

# The influence of metahalloysite addition on tobermorite formation studied by X-ray powder diffraction and scanning electron microscope

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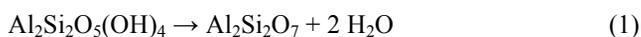
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**Abstract.** This paper presents the results of the studies carried out in the model systems and concerning the tobermorite synthesis with an addition of metahalloysite. Quartz sand and quicklime were the main raw material constituents. The mixtures in the form of slurries underwent hydrothermal treatment with an addition of metahalloysite (5%, 10%, 15%, 20% and 30%) for 4 hours and 12 hours. The resultant composites were analysed for their phase composition using X-ray powder diffraction. The microstructure was examined using the Scanning Electron Microscope. Tobermorite was the principle reaction product. When 30% metahalloysite was added to the mixture containing CaO and SiO<sub>2</sub>, the formation of katoite was found.

## 1 Introduction

Tobermorite is the principal phase formed in autoclaved building composites, the one which provides the final products with appropriate mechanical properties. Until now three tobermorite phases have been distinguished on the basis of their basal spacing: 14Å tobermorite- Ca<sub>5</sub>Si<sub>6</sub>O<sub>16</sub>(OH)<sub>2</sub>·7H<sub>2</sub>O, 11 Å tobermorite- Ca<sub>5</sub>Si<sub>6</sub>O<sub>16</sub>(OH)<sub>2</sub>·5H<sub>2</sub>O and water free 9 Å tobermorite Ca<sub>5</sub>Si<sub>6</sub>O<sub>16</sub>(OH)<sub>2</sub>. The most important type is 11Å tobermorite, which is the major phase found in aerated autoclaved concretes. Understanding the mechanism of tobermorite formation in the autoclave process is very important for the production of AAC [1-5]. Huston et al. [6] stated, that tobermorite formation proceeds in three stages: formation of amorphous C-S-H phase, increase in semi-crystalline tobermorite content and its crystallization. Numerous studies shown, that reactive silica, aluminium, Na and K or sulphates compounds have significant influence on tobermorite synthesis [6-9].

The tobermorite was synthesized with an addition of metahalloysite. Metahalloysite was obtained by dehydroxylation of halloysite [10-11]. This reaction can be presented as the schematic formula



Since tobermorite is important phase of autoclaved building composites, the influence of metahalloysite addition and autoclaving time on this phase formation in constant autoclaving

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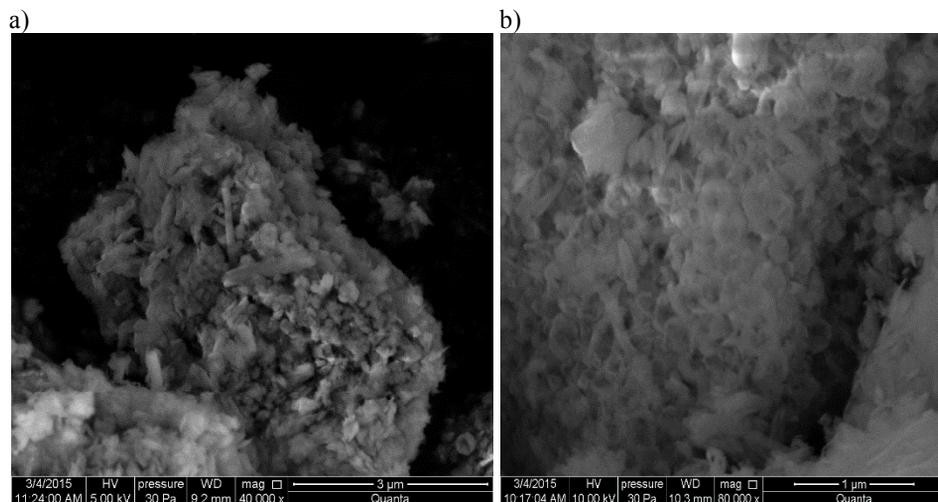
conditions corresponding to saturated water vapour pressure at temperature of 180°C were examined.

## 2 Materials, methods and samples preparation

Raw materials used to obtain autoclaved composites included silica sand and quicklime. The silica sand chosen met the PN-EN 196-1 criteria. Grains with the size less than 0.5 mm were ground to reach the Blain fineness of 6560 cm<sup>2</sup>/g. The quicklime was obtained by subjecting pure calcium carbonate to the heat of 1000°C for 2 h. Natural halloysite, used to obtain the metahalloysite, came from the Dunino mine, near Legnica. Metahalloysite was obtained by thermal treatment of halloysite at the temperature of 750°C for 2 hours. This mineral was used as an admixture 5%, 10%, 15%, 20% and 30% by weight of the joint weight of CaO and SiO<sub>2</sub>.

