite, a mineral belonging to a group of calcium silicate hydrates (C-S-H), is very rare in nature but plays an important role in several technical applications in building chemistry, mainly in hydration processes of Portland cement and production of autoclaved aerated concrete.

Tobermorite was firstly described by Heddle in 1880 [1]. The natural samples were found in three different localities near towns Tobermory and Dunvegan in Scotland. Generally the mineral could be formed in places with possible hydrothermal activity (i.e. in cavities in alkaline rocks, where was formed by hydrothermal alteration or in places where the hydrothermal fluids react with calcium silicate minerals) [2]. Till now, three main different phases of crystal structure have been described. The type of the structure is associated with the different degree of hydration, 9 Å tobermorite also called riversideite (Ca₅Si₆O₁₆(OH)₂), 11 Å tobermorite (Ca₅Si₆O₁₇·5H₂O) and 14 Å tobermorite also called plombierite (Ca₅Si₆O₁₆(OH)₂·7H₂O). The denomination of phases is related to characteristic d₀₀₂ values in the powder diffraction pattern, 9.3 Å, 11.3 Å and 14.0 Å from the least to the most hydrated form [3]. The most important phase is 11 Å tobermorite which crystallizes in orthorhombic or monoclinic form. The monoclinic form was found by Henmi and Kusachi [4] and was named clinotobermorite. The crystal structure of natural 11 Å tobermorite structure was firstly described by Megaw and Kelsey [5] and then by Hamid [6]. However, the detailed description of the real structure of both orthorhombic and monoclinic form was solved by Merlino et al. [7, 8] using order-disorder theory. The basic structure is build up by central CaO-octahedra layer attached from both sides with infinite silicate double chains composed of condensed dreierketten units along the *b* axis. Each



dreierketten unit consists of two paired tetrahedra pointing towards to Ca-layer and one bridging tetrahedron oriented to the interlayer. The composite layers consist of one calcium layer and two silicate layers bounded together by the interlayer containing mainly calcium ions and water molecules. Depending on the dehydration behaviour, the two types of 11 Å tobermorite, normal and anomalous type, can be distinguished. During the dehydration process the normal 11 Å form loses its interlayer water and transforms to a 9 Å tobermorite, while the anomalous one is affected by the dehydration process, but the formed crystalline structure is not 9 Å tobermorite [9]. At the temperatures above 800°C, both types recrystallize to new phase called wollastonite (CaSiO₃) [2].

The hydrothermal synthesis of tobermorite in various laboratory conditions has been extensively studied [10-14]. Generally, Ca(OH)₂ and SiO₂ react to form C-S-H phases under hydrothermal conditions. At the beginning of the reaction, the solution is saturated with lime so the Ca-rich phases like C-S-H (II) (C/S ratio around 1.5) and α-C₂S hydrate are formed. Whereas the temperature in the system start increases, the solubility of CaO decrease and the increase of SiO₂ solubility occur simultaneously. The next step of the hydrothermal reaction is the reduction of the C/S ratio to 1.25 and the creation of C-S-H (I) phase. In the final stage of the reaction, the C/S ratio drops to the optimal value for tobermorite formation (i.e. between 0.8-1) and the C-S-H (I) phase recrystallize to 11 Å tobermorite [15]. The whole reaction is schematically shown in equation (1). The course of the reaction is affected by many factors. The reaction temperature and pressure are one of the most important factors, temperatures between 120°C and 200°C and saturated steam pressure has been reported as the optimal. The reaction temperature and the reaction time are strongly depended on the particle size of SiO₂ [13, 15]. Generally, with higher temperature and longer reaction time the recrystallization of tobermorite to other calcium silicate hydrate, xonotlite (Ca₆Si₆O₁₇(OH)₂), is favoured. Besides mentioned factors, the amount of added water to reaction system plays also an important role in the final yield of the hydrothermal reaction [16].



The formation of tobermorite under the hydrothermal conditions is beside shown the strong dependence on the reaction temperature, time and especially on the solubility of SiO₂ source. Therefore, the main aim of the present work was to study the influence of SiO₂ particle size distribution together with the starting concentration in the aqueous solution. The influence of reaction time was also examined.

