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Hydrothermal reaction products of brick recyclates

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Abstract. This paper deals with possibilities of the brick-grind-dust application as a precursor for hydrothermal synthesis. Currently, this brick dust is partially reused in brick masonry or buried to the landfill site. The basic idea of this paper was to examine possibilities of the reaction of phases in brick dust with lime under hydrothermal conditions. The aim of the work was to find out an optimal ratio between lime and brick dust for maximal production of tobermorite. Physical and chemical properties of the brick-grind-dust were studied, and then a series of samples in autoclaves were prepared. The maximum amount of tobermorite after 24 hours of reaction was found in samples with addition of 25% lime. Phase composition of raw material and products of hydrothermal synthesis were analysed by powder X-ray diffraction analysis and differential thermal analysis. Structure of prepared samples was observed by scanning electron microscope.

1. Introduction

The tobermorite ($Ca_5Si_6O_{16}(OH)_2 \cdot 5H_2O$) is one of the basic mineralogical phase occurring in autoclaved aerated concrete and other naturally occurring minerals. Calcium silicate hydrates (CSH), or calcium silicate aluminate hydrates (CSAH) phases are quite explored area because their synthetical analogical structures are obtained as hydration products of cementitious building materials. The final structure and type of CSH or CSAH phases depend on the chemical and phase composition of the starting material and many other conditions such as amount of water, temperature, pressure, and reaction time [1].
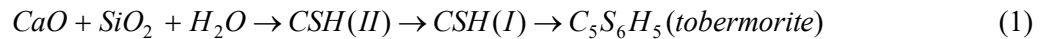
The reaction conditions necessary for tobermorite formation are called hydrothermal conditions (environment of saturated steam) and the ideal temperatures range is between 173°C and 197°C roughly. This temperature range is given by the intersection of the temperature solubility dependence of CaO (decreasing with temperature) and the temperature solubility dependence of SiO_2 (increasing with temperature) [2]. The intersection of solubility CaO and SiO_2 is shown in the figure 1. Calcium to Silicone ratio (Ca/Si = 5/6) of forming tobermorite, comes from its chemical formula. The temperature range and Ca /Si ratio needed to form tobermorite and others CSH phases are shown in figure 2 [3].

Production of building materials requires their stability, which is closely linked with phase stability. In autoclaved aerated concrete tobermorite is the desired phase, but there is a possibility of conversion into the other CSH mineral, xonotlite ($Ca_6Si_6O_{17}(OH)_2$). The stability of tobermorite can be ensured by the presence of aluminum and iron cations, which affect the transfer of tobermorite to xonotlite [4, 5].

The formation of tobermorite is described in the literature by two possible mechanisms according to the presence of aluminum ions. In the first case, without aluminum ions, tobermorite crystalizes from CSH gel via reaction described in equation 1. In the presence of aluminum ions is tobermorite created by two paths that run simultaneously. One possibility is the reaction through the CSH gel as written

above. The second possibility is that reaction proceeds through the mineral phase katoite (a type of hydrogarnet) and crystallization of tobermorite is solution controlled [4].

$$CaO + SiO_2 + H_2O \rightarrow CSH(II) \rightarrow CSH(I) \rightarrow C_5S_6H_5 (tobermorite) \qquad (1)$$

Traditionally used sources of SiO_2 in autoclaved aerated concrete described in literature are natural raw materials like a silica sand, kaolin, diatomaceous earth, crushed stone powder or same secondary raw materials represented by blast furnace slag, silica fume, fly ashes, ground glass waste, or porcelain [2, 6, 7, 8, 9]. Among the secondary raw materials brick grind dust can be included [10]. Burned brick can be used as a source of silicon oxide, aluminum oxide and iron oxide, in the form of mineral phases, if they are soluble. Soluble phases react under hydrothermal conditions to form new phases, potentially tobermorite, which they can stabilize to not to convert it into xonotlite [4, 5]. Brick-grind-dust is produced at the end of brick production when bricks are ground to achieve their high flatness. Brick dust is partially reused into the brick manufacturing process or buried to the land field site. Bricks are fired at a temperature of about 850-1000°C, so there is a possibility of a small amount of amorphous phase, depending on the feldspar content [11]. The amorphous content is potentially more reactive (more soluble under hydrothermal conditions) due to its disorder structure. A better solubility of the amorphous phase is shown in figure 1.
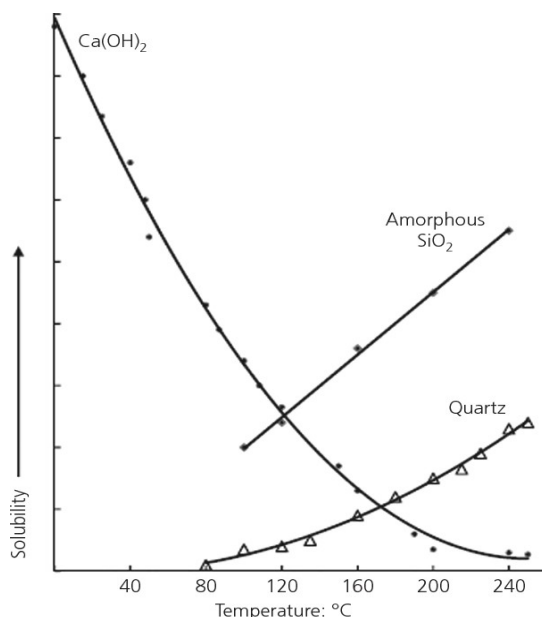

