# Application of Isomorphic Ca-Si Rocks for the Synthesis of α-C$_2$S Hydrate

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There are approximately 35 million t of carbonate opoka and 21 million t of chalk marl in Lithuania. These materials are suitable for the production of various hydraulic binders. In this work, the influence of burning temperature (700 °C – 950 °C) and duration (0.5 h – 2 h) on the calcination of isomorphic Ca-Si rocks was investigated. The goal was to prepare a mixture of opoka and chalk marl that would be reactive enough for the hydrothermal synthesis of various calcium silicate hydrates, as this would suggest another potential use of these stocks. It was determined that the largest amount of free CaO (59.09 %) is obtained after burning opoka for 2 h at 750 °C and after burning chalk marl for 2 h at 800 °C (84.22 %). The remaining CaO is bound to the structure of poorly crystalline pseudowollastonite, which transforms to wollastonite when the temperature of the thermal treatment is increased. Because the calcination temperature of both materials is similar, they can be burned simultaneously; this would significantly simplify the preparation procedure of these mixtures. The optimal temperature for burning the opoka – chalk marl mixture with a molar ratio of CaO/SiO$_2$ = 2 (62.8 % chalk marl and 37.2 % opoka) was determined to be 825 °C for 2 h. In this case, the amount of free CaO is the largest and the crystals of formed wollastonite are poorly crystalline. This blend was treated hydrothermally at 200 °C for 24 h. The dominant product of the synthesis was α-C$_2$S hydrate, which in literature was reported to be the main constituent in the production of new hydraulic binder.

*Keywords*: opoka; thermal treatment; α-C$_2$S hydrate; X-ray diffraction; hydrothermal synthesis.

## 1. INTRODUCTION

Since the development of ordinary Portland cement (OPC) roughly 175 years ago, it has become the most popular hydraulic binder worldwide. Annual production of this material is estimated at 3 Gt [1]. OPC is the number one binder used in concrete for construction because of its durability, universality, and relatively low cost. Its low price is determined by the worldwide availability of materials suited for its production, and local production significantly reduces the transportation cost.

However, the OPC industry faces a few disturbing problems. Because of the vast production amounts and the high temperature at which clinker (an intermediate product of producing Portland cement) must be burned, worldwide energy consumption of this industry approaches

10 – 11 EJ (10 – 11 × 10$^{18}$ J), corresponding to 2 % – 3 % of global energy usage. For every tonne of OPC produced, 0.87 t CO$_2$ is released, accounting for 5 % of manmade CO$_2$ emissions [2]. Many possible solutions for these problems have been suggested, but most of these are still in a theoretical stage. For example, in a process offered by Calera Corp. [3], CO$_2$ is mineralized in an aqueous precipitation process. Carbon dioxide reacts with calcium or magnesium in, for example, brines, resulting in carbonates, which can be used as building material. To what degree Calera is able to reduce significant amounts of CO$_2$ is an open question at this time [4]. A more realistic way is to use alternative raw materials, which could be in some cases

waste materials from other industries, such as bottom ash from municipal solid waste incinerators, residues from reprocessing salt slag, fly ash, paper residuals, used concrete, etc. [5]. However, these residuals can replace only a small part of the initial raw material mixture. A few alternative binders (calcium aluminate cements, supersulphated cements, alkali-activated cements, etc.) have been known for decades, but they are not widely used because of some negative properties: a decrease in strength of hardened cement stone is observed in case of calcium aluminate cements, hardened calcium sulfoaluminate cements exhibit shorter lifetime comparing to ordinary Portland cement, alkali – activated and supersulfated binders demonstrate relatively slow hardening [6 – 10].

In 2010, scientists of Karlsruhe Institute of Technology announced that synthesized α-C$_2$S hydrate, when milled with sand, exhibits hydraulic properties. A new type of cementitious material, named "Celitement", has been developed. Unlike ordinary Portland cement, the C-S-H phase is formed during the production of the binder and not during the hardening of concrete [10]. Initial tests showed its high chemical resistance and low carbonation rate due to low porosity [12], and its other important properties are similar to those of OPC. The cost of this material is mitigated by the lower thermal treatment of the intermediate product (α-C$_2$S hydrate is hydrothermally synthesized at 200 °C, whereas OPC clinker is burned at 1450 °C), and the release of CO$_2$ is decreased by 50 %. The raw materials needed for its production – carbonate rocks and quartz sand – can be found in most regions of the world.

α-C$_2$S hydrate is a common compound formed during the hardening of autoclaved calcium silicate products. It

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can also be obtained as a product of the hydration of cement minerals ($Ca_2SiO_4$, $Ca_3SiO_5$) and OPC slurries at $130\,°C - 220\,°C$ in a saturated water steam atmosphere [13 – 15]. This compound was reported to form after 1 day of hydrothermal treatment of β-$C_2S$ at $150\,°C$ keeping water/solid ratio of 20 [16]. α-$C_2S$ hydrate can also be hydrothermally synthesized directly from CaO and $SiO_2$, but the amount of obtained α-$C_2S$ hydrate depends on the activity of used $SiO_2$ [17]. In mixtures where molar ratio $CaO/SiO_2 = 2$, the mentioned compound was identified after 24 h of hydrothermal treatment at $200\,°C$ when using amorphous $SiO_2$. In slurries it forms through an intermediate phase – C-S-H (II) and remains stable until an excess of $Ca(OH)_2$ is present. In case of excess of $SiO_2$ α-$C_2S$ hydrate transforms to the calcium silicate hydrates of lower basicity. In addition, the formation of α-$C_2S$ hydrate depends on the CaO component used for the hydrothermal synthesis. This compound was reported to be a dominant product of the hydrothermal synthesis after 18 h at $200\,°C$ when using $CaCO_3$ (burnt for 4 h at $1000\,°C$), while in case of $Ca(OH)_2$ the same result only with larger crystals was obtained after 162 h [18].

