

Synthesis of Tobermorite Structure with Non-traditional Silica Components

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Abstract—The main aim of the article is research of kinetics of creation of calcium silicate hydrate (CSH) and calcium aluminate hydrate (CAH) phases in the autoclaved aerated concrete in dependence on type of raw materials. Regarding materials, this will be unique combinations of lime with fly ash, quartz sand or silica fume. The aim will be to prove the influence of ratio of individual types of materials on the CSH phase to determine optimal combinations of raw materials. The research focuses first on detailed analysis of the used materials. Next focus is kinetics of the creation of microstructures of silicate phases under ideal conditions of small-sized autoclave reactors (250 ml, 190 °C, 1.3 MPa). The produced samples are further analysed using of x-ray diffraction (XRD) and scanning electron microscopy (SEM) for qualitative valuation of created microcrystalline phases. The results show that the most suitable non-traditional silica component is ash from coal combustion. The optimal combination of amorphous and crystalline silicon in combination with Al₂O₃ provided the highest proportion of synthesized tobermorite even in more economical autoclaving variants.

Keywords— autoclaved aerated concrete; tobermorite; calcium sulfate; fly ash; silica fume.

I. INTRODUCTION

The needs of the end user should be always considered in order to sustain the development of civil engineering production. Today's trend is to look at the price of a product first and only subsequently value its quality. It is therefore critical to find the ways to maintain the low price level of the product without compromising its technical properties. One of the ways to achieve this result is to use low-cost materials that are in general by-products of industrial production or waste products. Among such materials are, for example, ashes from coal burning that takes place at high-temperature or through the fluid method. The production of autoclaved aerated concrete (AAC) is one of the many civil engineering fields where these by-product materials can be used.

AAC is a lightweight construction material with excellent thermal and technical properties in relation to its strength, is excellently workable and economically feasible. It is a material with long tradition, beginning in 1924, yet its potential can still be used today. Pure materials, meaning lime and quartz sand, were used since the beginning of production. The current trend is to find way to replace these more expensive materials with cheaper alternatives. It must be mentioned that ash from the high-temperature coal burning (fly ash) is also regularly used in AAC production. Nowadays the production of this ash is being limited, increasing the demand and, as a result, increasing its price. To the contrary, the production of fluidized bed

combustion ashes, which are the by-products of burning coal in heat-production plants and power plants, is increasing. These products have lower usability but they are suitable in terms of price and CaO content.

One of the most important mechanical properties of each material is strength. In case of AAC, the carrier of strength is the mineral tobermorite. This mineral forms through the reaction of silica oxides and calcium in hydrothermal conditions. It belongs to the group of calcium hydrosilicates, with the chemical formula Ca₅Si₆O₁₆(OH)₂·4H₂O. This paper further covers the selection of materials suitable for AAC design. The selection process emphasizes the use of economically more suitable silica materials, particularly coal burning ashes. Upon sustaining these conditions, it is possible to increase competitiveness at the market as well as profits.

A. Tobermorite Formation

The molar ratio of CaO/SiO₂ and the temperature of the hydrothermal processes are the key elements for the formation of tobermorite. Some initial phases may already occur due to atmospheric conditions, such as CSH, as well as by the hydration of cement. These are phases similar to tobermorite in terms of their structure, however, their crystalline grid is not as perfectly developed. Tobermorite is formed at a certain temperature inside the autoclave and a specific molar ratio of components. However, tobermorite is only a transitional phase, because

it further crystallizes into xonotlite, which is undesirable due to its lower strength. It is therefore important to set the autoclave timing in a way that maximizes the amount of tobermorite and minimizes the formation of xonotlite. Fig.1 shows the formation areas of the calcium hydrosilicates depending on temperature and molar ratio [1].