2. Experimental

2.1. Materials and synthesis

For the synthesis of a mineral tobermorite under the hydrothermal conditions, two types of silica sources, silica sand Dorsilit and specially crushed quartz sand, were chosen as starting materials. The average particle size (d₅₀) of silica sources is 5.29 μm for silica sand Dorsilit and 20.24 μm for specially crushed quartz sand. As the source of calcium oxide, the grounded CaCO₃ calcinated at 1000°C for 1 hour was used. The amount of CaO in calcinated limestone was determined to be higher than 97%. All the starting mixtures were mixed using the same C/S ratio equal to 0.83. The method of synthesis used in this study was inspired by Diamond et al. [17]. Required quantity of CaO was mixed with freshly-boiled distilled water (to suppress the undesirable carbonization) and stirred for 3 minutes. Then the calculated amount of SiO₂ was added to the mixture and was mixed for 5 more minutes. Used water-to-solid (w/s) ratio was set in a range from 1.5 to 15 ml/g. Hydrothermal reactions were carried out in a Teflon-lined laboratory autoclave placed in a conventional dryer. Prepared slurries were hydrothermally treated at 180°C and autogenous pressure for 1 and 5 days. Synthesized products were dried at 50°C for 12 hours.

2.2. Characterization of synthesized products

The phase composition of synthesized products was determined by X-ray diffraction analysis (XRD). Data were collected by X-ray diffractometer Empyrean (Pananalytical) using Cu K α radiation. For selected samples, a thermogravimetric and differential thermal analysis was performed using TG-DTA instrument Q 600 (TA Instruments). Analyses was run in Pt crucibles and were heated with the rate of 10°C/min from 20°C to 1000°C under the Ar atmosphere. The morphology of these chosen samples was observed by scanning electron microscopy (SEM) using microscope ZEISS EVO LS 10.

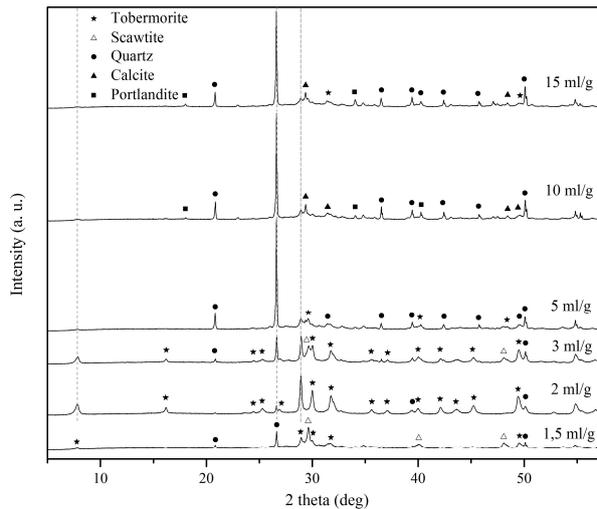


Figure 1. XRD patterns of samples synthesised for 1 day using specially crushed quartz sand and different w/s ratios (1.5–15 ml/g).

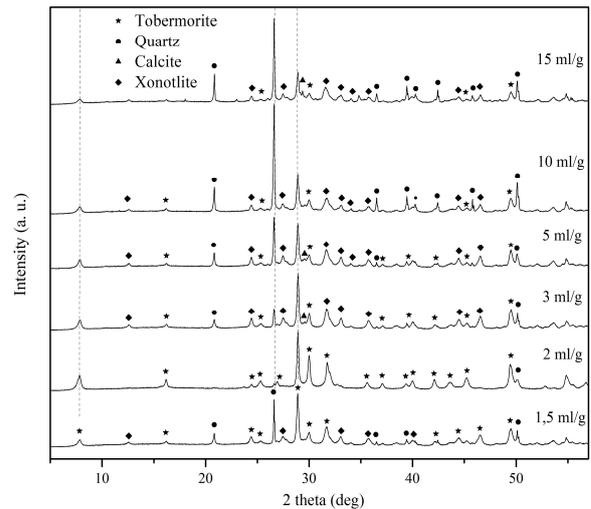


Figure 2. XRD patterns of samples synthesised for 5 days using specially crushed quartz sand and different w/s ratios (1.5–15 ml/g).