However, authors emphasize, that it is difficult to obtain only α-$C_2S$ hydrate using natural raw materials – it often forms along with other calcium silicates and portlandite [19].

However, the properties and quality of the raw materials determine the duration and temperature of hydrothermal reactions, and this along with the temperature of calcination can have a critical impact on the price of the product. The use of carbonate rocks is recommended, because burning them gives the maximum amount of reactive CaO at relatively low temperatures. A positive economic effect could be achieved using natural isomorphic Ca-Si rocks as initial materials; there would be no need to prepare them separately and homogenize afterwards. Two of these raw materials are found in Lithuania: opoka (industrial stock of approximately 35 million t) and chalk marl (approximately 21 million t).

Opoka is a silica-calcite sedimentary rock that is found in south-eastern Europe and Russia [20]. In addition to its known possible uses for the removal of phosphates [21] from water and being a useful pozzolanic additive in the production of pozzolanic Portland cement [22], it has also been reported as a prospective material for the hydrothermal synthesis of various calcium silicate hydrates [23]. A part of $SiO_2$ is in amorphous state in opoka and could intensify formation of C-S-H, similar as a nanodispersive $SiO_2$ in production of autoclaved aerated concrete [24]. However, in order to achieve high reactivity of opoka, it is necessary to establish its favorable calcination conditions.

The aim of this work was to develop an active material mixture (using natural isomorphic Ca-Si rocks) suited for the hydrothermal synthesis of the calcium silicate hydrates with a Ca/Si ratio of 2.

## 2. EXPERIMENTAL

Opoka and chalk marl samples were taken from the Stoniskis-Zemaitkiemis and Juodziai quarries in Lithuania and milled in ball mills until reaching $S_a = 970$ $m^2/kg$ and $890$ $m^2/kg$, respectively. The chemical composition of the materials is shown in Table 1.

The particle size distribution of opoka (Fig. 1) was determined to be as follows: 50 % particles with a diameter of 16.1 µm, 25 % with a diameter of 4.6 µm, and 10 % with a diameter of 1.9 µm. Average particle size was determined to be 28.36 µm.
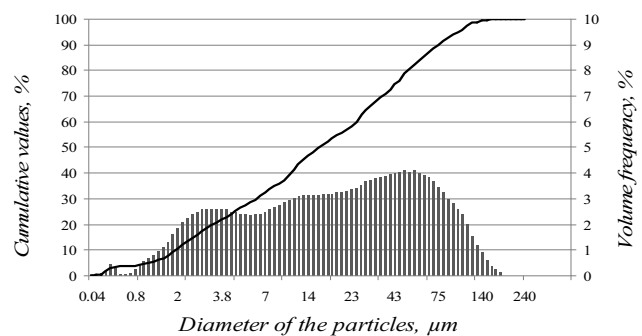


**Fig. 1.** Particle size distribution of opoka

The results of the chemical analysis of the opoka were confirmed by X-ray powder diffraction (XRD) analysis (Fig. 2); most of the opoka consisted of $SiO_2$. Four different modifications of $SiO_2$ were identified: quartz, cristobalite, tridymite, and amorphous (8.74 %, 27.30 %, 5.44 %, and 25.10 %, respectively) (Fig. 3). Carbonates were found in two different compounds: calcite and dolomite.
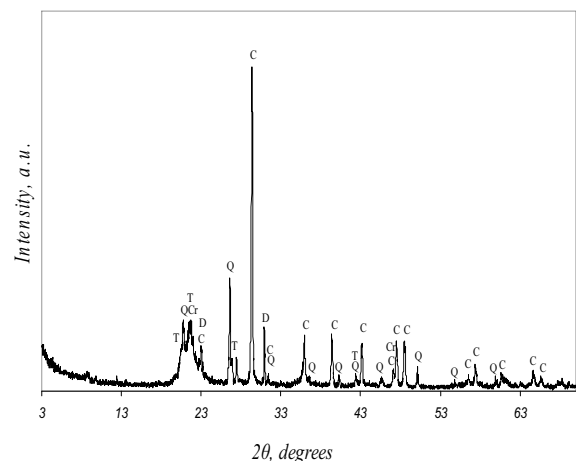