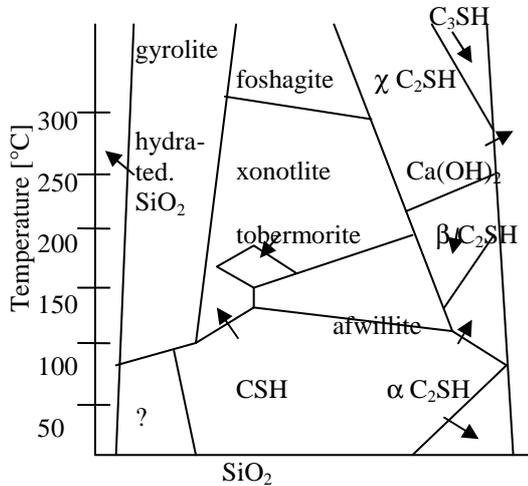
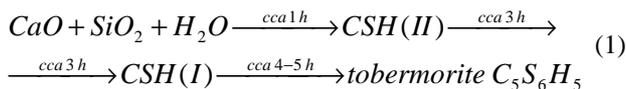


Fig. 1. Phase diagram CaO – SiO₂ – H₂O according to Bessey [1]

As it is apparent from the phase diagram, the mineral gyrolite might form in the case of C/S ratios lower than 0.5. Further, there is the desired mineral tobermorite with the ratio of 0.8–1.0. Afwillite may form in the case of ratios exceeding 1.5. Hydrogarnets may also form within the system CaO – SiO₂ – Al₂O₃ – H₂O. The content of Al₂O₃ in the CaO – SiO₂ – the H₂O system is critical to the formation of tobermorite. In the case of absence of Al₂O₃, tobermorite is formed from CSH gel, according to the equation 1:



However, when Al₂O₃ is present, tobermorite forms within the CaO – SiO₂ – Al₂O₃ – H₂O in two ways. (1) Tobermorite formation from the CSH phase: CSH → tobermorite, (2) Tobermorite formation from katoite: SiO₂, katoite, hydrogarnet, CSH → Si₄⁺, Ca₂⁺, Al₃⁺, OH⁻. The first phase is a transformation within the solid state. The second is a transformation from a solid matter → solution, where tobermorite crystallizes from a solution. These processes take place at the same time [2].

B. The Effect Of Silica Materials

The first of the four crucial aspects affecting the formation of tobermorite is the character of the initial silica material. The main characteristics are their mineralogical character, amorphous or crystalline form of the material and specific surface area. The character of the

silica material primarily affects the properties of the formed CSH gels (Fig. 2).

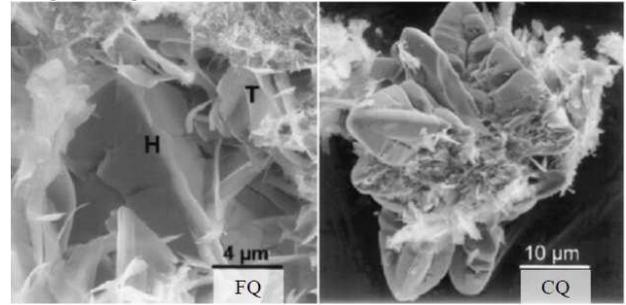


Fig. 2. Microscopic image of hydrographic decomposition by using fine FQ and coarse silicate CQ (H - hydrogarnet, T - tobermorite) [3]

When using crystalline quartz, in the form of ground quartz sand, the gels form in the molecular C/S ratio ≈ 1.69, meaning they are calcium-rich. Shorter chains characterize these gels. On the contrary, when using amorphous quartz, the forming gels with a C/S ≈ 0.81 ratio are silicon-rich and have long chains that less easily crystallize [4]. The result is a different rate of dissolving the silica material and therefore saturating the solution with these ions. Amorphous materials are more natural to dissolve, they saturate the solution with Si₄⁺ ions to a more considerable extent, and the CSH phases contain more of them. On the other hand, crystalline materials dissolve more slowly, a more considerable amount of the Ca₂⁺ ions are used for the formation of CSH phases, and these are therefore less branched and easier to crystallize into tobermorite [5].

The addition of amorphous silica in the form of ash can increase the rate of the tobermorite formation but, in the end, produces less of it. This way the ash decreases both the strength and the volumetric weight of the final product. [6, 7]. At the same time, the final product contains ash particles that failed to react, causing less connection between the crystals. This microstructure also results in increased absorbing power and shrinkage [8], [9]. Particle size affects the dissolving of silicon ions into the solution and therefore the formation of CSH phases (Fig. 3).