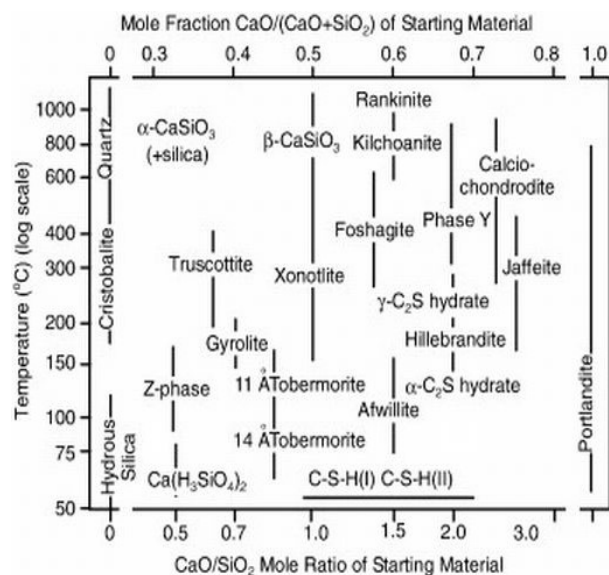**Figure 1.** Temperature dependence of solubility of $Ca(OH)_2$ and SiO_2 [2].

Figure 2. Phase changes in system $CaO/SiO_2/H_2O$ at elevated temperatures [3].

2. Materials and methods

Starting material was brick-grind-dust from brick factory Hevlín (company HELUZ). The specific surface of brick dust was 7300 cm²·g⁻¹ (Blaine). Particle size composition of the fraction less than 0.63 μm (the content of this fraction was approximately 66%) was analysed by particle size laser diffraction analysis (HELOS Sympatec) (figure 3). D_{50} of this fraction was 4.19 μm. Chemical composition of brick-grind-dust was analysed by energy-disperse X-ray fluorescence analysis (by spectrometer VANTA VCR) and is given in table 1. Phase composition of brick-grind-dust was analysed by powder X-ray diffraction analysis (XRD) (Empyrean, Panalytical). For the determination of amorphous content the Rietveld analysis was conducted. Results of phase analysis of the brick-grind-dust are in table 2.
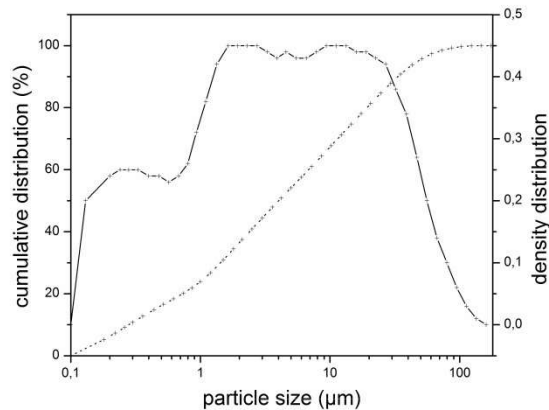
Figure 3. Particle size distribution of brick-grind-dust.

Table 1. Elemental composition of brick-grind-dust (LE = light elements).

Element	Si	Ca	Al	Fe	Mg	K	S	Ti	P	LE
(%)	22.82	8.21	8.19	4.4	2.84	2.38	0.66	0.51	0.06	49.93

Table 2. Phase composition of brick-grind-dust.

Phase	Amorphous	Quartz	Albite	Augite	Muscovite	Orthoclase	Akermanite	Hematite
(%)	28.5	30.4	17.1	5.6	11.2	2.0	4.3	0.9

As a source of calcium ions the limestone from Vitošov was used. Limestone was heated to 1000°C for two hours. The purity of the lime used was greater than 97% CaO determined by thermogravimetric and differential thermal analysis (TG-DTA analysis).

