

Hydrothermal Synthesis and Characterization of Na^+ and $[\text{Al}^{3+} + \text{Na}^+]$ -substituted Tobermorite in $\text{CaO-SiO}_2\cdot n\text{H}_2\text{O-H}_2\text{O}$ System

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The influence of Na^+ and $[\text{Na}^+ + \text{Al}^{3+}]$ additives on the formation of 1.13 nm tobermorite in the environment of saturated steam at a temperature of 175 °C was determined in this paper. The composition of initial mixtures corresponded to the molar ratios of $\text{CaO/SiO}_2 = 0.83$ ($\text{C/S} = 0.83$) or $\text{CaO}/(\text{SiO}_2 + \text{Al}_2\text{O}_3) = 0.83$ ($\text{C}/(\text{S} + \text{A}) = 0.83$) and $\text{Al}_2\text{O}_3/(\text{SiO}_2 + \text{Al}_2\text{O}_3) = 0.025$ ($\text{A}/(\text{S} + \text{A}) = 0.025$) when amorphous silica was used as an SiO_2 component. The amount of NaOH additive corresponding to 1, 3, 5, 7 or 10 % Na_2O from the mass of dry materials was added. Isothermal curing durations were as follows: 2, 4, 8, 16, 24 hours. According to the obtained results the NaOH additive stabilises semi-amorphous calcium silicate hydrate C-S-H(I) and retards its crystallisation into tobermorite. A bigger impact on hydrothermal reactions is made by an additive of $\gamma\text{-Al}_2\text{O}_3$, which considerably speeds up the formation of tobermorite, whereas a complex additive of $[\text{Al}^{3+} + \text{Na}^+]$ positively impacts the formation and crystallinity of 1.13 nm tobermorite when the durations of synthesis are short. Due to Al^{3+} insertion into a crystal lattice, 1.13 nm tobermorite of a mixed thermal type forms in stirred suspensions, and $[\text{Al}^{3+} + \text{Na}^+]$ insertion creates conditions for the formation of anomalous tobermorite.

Keywords: tobermorite; calcium silicate hydrate; Na^+ -substituted tobermorite, $[\text{Al}^{3+} + \text{Na}^+]$ -substituted tobermorite, thermal type.

INTRODUCTION

When hydrous suspensions of calcium and silicon compound mixtures are under hydrothermal curing or silica products are cured in autoclaves, the formation of minerals of the tobermorite group depends on a mixture composition, SiO_2 nature, fineness of raw material particles, conditions of synthesis and various additives. The latter or impurities very often change the process of formation of new compounds as well as their properties.

As it has been known for a long time, aluminium ions Al^{3+} can get inserted, in an isomorphous manner, into the structure of 1.13 nm tobermorite by replacing Si^{4+} in it [1–5]. This additive accelerates the formation of 1.13 nm tobermorite, increases its stability and changes some properties of the compound. D. S. Klimesch analysed the systems of $\text{CaO-SiO}_2\text{-H}_2\text{O}$ and $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-H}_2\text{O}$ and noted that upon heating 1.13 nm tobermorite the additive of aluminium raised the temperature of transformation into β -wollastonite from 830 °C to 870 °C [6]. R. Šiaučiūnas [3], also E. Rupšytė [5] proved this effect to be typical not for 1.13 nm tobermorite but for semi-amorphous compound C-S-H(I) the stability of which is also enhanced by Al^{3+} ions.

Partial silicon substitution by aluminium results in the formation of normal tobermorite, whereas addition of alkalis into initial mixtures produces anomalous tobermorite [7, 8]. As indicated by the authors, a big C/S ratio (1.0), short duration of curing, low temperature, Al insertion, stirring, fine particles of quartz, if any, create conditions for the formation of normal tobermorite. A low C/S ratio (0.8), high temperature, long duration and aluminium together with alkalis enhance the possibility for 1.13 nm tobermorite of an anomalous thermal type to be formed. In

this tobermorites the basic inter-planar distance does not decrease from 1.13 nm to 0.93 nm due to the presence of $\equiv\text{Si-O-Si}\equiv$ (Al) bridges between the tetrahedron chains and double chains forms. They make the structure very rigid, like in zeolites.

An additive of Na_2O also has an impact on the formation and properties of calcium silicate hydrates. Sodium compounds can be used as alkaline activators, particularly with compounds having hydraulic properties, and such impurities are always present in Portland cement.

According to the research done by C. A. Langton [9], when the content of Na_2O additive is not above 10 % and the content of SiO_2 is equal to 55 % no other mineral, except C-S-H(I), forms. Upon increasing the content of Na_2O during autoclave treatment pectolite also forms, which is confirmed by W. Nocun-Wczelik's research [10]. When treating the molar mixtures of low basicity ($\text{C/S} = 0.67$) with an additive of NaOH at a temperature of 200 °C, after 24 h the author obtained a small amount of the Z-phase together with 1.13 nm tobermorite of a low degree of crystallinity. Meanwhile when the ratio of C/S is 0.83, xonotlite and pectolite form. A subsequent increase of calcium oxide content results in the increase of xonotlite part in products.

Sodium ions may get inserted into a lattice of C-S-H(I) or tobermorite crystals but do not form any solid solutions with other crystalline calcium silicates hydrates, such as xonotlite or foshagite [11, 12]. The research done by S. Hong shows that very small amount of alkaline metals may pass from their solutions into calcium silicate hydrate or calcium aluminosilicate hydrate gels, which depends on the ratio of C/S and the content of aluminium in gel [13].

The ion exchange capacity of pure 1.13 nm tobermorite is small, and the insertion of Al^{3+} ions into a crystalline lattice increases it insignificantly. However, simultaneous insertion of Na^+ ions enhances this property nearly tenfold [14].

