

MONITORING THE EFFECT OF QUARTZ-SAND REPLACEMENT BY AMORPHOUS-SILICA RAW MATERIAL ON THE MICROSTRUCTURE OF CALCIUM SILICATE COMPOSITES

OPAZOVANJE UČINKA ZAMENJAVE KREMENČEVEGA PESKA S SUROVIM AMORFNIM SILIKATOM NA MIKROSTRUKTURO KALCIJ-SILIKATNIH KOMPOZITOV

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Quartz sand is the main raw material for the production of autoclaved calcium silicate composites. However, its resources are rapidly dwindling and alternative siliceous raw materials need to be sought and tested for replacement. Most often, they are raw materials containing amorphous silica. Amorphous silica is more readily soluble than crystalline silica and may thus contribute to the formation of a superior microstructure of the calcium silicate composite through calcium hydrate phases. This paper is focused on determining the optimal replacement rate of the amorphous-silica raw material replacing the crystalline silica sand, while describing changes in the microstructure of calcium silicate composites. The replacement was graded at (0, 25, 50, 75 and 100) %. Hydrothermal-treatment conditions were based on a real production of autoclaved aerated concrete, so a temperature of 190 °C and an isothermal holding time of 7 h were chosen. To study the effect of the ratio of raw materials on the microstructure, an X-ray diffraction analysis supported by scanning-electron-microscopy images was used.

Keywords: calcium silicate composite, glass, tobermorite

Kremenčev pesek je glavna osnovna surovina za izdelavo kalcij-silikatnih (Ca-Si) kompozitov v avtoklavih. Ker pa njegova najdišča hitro izginjajo, je potrebno za njegovo zamenjavo najti in preiskati alternativne surovine na osnovi silikatov. Najpogostejše osnovne surovine vsebujejo amorfn kremen. Ta je lažje topen kot kristalinični in tako prispeva k tvorbi boljše mikrostrukture Ca-Si kompozita preko kalcij-hidratnih faz. Ta članek se osredotoča na opis določitve optimalnega razmerja zamenjave kristaliničnega kremenčevega peska z amorfnim kremenčevim peskom in s tem povezanimi spremembami mikrostrukture Ca-Si kompozitov. Izbrana razmerja so bila (0, 25, 50, 75 in 100) %. Izbrani pogoji hidrotermalne obdelave so temeljili na realni proizvodnji prezračenega cementa v avtoklavih, to je temperaturi 190 °C in izotermnem času zadrževanja 7 h na tej izbrani temperaturi. Vpliv na mikrostrukturo izdelanih kompozitov so študirali z rentgensko difrakcijo (XRD), podprto s posnetki, izdelanimi z vrstičnim elektronskim mikroskopom.

Gljučne besede: kompozit na osnovi kalcijevega silikata, steklo, Ca-Si-hidratni mineral (tobermorit)

1 INTRODUCTION

Calcium silicate composites, such as autoclaved aerated concrete (AAC), are made from a silica component and lime, or other raw materials such as cement, gypsum and aluminium powder. Only siliceous raw materials and lime were used for this research; therefore, attention will be paid to the interaction of these raw materials.

The siliceous component, a natural source of the primary raw material, is most often found in the crystalline form. Crystalline silica (SiO_2) is poorly reactive and its interaction with lime (CaO) is possible under hydrothermal conditions. The high pressure, temperature and presence of steam during the autoclaving of calcium silicate composites promote the solubility of crystalline SiO_2 , thereby reacting with lime and H_2O to form new calcium hydrosilicate phases (CSH). Tobermorite is considered an important CSH phase. Tobermorite

($5\text{CaO} \cdot 6\text{SiO}_2 \cdot 5\text{H}_2\text{O}$) represents functional binders in lime silicate materials. Its quantity and quality then define the resulting material properties.¹⁻⁶

Secondary raw materials have been used in the production of lime-silicate composites for many years, in the process of research and application. However, most often these are ashes.³⁻⁵ Other, alternative secondary raw materials have been investigated so far on a smaller scale. For example, P. Walczak et al.⁶ focused on the possibility of using ground waste glass in the AAC technology. Their research suggests that glass has a potential for use in the AAC technology. Therefore, this paper focuses on the research of the influence of ground container glass. Glass as a raw material is more often used in cementitious composites.^{7,8}

Influence of the SiO_2 morphology

Secondary raw materials are often characterized by the content of amorphous SiO_2 . Amorphous SiO_2 is more soluble than crystalline SiO_2 and thus more reactive. S. Haastrup et al.⁹ describe the kinetics of a CSH gel