Tobermorite was synthesized at the CaO/SiO<sub>2</sub> molar ratio of 0.86. The ratio of water *w* to the amount of solid constituents *s* was 2 (W/S=2). The constituents were placed in plastic containers and homogenized for 5 minutes. Metahalloysite was added towards the end of mixing the main components. The slurries were then poured into PTFE moulds and moved into a laboratory autoclave and held at 180°C for 4 and 12 hours at a saturated steam atmosphere. The temperature in the autoclave was elevated with the rate of 1.5°/min. The specimens were dried under vacuum to prevent them from being contaminated with CO<sub>2</sub>.

The phase composition and the microstructure of the composites was examined using an X-ray diffraction method (EMPYREAN manufactured by PANalytical) and scanning electron microscope (Quanta 250 FEG manufactured by ThermoFisher Scientific) in the low vacuum mode. The steam atmosphere was 30 Pa. The microstructure of halloysite and metahalloysite are shown in Fig.1a and Fig.1b respectively. Details of raw material composition are given in Table 1.



**Fig. 1.** The microstructure of a) halloysite b) metahalloysite.

Halloysite is consist of irregular forms and spatially dispersed tubes. Metahalloysite is amorphous and the particles with tubular morphology, typical for halloysite, are not found.

**Table 1.** Chemical composition of raw materials as determined by X-ray fluorescence.

Oxide [%]	Quicklime	Quartz	Metahalloysite
SiO <sub>2</sub>	NS*	99.6	49.6
K <sub>2</sub> O	NS*	NS*	0.1
TiO <sub>2</sub>	NS*	NS*	2.0
Al <sub>2</sub> O <sub>3</sub>	NS*	NS*	41.5
Fe <sub>2</sub> O <sub>3</sub>	NS*	NS*	5.7
P <sub>2</sub> O <sub>5</sub>	NS*	NS*	0.8
CaO	99.8	NS*	0.3

NS\* - not studied

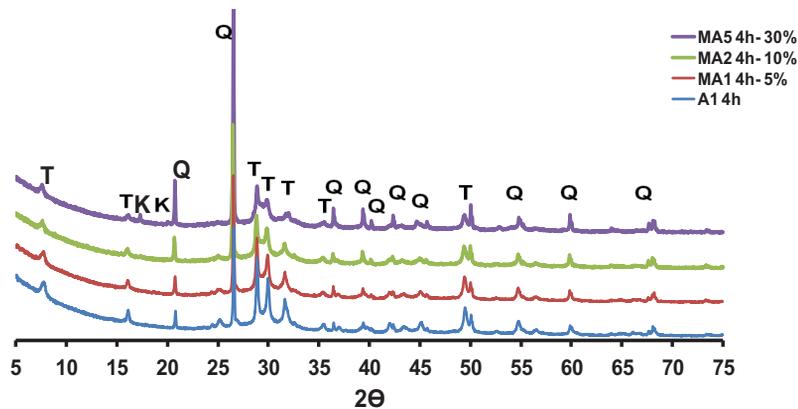
### 3 Results

Sample designations and metahalloysite percentage share in mixes composed of quicklime and silica are given in Table 2.

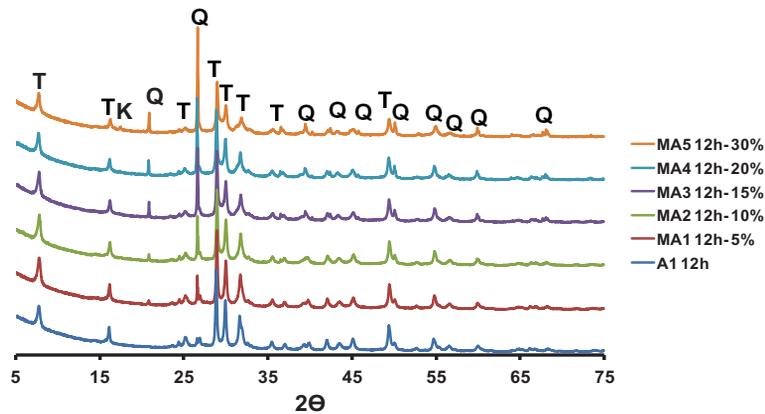
**Table 2.** Designation of autoclaved mixes with metahalloysite.

Designation of samples	A1	MA1	MA2	MA3	MA4	MA5
Metahalloysite content [%]	0	5	10	15	20	30

Phase compositions of mixes composed of quartz sand and CaO with metahalloysite after 4h and 12h of autoclaving process are presented on Figs. 2-3.