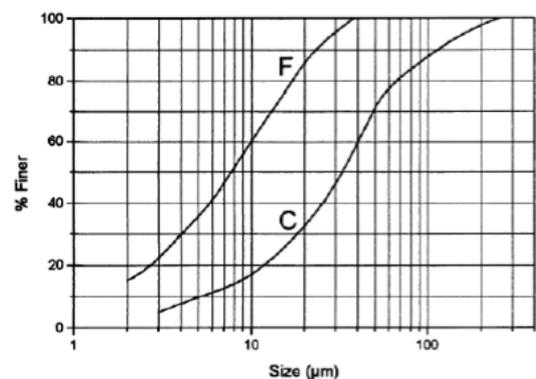


Fig. 3. Distribution of particles of siliceous materials (F - fine, C - course) [3]

The saturation of the solution with silicon and calcium ions is closely related. Portlandite cannot be dissolved until the Ca₂⁺ ions are to a certain degree used up, for example by the formation of the CSH gel. The solubility of silica, and thus also of portlandite, decreases with the increased size

of grain [10]. Particle size also has a particular effect within the hydrothermal conditions. The ability to decompose hydrogarnet (that crystallizes into tobermorite) decreases with the dropping specific surface area of silicates. As a result, the product, therefore, contains less of these phases [11], [3] However, quartz sand with a smaller specific surface area forms more crystalline tobermorite and can contain more massive quantities of it during more extended autoclave periods. The consequence could be a delayed transformation of tobermorite into xonotlite [12].

C. The Effect of Hydrothermal Processes

During hydrothermal synthesis, recrystallization occurs in the sense of Rabinder theory. The beginning of the crystallization is the end of the hydration of CaO and thus the formation of a spatial macrostructure from the Ca (OH)₂ crystals. A continual transformation of crystalline phases takes place over the course of autoclaving, without achieving a balanced state. The specific surface area of crystals increases at the beginning of the hydrothermal synthesis, due to the crystallization of material and the creation of microstructure. In later stages, the phenomenon of the crystals growing larger and decreasing of their specific surface area takes place. This phenomenon can be observed after 20 hours of autoclaving [1].

The extension of the period of isothermal endurance causes an improvement of mechanical properties and mineralogical composition. More extended hydrothermal treatment enables better crystallization of tobermorite, when its crystals are larger and fit better together. This way they create a more homogenous microstructure, resulting in improvement of the mechanical properties of the AAC. Xonotlite may form upon the isothermal period of approximately 20 to 72 hours and sufficient supply of CaO, which is however undesirable due to its lower mechanical strength in comparison to tobermorite [1].

If we increase the pressure autoclaving so it may cause the break of the crystals resulting in the opposite effect as prolonged isotherm. Therefore, it is necessary to find the optimal autoclave regime to achieve the best mineralogical composition and the resulting mechanical properties [13]. The temperature of the hydrothermal reaction mainly affects the rate of dissolution of the siliceous raw materials. At a temperature of 150 °C and 24 hours, CSH and C₂SH with a higher Ca²⁺ content are formed. This reaction causes the slow dissolution of the quartz [14].

II. MATERIAL AND METHOD

A. Testing Methodology

The methodology of tests performed about this paper was divided into two parts. The first part regarded analysis of entry materials, where each raw material was subjected to chemical analysis (XRD – RTG diffraction analysis) to identify the number of oxides. The specific surface area was established using the permeable method according to Blaine and laser granulometry. Quicklime was selected as a basic raw material for increasing the content of calcium oxide in the mixture. Quartz sand (representing the crystalline type) and silica fume (representing the amorphous type) were

selected for the experimental part as the main representatives of silica compounds with a high content of SiO₂. Fly ash from coal burning was selected as the representative of by-product materials.

The second part of the performed tests was focused on synthesizing tobermorite. A combination of quicklime and silica materials in the variable molar C/S ratio of 0.73 and 1.00 was used for the synthesis. In the first phase, the materials were left to rest, causing the initial formation of the CSH products during this process. Subsequently, the samples (20x20x100 mm) were treated hydrothermally over the course of 4, 8 and 16 hours since the beginning of autoclaving in hydrothermal reactors (Teflon inner vessel, external stainless steel pressure vessel) with the volume of 250 ml at 190°C.



Fig. 4. Autoclave reactor (250 ml)

After autoclaving, the final product was dried at 60°C to constant weight. Next step was grinding of the test sample to the particle size lower than 0.063 mm. Powdered sample was subjected to the X-ray diffraction analysis to determine the mineralogical composition. For the SEM analysis were used samples of size approx. 5x5x5 mm. SEM at a magnification of 5000x and 1000x was used for qualitative valuation of created microcrystalline phases.