3. Results

3.1. Synthesis of tobermorite using specially crushed quartz sand

The solubility of silica source is affected by the amount of added water to the reaction system. For the examination of the influence of w/s ratio on tobermorite formation, six samples with different w/s ratio were used (1.5, 2, 3, 5, 10 and 15 ml/g). Figure 1 shows the XRD patterns of samples prepared from the mixture of specially crushed sand and calcinated CaCO₃ hydrothermally treated for 1 day. It is obvious that after a one day of hydrothermal reaction the different w/s ratio strongly affects the phase composition of prepared samples. With the increasing amount of water in the system the amount of prepared tobermorite strongly decrease. The XRD results show the presence of crystalline tobermorite only in samples prepared with w/s ratio between 1.5–3 ml/g. The highest yield of tobermorite formation after 1 day of hydrothermal treatment was observed with the use of w/s ratio of 2 ml/g. In samples with higher w/s ratio, the starting materials are the only detected. If the reaction time is prolonged from one to five days, the amount of tobermorite in samples is increased. The highest amount of tobermorite is still found in the sample prepared with w/s ratio of 2 ml/g. In some samples, part of crystalline tobermorite was transformed into xonotlite. The unreacted SiO₂ is still the main phase even after five days of the treatment. Except the unreacted starting materials, the CO₂ bearing compounds like calcite and scawtite (Ca₇(Si₆O₁₈)(CO₃)·2H₂O) were presented in some samples. The contamination is caused by the reaction of wet samples with air containing CO₂ during the preparing process and mainly during the drying of prepared products [18].

The influence of reaction time on morphology of formed tobermorite particles was observed on samples with the highest amount of tobermorite determined from XRD analysis. Therefore,

the samples prepared with the used w/s ratio 2 ml/g were analysed by SEM and the images are given in Figure 3 and Figure 4. It could be seen, that the SiO_2 particles from the starting material are covered with tobermorite platelet-like crystals. The crystals in sample hydrothermally treated for 1 day are longer and could be better distinguished than the crystals in sample that was autoclaved for 5 days. The higher degree of agglomeration of platelet tobermorite particles could be here also observed. The various length of the hydrothermal reaction showed the differences in the morphology of prepared tobermorite crystals. No other significant phases could be detected from the SEM images.

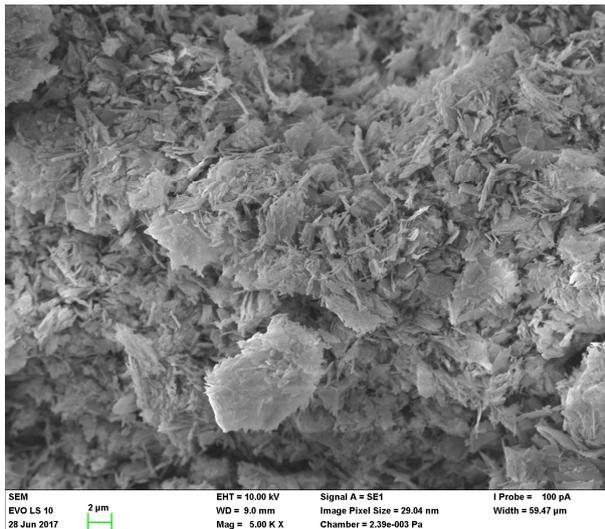


Figure 3. SEM images of samples synthesised for 1 day using specially crushed quartz sand and w/s ratio 2 ml/g.

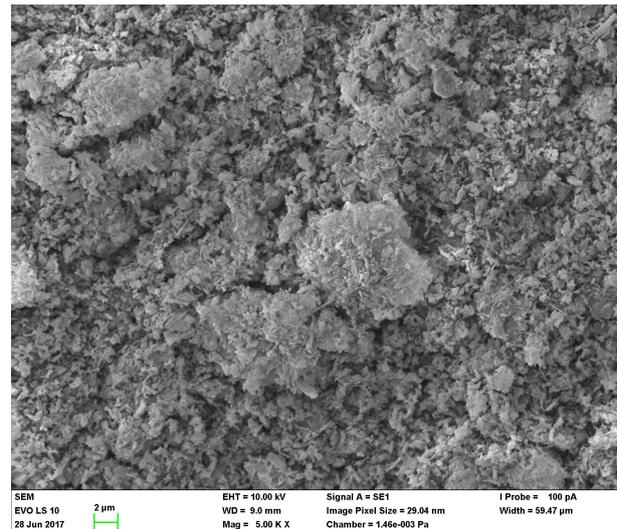


Figure 4. SEM images of samples synthesised for 5 days using specially crushed quartz sand and w/s ratio 2 ml/g.