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Table 1: Basic characteristics of raw materials

	Bulk density (g/cm ³)	Specific surface (cm ² /g)	SiO ₂ (%)	Al ₂ O ₃ (%)	K ₂ O (%)	Na ₂ O (%)	Fe ₂ O ₃ (%)
Quartz sand	2.70	3080	92.91	2.53	1.53	0.70	0.84
		6080					
Glass	2.56	2930	69.73	1.76	0.88	12.20	0.41
		6160					

formation from amorphous microsilica. The CSH phase formed at a molar ratio Ca/Si <1 corresponds to the structure of tobermorite. They also state that the solubility of silica indicates the rate of the reaction of CaO and SiO₂. The CSH phase formed from crystalline SiO₂ contains a high amount of Ca(OH)₂, while the CSH formed from the reaction of amorphous SiO₂ contains a high amount of SiO₂.^{13,14} The presence of SiO₂ may slow down the crystallization of CSH into tobermorite. Consequently, when using crystalline SiO₂, the reaction is slower, but it may lead to the formation of more crystalline tobermorite. J. Fleischhacker¹⁵ describes, in his work, that the use of amorphous microsilica in a lime-silicate composite led to the formation of tobermorite only after a prolongation of the hydrothermal treatment to 16 hours and an increase in the Ca/Si molar ratio to 1.0, otherwise tobermorite was not detected.

Influence of the fineness of siliceous raw materials on the formation of tobermorite

The quartz grain size affects the rate of the formation of CSH phases and hence the amount or morphology of CSH^{10,11}. S. Bernstein et al.¹⁰ investigated the effect of the quartz grain size on the formation of 1.13-nm tobermorite in the AAC technology. They examined the difference between grain sizes of 8 μm and 16 μm. They found that the use of 8-μm grains allowed a faster formation of tobermorite than 16-μm grains. N. Isu et al.¹² also found that finer quartz accelerated the formation of tobermorite, but also found that in the case of finer quartz, the crystallinity of tobermorite was lower than in the case of coarse quartz.

2 EXPERIMENTAL PART

The main aim of this paper is to understand the changes in the microstructure of the sand-lime composite due to the gradual substitution of sand with ground glass. Another aim is to monitor the changes in the microstructure as well as physical and mechanical changes of samples based on the change in the specific surface area.

Raw materials

The samples were made from lime and silica components. Quartz sand was used as the reference silica component, and ground container glass was used as the substitute raw material. Two fineness values were chosen; quartz sand and glass had similar fineness values. The fineness was chosen to be 3000 cm²/g and

6100 cm²/g. The basic characteristics of the raw materials are shown in **Table 1**. Glass substitutions were chosen on a scale of 0–100 %, namely (0, 25, 50, 75 and 100) %.

The particle size and distribution were determined using a Malvern Mastersizer 2000. The resulting particle distribution is shown in **Figure 1**.

Sample preparation

The lime and silica components were mixed to achieve the desired molar ratio of Ca/Si 0.83 based on a 1.1-nm tobermorite molar ratio. The dry mixture was carefully homogenized and then water was added to form a liquid consistency. The water coefficient of the dry mix (*w*) ranged from *w* = 0.60 to 0.80 [–], with the coarser silica component being mixed with *w* = 0.60–0.66 and the finer silica component with *w* = 0.73–0.8 [–].

The liquid suspension was poured into molds of 20 × 20 × 100 mm. After 24 h, the samples were removed from the molds and subjected to a hydrothermal treatment in a laboratory autoclave at 190 °C for 7 h. The conditions of autoclaving were based on a real production of AAC.

Methods

The basic physical and mechanical properties of the samples were determined, namely the bulk density and compressive strength, according to standard EN 206+A1 Concrete – Specification, performance, production and conformity.