B. Materials Used

High-temperature fly ash, quicklime, quartz sand and silica fume were used for the experimental part. The properties of the individual materials can influence their behavior in the mix, together with other components, and determine the possibility of their use. For these reasons, it is necessary to carry out tests on input raw materials. In addition to mechanical properties, the addition of alternative raw materials (fly ash) can also influence the growth of mosses in building structures, for example. The use of fly ash in mixtures leads to environmental protection. For the fly ash process, the definition of 3R (Reuse, Recycle and Reduce) is sometimes used.

The input materials were subjected to chemical analysis. This analysis was necessary for the design of the formulae for the preparation of tobermorite. The individual percentage representation of the materials was tied to the molar C/S ratio of the individual formulae. Table 1 shows the chemical composition and loss on ignition (LOI) of the entry materials with their respective amounts of oxides.

Particle density and specific surface area of the entry materials were also established (see Table 2). Specific surface area influences the solubility of materials and thus

also the saturation of the solution with calcium and silicon ions. Specific surface area of materials was established using the Blaine's permeability method. Laser granulometry was used in order to establish the specific surface area of silica fume, where the surface is calculated as the sum of the surfaces of spherical particles.

TABLE I.
THE CHEMICAL COMPOSITION OF ENTRY MATERIALS

Material	Free CaO	Tot. CaO	SiO ₂	Al ₂ O ₃	SO ₃	LOI
Fly ash	0.05	3.44	58.80	19.70	0.18	1.43
Quicklime	85.30	86.10	1.18	0.56	0.38	2.70
Quartz sand	0.05	0.17	86.10	5.47	0.17	1.12
Silica fume	0.12	0.40	93.20	0.23	0.29	2.69

TABLE II.
PARTICLE DENSITY AND SURFACE OF ENTRY MATERIALS

Material	Particle Density [g·cm ⁻³]	Spec. Surface Area [cm ² ·g ⁻¹]
Fly ash ¹⁾	1.97	2,800 ¹⁾
Quartz sand ¹⁾	2.72	3,500 ¹⁾
Silica fume ²⁾	2.32	15,200 ²⁾
Quicklime ¹⁾	3.20	4,800 ¹⁾

Methods of stimulation of the specific surface area:
¹⁾ Blaine's permeability method, ²⁾ Laser granulometry.

III. RESULTS AND DISCUSSION

The experimental part was focused on observation of the effects influencing the formation of tobermorite. The formation of tobermorite phases in the C – A – S – H system depends on the molar ratio of CaO/SiO₂. Molar ratios of C/S = 0.73 and 1.00 with higher content of calcium oxide were selected to evaluate the effect of the ratio. Formulae for the preparation of tobermorite from the selected silica compounds and additives were designed by the established amount of oxides for the given molar ratios. Fly ash, quartz sand, and silica fume were selected as the silica compounds. Table 3 below shows the composition of the material mixtures, calculated by the chemical analysis of these materials and molar ratios.

XRD analyses were performed for all proposed formulae. Fig. 5-10 show an example of roentgenograms and Tables 4-6 show the results of mineralogical analyses of the samples by the individual silica materials.

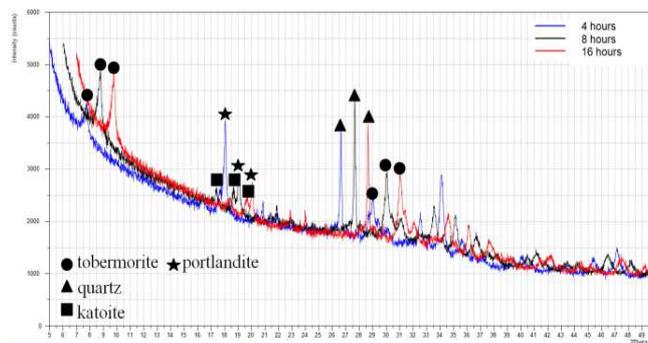


Fig. 5. Combination of roentgenograms of a sample using fly ash autoclaved at the temperature of 190 °C with a molar ratio of C/S = 0.73