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Recently, 1.13 nm tobermorite has also been synthesised from the natural materials trachyte [15], riverbed sediments [16] containing aluminium impurities. An activator, NaOH, is added to the raw material mixtures in order to speed up a reaction.

However, all the mentioned research works lack integrated data about the impact of additives containing Na^+ ions or $[\text{Na}^+ + \text{Al}^{3+}]$ ions on the formation of tobermorite when amorphous silica is used as a component of SiO_2 . The aim of this work is to investigate the impact of NaOH (when used alone and with $\gamma\text{-Al}_2\text{O}_3$) on the mineral composition and properties of products obtained during the synthesis of CaO and amorphous silica mixtures at a temperature of 175 °C.

EXPERIMENTAL

Ground materials were used: CaO, derived upon heating reagent grade CaCO_3 for 6 h at a temperature of 1000 °C, ($\text{CaO}_{\text{free}} = 98.42\%$, specific surface area $S_s = 563 \text{ m}^2/\text{kg}$); reagent $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ (loss on ignition = 22.8 %, $S_s = 1235 \text{ m}^2/\text{kg}$); solution of reagent NaOH ($C_{\text{NaOH}} = 6.2\%$).

The molar ratios of initial mixtures: $C/(S+A) = 0.83$ and $A/(S+A) = 0$ or 0.025 (where: C – CaO, S – SiO_2 , A – Al_2O_3). Water was poured onto the carefully homogenised mixtures by adding the required amount of NaOH solution to have the equivalent content of Na_2O in suspensions of 0, 1, 3, 5, 7, respectively and up to 10 % of dry substances and the ratio of water and solid substances W/S in suspensions equal to 10. Syntheses were carried out in the medium of saturated steam at a temperature of 175 °C in unstirred suspensions, and with isothermal curing durations of 2, 4, 8, 16 or 24 hours. The mentioned durations in stirred suspensions were 24 or 32 hours. The products of synthesis were rinsed with ethyl alcohol to prevent carbonisation, dried at a temperature of 100 °C – 105 °C up to the constant mass and sieved through sieve No 008.

The X-ray powder diffraction (XRD) data were collected with DRON-6 X-ray diffractometer with Bragg-Brentano geometry using Ni-filtered Cu K_α radiation and graphite monochromator, operating with the voltage of 30 kV and emission current of 20 mA. The step-scan covered the angular range $2^\circ - 60^\circ$ (2θ) in steps of $2\theta = 0.02^\circ$. Differential scanning calorimetry (DSC) tests were carried out on a analyzer Dupont 990 (USA) with computer control. The rate of temperature increase was 10 °C/min. Specific surface area determinations were carried with ENV 197-1 (by Blaine method). SEM was carried out with Oxford ISIS Leo 440i D. Magnification – 5000 $\times$, operating voltage – 20 kV, working distance between the sample and lens – 10 mm, sample materials were covered with gold, detector – SE, environment – high vacuum (HV).

RESULTS AND DISCUSSION

Synthesis in unstirred suspensions

Hydrothermal reactions rapidly occur in CaO mixtures with amorphous silica – the initial substances react completely already during the first two hours of isothermal during in the medium of saturated steam at a temperature

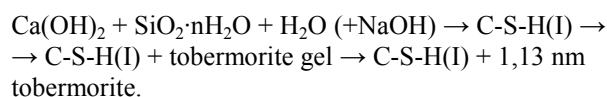
of 175 °C, which results in the formation of semi-crystalline calcium silicate hydrate C-S-H(I) ($d = 0.304$; 0.279; 0.182 nm). An additive of NaOH does not have a noticeable influence on the mineral composition of products as also only C-S-H(I) forms. However, by getting inserted into the structure of C-S-H(I) it influences the temperature of re-crystallisation of this compound into wollastonite, which falls from 837 °C to 757 °C (Fig. 1, b, curves 1, 2).

Upon extending the duration of synthesis up to 4 hours no new derivatives form, but changes occur in the structure of C-S-H(I), i. e. a degree of crystallinity increases. This is proved by an increase in the intensity of 0.304 nm X-ray diffractive peak, and in particular by the origination of a new peak of 0.73 nm, which is typical of the whole group of tobermorite minerals showing certain orderliness in the ab plane. In DSC curves the impact of NaOH remains the same – the temperature of C-S-H(I) transition into wollastonite is reduced from 844 °C to 757 °C (Fig. 1, b, curve 3).

Upon extending the duration of hydrothermal curing up to 8 hours, there forms the rudiments of 1.13 nm tobermorite, i. e. tobermorite gel ($d = 1.13$; 0.73; 0.307; 0.182 nm), which is characterised by a broad 1.13 nm peak. A small content of Na_2O additive (1 % or 3 %) does not hinder the formation of this compound. Upon adding more of the additive (5 % – 10 %) no tobermorite gel forms and the only product that remains is C-S-H(I), like in the case of four-hour duration (Fig. 1, a, curve 4).

When a synthesis is carried out for 16 hours, crystalline 1.13 nm tobermorite ($d = 1.13$; 0.307; 0.297; 0.182 nm) already forms (Fig. 2, a, curve 1). A product of a similar composition is obtained upon adding 5 % of Na_2O to the mixture. However, if the content of this additive is increased to 7 % or 10 %, only tobermorite gel forms (Fig. 2, a, curves 3–4) and the exothermal effect's temperature again significantly falls: from 840 °C to 761 °C.

