

THE INFLUENCE OF STIRRING AND γ - Al_2O_3 OR Na_2O ADDITIVES ON THE GYROLITE FORMATION IN THE CaO -QUARTZ- H_2O SYSTEM

KESTUSIS BALTAKYS, RAIMUNDAS SIAUCIUNAS

Department of Silicate Technology, Kaunas University of Technology, Radvilenu 19, LT - 50270 Kaunas, Lithuania

E-mail: kestutis.baltakys@ktu.lt

Submitted September 29, 2006; accepted November 28, 2006

Keywords: Gyrolite; Z-phase; C-S-H(I); Calcium-silicate-hydrate; X-Ray diffraction

The influence of stirring and γ - Al_2O_3 or Na_2O additives on the gyrolite ($\text{Ca}_{16}\text{Si}_{24}\text{O}_{60}(\text{OH})_8 \cdot 14\text{H}_2\text{O}$) formation process in the CaO -quartz- H_2O mixture has been examined. The molar ratios of primary mixtures were $\text{CaO}/(\text{SiO}_2 + \text{Al}_2\text{O}_3) = 0.66$ and $\text{Al}_2\text{O}_3/(\text{SiO}_2 + \text{Al}_2\text{O}_3) = 0$ or 0.025 . Water/solid ratio of the suspension was equal to 10.0. Hydrothermal synthesis has been carried out in rotating autoclave (10 rpm) under the saturated steam pressure at 200°C ; the duration of isothermal curing was 2, 4, 6, 8, 16, 24, 32, 48, or 72 hours. It has been found that in the pure mixture the presence of stirring has not positive influence on the gyrolite formation. Even after 72 h hydrothermal treatment at 200°C 1.13 nm tobermorite ($\text{Ca}_3\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$) dominates in the products. In the stirred CaO -quartz- Na_2O - H_2O system gyrolite formed more quickly - 24 hours of isothermal curing at 200°C than in the unstirred suspension - 32 h. The results show that the addition of γ - Al_2O_3 in the CaO -quartz- Na_2O - H_2O suspension stabilizes gyrolite and prevents its transformation to pectolite ($\text{NaCa}_2\text{Si}_3\text{O}_8(\text{OH})$).

INTRODUCTION

Gyrolite ($\text{Ca}_{16}\text{Si}_{24}\text{O}_{60}(\text{OH})_8 \cdot 14\text{H}_2\text{O}$), a calcium silicate hydrate, rarely occurs as a natural mineral in association with zeolites [1]. Recently, the interest in gyrolite increases because the new possibilities of application were found: it may be used reduce heavy metal ions and remove them from wastewaters [2] and it is known for its selectivity to DNA clearance [3].

Meanwhile, hydrothermal synthesis of gyrolite is a long and complex process. Gyrolite was first synthesized by Flint et al. (1938) [4] and subsequently by Taylor (1964) [5] Meyer and Jaunarajs (1961) [6], Števela and Petrovič (1983) [7] and Jauberthie (1996) [8]. They reported the stability of gyrolite under saturated water vapor pressure between 120 and 200°C . Above 200°C , truscottite ($\text{Ca}_{14}\text{Si}_{24}\text{O}_{58}(\text{OH})_8 \cdot 2(\text{H}_2\text{O})$) is the stable phase, although gyrolite can be metastably produced up to 270°C . Their formation, stability and phase relationship were studied and plotted in phase equilibrium diagrams by Roy and Harker [9], Harker [10] and Taylor [5]. However, almost all of these tests were performed with SiO_2 component using its active forms such as amorphous SiO_2 , finely dispersed aerosil, silicic acid.

The results of the research showed that in the unstirred suspension optimal temperature of gyrolite synthesis is rather high (approximately 200°C) and the duration is long (about 32 h) when amorphous $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ is used as SiO_2 component [11, 12]. More-

over, there is little data (and it is not comprehensive) about the synthesis of gyrolite and the sequence of the formed intermediate/new compounds and the influence of additives on it, when a less active but the most common natural form of SiO_2 - quartz is used [11, 13].