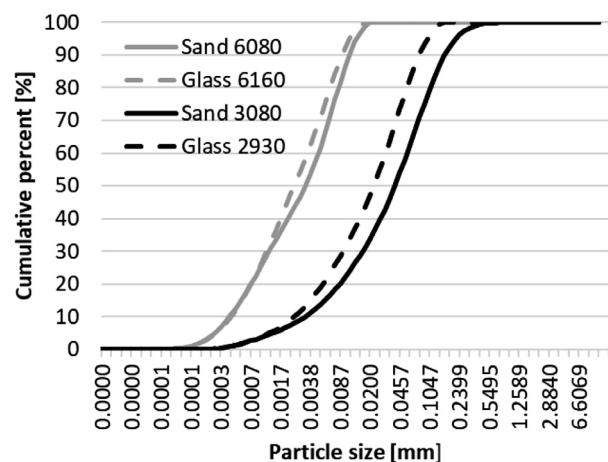


Figure 1: Granulometric curves of quartz sand and glass

The microstructure study was performed using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The clean cores of the samples were ground using a grinding mill to a size of <0.5 mm. The resulting powder was then ground in a McCrone mill to a particle size of <20 μm, in an isopropanol solution with a standard addition, to more accurately determine the amounts of minerals. Calcium fluoride (CaF₂) was chosen as the standard. The resulting suspension was dried in a drying room to a steady weight. The sample thus prepared was loaded into an Empyrean Analytical machine for an XRD analysis.

3 RESULTS

Physical/mechanical properties

The influence of the amount of the glass substituting the sand was investigated, while the influence of the fineness of the siliceous raw material on the basic physical/mechanical properties was studied. The emphasis was placed on the compressive strength.

The bulk density of the samples (Figure 2) with a fineness of 3000 cm²/g of the silica input component is, according to the results, unchanged with respect to the glass amount substituting the sand. Differences in the bulk-density values are within 5 %. The bulk-density difference for the samples with a fineness of 6100 cm²/g is already around 7 %, while the highest values are achieved by the samples with a 100-% glass substitution of the sand.

With respect to the compressive-strength values, some dependence on the glass substitution of the sand was observed for the samples with a 3000-cm²/g silica fineness (Figure 3). The reference strength was the highest. Then the strength gradually decreased with the increasing glass substitution of the sand. The sample with a 50-% substitution achieved only half the value of the compressive strength of the reference sample. Further, there was only a slight increase with the increasing glass-to-sand ratio of a sample. The samples with the siliceous raw material with a fineness of

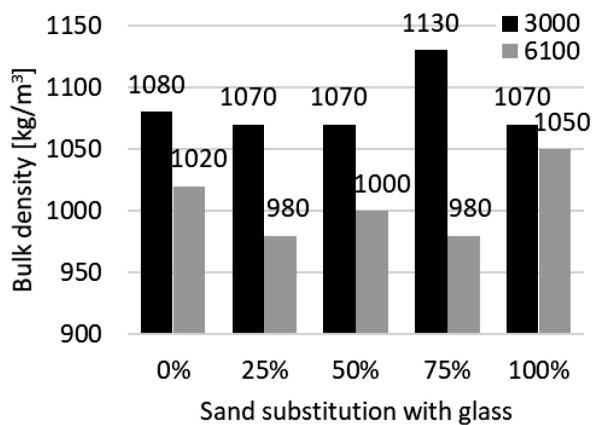


Figure 2: Bulk density of the samples

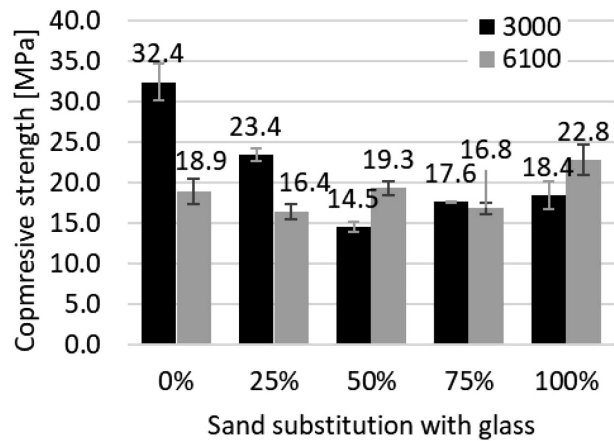


Figure 3: Compressive strength of the samples

6100 cm²/g achieved a relatively constant strength without the influence of the amount of the glass substitution of the sand.

Microstructure

The data from diffractograms were evaluated according to the intensity and position of diffraction lines, but also according to Ritveld refinement of the contained tobermorite. The quantitative analysis was considered a priority of this paper. The results were supported by SEM images.