Upon extending the duration of hydrothermal curing in the medium of saturated steam up to 24 hours, the crystallinity degree of the formed tobermorite increases in the mixtures without any additives (Fig. 3, curve 1), but there remains some non-recrystallised C-S-H(I). Upon adding 5 % of Na_2O additive the crystallinity degree of 1.13 nm tobermorite nearly does not change (Fig. 3, curves 2–3), whereas upon increasing the content of this additive the crystallinity degree of tobermorite starts decreasing (Fig. 3, curve 4). In summary of research results it can be stated that under the investigated conditions the reactions of calcium silicate hydrates formation in CaO and amorphous silica mixtures with and without the NaOH additive take place according to the same scheme:



The influence of an amount of NaOH additive on the mineral composition and duration of compounds existence of the products obtained during hydrothermal synthesis at a 175 °C temperature can be represented by this scheme (Fig. 4).

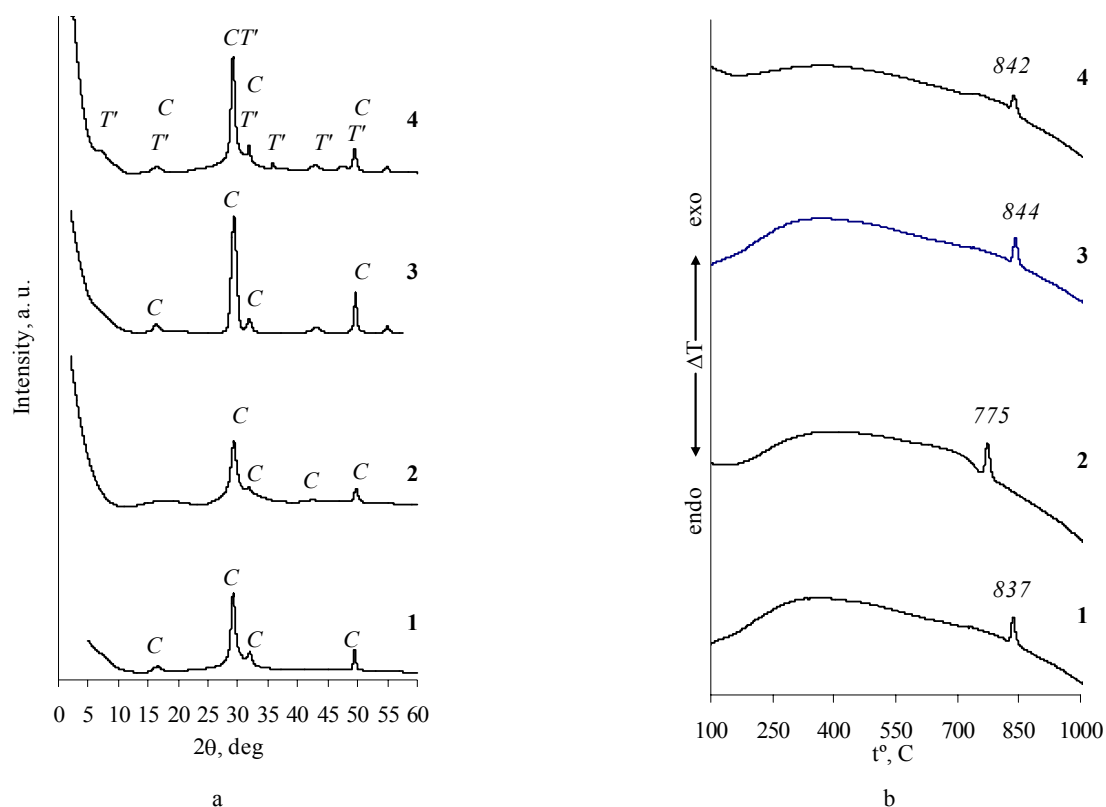


Fig. 1. XRD patterns (a) and DSC curves (b) of synthesis products, when duration of curing and Na_2O content: 1 – 2 h, $\text{Na}_2\text{O} = 0\%$; 2 – 2 h, $\text{Na}_2\text{O} = 5\%$; 3 – 4 h, $\text{Na}_2\text{O} = 0\%$; 4 – 8 h, $\text{Na}_2\text{O} = 0\%$. Indexes: C – C-S-H(I); T' – tobermorite gel