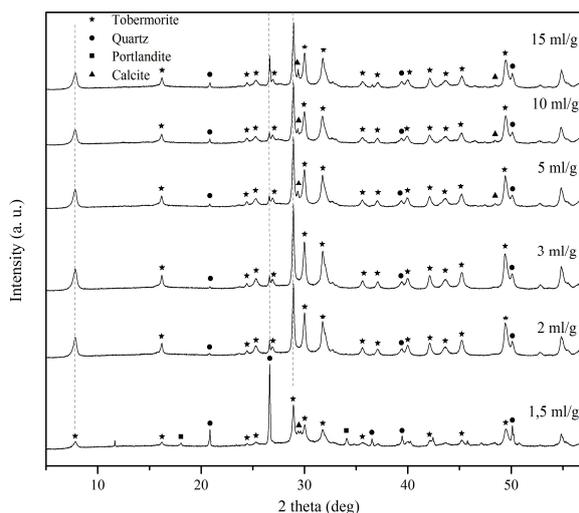


Figure 5. XRD patterns of samples synthesised for 1 day using silica sand Dorsilit and different w/s ratios (1.5–15 ml/g).

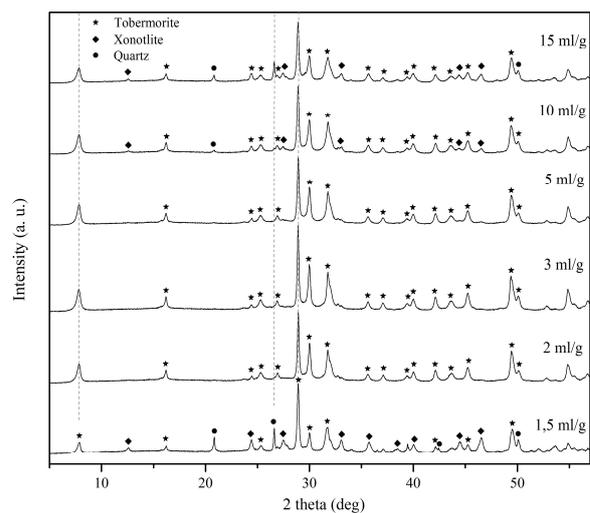


Figure 6. XRD patterns of samples synthesised for 5 days using silica sand Dorsilit and different w/s ratios (1.5–15 ml/g).

3.2. Synthesis of tobermorite using silica sand Dorsilit

Results of the XRD analysis on samples prepared using silica sand Dorsilit are shown in Figure 5 and Figure 6. After one day of hydrothermal reaction, tobermorite is present in all samples. The influence of w/s ratio is consistent with the trend observed in the samples prepared using specially crushed silica sand. It was also determined that with the increasing w/s ratio the amount of prepared tobermorite phase decreased. None of the prepared samples is phase pure and the presence of the starting materials is determined. Prolonging the reaction time from one to five days allowed the reaction to proceed, so the amount of tobermorite phase is higher in all samples independently of the w/s ratio. The only detected crystalline phase, in samples with w/s ratio from 2 to 5 ml/g, was tobermorite. Conversion to xonotlite appears only in samples with higher w/s ratio, but the amount of crystallized xonotlite is almost negligible. No CO₂ bearing phases were detected after five days of hydrothermal reaction.

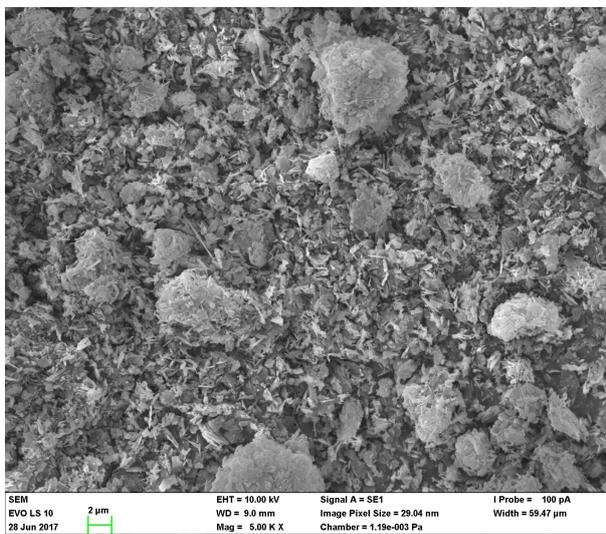


Figure 7. SEM images of samples synthesised for 1 day using silica sand Dorsilit and w/s ratio 3 ml/g.