In order to use more broadly gyrolite in practice the manufacturing of this material must be cut in price, i.e., by reduction of the duration of hydrothermal treatment and/or its temperature. As in the case of other heterogeneous chemical reactions, also calcium silicate hydrates formation is faster when the reaction mixture is stirred [14, 15]. However, no data is available about the influence of stirring on gyrolite synthesis in the CaO -quartz- H_2O suspension and the influence of γ - Al_2O_3 and Na_2O additives on it. It is necessary to seek the additives which can positively enhance or facilitate the formation of gyrolite.

The aim of this work was to determine the parameters of gyrolite hydrothermal synthesis in the stirred CaO -quartz- H_2O suspension and to examine the influence of γ - Al_2O_3 and Na_2O additives.

EXPERIMENTAL

In this paper the following raw materials were used: fine-grained quartz (99.5 % Reachim, Russia; specific surface area $S_a = 1100 \text{ m}^2/\text{kg}$), after grinding, washing off from iron impurities by hydrochloric acid; calcium oxide (99.5 % Reachim, Russia; $S_a = 548 \text{ m}^2/\text{kg}$)

produced by calcinations of calcium carbonate at 1000°C for 6 hours; NaOH solution (Delta Chem, Czech Republic; $c = 1.04\%$); $\gamma\text{-Al}_2\text{O}_3$ (Lachema, Czech Republic;) obtained by heating $\text{Al}(\text{OH})_3$ for 5 hour at 550°C ($S_a = 712\text{ m}^2/\text{kg}$).

The molar ratios of primary mixtures were $C/(S + A) = 0.66$ and $A/(S + A) = 0$ or 0.025 ($C\text{-CaO}$, $S\text{-SiO}_2$, $A\text{-Al}_2\text{O}_3$). The amount of NaOH, corresponding to 5 % of Na_2O from the mass of dry materials, added in the form of solution and additionally added necessary quantity of water that water/solid ratio of the suspension was equal to 10.0. Hydrothermal synthesis has been carried out in rotating autoclave A-08 (10 rpm) under the saturated steam pressure at 200°C temperature; the duration of isothermal curing was 2, 4, 6, 8, 16, 24, 32, 48, or 72 hours. The products of the synthesis was filtered, rinsed with ethyl alcohol to prevent carbonization of material, dried at a temperature of $100^\circ\text{C} \pm 5$, and sieved through a sieve with a mesh width of 50 μm .

The X-ray powder diffraction (XRD) data were collected with DRON-6 X-ray diffractometer with Bragg-Brentano geometry using Ni-filtered $\text{Cu K}\alpha$ radiation and graphite monochromator, operating with voltage of 30 kV and emission current of 20 mA. The step-scan covered the angular range $2\text{-}60^\circ$ (2θ) in steps of $2\theta = 0.02^\circ$. For diffraction profile refinement under the pseudoVoigt function and for description of the diffractive background under the 3rd degree Tchebyshev polynomial, we used a computer program X-fit [16].

Simultaneous thermal analysis (STA: differential scanning calorimetry-DSC and thermogravimetry-TG) was also employed for measuring the thermal stability and phase transformation of synthesized products at a heating rate of $15^\circ\text{C}/\text{min}$, the temperature ranged from 30°C to 1000°C under air atmosphere. The test was carried out on a Netzsch instrument STA 409 PC Luxx. The ceramic sample handlers and crucibles of Pt-Rh were used.

Scanning electron microscopy (SEM) (Oxford ISIS Leo 440 i) coupled with energy dispersive X-ray spectrometer (EDS) was performed using a accelerating voltage of 20 kV and a working distance of 10 mm for SEM observation and a 200 s accumulation time for EDS analysis.

The specific surface area of the raw materials was determined by the Blaine's method with air permeability apparatus (Model 7201, Toni Technik Baustoffprüf-systeme GmbH).

RESULTS AND DISCUSSION

XRD, SEM and DSC analysis showed that stirring does not have positive influence in the CaO -quartz- H_2O system because gyrolite does not form even after 72 h

hydrothermal treatment at 200°C and in the products dominate 1.13 nm tobermorite which is hard to disrupt (Figures 1a, c, e).

The dehydration of 1.13 nm tobermorite with $C/S = 0.66$ proceeds in a different way than 1.13 nm tobermorite with $C/S = 0.83$. The latter has characteristic sharp endothermic effect at 220°C , which is related to the loss of 4.5 molecules of water. Meanwhile, in the sample with $C/S = 0.66$, this effect was not observed and analogical quantity of water ($\sim 6\text{-}7\%$) is loosed in the temperature range from 125 to 280°C (Figure 1c).

