The influence of different types of siliceous raw materials on tobermorite formation in lime-silica composite

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Abstract: - Autoclaved aerated concrete (AAC) is ecological building material with useful properties. The main mineral compound of AAC is tobermorite, it increases its mechanical properties. There is examined the usage of nature and artificial siliceous materials in this study. Main aim of the study is to demonstrate the influence of individual types of materials on the tobermorite creation and to determine optimal lime/silica ratio. First step of the research focuses on analysis of the used materials. In the second step on the creation of calcium hydrosilicate phases under ideal conditions (temperature of 190 °C, pressure of 1.3 MPa) of autoclave reactors (volume of 250 ml). The autoclaved samples are next analyzed by X-ray diffraction and scanning electron microscopy for qualitative evaluation of created mineral phases. The results show that the most suitable non-traditional silica component is coal fly ash. Fly ash has the optimal combination of amorphous and crystalline SiO_2 in combination with Al_2O_3. These properties provided the highest proportion of created tobermorite even in more energy-saving autoclaving mode.

Key-Words: - autoclaved aerated concrete, tobermorite, fly ash, quartz sand, silica fume, hydrothermal conditions, calcium hydrosilicates.

1 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. Including, 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-products 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 should 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 coal burning 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 $Ca_5Si_6O_{16}(OH)_2 \cdot 4H_2O$.

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 ashes. Upon sustaining these conditions, it is possible to increase competitiveness at the market as well as profits.

1.1 Tobermorite Formation

The molar ratio of CaO/SiO$_2$ 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 at a specific molar ratio of components. However, tobermorite is only a transitional phase, because it further crystalizes to 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]
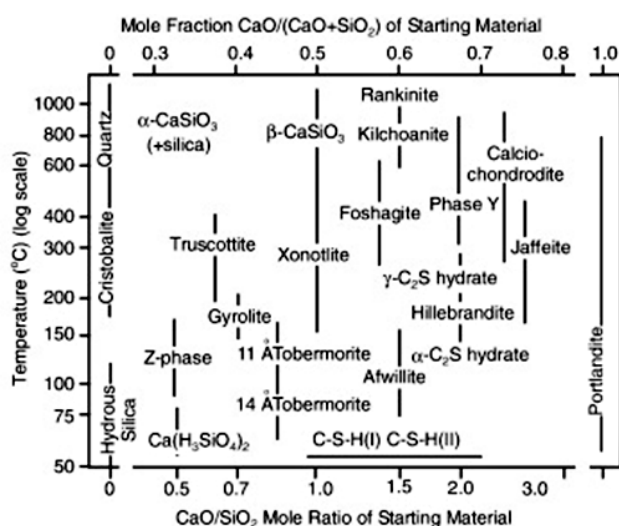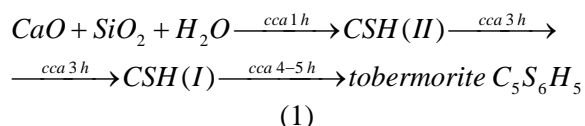

Fig. 1. CaO – SiO$_2$ – H$_2$O phase diagram [1]

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 – SiO$_2$ – Al$_2$O$_3$ – H$_2$O.

The content of Al$_2$O$_3$ in the CaO – SiO$_2$ – H$_2$O system is critical from the point of view of the formation of tobermorite. In the case of absence of Al$_2$O$_3$, tobermorite is formed from CSH gel, according to the equation 1:

$$CaO + SiO_2 + H_2O \xrightarrow{cca\,1\,h} CSH(II) \xrightarrow{cca\,3\,h}$$
$$\xrightarrow{cca\,3\,h} CSH(I) \xrightarrow{cca\,4-5\,h} tobermorite\ C_5S_6H_5$$
$$(1)$$

However, when Al$_2$O$_3$ is present, tobermorite forms within the CaO – SiO$_2$ – Al$_2$O$_3$ – H$_2$O in two ways. (1) Tobermorite formation from the CSH phase: CSH → tobermorite, (2) Tobermorite formation from katoite: SiO$_2$, katoite, hydrogarnet, CSH → Si^{4+}, Ca^{2+}, Al^{3+}, 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]