**Fig. 2.** XRD curve of raw opoka. Indexes: C – calcite; Q – quartz; D – dolomite; Cr – cristobalite; T – tridymite

**Table 1.** Chemical composition of opoka and chalk marl

| Material | Oxides, wt. % | | | | | | Anions, wt. % | | Ignition losses, wt. % |
|---|---|---|---|---|---|---|---|---|---|
| | CaO | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MgO | $K_2O$ | $F^-$ | $SO_3^{2-}$ | |
| Opoka | 22.64 | 52.56 | 2.42 | 0.78 | 0.61 | 0.62 | 0.12 | 0.45 | 18.97 |
| Chalk marl | 51.87 | 3.72 | 0.87 | 0.42 | 0.29 | 0.12 | 0.17 | < 0.1 | 41.99 |

In the curves of simultaneous thermal analysis (STA), it can be seen that calcination in opoka started at a relatively low temperature of 665 °C and ended at 763 °C.
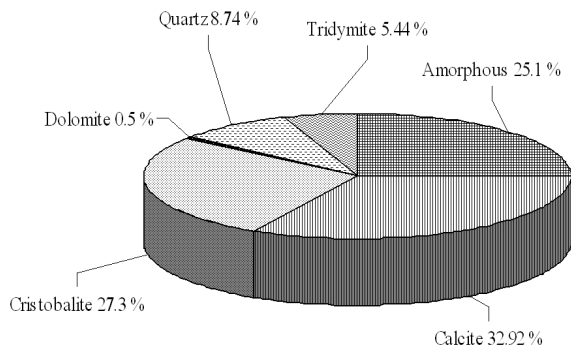


**Fig. 3.** Mineral composition of opoka

The mass loss was 16.41 %, which equals to the 37.32 % of $CaCO_3$ being in the material. An exothermal peak at 895 °C shows the reaction between CaO and $SiO_2$ in which wollastonite ($CaO \cdot SiO_2$) was formed (Fig. 4).
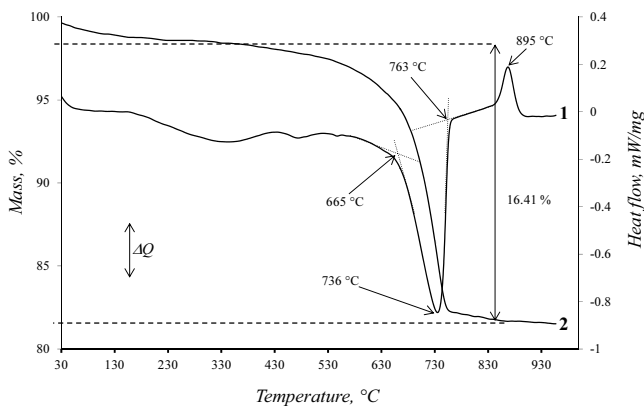


**Fig. 4.** STA curves of raw opoka. Indexes: 1 – DSC, 2 – TG

Only $CaCO_3$ and traces of quartz were identified in the XRD curves of the chalk marl (Fig. 5). According to STA results, calcination in latter material starts at 670 °C and ends at 840 °C (Fig. 6). The mass loss during this process is 40.96 %; thus, there is 93.09 % $CaCO_3$ in the chalk marl.
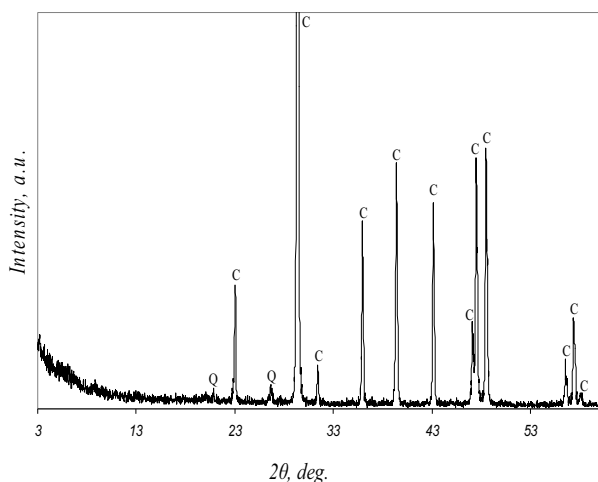


**Fig. 5.** XRD curve of raw chalk marl. Indexes: C – calcite; Q – quartz

Dry pellets of the opoka-chalk marl mixture of a diameter of approximately 1.5 cm were formed and burned

at 700 °C – 950 °C (at intervals of 50 °C) in automatic laboratory kiln (SNOL 8,2/1100) for periods of 0.5, 1 and 2 h.
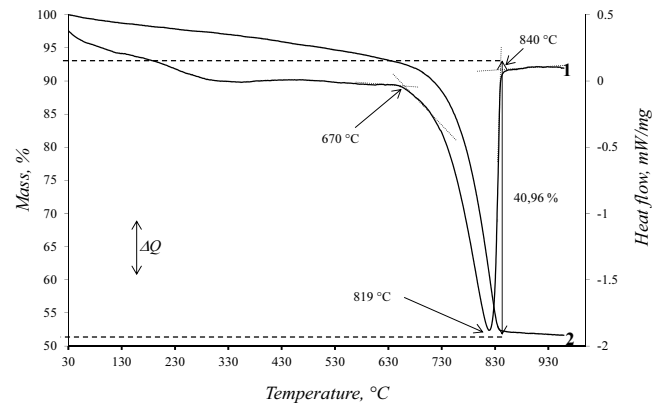


**Fig. 6.** STA curves of raw chalk marl. Indexes: 1 – DSC, 2 – TG

The XRD data were collected with a DRON-6 X-ray diffractometer with Bragg-Brentano geometry using $CuK_\alpha$ radiation and a graphite monochromator, operating with a voltage of 30 kV and emission current of 20 mA. The step – scan covered the angular range of 2°– 60° ($2\theta$) in steps of $2\theta = 0.02°$.