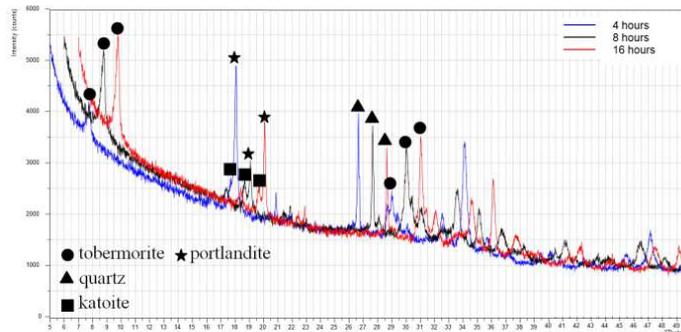


Fig. 6. Combination of roentgenograms of a sample using fly ash autoclaved at the temperature of 190 °C with a molar ratio of C/S = 1.00

TABLE III.
FORMULAE FOR THE PREPARATION OF TOBERMORITE WITHOUT ADDITIVES

		Molar C/S ratio		
		0.73	1.00	
Amount of Material [%]	1	Quicklime	30.04	37.70
		Fly ash	69.96	62.30
	2	Quicklime	40.68	48.54
		Quartz Sand	59.32	51.46
	3	Quicklime	42.52	50.46
		Silica Fume	57.48	49.54

TABLE IV.
MINERALOGICAL COMPOSITION OF SAMPLES BY FLY ASH

C/S ratio	4 hours		8 hours		16 hours	
	0.73	1.00	0.73	1.00	0.73	1.00
Quartz	++	++	++	++	++	++
Tobermorite	++	++	++	+++	++	+++
Katoite	+	+	+	+	+	+
Portlandite	++	+++	+	++	+	++
Amorphous phase	++	++	++	++	++	++

+++ the phase forms the majority part
 ++ the phase is present in a considerable amount
 + the phase is present in a minor amount

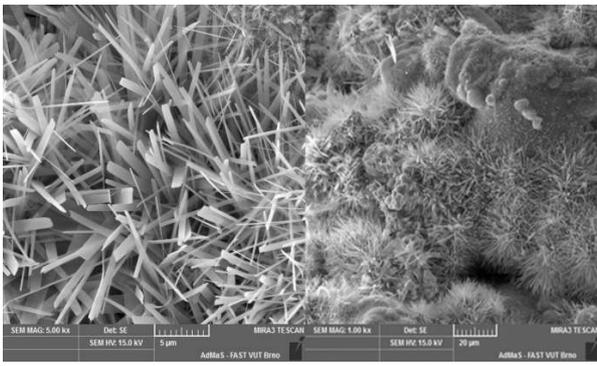


Fig. 7. SEM image of a sample created using fly ash without additives, autoclaved for 16 hours at the temperature of 190 °C.

Based on the evaluation of the roentgenograms (Fig. 5 and 6), we can generally conclude that the amount of tobermorite gradually increased with the duration of the hydrothermal synthesis, as well as that the amount of silica slightly decreased. The content of portlandite after 8 hours of autoclaving decreased rapidly. Katoite remained in the samples throughout the synthesis, and its content decreased slightly. The amount of tobermorite increased with the rising temperature and more extended autoclaving period, as well as with higher molar ratio C/S. The highest amount of tobermorite was observed in the mixture with the molar ratio of C/S = 1.00 treated hydrothermally at the temperature of 190 °C over the course of 8 hours.

Observation of the microstructure using an SEM (see Fig. 7) also reveals the high content of tobermorite phases. Small pointy crystals of tobermorite thickly cover the surface of the sample. Their length exceeds the width due to the content of aluminum that accelerates the crystallization of tobermorite.