Samples were prepared in laboratory steel autoclaves with Teflon linings. Brick-grind-dust and lime were mixed in different Ca/Si ratios (see table 3). Amount of water was constant in all samples (100 ml). After two minutes of mixing of starting mixture, autoclaves were closed and placed to laboratory dryer set up to 180°C for a different time, 24, 48, 72 and 120 hours. After this heat treatment the autoclaves were cooled to the laboratory temperature and the reaction products were filtered on a Büchner funnel and dried at 60°C. After drying the prepared samples were crushed in a mortar and analysed. Phase composition was analysed by XRD analysis. Selected samples were analysed by TG-DTA analysis (TA Instruments Q600) and scanning electron microscope (SEM, ZEISS EVO LS 10).

Table 3. The starting composition of samples.

Sample	10_%_CaO	15_%_CaO	20_%_CaO	25_%_CaO	30_%_CaO	37,5_%_CaO	50_%_CaO
CaO (g)	2	3	4	5	6	7.5	10
Br.dust (g)	18	17	16	15	14	12.5	10
Ca/Si	0.71	0.91	1.14	1.40	1.70	2.24	3.49
H_2O (g)	100						

3. Results and discussion

According to chemical analysis the Ca/Si ratio in brick dust is 0.36. Stoichiometric ratio origine from the tobermorite formula is 0.83, but this value comes from a clear system which should contain only reactive CaO, SiO_2 and H_2O. Drochytka in his publication Pórobeton [12] describes a phase diagram

CaO–SiO$_2$–H$_2$O by Bessey. There is a possibility to create tobermorite from ratio ranging from 0.8 to 1.0 in the system which contains only CaO, SiO$_2$ and H$_2$O. Brick dust is composed of at least eight mineral phases. Some minerals, containing calcium and silicon, do not react under hydrothermal conditions and could be found in the sample even after the reaction. To find the optimum lime addition to the system based on brick dust, an addition of 10 to 50% CaO has been proposed. Resulting Ca/Si ratios are given in table 3. The idea of the experiment was to obtain the highest amount of tobermorite as possible without the traces of unreacted portlandite.

The phase composition of prepared samples was analysed by XRD analysis. In figure 4, the diffractograms of samples hydrothermally cured for 24 hours are shown. There are same phases originated from the brick-grind-dust like muscovite, quartz, albite and akermanite. Additionally after hydrothermal synthesis the presence of tobermorite, katoite and hibschite were observed. There is an increase in the tobermorite peak intensity in samples prepared using up to 25% of CaO. With more added lime the intensity is decreasing. Calculated ratio for the sample with 25% addition of CaO comes from XRF spectra of brick and CaO addition results in 1.4. Along with the increasing amount of added lime, the intensity of portlandite peaks is increasing. For samples containing 15% and 20% lime, portlandite diffraction is almost insignificant. The intensity of calcite peak is also increasing with lime addition. With increasing lime content, a slight increase in hibschite peaks may be observed at the expense of katoite. This observation corresponds to the theory of the formation of tobermorite over the katoite which was mentioned by Matsui et. al. [4]. With the increase in lime content, the dissolution rate of the muscovite, quartz and feldspar increase. For the maximum possible yield of tobermorite after 24 hours, the most suitable addition of CaO is in the range 20–25% CaO.

A mixture containing 25% CaO was subjected to another experiments, which extended the reaction time to up to 48, 72 and 120 hours. The diffractograms are shown in figure 5. The diffraction spectrum shows that portlandite peaks are lost after 48 hours. The intensity of calcite diffraction is approximately the same after all reaction times. This amount of calcite is probably a product of portlandite carbonation because of CO$_2$ content in the air. The amount of tobermorite increases in time, while the amount of quartz decreases. The biggest change is apparent after 48 hours, and after prolongation of the reaction, the phase composition of the prepared samples is comparable. There is no conversion of tobermorite into xonotlite, even after the 120 hours of reaction. The influence of the aluminium and iron presence in the reaction system to prevent transformation of tobermorite to xonotlite is in good agreement with the results published earlier [4, 5].
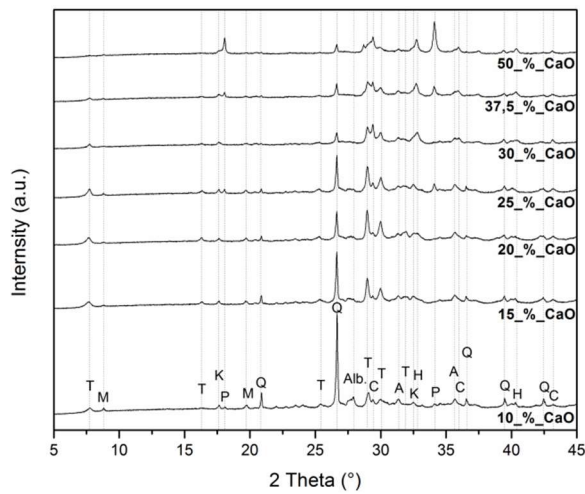
Figure 4. Comparison of diffractograms for different CaO concentrations, 24 hours of reaction.