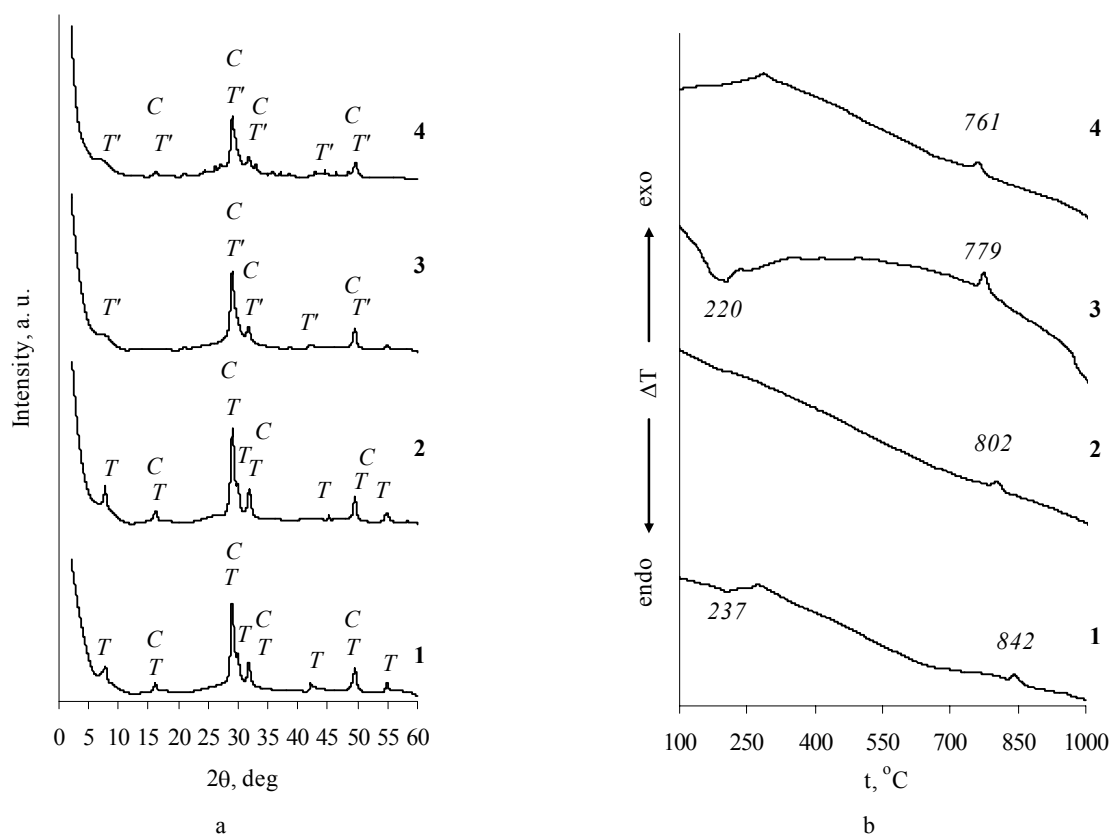


Fig. 2. XRD diffraction patterns and DSC curves of synthesis products from $\text{CaO-SiO}_2 \cdot n\text{H}_2\text{O}$ mixtures. Temperature – 175°C when duration of curing is 16 h and Na_2O content, %: 1 – 0; 2 – 5; 3 – 7; 4 – 10. Indexes: C – C-S-H(I), T' – tobermorite gel, T – 1.13 nm tobermorite

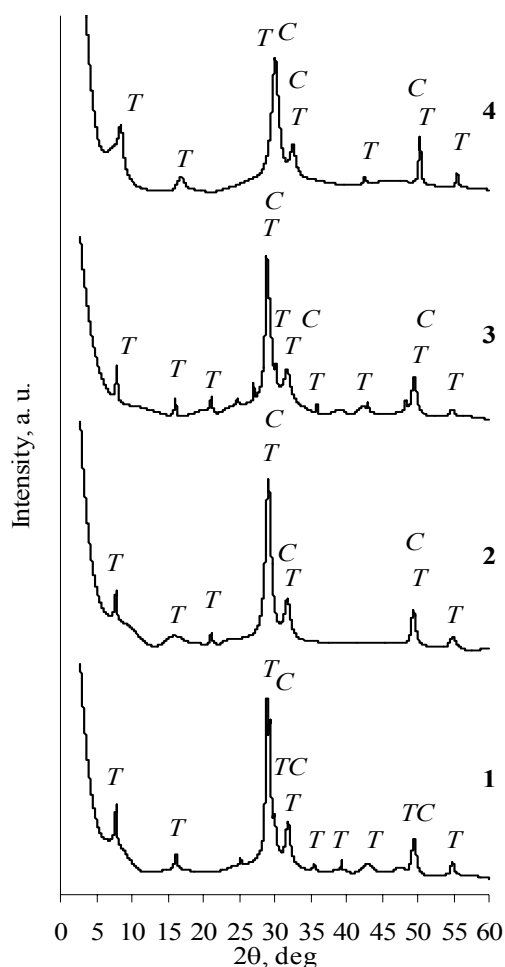


Fig. 3. XRD patterns of synthesis at 175 °C temperature products from CaO and SiO₂·nH₂O mixtures when duration of curing is 24 h and Na₂O additive content, %: 1 – 0; 2 – 1; 3 – 5; 4 – 10. Indexes: T – 1.13 nm tobermorite, C – C-S-H(I)

The amount of Na₂O additive up to 5 %, in fact, has no influence on the crystallinity of tobermorite, but upon adding more alkalis in the initial mixtures it stabilises C-S-H(I) and impedes the re-crystallisation of this compound into tobermorite gel and later – into 1.13 nm tobermorite.

The majority of industrial silicate raw materials are

polluted with aluminium impurities and therefore a complex influence of Al³⁺ and Na⁺ ions on the formation of tobermorite was investigated.

In the environment of saturated steam at a temperature of 175 °C 1.13 nm tobermorite and C-S-H(I) already formed after two hours of synthesis in both CaO-SiO₂·nH₂O mixtures with γ-Al₂O₃ and those containing also NaOH additive.

After 4 h of isothermal curing the crystallinity degree of 1.13 nm tobermorite is directly dependent on the amount of NaOH additive: the larger is the amount of Na⁺ ions in the initial suspension the larger amount of tobermorite is obtained and its degree of crystallinity also increases (Fig. 5, a, curves 1–4). Yet, a certain amount of C-S-H(I) remains but its content respectively decreases with a content of NaOH additive increasing. This is demonstrated by the decreasing exothermal effect in DSC curves at a temperature of 845 °C–757 °C (Fig. 5, b, curves 1–4).

Upon extending the duration of synthesis up to 8 hours, practically the whole C-S-H(I) transforms into 1.13 nm tobermorite from CaO-SiO₂·nH₂O-Al₂O₃-H₂O mixture (without any NaOH additive). This is testified to the fact that no exothermal effect of wollastonite formation practically remains in DSC curves (Fig. 5, b, curve 1).

This is the reason why NaOH doesn't influence anymore the composition of hydrothermal reaction products – in all cases there was obtained 1.13 nm tobermorite of high crystallinity degree (Fig. 5, a, curves 2–4). Amount and degree of crystallinity were determined by intensity of 1.13 nm and 0.297 nm peaks on XRD patterns. It remained single phase after 16 h and 24 h of hydrothermal curing in the medium of saturated steam at 175 °C temperature.