In the presence of 2.6 % $\gamma\text{-Al}_2\text{O}_3$ in the CaO -quartz- H_2O mixture, already after 72 h of isothermal curing, a smaller quantity of 1.13 nm tobermorite forms, because in XRD pattern basic reflection with d -spacing-1.13 nm was less intensive as compared with a pure system (Figure 1b). Furthermore, the low-intensity basic reflection with d -spacing-2.2 nm shows the beginning of gyrolite gel formation.

The DSC analysis confirmed the results obtained by XRD: the DSC curve exhibits the exothermic peak at 861°C , characterizing the transformation of gyrolite gel into wollastonite and the endothermic effect at 224°C , characteristic to 1.13 nm tobermorite (Figure 1d).

As far as we know it is the first evidence of positive influence of $\gamma\text{-Al}_2\text{O}_3$ on gyrolite synthesis because in the unstirred suspensions this additive stimulates the formation of $C\text{-S-H(I)}$, calcium aluminum silicate hydrates, 1.13 nm tobermorite and xonotlite [11, 12].

Already in 1974, Taylor [17] noted that at temperatures higher than 150°C tobermorite is thermodynamically unstable in the mixtures with $C/S > 0.8$ and transfers to xonotlite. The results of the tests performed by us showed [11, 12] that in the unstirred suspensions this tendency proves out also in the mixture with lower C/S ratio according to the stoichiometry of gyrolite: tobermorite transfers into xonotlite when the synthesis is proceeding for 48 h.

Moreover, in the stirred suspensions and after prolonged synthesis (72 h), 1.13 nm tobermorite becomes unstable and transfers into a compound with the stoichiometry corresponding to the molar ratio of the primary mixture - gyrolite.

Scanning electron microscopy (SEM) showed that in the products with $\gamma\text{-Al}_2\text{O}_3$ are much shorter, needle-shaped tobermorite crystals comparing with the pure system (Figures 1e,f). Meanwhile, between and near these crystals, there are very small plate crystallites characteristic to gyrolite gel.

Analogical research was performed with Na_2O additive. It has been determined that in the stirred CaO -quartz- Na_2O - H_2O suspension, almost all quartz reacts during the first 2 hours of hydrothermal treatment: endothermic effect at 573°C was not identified in the DSC curve, and only small-intensity basal reflection of