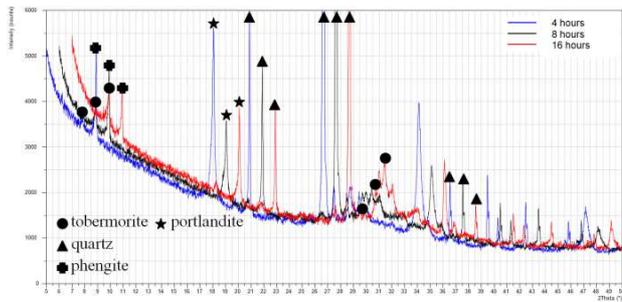


Fig. 8. Combination of roentgenograms of a sample using quartz sand autoclaved at the temperature of 190 °C with a molar ratio of C/S = 0.73

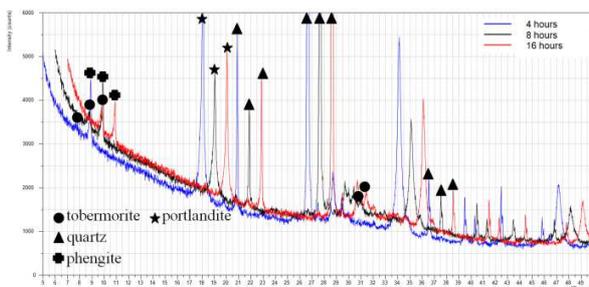


Fig. 9. Combination of roentgenograms of a sample using quartz sand autoclaved at the temperature of 190 °C with a molar ratio of C/S = 1.00

TABLE V.
MINERALOGICAL COMPOSITION OF SAMPLES BY QUARTZ SAND

C/S ratio	4 hours		8 hours		16 hours	
	0.73	1.00	0.73	1.00	0.73	1.00
Quartz	+++	+++	+++	++	++	++
Tobermorite	+	+	++	++	++	++
Katoite	++	++	++	++	++	++
Portlandite	+++	+++	++	++	++	++
Amorphous phase	++	++	++	++	++	++

+++ the phase forms the majority part
 ++ the phase is present in a considerable amount
 + the phase is present in a minor amount
 - the phase is not present

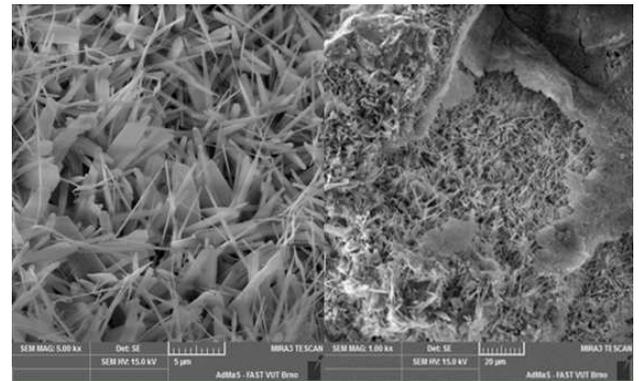


Fig. 10. SEM image of a sample created using quartz sand without additives, autoclaved for 16 hours at the temperature of 190 °C.

Based on the roentgenograms (Fig. 8 and 9) we can conclude that the majority part of the mineralogical composition in the samples created using quartz sand at low molar C/S ratios and shorter autoclaving period forms the unreacted silica and portlandite, and in the lesser amount, they contain tobermorite and phengite. The presence of unused portlandite in the sample was caused by the low solubility of silica in the solution, thus having limited its ability to react with silica forming CSH phases. Samples also included phengite, a mineral contained in the used quartz sand. Tobermorite was formed after 8 hours of autoclaving, and its amount slightly increased with the course of the hydrothermal synthesis.

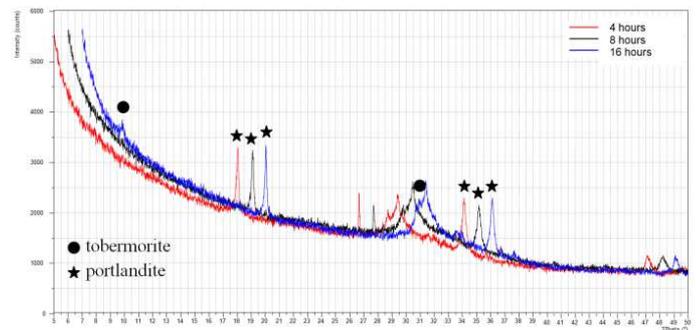


Fig. 11. Combination of roentgenograms of a sample using silica fume autoclaved at the temperature of 190 °C with a molar ratio of C/S = 0.73