In summary it can be stated that γ-Al₂O₃ stimulates the formation of tobermorite in CaO mixtures with SiO₂·nH₂O. Na⁺ ions get inserted into the structure and neutralise a negative charge in silicate chains due to Si⁴⁺ replacement with Al³⁺. At the beginning of synthesis NaOH additives in CaO-SiO₂-Al₂O₃-H₂O mixtures stimulate tobermorite formation. After 8 hours of synthesis the latter compound becomes the only one in the mixtures without NaOH additive and therefore it's not worth while additionally inserting alkalis during long-lasting synthesis.

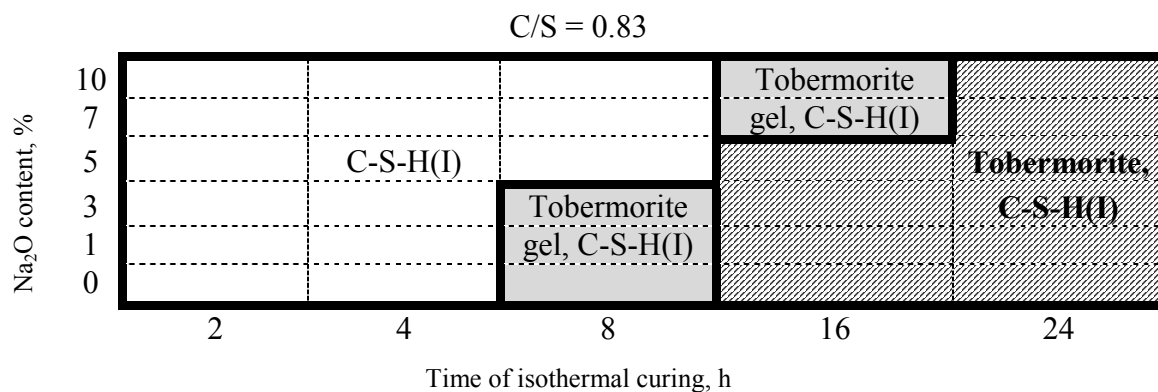


Fig. 4. Influence of sodium oxide quantity and duration of synthesis at 175 °C temperature on the mineral composition of products

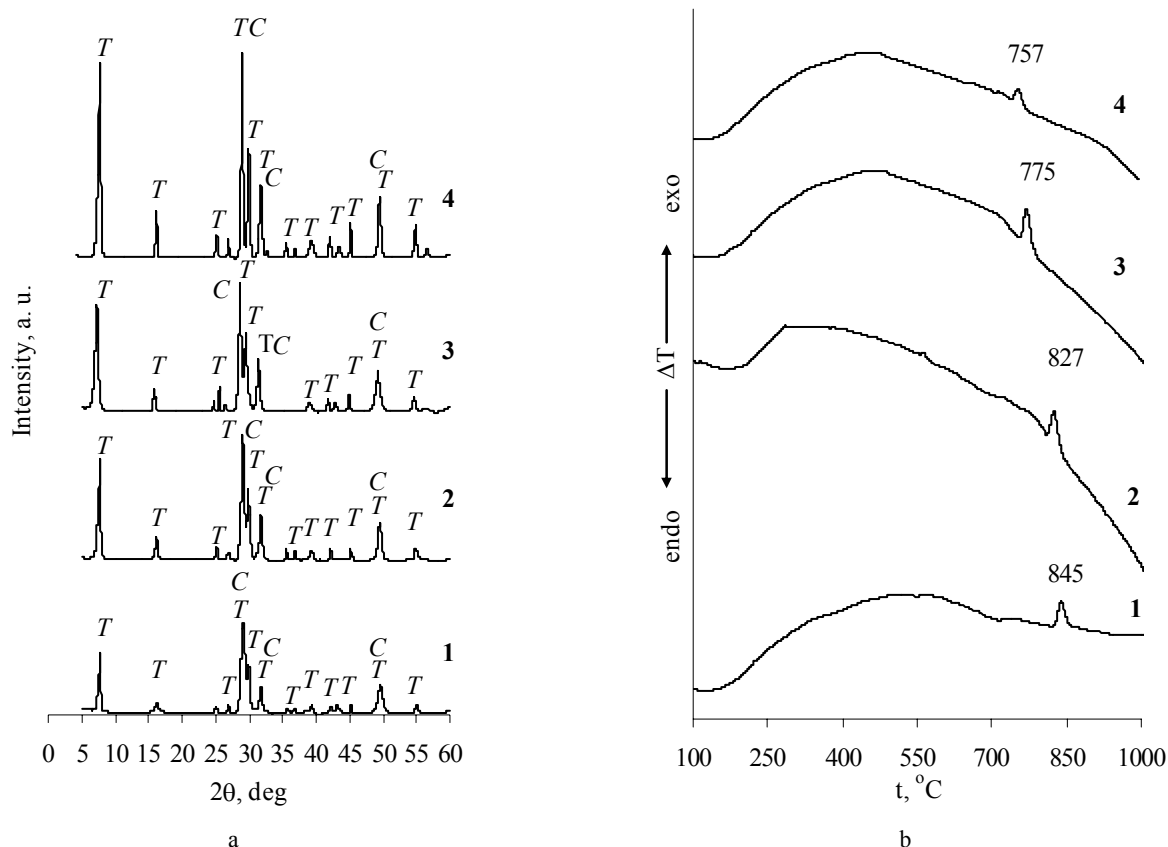


Fig. 5. XRD patterns (a) and DSC curves (b) of synthesis products from CaO and amorphous silica mixtures with $\gamma\text{-Al}_2\text{O}_3$ additive when synthesis duration is 4 h. Amount of Na_2O added, %: 1 – 0; 2 – 1; 3 – 5; 4 – 10. Indexes: T – 1.13 nm tobermorite, C – C-S-H(I)