Figure 5. The diffractograms of samples prepared with 25 % of CaO for different time of reaction.

Markers: T – 11 Å tobermorite, M – muscovite, K – katoite, P –portlandite, Q – quartz, Alb. – albite, C – calcite, A – akermanite, H – hibschite.

The morphology of the brick-grind-dust can be described as angular fine particles with different shape and size (see figure 6). After 24 hours of hydrothermal conditions (figure 7), crystals on the surface of bricks-grind-dust particles are formed. Their morphology and shape of the crystals is difficult to describe even with a magnification of 20 000 ×. With increasing reaction time (figure 8), plates or flakes of tobermorite crystallized. This structure is very similar to the structure described in the article by Gutovic et al. [10], where brick recycles with Portland cement under hydrothermal conditions were studied.
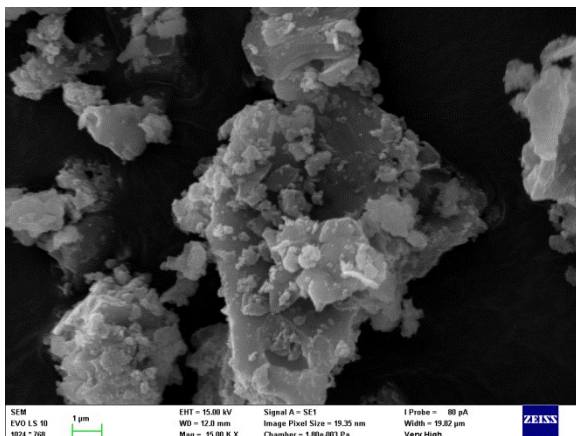

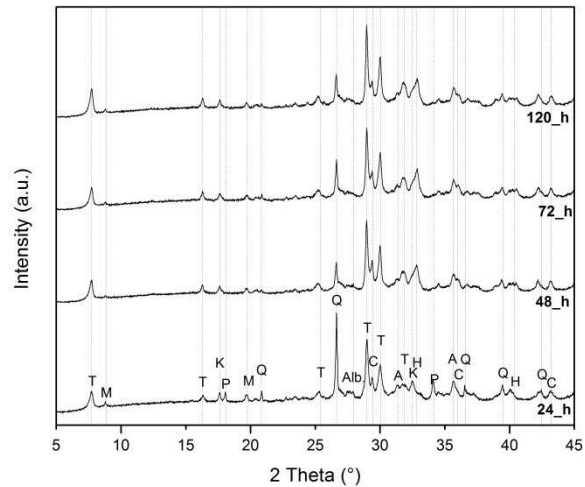**Figure 6**. Brick dust before reaction (mag. 15 000×).
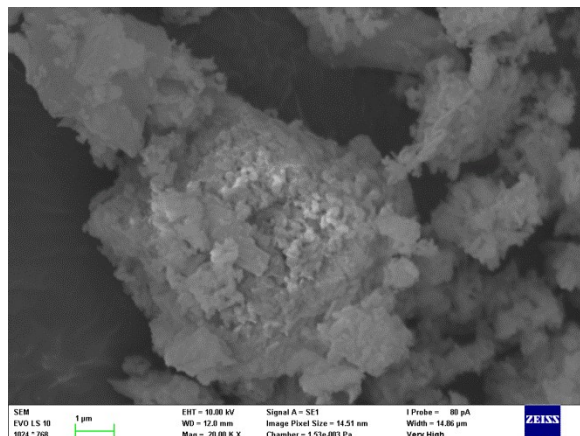
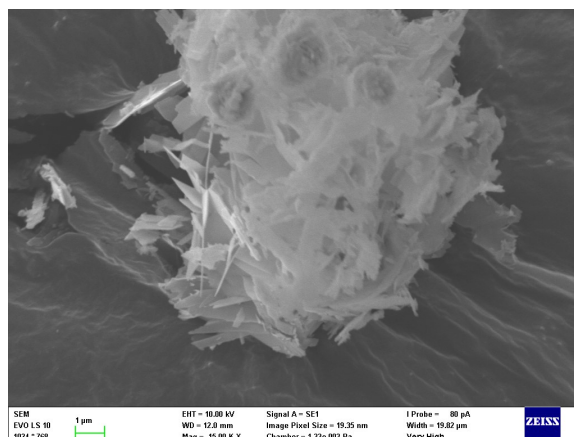**Figure 7.** Brick dust after 24 hours of the hydrothermal reaction (mag. 20 000×).