An XRD 3003 TT diffractometer (GE Sensing & Inspection Technologies GmbH) with a $\theta$-$\theta$ configuration and $CuK_\alpha$ radiation ($\lambda = 1.54$ Å) was also used. The angular range was from 5° to 70° $2\theta$, with a step width of 0.02° and a measuring time of 6 seconds per step. Autoquan software was used for Rietveld analysis.

X-ray fluorescence analysis (XRF) was performed using S4 Explorer and $CuK_\alpha$ radiation, operating with a voltage of 20 kV and emission current of 5 mA.

Simultaneous thermal analysis (STA) was also used for measuring the thermal stability and phase transformation of samples at a heating rate of 15 °C /min; the temperature ranged from 30 °C to 1000 °C under air atmosphere. The tests were carried out on a Netzch instrument, STA 409 PC Luxx. Ceramic sample handlers and crucibles of Pt-Rh were used.

The particle size distribution of materials was measured using a CILAS 1090 LD particle size analyser, which has a sensitivity range from 0.04 μm to 500 μm. Water was used as the carrier liquid. The particles were dispersed by ultrasound for 2 minutes while the obscuration of particles in water reached 14 %. The ultrasound duration during the measurement was 70 seconds. The standard operating procedure used was the Fraunhöfer method.

The amount of free CaO was determined following the standard ASTM C114-11b.

## 3. RESULTS AND DISCUSSION

The amounts of free CaO and CaO in carbonates were determined in burnt opoka and chalk marl. Also, the quantity of CaO bound to the structure of calcium silicate (formed during the thermal treatment) was calculated. The values are expressed as a percentage of the total CaO present in the material and are given in Table 2. Decomposition of the $CaCO_3$ in opoka practically ended at 800 °C after 2 h or at 850 °C after 0.5 h. It should be noted that CaO, formed during calcination, is very active; therefore, it rapidly reacts with $SiO_2$. At 700 °C, about 20 % of the total CaO was bound into the structure of

newly formed compounds. The rate of this process increased with elevating temperatures. Consequently, the amount of free CaO started to decrease with a further increase in temperature (Fig. 7). The main newly formed compound during the burning of opoka at $750\,°C - 850\,°C$ was calcium silicate, which is referred to as "pseudowollastonite" (Fig. 7, a, curves 1 and 2). Elevating the temperature favoured its transformation to wollastonite (Fig. 7, a, curve 3). The growing intensity of its peaks suggests that the amount of this calcium silicate as well as the size of its crystals increased (Fig. 7, a, curve 4).

**Table 2.** Variation of CaO amount during calcination of opoka and chalk marl

| Temperature, ºC | Duration, h | Opoka | | | Chalk marl | | |
|---|---|---|---|---|---|---|---|
| | | $CaO_{carb.}$ | $CaO_{free}$ | $CaO_{silic.}$ | $CaO_{carb.}$ | $CaO_{free}$ | $CaO_{silic.}$ |
| 700 | 0.5 | 56.23 | 25.73 | 18.03 | 91.28 | 1.81 | 6.91 |
| | 1 | 45.27 | 30.52 | 24.21 | 87.85 | 3.65 | 8.50 |
| | 2 | 36.91 | 39.89 | 23.20 | 76.39 | 12.74 | 10.,87 |
| 750 | 0.5 | 25.96 | 42.54 | 31.50 | 84.45 | 5.12 | 10.43 |
| | 1 | 19.64 | 48.42 | 31.94 | 69.79 | 18.71 | 11.50 |
| | 2 | 13.26 | 59.09 | 27.64 | 43.09 | 45.39 | 11.52 |
| 800 | 0.5 | 12.07 | 48.99 | 38.94 | 62.11 | 25.42 | 12.47 |
| | 1 | 8.68 | 35.98 | 55.33 | 37.39 | 50.85 | 11.76 |
| | 2 | 7.37 | 27.16 | 65.47 | 5.52 | 84.22 | 10.26 |
| 850 | 0.5 | 5.17 | 16.58 | 78.26 | 33.24 | 57.35 | 9.41 |
| | 1 | 4.31 | 13.76 | 81.93 | 6.81 | 82.25 | 10.94 |
| | 2 | 4.37 | 13.22 | 82.41 | 2.09 | 88.54 | 9.37 |
| 900 | 0,5 | 3.54 | 12.47 | 83.98 | 8.59 | 81.36 | 10.05 |
| | 1 | 2.95 | 10.91 | 86.14 | 1.45 | 89.63 | 8.92 |
| | 2 | 3.06 | 9.90 | 87.05 | 0.61 | 88.99 | 10.40 |
| 950 | 0.5 | 2.43 | 9.13 | 88.44 | 1.47 | 87.50 | 11.04 |
| | 1 | 2.11 | 8.90 | 88.98 | 0.00 | 85.19 | 14.81 |
| | 2 | 1.89 | 8.36 | 89.75 | 0.00 | 83.17 | 16.83 |