1.2 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).
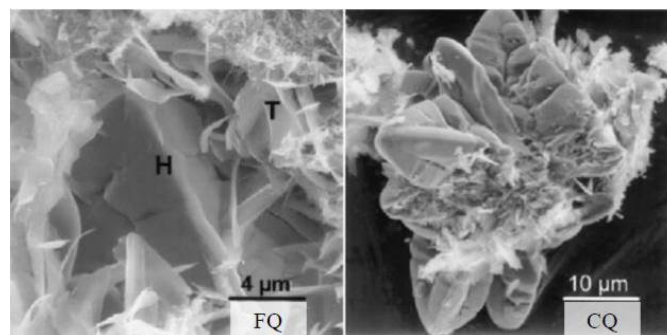

Fig. 2. Hydro graphic desintegration by using fine quartz (FQ) and coarse quartz (CQ), H - hydrogranate, T - tobermorite [3]

While 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. [4] These gels are characterized by shorter chains. On the contrary, while using amorphous quartz, the forming gels with a C/S ≈ 0.81 ratio are silicon-rich and have long chains that less easily crystalize. The result is a different rate of the silica material dissolving and therefore saturating the solution with these ions. Amorphous materials are easier to dissolve, they saturate the solution with Si4+ ions to a larger extent and the CSH phases contain more of them. On the other hand, crystalline materials dissolve more slowly, a larger 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).
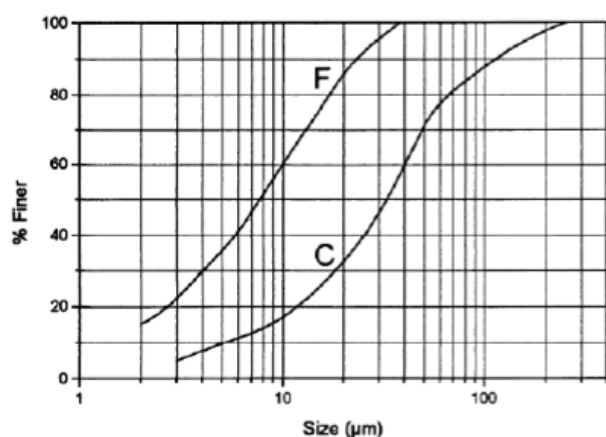

Fig. 3. Particles size distribution of silica materials (F - fine, C - coarse) [3]

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 increase of grain size. [10] Particle size also has a certain effect within the hydrothermal conditions. The ability to decompose of 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 larger quantities of it during longer autoclave periods. The consequence could be a delayed transformation of tobermorite into xonotlite. [12]

1.3 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 balance state. The specific surface area of crystals increases in 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. Longer 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 sufficiently supply CaO, which is however undesirable due to its lower mechanical strength in comparison to tobermorite. [1]

If we increase the pressure of autoclaving 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]

2 MATERIAL AND METHOD

2.1 Testing Methodology

The methodology of tests performed in this paper was divided into two parts. The first part regarded analysis of input materials, where each raw material was subjected to chemical analysis in order to identify the amount of oxides. Specific surface area was established using 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 high content of SiO_2. 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 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 volume of 250 ml at 190°C.

Fig. 4. Used autoclave reactor (250 ml), components (left), before inserting a sample and closing (right)

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 (XRD) in order to determine the mineralogical composition. For the scanning electron microscopy (SEM) were used samples of size approx. 5x5x5 mm. SEM at magnification of 5000x and 1000x was used for qualitative valuation of created microcrystalline phases.

2.2 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 behaviour in the mixture together with other components and determine the possibility of their usage. 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 on 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. [15]

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 input materials with their respective amounts of oxides.

Table 1. Chemical composition of raw materials

Material	Free CaO	Tot. CaO	SiO_2	Al_2O_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

Particle density and specific surface area of the input 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 was calculated as the sum of the surfaces of spherical particles.

Table 2. Particle density and specific surface area of used raw 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.		

3 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/SiO_2. 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 based on 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 on the basis of the chemical analysis of these materials and molar ratios.