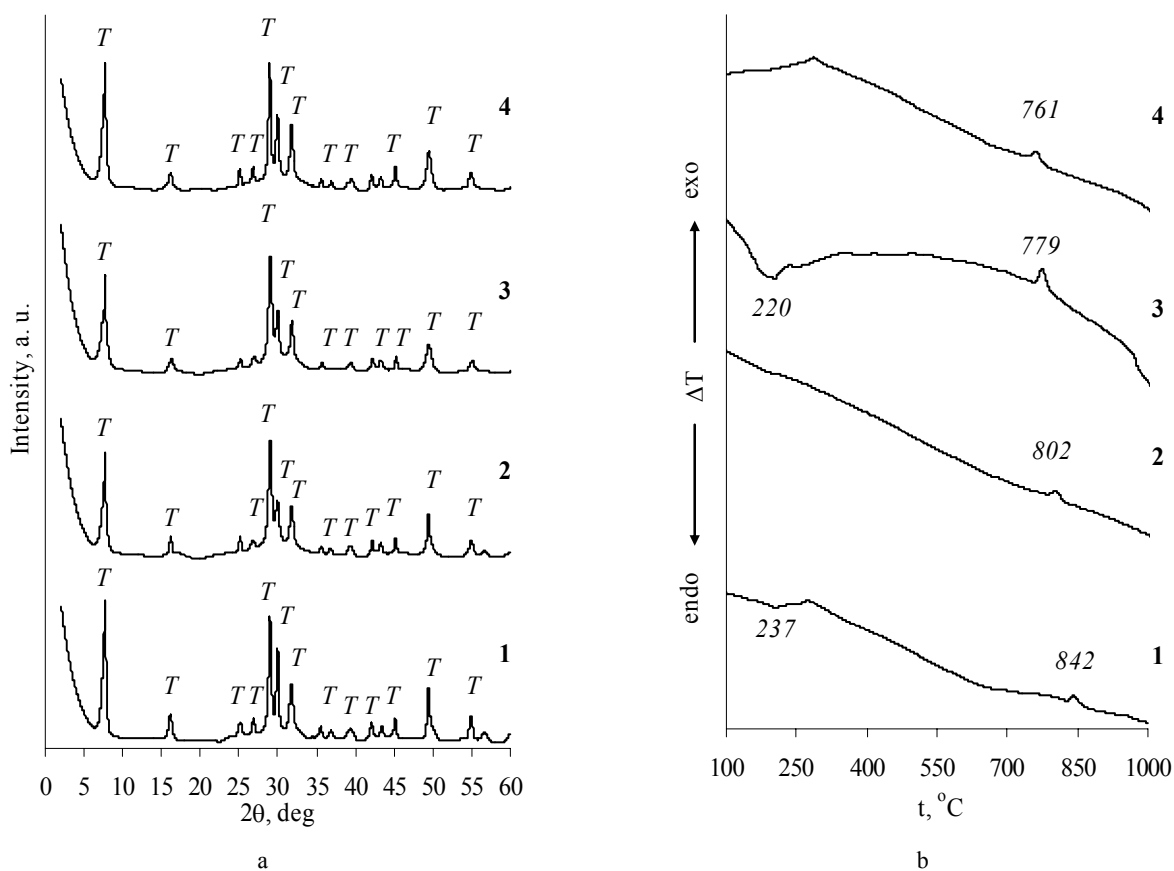


Fig. 6. XRD patterns (a) and DSC curves (b) of synthesis products from CaO and amorphous silica mixtures with $\gamma\text{-Al}_2\text{O}_3$ additive when synthesis duration is 8 h. Amount of Na_2O added, %: 1 – 0; 2 – 1; 3 – 5; 4 – 10. Indexes: T – 1.13 nm tobermorite

Synthesis in stirred suspensions

The influence of γ - Al_2O_3 and NaOH additives on the mineral composition of the obtained product becomes especially apparent after a longer synthesis when suspensions are stirred. Considering the fact that the best crystallised 1.13 nm tobermorite was obtained in unstirred suspensions with a 5 % content of Na_2O , only this amount of additive was used. Mixtures with the molar ratios of $\text{C/S}=0.83$ and $\text{C/(S+A)}=0.83$ and $\text{A/(S+A)}=0.025$ were synthesised. Syntheses with and without NaOH additive were carried out simultaneously.

After 24 h of hydrothermal synthesis at 175 °C temperature, CaO and amorphous silica mixtures without additives produced 1.13 nm tobermorite of a low degree of crystallinity having a 1.13 nm peak of medium intensity but wide and interrelated peaks of 0.307 nm and 0.297 nm (Fig. 7, curve 1). Upon adding γ - Al_2O_3 additive, after 24 h of treatment tobermorite of a high degree of crystallinity was obtained in both cases – with and without the Na_2O additive (Fig. 7, curves 2, 3). Upon extending the duration of isothermal curing up to 32 h the composition of synthesis products in the mixture has not changed. Upon adding 5 % of Na_2O of the dry substance mass, it has intensified hydrothermal reactions – 1.13 nm tobermorite started re-crystallizing into thermodynamically most stable monobasic calcium silicate hydrate – xonotlite (Fig. 7, curve 5).