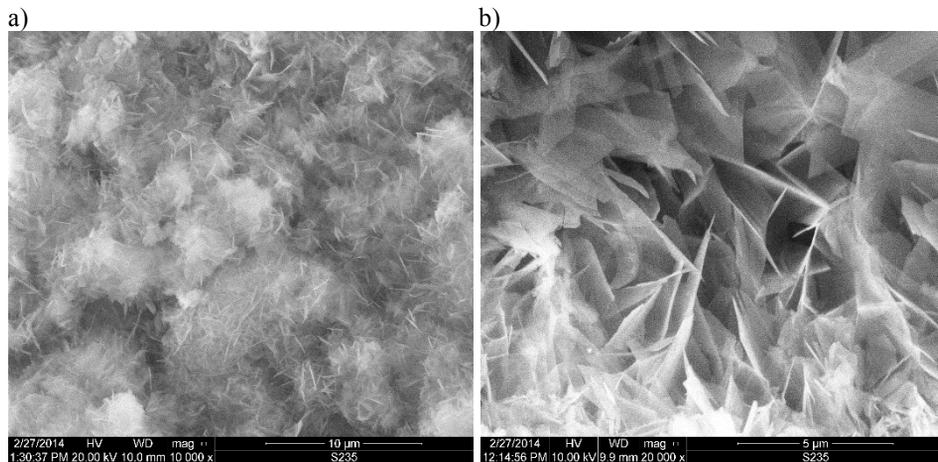
**Fig. 2.** X-ray diffraction patterns of mixes with metahalloysite addition, autoclaving time 4 hours. T- tobermorite, K- katoite, Q- quartz.



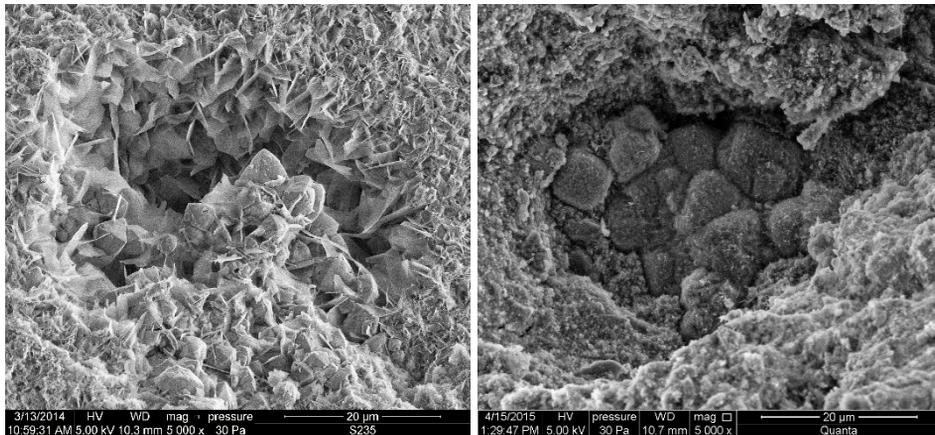
**Fig. 3.** X-ray diffraction patterns of mixes with metahalloysite addition, autoclaving time 12 hours. T- tobermorite, K- katoite, Q- quartz.

X-ray pattern analysis (Figs. 2,3) shown that primary synthesis product in samples with metahalloysite is tobermorite. Except this phase, quartz is also present, but the intensity of this phase decreased with reaction time (after 12 hours). Katoite occurs in samples with 30% of metahalloysite after 4 hours. This phase appears when Al/(Al+Si) molar ratio exceeds 0.15. Hydrogarnet did not disappear after 12 hours. According to Klimesh et al. [12-16], katoite is indirect phase in tobermorite formation. Hydrogarnets durability decreases with increase in silica content and the extension of autoclaving time. Metahalloysite was not present in any sample. It means that this mineral completely reacted, and SiO<sub>2</sub> contained in metahalloysite is more reactive than quartz sand, therefore it quickly reacts with calcium ions.

Microscopic examinations confirmed the phase composition results from the XRD analysis. Figs. 4-5 show SEM selected images of the morphology of calcium silicate hydrates (C/S= 0.86) with metahalloysite. Observations under scanning electron microscope have shown, that time of synthesis and presence of mineral additions influence on products morphology. After 4 hours of autoclaving process, poorly crystallized calcium silicate hydrates are observed. Well-developed concentrations of tobermorite were observed in the samples without metahalloysite after 12 hours. In the sample containing 30% of metahalloysite, tobermorite is accompanied by hydrogarnets. The typical octahedral morphology of hydrogarnet occurring in twinned crystals is illustrated in Fig.5. Tobermorite occurs in the form of flattened laths.



**Fig. 4.** Microstructure of reference sample after a) 4 hours b) 12 hours.



**Fig. 5.** Microstructure of sample with 30% of metahalloysite addition.

## 4 Analysis of the results

Tobermorite under hydrothermal conditions can be synthesized with an addition of clay mineral such as metahalloysite. Test results of samples with metahalloysite addition shown, that variable phase composition is obtained depending on the amount of used metahalloysite. Only tobermorite and quartz are observed in samples with metahalloysite addition in amount to 20%. Metahalloysite addition higher than 20% caused, except tobermorite, also katoite formation. Microstructure analysis under scanning electron microscope shown, that extension of hydrothermal treatment time favours the formation of calcium silicate hydrates with ordered structure. Hydrogarnets crystals in the form of rhombic octahedron were present in samples with 30% of metahalloysite addition.

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