Here: $CaO_{carb.}$ – amount of CaO bound in carbonates, wt. %; $CaO_{free}$ – amount of free CaO, wt. %; $CaO_{silic.}$ – amount of CaO bound in the structure of silicates, wt. %.
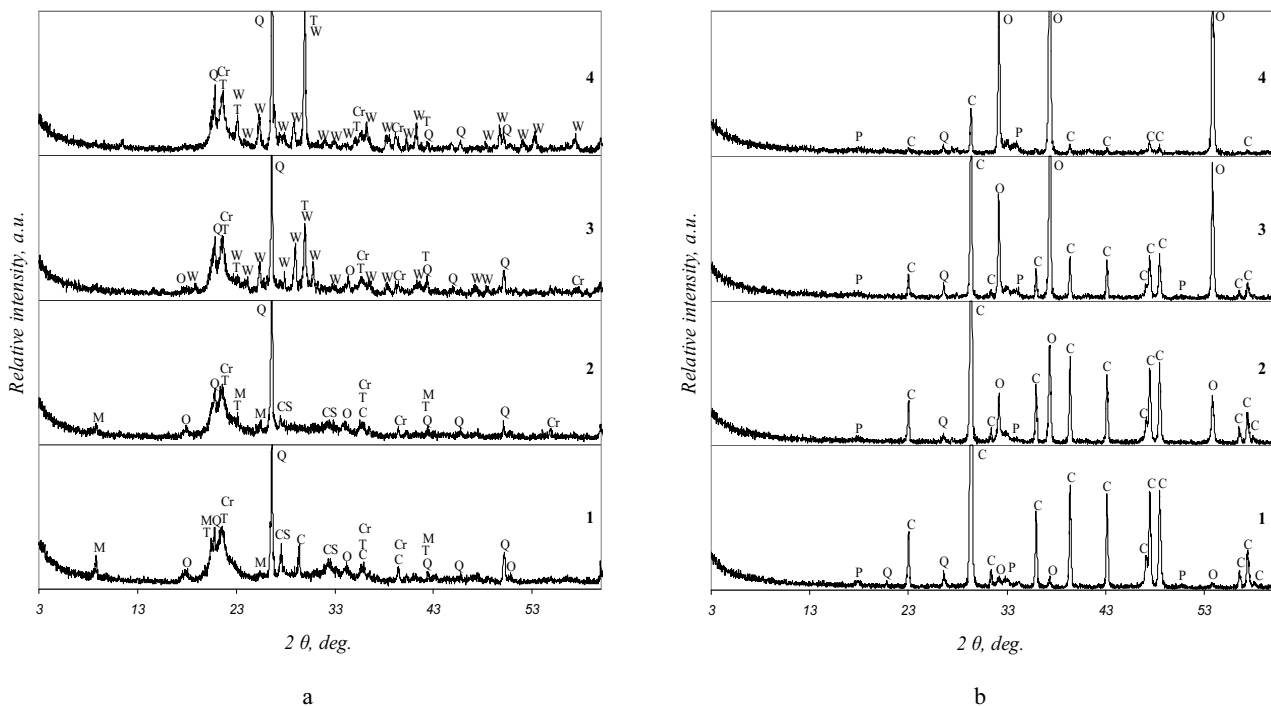


**Fig. 7.** XRD curves of burnt (1 h) opoka (a) and chalk marl (b). Indexes: 1 – 750 °C, 2 – 800 °C, 3 – 850 °C, 4 – 900 °C; Q – quartz, M – muscovite, Cr – cristobalite, D – dolomite, C – calcite, CS – calcium silicate ("pseudowollastonite"), O – calcium oxide, W – wollastonite

**Table 3.** Variation of CaO amount in burnt opoka – chalk marl mixture and amount of total CaO
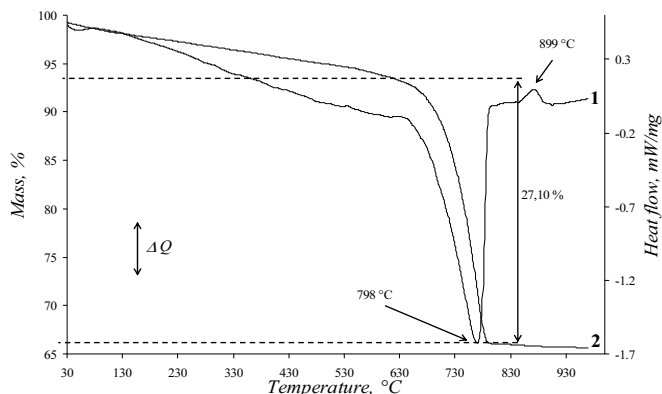
| Temperature, °C | Ignition losses, wt. % | Variation of CaO amount in the mixture, wt. % | | | Amount of total CaO, wt. % | | |
|---|---|---|---|---|---|---|---|
| | | CaO$_{carb.}$ | CaO$_{free}$ | CaO$_{silic.}$ | CaO$_{carb.}$ | CaO$_{free}$ | CaO$_{silic.}$ |
| 775 | 12.30 | 17.84 | 17.05 | 26.68 | 28.98 | 27.69 | 43.33 |
| 800 | 4.99 | 6.68 | 26.77 | 28.12 | 10.85 | 43.48 | 45.67 |
| 825 | 1.36 | 1.75 | 31.20 | 28.62 | 2.84 | 50.67 | 46.48 |
| 850 | 1.11 | 1.37 | 29.10 | 31.10 | 2.22 | 47.26 | 50.51 |