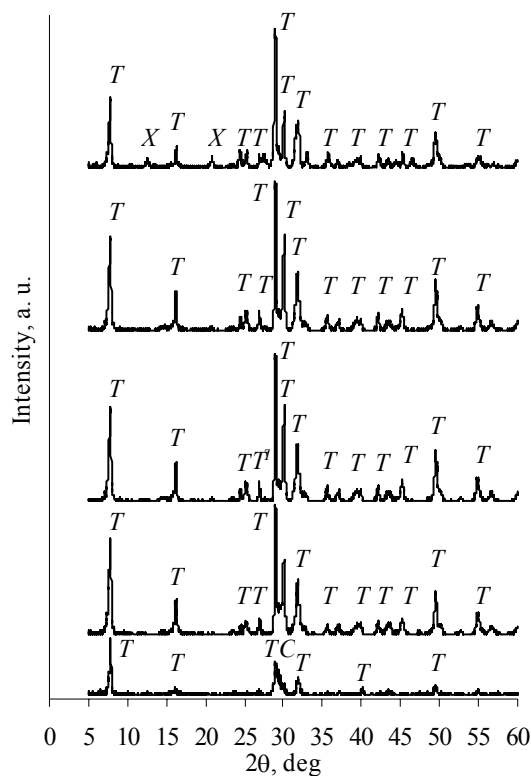
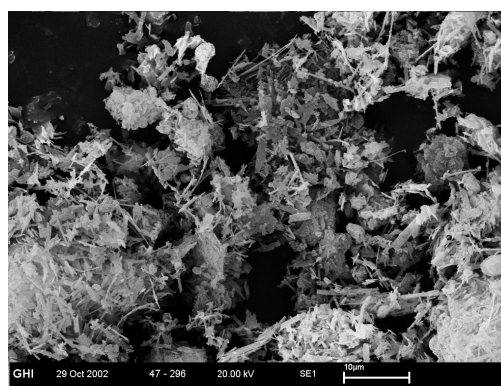
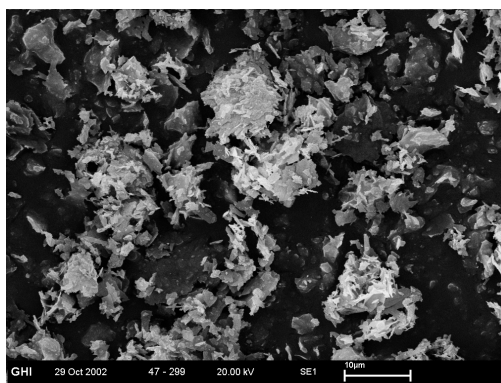


Fig. 7. XRD diffraction patterns of synthesis products at 175 °C temperature, when composition of initial mixtures $\text{C/(S+A)}=0.083$, amount of additives and synthesis duration: 1 – $\text{A/(S+A)}=0$, $\text{Na}_2\text{O}=0\%$, $\tau=24$ h; 2 – $\text{A/(S+A)}=0.025$, $\text{Na}_2\text{O}=0\%$, $\tau=24$ h; 3 – $\text{A/(S+A)}=0.025$, $\text{Na}_2\text{O}=5\%$, $\tau=24$ h; 4 – $\text{A/(S+A)}=0.025$, $\text{Na}_2\text{O}=0\%$, $\tau=32$ h; 5 – $\text{A/(S+A)}=0.025$, $\text{Na}_2\text{O}=5\%$, $\tau=32$ h. Indexes: T – 1.13 nm tobermorite, C – C-S-H(I), X – xonotlite

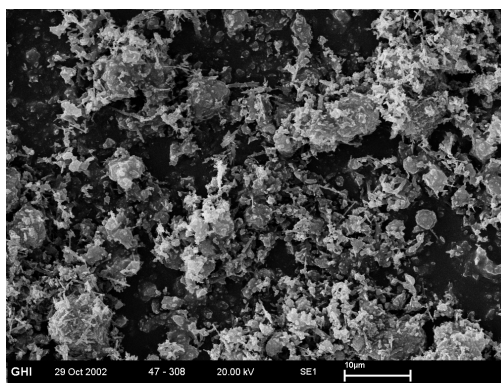
At a temperature of 175 °C from CaO and amorphous silica mixtures 1.13 nm tobermorite forms crystals of up to 10 micrometer in length shaped like needles and plate-shaped ones of 4 μm –6 μm (Fig. 8, a); however the majority of them are bound into large agglomerates by semi-amorphous C-S-H(I) that has not managed to re-crystallise yet. Thus, as confirmed by SEM investigation, an isomorphous mixture of 1.13 nm tobermorite and C-S-H(I) forms in $\text{CaO-SiO}_2\text{-nH}_2\text{O-H}_2\text{O}$ system during 24 h at a temperature of 175 °C. Upon adding γ - Al_2O_3 additive into the system, no accumulations of amorphous particles are detected any more. The morphology of 1.13 nm tobermorite also changes – needle-shaped crystals are not present any longer and the plates enlarge to 8 μm –10 μm (Fig. 8, b).



a



b



c

Fig. 8. SEM micrographs (magnification – 5000 $\times$) of synthesis products from mixtures with molar ratio $\text{C/(S+A)}=0.83$, when duration is 24 h, and sort of additives: a – without additives; b – with γ - Al_2O_3 ; c – with γ - Al_2O_3 and 5 % Na_2O

Upon adding the amount of NaOH accounting for 5 % of Na₂O of dry substances into the mixture the composition of which can be described by the molar ratio of C/(S+A)=0.83 and A/(S+A)=0.025, the dimensions of 1.13 nm tobermorite plates decrease twofold or threefold – their diameter reaches only 3 µm – 5 µm (Fig. 8, c).

Thermal type of 1.13 nm tobermorite

1.13 nm tobermorite may be of three types: normal, mixed and anomalous. The type is determined according the fact whether its crystal lattice shrinks from 1.13 nm to 0.9 nm or not upon heating this compound at a temperature of 300 °C. Tobermorite synthesised from pure mixtures that do not contain any additives is normal (Fig. 9, curve 1).