Diffraction lines of 1.1-nm tobermorite were detected in all samples. Further, quartz, orthoclase, calcite, a CaF₂ addition and amorphous phases were detected. The intensity of the tobermorite diffraction lines (Figure 4) varied depending on the amount of glass and the fineness of the silica component. The changes were not constant. The reference sample with the coarser silica raw material achieved a high-intensity diffraction line. Then, with the 25-% substitution, the intensity decreased and with 50-%, 70-% and 100-% glass amounts, there was a

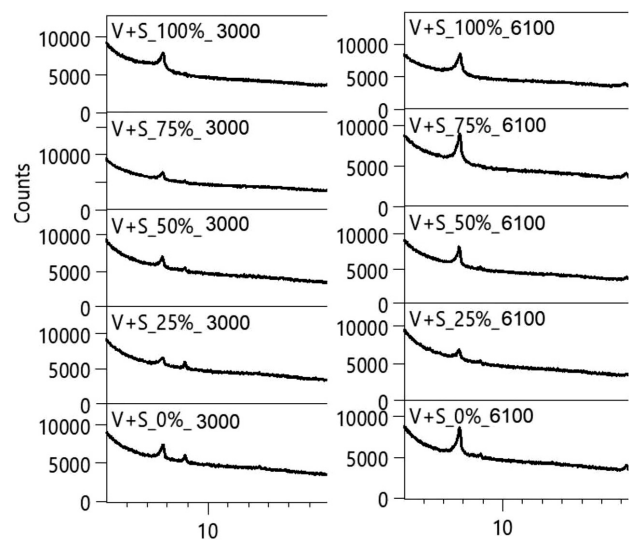


Figure 4: XRD diffractograms – isolated tobermorite diffraction lines

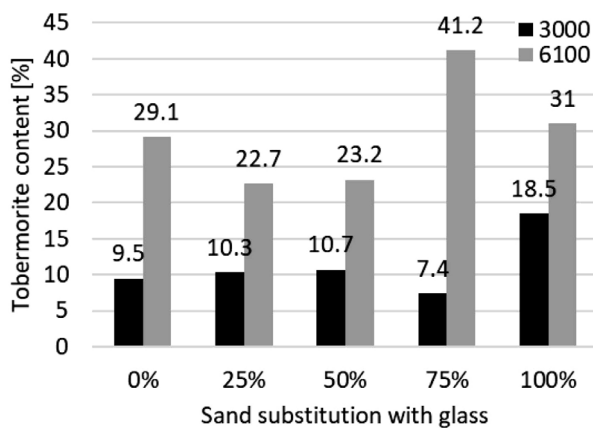


Figure 5: Tobermorite contents in the samples

gradual increase. Intensities were detected in the samples with a finer raw material, but for the sample with a 100-% glass amount, it decreased again. Lastly, an increase in the intensity of the tobermorite diffraction

line was observed with an increased specific surface area of the siliceous raw material.

The quantitative XRD analysis gave interesting results. The samples with a basic fineness of 3000 cm²/g up to a glass content of 75 % did not show any significant change in the amount of tobermorite. However, the 100-% substitution caused an increase in the amount of tobermorite by almost 100 % compared to the reference sample. Another significant difference in the amount of tobermorite was observed due to different fineness values of the siliceous raw materials. The samples with a finer silica component generally contained 12–34 % more tobermorite. The largest amount of tobermorite was found in the sample with the 75-% glass amount and with a fineness of 6500 cm²/g.

Scanning electron microscopy

In the paper, SEM images of the samples with 0, 50 and 100 % of glass are presented to show the nature of the change in the morphology of tobermorite.