Table 3. Shares of raw materials in the different formulas

			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

XRD analysis 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 on the basis of the individual silica materials.
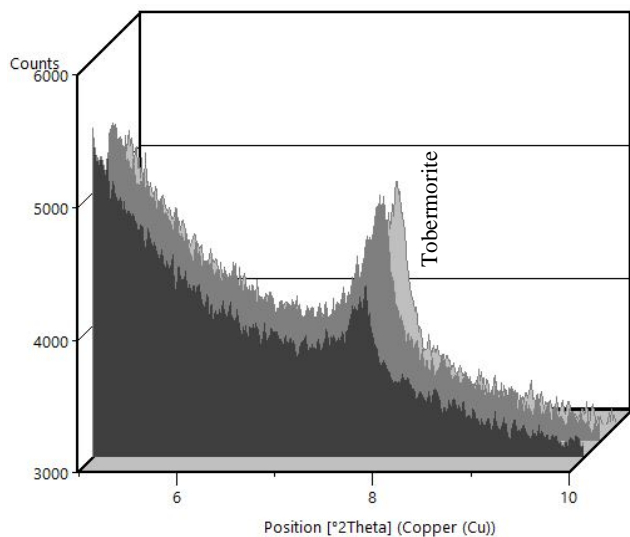

Fig. 5. Combination of XRD results of samples based on fly ash and lime (C/S = 0.73)
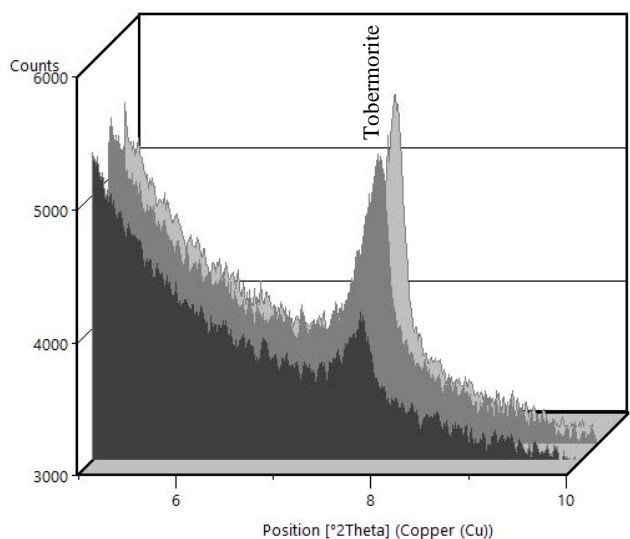

Fig. 6. Combination of XRD results of samples based on fly ash and lime (C/S = 1.00)

Table 4. Main mineralogical composition of samples based on fly ash (intensity of peaks)

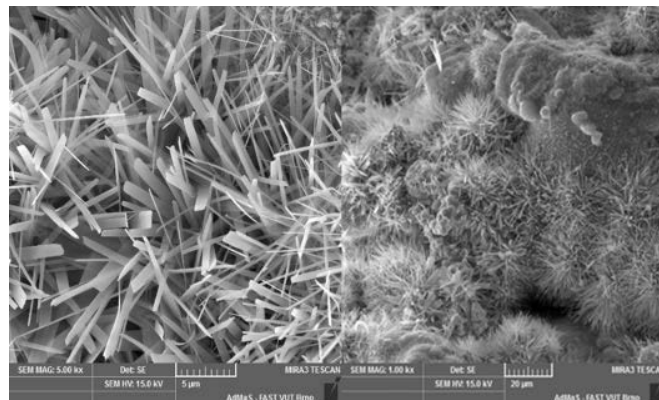|	4 hours		8 hours		16 hours	
C/S ratio	**0.73**	**1.00**	**0.73**	**1.00**	**0.73**	**1.00**
Tobermorite	4700	4200	5000	5300	5000	5500
Quartz	3700	4000	4300	3800	4000	3500
Katoite	2700	2700	2800	2600	2600	2600
Portlandite	4000	5000	3000	3100	2800	3800

Fig. 7. SEM image of a sample based on fly ash, autoclaved for the 16 hours.