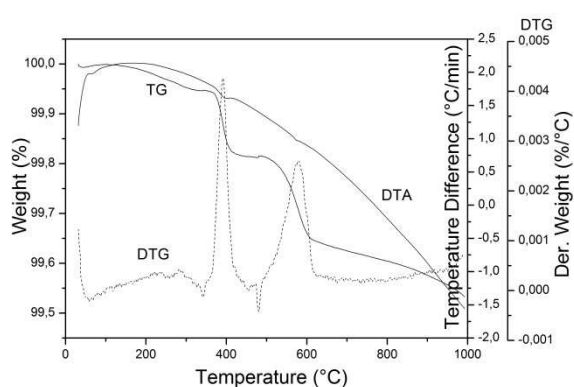**Figure 8.** Brick dust after 120 hours of the hydrothermal reaction (mag. 15 000×).

Figure 9. Thermogravimetric and differential thermal analysis of brick-grind-dust (exo up).
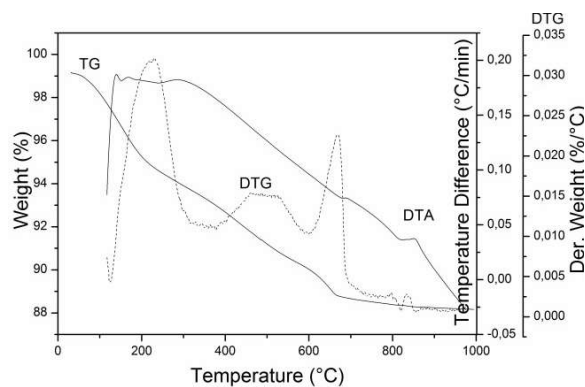
Figure 10. Differential thermal analysis after 120 hours of reaction (exo up).

Sample after 120 hours of reaction and unreacted brick dust was analyzed by TG-DTA analysis. From the figure 9 it is obvious, that brick dust contains little amount of water probably bonded in a C–(A)–S–H phases or in a structure of gypsum which is lost between 50°C and 250°C. With increasing temperature, two more peaks are observed on DTG curve. First, there is a peak of dehydroxylation of portlandite above 400°C, then above 600°C decomposition of carbonates occur. After 120 hours of reaction (figure 10) loss of water between 50°C and 250°C from C–(A)–S–H phases is observed because a part of the structurally bonded water is included in the tobermorite structure. Finally, tobermorite recrystallizes to wollastonite above 850°C, which is described by Huang et al. [13]. This is observable as the exothermic peak on DTA at this temperature. Shaw et al. [14] describe this conversion of tobermorite to wolastonite by the differential scanning calorimetry/thermogravimetric analysis. Shaw et al. describe this fact on the natural minerals and Huang et al. describe this effect on the system based on pure precursor. The amount of tobermorite which is prepared from brick-grin-dust is probably smaller, due to presence of non-reactive phases. Therefore, the phenomena on the DTA curve are not very pronounced and differential scanning calorimetry should be probably better method for tobermorite characterization.

4. Conclusion

The reaction of a fine fraction of brick recyclates with calcined limestone in hydrothermal conditions results in a production of new minerals: tobermorite, katoite and hibschite. The optimal amount of burned lime was found in range of 20–25% of CaO. When 25% of CaO or more was used, then some

amount of portlandite was found, which is undesirable for potential application in autoclaved aerated concrete.

The presence of tobermorite was also observed by TG–DTA analysis, whereby at temperatures around 850°C the recrystallization of tobermorite into wollastonite occur. Reaction time plays the greatest role in terms of the morphology of prepared tobermorite. After 24 hours, the structure of the reaction products was not fully developed. After 120 hours of reaction, the platelet crystals of tobermorite were already well developed.

Subsequent aim for the research of this topic would be the reduction of amount of portlandite in final product because of stability. Next step is to prepare autoclaved aerated concrete with brick-grind-dust and test the mechanical properties of them.

Acknowledgment

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