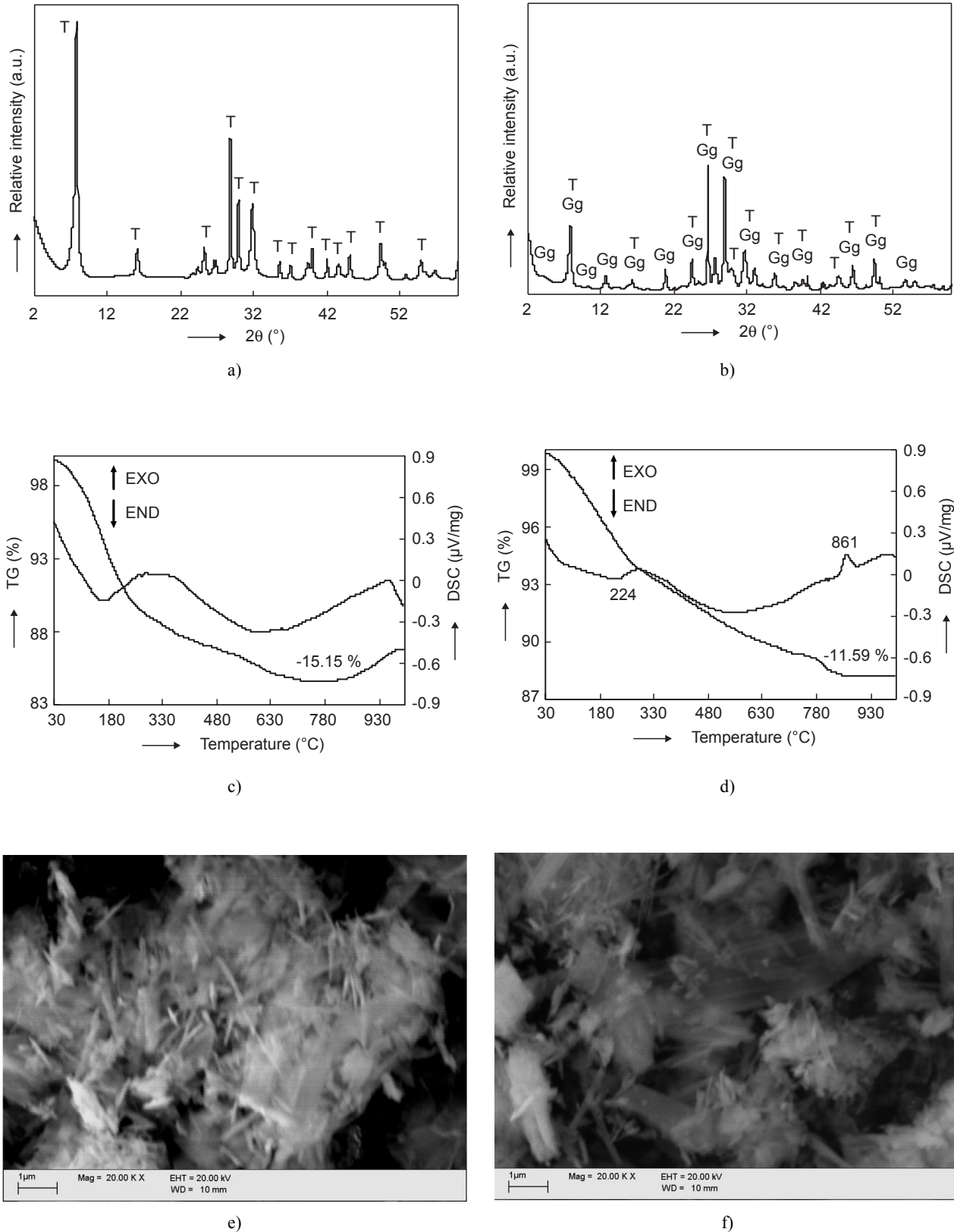


Figure 1. X-ray diffraction patterns (a - pure CaO–quartz–H₂O system; b - with γ -Al₂O₃ additive), DSC curves (c - pure CaO–quartz–H₂O system; d - with γ -Al₂O₃ additive) and SEM pictures (e - pure CaO–quartz–H₂O system; f - with γ -Al₂O₃ additive) of the synthesis products. Duration of hydrothermal treatment at 200°C temperature is 72 hours. T:1.13 nm tobermorite, Gg:gyrolite gel.

quartz with d -spacing 0.334 nm appeared in the X-ray diffraction pattern (Figure 2, curve 1). In the synthesis products alone C-S-H(I) is identified (Figure 2, curve 1, exothermic peak at 784°C temperature). At a longer time of synthesis (8 hours) all quartz reacts (Figure 2, curve 4). Therefore, it is not coincidence that basic reflections, characteristic to gyrolite gel (d -spacing-2.2 nm) and Z-phase (d -spacing-1.5 nm), start dominating in the X-ray diffraction pattern of the reaction products (Figure 2, a, curve 4). This is confirmed by DTA

data as well: exothermic peak at $\sim 797^\circ\text{C}$ becomes wider and lower (Figure 2b, curve 4). However, in the unstirred suspensions at the temperature of 200°C the traces of low base calcium silicate hydrates appeared only after 16 h of isothermal curing [14].

It was determined that after prolonged hydrothermal treatment up to 16 hours, gyrolite starts to dominate in the products although quite large quantity of Z-phase remains (Figure 2, curve 5). It should be noted that Z-phase finishes transferring into gyrolite after 24 hours