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 longer 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 revealed high content of tobermorite phases. The surface of the sample was thickly covered by small pointy crystals of tobermorite. Their length surpassed the width due to the content of aluminium that accelerated the crystallization of tobermorite.
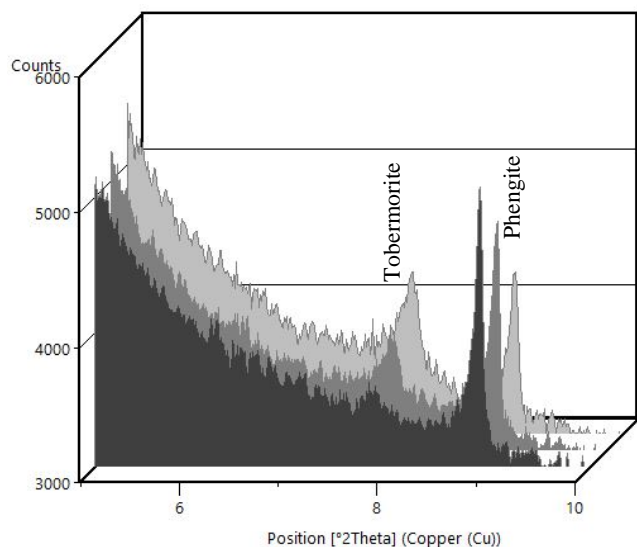
Fig. 8. Combination of XRD results of samples
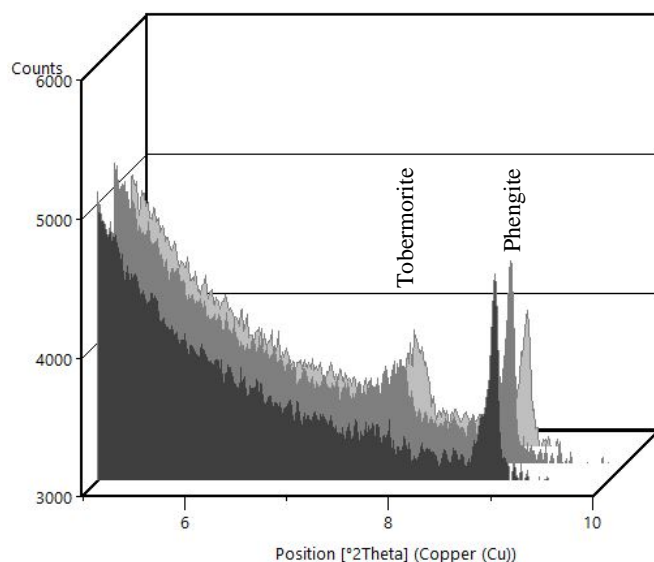based on quartz sand and lime (C/S = 0.73)

Fig. 9. Combination of XRD results of samples
based on quartz sand and lime (C/S = 1.00)

Table 5. Main mineralogical composition of
samples based on quartz sand (intensity of peaks)

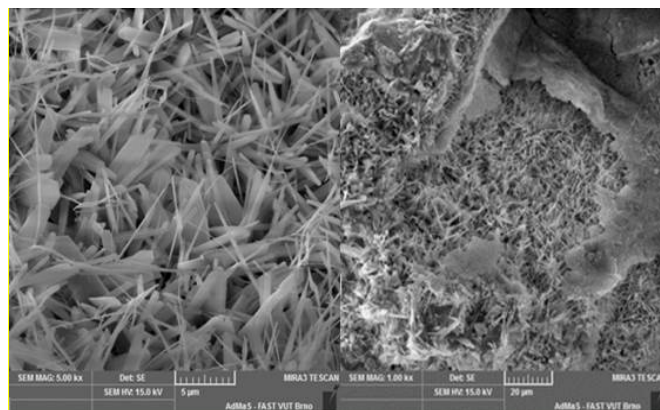| C/S ratio	4 hours		8 hours		16 hours	
	0.73	1.00	0.73	1.00	0.73	1.00
Tobermorite	3600	3500	3900	3800	4300	4000
Phengite	5100	4500	4800	4500	4300	4000
Quartz	>6000					
Portlandite	5100	5900	3500	4700	3800	5300

Fig. 10. SEM image of a sample based on quartz
sand, autoclaved for the 16 hours.

Based on the roentgenograms (Fig. 8 and 9) we can
conclude that the major part of the mineralogical
composition in the samples created using quartz
sand at low molar C/S ratios and shorter autoclaving
period formed the unreacted silica and portlandite,
and in lesser amount they contained tobermorite and
phengite. The presence of unused portlandite in the
sample was caused by 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
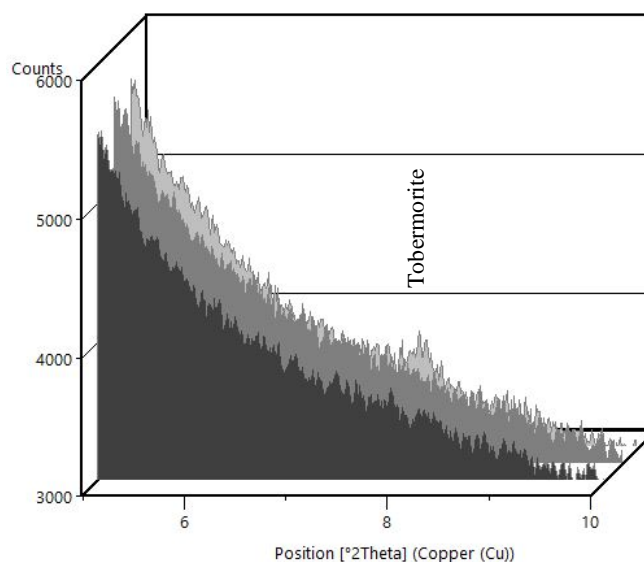the course of the hydrothermal synthesis.