Indexes: CaO$_{carb.}$ – amount of CaO bound in carbonates, wt. %; CaO$_{free}$ – amount of free CaO, wt. %; CaO$_{silic.}$ – amount of CaO bound in the structure of silicates, wt. %.

It is worth mentioning that after burning opoka in 700 °C – 900 °C, all crystalline $SiO_2$ modifications (quartz, tridymite, cristobalite) were identified in XRD curves. This suggests that CaO, formed during the calcination, first of all reacts with amorphous $SiO_2$.

In the case of chalk marl, calcination starts at 700 °C: the portion of CaO in carbonates was reduced from 91.28 % (0.5 h) to 76.39 % (2 h) (Table 2). Due to low amounts of acidic oxides in marl (9.73 %), the change in the quantity of bound to other compounds CaO was almost trivial (Table 2). In addition to depending on temperature, the degree of calcination also depends on the duration of isothermal treatment.

Thus, the highest amount of free CaO (59.09 %) was identified in opoka after 2 h of thermal treatment at 750 °C. In chalk marl, the highest amount of free CaO (88.54 %) was identified after 2 h at 850 °C. However, a sufficiently high amount of free CaO was obtained after burning chalk marl at 800 °C for 2 h (84.22 %). For this reason, a further increase in the calcination temperature is not recommended, because the size of the crystals of the newly formed compounds increases and as a result its reactivity under hydrothermal conditions will be reduced.

STA analysis data showed that the burning process of the mixture (Fig. 8) was very similar to the burning process of opoka: the CaO that is formed reacts with $SiO_2$ and forms wollastonite (exothermal effect at 899 °C in the DSC curve).

The mixture of opoka and chalk marl was burned at 775 °C – 850 °C (at intervals of 25 °C). Products were analysed using chemical and XRD analysis. The results showed that the optimal burning temperature for this mixture was 825 °C: calcination was almost over and the amount of free CaO increased to 50.67 % of total CaO (Table 3).

Wollastonite started forming at 775 °C in the mixture (because of the excess of CaO, it was formed at a lower temperature than when only opoka was used). However, the intensity of peaks representing this silicate remained relatively low even after burning at 825 °C (Fig. 9). This means that silicates with deformed crystal lattice formed during the calcination. The intensity of calcite peaks in XRD curves consistently decreased as temperature rose during the thermal treatment. They were not identified after burning the mixture at 825 °C for 2 h.



**Fig. 8.** STA curves of opoka – chalk marl mixture. Indexes: 1 – DSC, 2 – TG
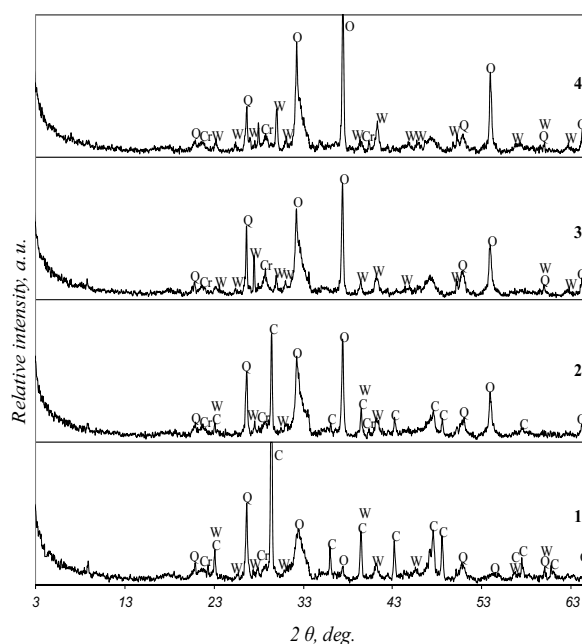


**Fig. 9.** XRD curves of burnt (1 h) opoka – chalk marl mixture. Indexes: 1 – 775 °C, 2 – 800 °C, 3 – 825 °C, 4 – 850 °C; Q – quartz, Cr – cristobalite, C – calcite, O – calcium oxide, W – wollastonite

The similarity of the burning temperatures for both raw materials suggests that it would be effective to prepare the mixture first, before using the thermal treatment. For this reason, we prepared the mixture of both materials with a Ca/Si ratio of 2 (calculations were made according to the results of chemical analysis of these materials). The composition was 62.8 % chalk marl and 37.2 % opoka (by mass). This mixture consisted of 40.99 % CaO, 21.88 % $SiO_2$, and 3.03 % other oxides; ignition losses accounted for 33.43 %.

According to the results described above, the most favourable temperature for thermal treatment of the opoka-chalk marl mixture was 825 °C, and the optimal duration was 2 h; these conditions ensured the maximum amount of free CaO in the mixture.