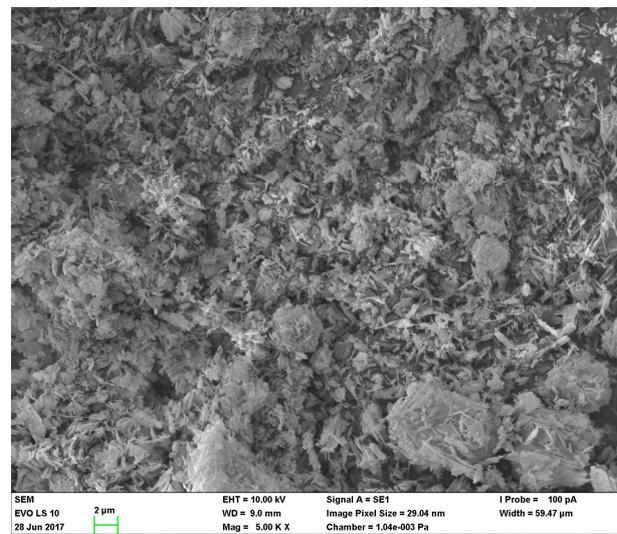


Figure 8. SEM images of samples synthesised for 5 days using silica sand Dorsilit and w/s ratio 3 ml/g.

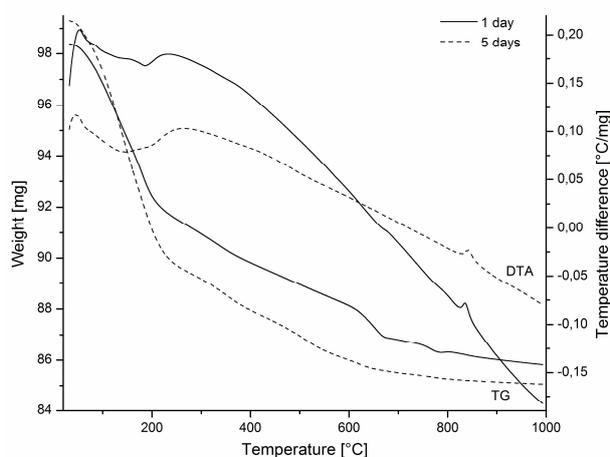


Figure 9. TG-DTA curves of samples synthesised for 1 and 5 days using specially crushed quartz sand and w/s ratio 2 ml/g.

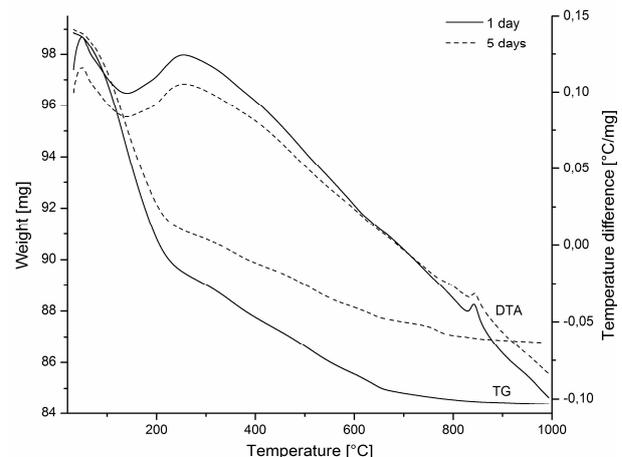


Figure 10. TG-DTA curves of samples synthesised for 1 and 5 days using silica sand Dorsilit and w/s ratio 3 ml/g.

The morphology of prepared tobermorite using silica sand Dorsilit as a starting source of SiO_2 were studied on the samples with the w/s ratio 3 ml/g. It was found that the prepared tobermorite phases crystallized in the platelet form particles independently of the reaction time (Figure 7 and 8). Observed morphology is almost the same as in case of the synthesis with specially milled quartz sand after five days of hydrothermal reaction.