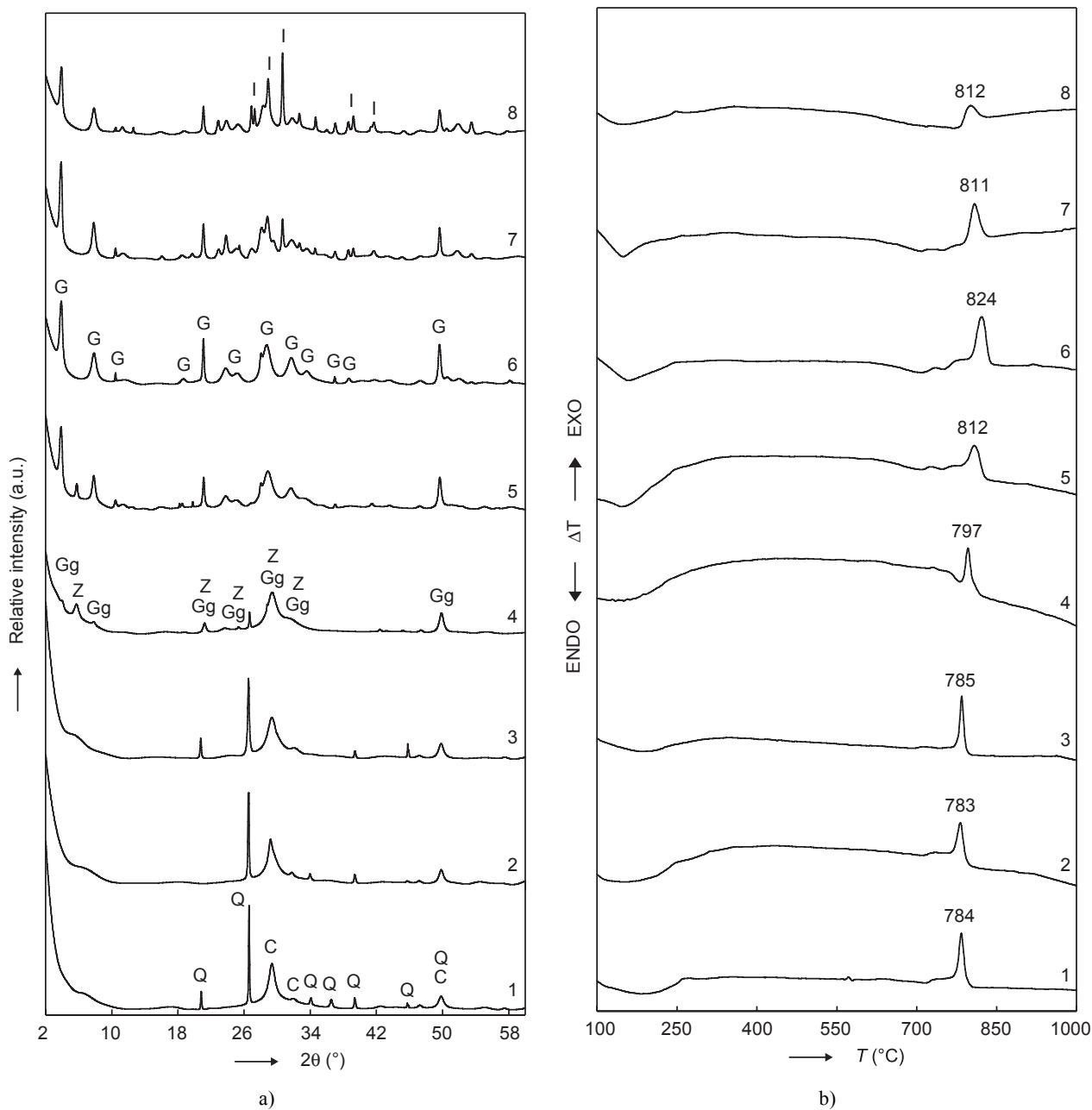
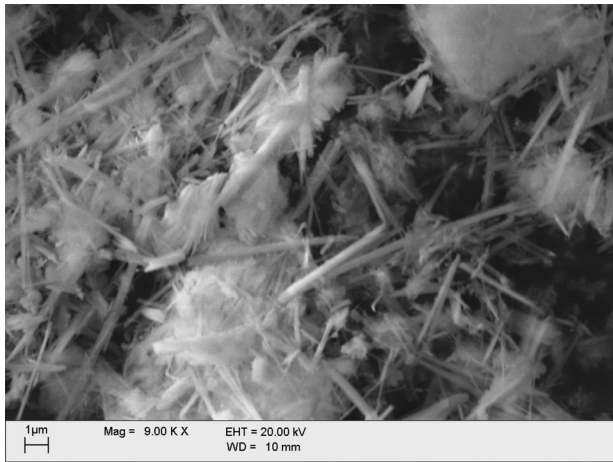