Fig. 11. Combination of XRD results of samples
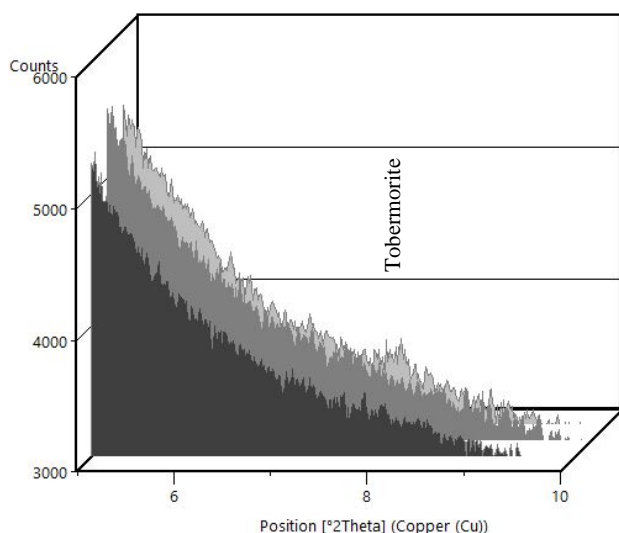based on silica fume and lime (C/S = 0.73)

Fig. 12. Combination of XRD results of samples based on silica fume and lime (C/S = 1.00)

Table 6. Main mineralogical composition of samples based on silica fume (intensity of peaks)

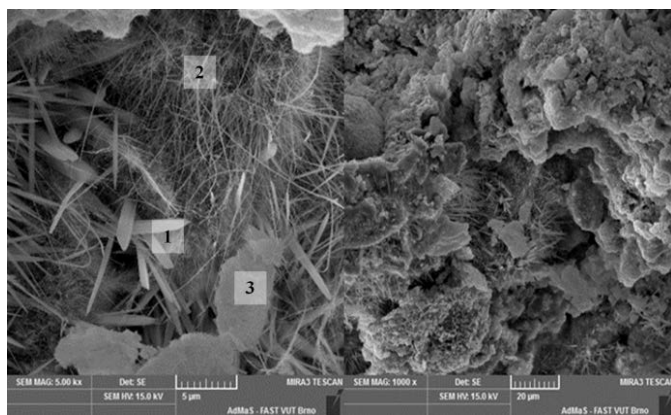| C/S ratio	4 hours		8 hours		16 hours	
	0.73	1.00	0.73	1.00	0.73	1.00
Tobermorite	-	-	-	-	3800	3600
Portlandite	3400	5500	3400	5500	3400	5300

Fig. 13. SEM image of a sample based on silica fume, autoclaved for the 16 hours.
(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-crystalized 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 high content of SiO_2. These calcium hydrosilicates are less capable of crystalizing into tobermorite.

Tobermorite was formed only after 16 hours of autoclaving and in trace amounts.

4 CONCLUSIONS

Using the aforementioned analysis, 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 the highest amounts while fly ash was used. The character of silicon dioxide and the content of aluminum oxide in the ash accelerated its crystallization, which was also confirmed by the presence of katoite. Tobermorite was formed in larger 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 by silicon ions, creating high-silica CSH phases that were less capable of crystalizing into tobermorite.

The major 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 SiO_2, CSH gel.

The samples containing silica fume as the silica compound were characteristic by high content of amorphous phase and unreacted portlandite. The cause was the high solubility of amorphous silicate. Together with portlandite, this co-created high-silica CSH phases that barely crystalized further. The trace amount of tobermorite was recorded at the 16-hour synthesis period. Due to this fact sample contained high amount of amorphous phase composed mostly of amorphous SiO_2 and CSH gel.

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