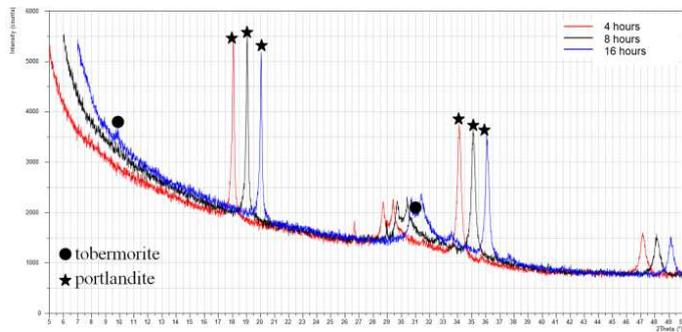


Fig. 12. Combination of roentgenograms of a sample using silica fume autoclaved at the temperature of 190 °C with a molar ratio of C/S = 1.00

TABLE VI
MINERALOGICAL COMPOSITION OF SAMPLES BY SILICA FUME

C/S ratio	4 hours		8 hours		16 hours	
	0.73	1.00	0.73	1.00	0.73	1.00
Tobermorite	-	-	-	-	+	+
Portlandite	++	+++	++	+++	++	+++
Amorphous phase	++++	++++	++++	++++	++++	++++

+++ the phase forms the majority part
 ++ the phase is present in a considerable amount
 + the phase is present in a minor amount
 - the phase is not present

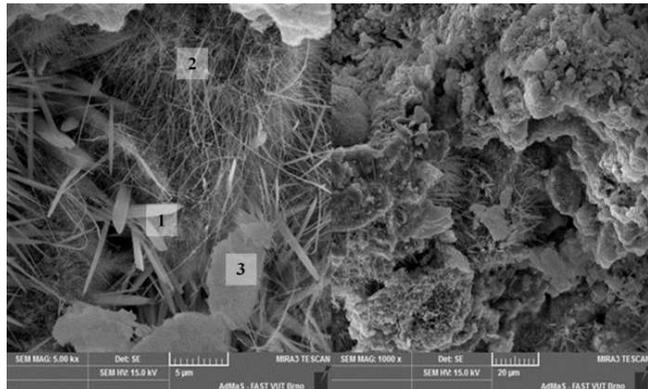


Fig. 13. SEM image of a sample created using silica fume without additives, autoclaved for 16 hours at the temperature of 190 °C. (1 – tobermorite, 2 – CSH (I), 3 – CSH gel)

Based on the completed roentgenograms (Fig. 11 and 12) we can conclude that the majority of the mineralogical composition of the samples created using silica fume form amorphous phases of silicon dioxide, non-crystallized CSH phases, portlandite and trace amounts of tobermorite. The high amount of amorphous phases is likely the result of the high solubility of the silicate used. That produced CSH phases with low molar C/S ratio, meaning with a high content of SiO₂. These calcium hydrosilicates are less capable of crystallizing into tobermorite. Tobermorite was formed only after 16 hours of autoclaving and in trace amounts.

IV. CONCLUSION

Using the analysis above, the effect of silicate species on tobermorite formation in the C - A - S - H system was observed without the use of additives. Tobermorite was formed in highest amounts when using fly ash. The character of silicon dioxide and the content of aluminum oxide in the ash accelerated its crystallization, also confirmed by the presence of katoite. Tobermorite was formed in more significant amounts at higher molar C/S ratio, due to the higher saturation of the environment with Ca₂⁺ ions. These were capable of reacting with the Si₄⁺ ions, creating CSH phases. The lower ratio caused oversaturation with silicon ions, creating high-silica CSH phases that are less capable of crystallizing into tobermorite.

The majority part of the sample's mineralogy created from quartz sand remained composed of mainly quartz and portlandite. The cause of the high amount of these minerals is the low solubility of quartz, resulting in the absence of Si₄⁺ ions necessary for the formation of CSH phases, in particular of tobermorite. Trace amounts of tobermorite were recorded at 190 °C and synthesis time of 16 hours. As a consequence is, that the sample contains a high amount of an amorphous phase mainly consisting of amorphous SiO₂, CSH gel. The samples are containing silica fume as the silica compound was characterized by high content of amorphous phase and unreacted portlandite. The cause is the high solubility of amorphous silicate. Together with portlandite, this co-created high-silica CSH phases that barely crystallized further. The trace amount of tobermorite was recorded at the 16-hour synthesis period. Due to this, the sample contains a high amount of amorphous phase composed mostly of amorphous SiO₂ and CSH gel.

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