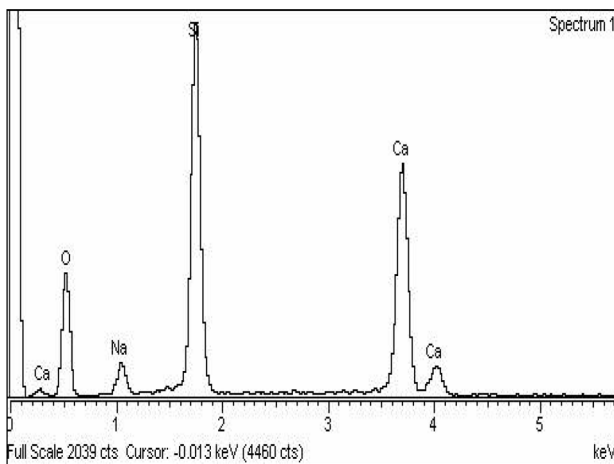
Figure 2. X-ray diffraction patterns (a) and DSC curves (b) of the synthesis products. Duration of hydrothermal treatment at 200°C temperature: 1-2 h, 2-4 h, 3-6 h, 4-8 h, 5-16 h, 6-24 h, 7-48 h, 8-72 h. Q: quartz, C: C-S-H (I), Z: Z-phase, Gg: gyrolite gel, G: gyrolite, I: pectolite.

of synthesis (as without stirring after 32 h) (Figure 2, curve 6). It should be underlined that gyrolite is metastable under given conditions because already after 48 h of isothermal curing the traces of new compound - pectolite are identified (Figure 2, curve 7).

The intensities of pectolite lines in X-ray diffraction pattern grows after prolonged synthesis for 72 h but the intensity of main gyrolite basic reflection decreases a little (Figure 2, curve 8). These data were confirmed by DTA measurements as well: a wide exothermic effect at 812°C, characterizing the transfer of low base calcium silicate hydrates into wollastonite, may be seen in Figure 2b, curve 8. A presence of two crystal morphologies can be seen in SEM micrographs: gyrolite plates and long, needle-shaped pectolite crystals that are formed on gyrolite plates and between them in the interlayers (Figure 3a). The results of EDS analysis confirmed that sodium enters into the structure of crystals after the long isothermal curing time (Figure 3b).



a)



b)

Figure 3. Scanning electron micrograph (a) and EDS analysis curve (b), 72 hours of isothermal curing at 200°C.

Thus, it has been determined that in the stirred CaO–quartz–Na₂O–H₂O system gyrolite is formed faster in 24 hours of isothermal curing at 200°C than in the unstirred suspension - 32 hours of synthesis. Moreover, in the stirred suspension gyrolite dominates longer as the main product (48 h, 200°C) as compared with an unstirred suspension (24 h, 200°C).

It should be stressed that the presence of γ -Al₂O₃ additive in the CaO–quartz–Na₂O–H₂O suspension stabilizes gyrolite and prevents its transformation to pectolite. Moreover, 1.13 nm tobermorite together with gyrolite were seen under all explored conditions (2-72 h, 200°C).

CONCLUSIONS

1. The presence of stirring does not have a positive influence on the crystallization of gyrolite in the CaO–quartz–H₂O system - it does not form even after 72 h hydrothermal treatment at 200°C and in the products 1.13 nm tobermorite dominate which is hard to disrupt.
2. γ -Al₂O₃ was found to have a favorable influence on gyrolite synthesis in the CaO–quartz–H₂O system: after 72 h of hydrothermal treatment at 200°C 1.13 nm tobermorite becomes unstable and begins to transfer into compound with the stoichiometric composition corresponding to the molar ratio of the primary mixture - gyrolite.
3. Na₂O additive more positively affects gyrolite synthesis in stirred suspensions than in the unstirred one: when 5 % of Na₂O was added in the CaO–quartz–H₂O system, gyrolite was formed faster - already after 24 hours of synthesis at 200°C. Moreover, in the stirred suspension gyrolite dominates longer as the main product (48 h, 200°C) when compared it with an unstirred suspension (24 h, 200°C).

Acknowledgement

The authors are very grateful to A. Baltusnikas - a Head of X-ray diffraction analysis laboratory of KTU for carrying out X-ray analysis experiments and for his constructive comments on the paper.