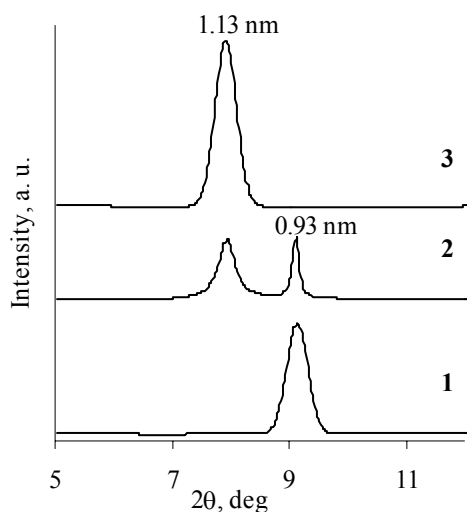


Fig. 9. Thermal type of tobermorite. XRD patterns after 3 h heating at 300 °C temperature. Duration of synthesis – 24 h and composition of initial mixtures: 1 – C/S=0.83, Na₂O=0 %; 2 – C/(S+A)=0.83 ir A/(S+A)=0.025, Na₂O=0 %, 3 – C/(S+A)=0.83 ir A/(S+A)=0.025, Na₂O=5 %

Meanwhile, upon adding γ-Al₂O₃ into initial mixtures, tobermorite of a mixed thermal type forms (Fig. 9, curve 2), whereas upon adding sodium hydroxide into it – anomalous one forms (Fig. 9, curve 3).

CONCLUSIONS

A content of NaOH additive above 5 % in CaO mixtures with amorphous silica slows down the formation of 1.13 nm tobermorite and stabilises C-S-H(I).

At the beginning, NaOH increases the amount and crystallinity degree of 1.13 nm tobermorite forming in CaO-SiO₂-nH₂O-Al₂O₃-H₂O mixtures but later its influence becomes insignificant.

Na⁺ ions that get inserted into a lattice of 1.13 nm tobermorite together with Al³⁺ ions reduce the size of the forming crystals.

When suspensions are stirred, due to Al³⁺ insertion into a structure 1.13 nm tobermorite of a mixed thermal type forms instead of the normal one, and in case of a complex [Al³⁺+Na⁺] substitution anomalous 1.13 nm tobermorite is obtained.

REFERENCES

1. **Kalousek, G. L.** Crystal Chemistry of Hydrous Calcium Silicates: I. Substitution of Aluminum in the Lattice of Tobermorite *Journal of American Ceramics Society* 40 1957: pp. 74–80.
2. **Diamond, S., White, J. L., Dolch, W. L.** Effects of Isomorphous Substitution of Hydrothermally Synthesized Tobermorite *American Mineralogist* 51 1966: pp. 388–401.
3. **Šiaučiusas, R.** Hydrothermal Synthesis of Al-substituted Calcium Silicate Hydrates and Getting of Effective Thermal-insulating Materials on Its Basis *PhD Dissertation* 1989, Kaunas (in Russian).
4. **Šiaučiusas, R., Sasnauskas, K., Balandis, A.** Research of Synthesis Processes of Low-base Calcium Silicate Hydrates with Addition of Al-bearing Components *Cheminė technologija* 2 1999: pp. 31–38 (in Russian).
5. **Rupšytė, E.** The Change of Properties and Mineralogical Composition of Calcium Silicate Hydrates during Carbonatisation *PhD Thesis* Kaunas, 2002 (in Lithuanian).
6. **Klimesch, D. S., Ray, A.** DTA-TG Study of the CaO-SiO₂-H₂O and CaO-Al₂O₃-SiO₂-H₂O Systems under Hydrothermal Conditions *Journal of Thermal Analysis and Calorimetry* 56 1999: pp. 27–34.
7. **El-Hemaly, S. A. S., Mitsuda, T., Taylor, H. F. W.** Synthesis of Normal and Anomalous Tobermorites *Cement and Concrete Research* 7 1977: pp. 429–438
8. **Hara, N., Inoue, N.** Thermal Behaviour of 11Å Tobermorite and Its Lattice Parameters *Cement and Concrete Research* 10 1980: pp. 53–60.
9. **Langton, C. A., White, E. L., Grutzeck, W. M., Roy, D. M.** High Temperature Cement with Geothermal Application *SPE Oilfield and Geothermal Chemistry Symposium* 28–30 May 1980. Stanford, USA.
10. **Nocun-Wzelik, W.** Effect of Some Additions on Autoclaved Calcium Silicate Hydrates *Cement and Concrete Research* 27 1997: pp. 83–92.
11. **El-Korashy Sabry, A.** Chemical Studies on the Reactions of Synthetic 1.13 nm Tobermorite with Alkali Metal Hydroxydes at Room Temperature *Monatshefte für Chemie* 128 1997: pp. 599–607.
12. **Nelson Eric, B., Kalousek George, L.** Effects of Na₂O on Calcium Silicate Hydrates at Elevated Temperatures *Cement and Concrete Research* 7 1977: pp. 689–694.
13. **Hong, S. Y., Glasser, F. P.** Alkali Sorption by C-S-H and C-A-S-H Gels Part II. Role of Alumina *Cement and Concrete Research* 32 2002: pp. 1101–1111.
14. **Siauciusas, R., Janickis, V., Palubinskaite, D., Ivanauskas, R.** The Sorption Properties of Tobermorite Modified with Na⁺ and Al³⁺ Ions *Ceramics-Silikaty* 48 2004: pp. 76–82.
15. **Youssef, H., Ibrahim, D., Komarneni, S., MacKenzie, K. J. D.** Synthesis of 11Å Al-substituted Tobermorite from Trachyte Rock by Hydrothermal Treatment *Ceramics International* 36 2010: pp. 203–209.
16. **Jing, Z., Jin, F., Yamasaki, N., Maeda, H., Ishida, E. H.** Potential Utilization of Riverbed Sediments by Hydrothermal Solidification and Its Hardening Mechanism *Journal of Environmental Management* 90 2009: pp. 1744–1750.