In order to check whether the isomorphic Ca-Si rocks, prepared following the conditions described above, are suitable for the synthesis of calcium silicate hydrates, the opoka-chalk marl mixture was milled to $S_a = 935$ m²/kg, mixed with water (w/s = 10), and treated isothermally for 24 h at 200 °C under an atmosphere of saturated water steam. The dominant product in the mixture after the synthesis was $\alpha$-C$_2$S hydrate; the intensity of the peaks ($d = 0.532, 0.422, 0.326, 0.288, 0.281, 0.266, 0.241, 0.177$ nm) representing this compound in XRD curve (Fig. 10) was relatively high. The formation of this calcium silicate hydrate was also proven using DSC: the endothermic effect at 481 °C corresponds to its dehydration (Fig. 11). The effect next to that one (419 °C) corresponds to the dehydration of portlandite. Hence, isomorphic Ca-Si rocks are suitable for the synthesis of $\alpha$-C$_2$S hydrate.
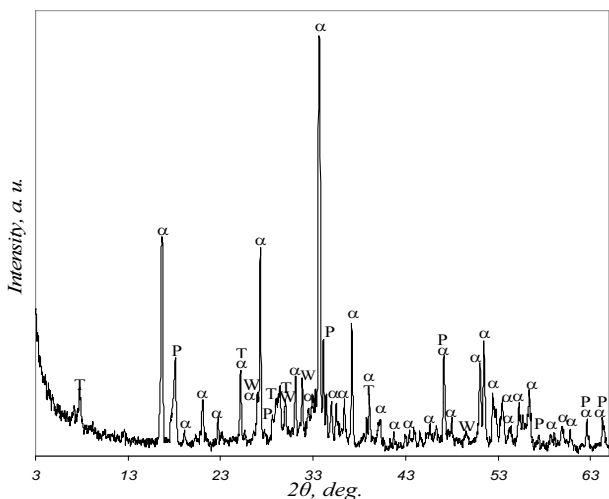


**Fig. 10.** XRD curve of the opoka-chalk marl mixture, treated hydrothermally at 200 °C for 24 h. Indexes: α – α-C$_2$S hydrate, T – tridymite, P – portlandite, W – wollastonite
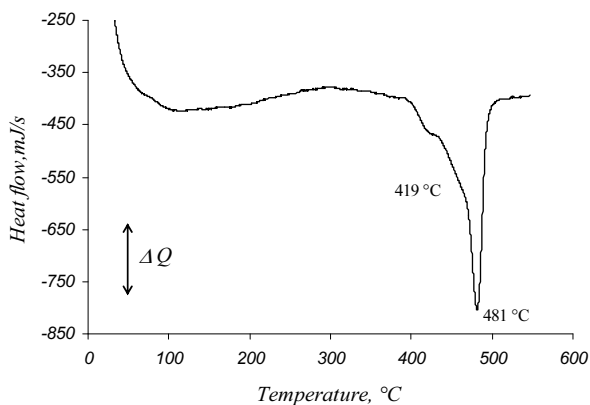


**Fig. 11.** DSC curve of the the opoka-chalk marl mixture, treated hydrothermally at 200 °C for 24 h

## 4. CONCLUSIONS

1. The process of the formation of free CaO during the calcination of isomorphic Ca-Si rocks depends on the temperature and duration of the thermal treatment. The largest portion of free CaO (59.09 %) in opoka forms after 2 h of thermal treatment at 750 °C, while a sufficient amount of it (84.22 %) in chalk marl is obtained after burning it for 2 h at 800 °C. Therefore, it is recommended that these rocks should be burned simultaneously; this would substantially simplify the technological process as well as reducing the required energy input.

2. The optimal temperature for the burning an opoka-chalk marl mixture with a molar ratio of CaO to SiO$_2$ of 2 was determined to be 825 °C with a duration of 2 h; this preparation yielded the maximum amount of free CaO. Furthermore, $\alpha$-C$_2$S hydrate formed in this mixture after it was treated hydrothermally at 200 °C for 24 h.

**REFERENCES**

1.  U.S. Geological Survey *Mineral Commodity Summaries* January, 2012: pp. 38 – 39.

2.  **Damtoft, J. S., Lukasik, J., Herfort, D., Sorrentino, D., Gartner, E. M.** Sustainable Development and Climate Change Initiatives   *Cement and Concrete Research*   38 (2) 2008: pp. 115 – 127.
    http://dx.doi.org/10.1016/j.cemconres.2007.09.008

3.  www.calera.com [Accessed November 3, 2013].

4.  **Carter, T.** In: Converting Carbon Emissions to Profitable Products [on-line]. Cement Sustainability Initiative Forum, Warsaw (2010).
    Available at:
    http://www.wbcsdcement.org/pdf/CSIForum2010/06%20CSI%20Carter%20100914.pdf. [Accessed December 8, 2011].

5.  Verein Deutscher Zementwerke (Ed.), Environmental Data of the German Cement Industry 2009, 2010: pp. 8.

6.  **Scrivener, K. L., Capmas, A.** Calcium Aluminate Cements. In: Hewlett, P. C. (Ed.). Lea's Chemistry of Cement and Concrete. Elsevier, Ltd., Oxford, UK, 1998: pp. 713 – 782.