3.3. TG-DTA analysis

For confirmation of the results from XRD analysis, TG-DTA measurements on samples with the highest yield of tobermorite (detected by XRD) were performed. The influence of particle size on thermal processes was also studied. The main weight loss on a TG curve occurs between 50°C and 250°C . The weight decrease is accompanied by the broad endothermic hump on a DTA curve presumably resulting from the loss of the loosely bound molecular water from tobermorite structure. The weight decrease is comparable in all four samples. In samples prepared using specially crushed silica sand, it is obvious that the amount of tobermorite increases with prolonged reaction time (Figure 9). This confirms the XRD analysis, whilst the results for the samples prepared using silica sand Dorsilit is opposite (Figure 10). The amount of tobermorite phase is lower in sample hydrothermally treated for 5 days. This difference could be caused by the additional carbonation of tobermorite during the sample storage. Between 250°C and 800°C , any remaining molecular water from tobermorite is lost. At about 850°C a sharp exothermic peak is detected indicating the recrystallization of tobermorite into wollastonite. Besides the changes connected with the presence of tobermorite, the presence of calcite is detected by the weight loss between 600°C and 650°C , where the decomposition of calcite takes place. Mentioned weight loss is most obvious in the sample prepared using specially crushed silica sand synthesised for one day.

4. Discussion

The formation of tobermorite in hydrothermal conditions is strongly affected by the average particle size of the used source of SiO_2 . Two sources differing in particle size were used to prove this fact. The experiments reveal that if the particle size is smaller the formation of tobermorite is easier and the yield of the reaction is higher. This result corresponds with previously reported studies [16, 19–21]. The rate of dissolution of quartz particles corresponds to particle size and it is time dependent, the finer particles have quicker dissolution, whilst the coarser one has the slower. So, the overall reaction is accelerated due to an increase in reactivity depending on particle size. According to the literature [21], when the SiO_2 source with the particle size higher than $10\ \mu\text{m}$ is used as a starting material, synthesized tobermorite decomposes to xonotlite. The result in this work is basically in good agreement with those found in the literature. Kikuma et al. [16] had proposed an explanation of this phenomenon. During the hydrothermal reaction non-crystalline C–S–H is formed as an intermediate phase before the crystalline calcium silicate hydrates occur. When the less soluble SiO_2 source is used, the C/S ratio in the non-crystalline C–S–H is higher and the reaction equation (1) proceeds towards xonotlite instead of tobermorite.

Another not negligible factor for all hydrothermal synthesis, including the formation of tobermorite, is the water-to-solid ratio. The obtained results indicate that the amount of prepared tobermorite significantly decreases with the increasing value of w/s ratio. The calcium and silicate ions concentration in the reaction solution probably plays an important role in tobermorite formation. These results tie well with previous study published by Kikuma et al. [16]. They have done an examination on the samples prepared from fine quartz with particle size $2\ \mu\text{m}$ and quicklime. The used w/s ratio was 1.7, 3, 6 and 9 ml/g and the measurements were done by in-situ time-resolved XRD. Based on the obtained results they suggested that the silicate ion concentration is differing according to the w/s ratio. They showed that the lower silicate ion concentration in the solution phase is important for the tobermorite formation under the hydrothermal conditions.

The influence of the particle size of SiO_2 source and reaction time on the morphology of prepared tobermorite was also observed. Tobermorite crystallises into the platelet-like crystals. The size of

formed crystals decreases with the increasing reaction time and they have a tendency to form aggregates after five days of hydrothermal reaction. The reaction of the coarser SiO₂ particles is slower so the aggregates are created after a longer reaction time. The formation of platelets crystals of tobermorite through the heterogeneous nucleation was also described by Bell and Adair [22].

5. Conclusions

Hydrothermal formation of mineral tobermorite in system CaO–SiO₂–H₂O was studied. Two important factors were mainly examined – the average particle size of SiO₂ source and the water-to-solid ratio. Based on experiments conducted at 180°C and an autogenous pressure with two different particle size of SiO₂ source, it can be shown that the SiO₂ source containing smaller particles accelerating the reaction. These could be attributed to a better solubility of finer quartz particles in a hydrothermal system. The formation of tobermorite is also significantly influenced by the changes in w/s ratio. The increase in the w/s ratio probably influences the calcium and silicate ions concentration in a solution, which plays an important role in a process of tobermorite formation. The ideal w/s ratio was almost independent of the used SiO₂ sources and lies in a range of 2 to 3 ml/g. Using the optimal w/s ratio and the prolonged reaction time from one to five days resulted in a preparation of samples containing phase pure tobermorite. In samples prepared with higher w/s ratio and longer reaction times the unfavourable formation of xonotlite occurs. This trend was more like observed in samples prepared from coarser SiO₂ source, which is probably caused by the higher C/S ratio in a system thanks to its lower solubility.

Acknowledgements

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