References

1. <http://mineral.galleries.com/minerals/silicate/gyrolite/gyrolite.htm>, as on 17 May 2006
2. Miyake M., Iwaya M., Suzuki T.: J.Am.Ceram.Soc. 73, 3524 (1990).
3. Winters M. A., Richter J. D., Sagar S. L., Lee A. L., Lander R. J.: Biotechnol.Prog. 19, 440 (2003).
4. Flint E. P., Mc Murdie H. F., Wells L. S.: J.Res.Nat.Bur. Stand. 21, 617 (1938).
5. Taylor H. F. W.: *The Chemistry of Cements*, vol. I, p.70, Academic Press, London 1964.

6. Meyer J. W., Jaunarajs K. L.: *Amer.Mineral.* 46, 913 (1961).
7. Števíla L. and Petrovič J.: *Cem.Concr.Res.* 13, 684 (1983).
8. Jaubertie R., Temimi M., Laquerbe M.: *Cem.Concr.Res.* 26, 1335 (1996).
9. Roy D. M., Harker R. I. in: *Proceedings of the Fourth International Symposium on the Chemistry of Cement*, p.196-201, D.C., Washington 1960.
10. Harker R. I.: *J.Am.Ceram.Soc.* 47, 521 (1964).
11. Siauciunas R., Baltakys K.: *Cem.Concr.Res.* 34, 2029 (2004).
12. Baltakys K., Šiauciunas R., Baltušnikas A.: *Chemical Technology 1*, 45 (2004). (in Lithuanian)
13. Nocun-Wczelik W.: *Cem.Concr.Res.* 29, 1759 (1999).
14. Baltakys K., Siauciunas R.: *J.Mater.Sci.* 41, 4799 (2006).
15. Taylor H. F. W., Roy D. M.: *Proceedings of 7th International Symposium on the Chemistry of Cement*, p. 112, Paris 1980.
16. Cheary R. W., Coelho A. A., Programs XFIT and FOURYA, deposited in CCP14 Powder Diffraction Library, Engineering and Physical Sciences Research Council, Daresbury Laboratory, Warrington, England 1996. (<http://www.ccp14.ac.uk/tutorial/xfit-95/xfit.htm>).
17. Taylor H. F. W. in: *6th International Congress on the Chemistry of Cement*, Research Institute VNIIESM of the Ministry of Building Materials Industry of the USSR, p. 43, Moscow 1974. (in Russian)

VLIV MÍCHÁNÍ A PŘÍDAVKU γ -Al₂O₃ NEBO Na₂O
NA VZNIK GYROLITU V SYSTÉMU
CaO–KŘEMEN–H₂O

KESTUSIS BALTAKYS, RAIMUNDAS SIAUCIUNAS

*Department of Silicate Technology,
Kaunas University of Technology,
Radvilenu 19, LT - 50270 Kaunas, Lithuania*

Byl zkoumán vliv míchání a přídavku γ -Al₂O₃ nebo Na₂O na proces tvorby gyrolitu (Ca₁₆Si₂₄O₆₀(OH)₈·14H₂O) ve směsi CaO–krystal–H₂O. Molární poměry primárních směsí byly CaO/(SiO₂ + Al₂O₃) = 0,66 a Al₂O₃/(SiO₂ + Al₂O₃) = 0 nebo 0,025. Poměr voda/pevný podíl suspenze byl roven 10,0. V rotačním autoklávu (10 otáček za minutu) za působení tlaku nasycené páry při 200°C byla provedena hydrotermální syntéza; délka izotermálního vytvrzování byla 2, 4, 6, 8, 16, 24, 32, 48, nebo 72 hodin. Bylo zjištěno, že v čisté směsi nemělo míchání pozitivní účinek na tvorbu gyrolitu. Dokonce i po 72 hodinách při 200°C ve výrobku převažuje 1,13 nm tobermorit (Ca₅Si₆O₁₅(OH)₂·5H₂O). V míchaném systému CaO–krystal–Na₂O–H₂O se gyrolit vytvořil rychleji - po 24 hodinách izotermického vytvrzování při 200°C a v nemíchané suspenzi po 32 hodinách. Výsledky ukazují, že přídavek γ -Al₂O₃ do suspenze CaO–krystal–Na₂O–H₂O stabilizuje gyrolit a brání jeho přeměně na pektolit (NaCa₂Si₃O₈(OH)).