7.  **Juenger, M. C. G., Winnefeld, F., Provis, J. L., Ideker, J. H.** Advances in Alternative Cementitious Binders *Cement and Concrete Research*   41   2011: pp. 1232 – 1243.
    http://dx.doi.org/10.1016/j.cemconres.2010.11.012

8.  **Singh, M., Garg, M.** Calcium Sulphate Hemihydrate Activated Low Heat Sulphate Resistant Cement *Construction and Building Materials*   16 (3)   2002: pp. 181 – 186.
    http://dx.doi.org/10.1016/S0950-0618(01)00026-5

9.  **Novak, D., Novak, R.** Practical Experience with a New Type of Supersulphated Cement   *Cement International* 4 (6)   2004: pp. 116 – 125.

10. **Matschei, T., Bellmann, F., Stark, J.** Hydration Behavior of Sulphate–Activated Slag Cements   *Advanced Cement Research*   18 (5)   2005: pp. 167 – 178.
    http://dx.doi.org/10.1680/adcr.2005.17.4.167

11. **Stemmermann, P., Schweike, U., Garbev, K., Beuchle, G.** Celitement – a Sustainable Prospect for the Cement Industry *Cement International*   8   2010: pp. 52 – 66.

12. **Stemmermann, P., Beuchle, G., Garbev, K., Schweike, U.** Celitement®—A New Sustainable Hydraulic Binder Based on Calcium Hydrosilicates *13th International Congress on the Chemistry of Cement* (July 3 – 8, 2011) Madrid, Spain: p. 158.

13. **Yanagisawa, K., Hu, X., Onda, A.** Hydration of β-dicalcium Silicate at High Temperatures under Hydrothermal Conditions *Cement and Concrete Research* 36 2006: pp. 810 – 816.
http://dx.doi.org/10.1016/j.cemconres.2005.12.009

14. **Luke, K.** Phase Studies of Pozzolanic Stabilized Calcium Silicates Hydrates at 180 °C *Cement and Concrete Research* 34 2004: pp. 1725 – 1732.
http://dx.doi.org/10.1016/j.cemconres.2004.05.021

15. **Colston, S. L., Barnes, P., Jupe, A. C.** An in-situ Synchrotron Energy-Dispersive Diffraction Study of the Hydration of Oil Well Cement Systems under High Temperature/Autoclave Conditions up to 130 °C *Cement and Concrete Research* 35 2005: pp. 2223 – 2232.
http://dx.doi.org/10.1016/j.cemconres.2004.09.005

16. **Hu, X., Yanagisawa, K., Onda, A., Kajiyoshi, K.** Stability and Phase Relations of Dicalcium Silicate Hydrates *Journal of the Ceramic Society of Japan* 114 (2) 2006: pp. 174 – 179.

17. **Siauciunas, R., Rupsyte, E.** Formation of High Basic Calcium Silicate Hydrates in Mixtures with Aluminium Additions *Chemical Technology* 4 (17) 2000: pp. 47 – 54 (in Lithuanian).

18. **Garbev, K., Gasharova, B., Beuchle, G., Kreisz, S., Stemmermann, P.** First Observation of $\alpha$-Ca$_2$[SiO$_3$(OH)](OH) – Ca$_6$[Si$_2$O$_7$][SiO$_4$](OH)$_2$ Phase Transformation upon Thermal Treatment in Air *Journal of American Ceramic Society* 91 (1) 2008: pp. 263 – 271.

19. **Garbev, K., Beuchle, G., Schweike, U., Stemmermann, P.** Hydration Behaviour of Celitement®: Kinetics, Phase Composition, Microstructure and Mechanical Properties *13th International Congress on the Chemistry of Cement* (July 3 – 8, 2011) Madrid, Spain: p. 159.

20. **Brogowski, Z., Renman, G.** Characterization of Opoka as a Basis for Its Use in Wastewater Treatment *Polish Journal of Environmental Studies* 13 (1) 2004: pp. 15 – 20.

21. **Johanson, L., Gustafsson, J. P.** Phosphate Removal Using Blast Furnace Slags and Opoka-Mechanisms *Water Research* 34 (1) 2000: pp. 259 – 265.
http://dx.doi.org/10.1016/S0043-1354(99)00135-9

22. **Kaminskas, R., Vektaris, B.** The Influence of Carbonate Opoka (Gaize) on the Hydration and Hardening of Portland Cement *Chemical Technology* 2 (11) 1999: pp. 65 – 74 (in Lithuanian).

23. **Siauciunas, R.** Synthesis of Tobermorite and Xonotlite Using Stoniskis – Zemaitkiemis Opoka *Chemical Technology* 3 (24) 2002: pp. 22 – 26 (in Lithuanian).

24. **Laukaitis, A., Keriene, J., Kligys, M., Mikulskis, D., Lekunaite, L.** Influence of Amorphous Nanodispersive SiO$_2$ Additive on Structure Formation and Properties of Autocalved Aerated Concrete *Material Science* (*Medžiagotyra*) 16 (3) 2010: pp. 257 – 263.