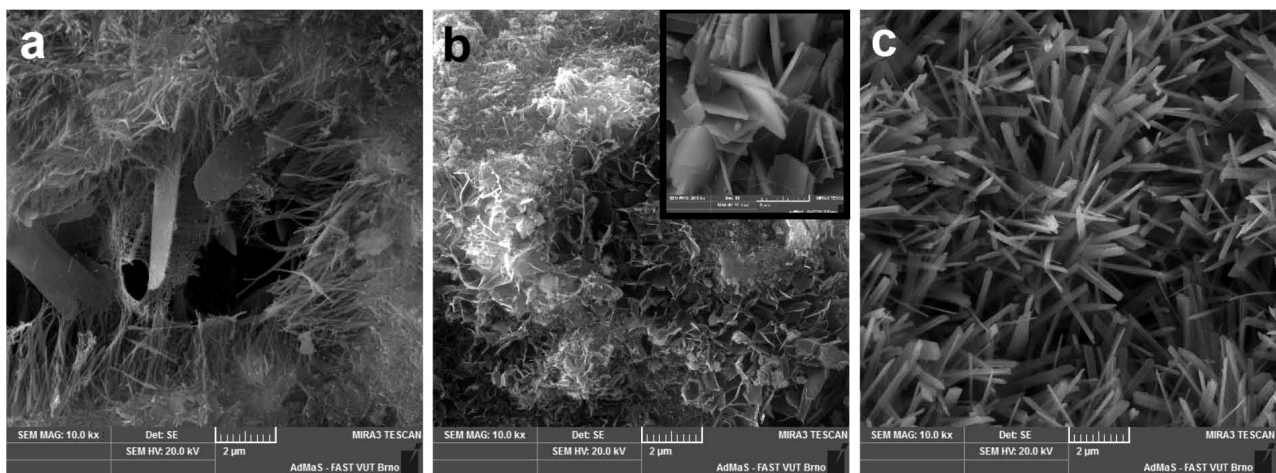


Figure 6: SEM images magnified 10k × – samples with a fineness of 3000 cm²/g: a) sample with 0 % of glass, b) sample with 50 % of glass, c) sample with 100 % of glass

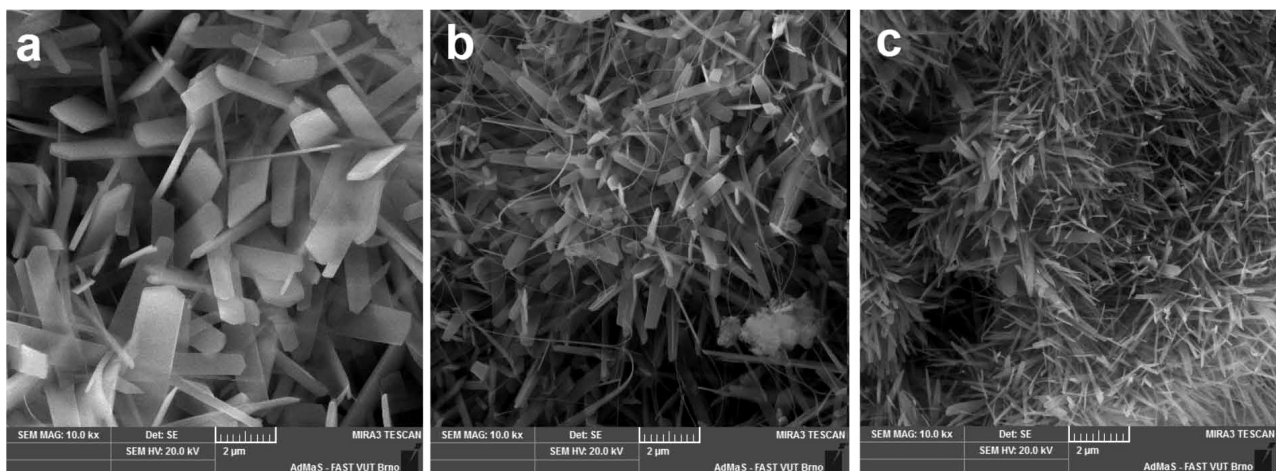


Figure 7: SEM images magnified 10k × – samples with a fineness of 6100 cm²/g: a) sample with 0 % of glass, b) sample with 50 % of glass, c) sample with 100 % of glass

For both fineness values used, the change in the morphology of tobermorite crystals depends on the amount of glass in the sample. Among the samples with a specific surface area of the silica raw material of 3000 cm²/g (**Figure 6**), the sample with 0 % of glass includes thick tobermorite crystals and a CSH gel connecting the aggregate grains as the binder. There are already two types of tobermorite morphology in the sample with 50 % of glass, in the form of thick plates and in the form of a "house of cards". In the 100-% glass sample, small and thin tobermorite crystals are evenly crystallized over the entire amorphous grain surface.

A comparison of the samples with the fineness values of silica material of 3000 cm²/g and 6100 cm²/g shows a change in the morphology of tobermorite (**Figure 7**). In the image of the sample with 0 % of glass and a higher fineness of the siliceous raw material, very well developed tobermorite crystals are visible, which are gradually smaller with an increasing amount of glass in the sample.

4 DISCUSSION

The use of glass as the substitute for silica sand had a significant effect on the resulting compressive strength of the samples, considering the basic fineness value of 3000 cm²/g. According to the above results, it can be said that up to 50 % of the glass substitution of the sand, the compressive strength decreases to almost half the strength of the reference lime-silicate composite. There may be several reasons for that. Although amorphous SiO₂ is more reactive, the CSH phases resulting from amorphous SiO₂ contain a higher SiO₂ ratio, thereby slowing down the development of tobermorite crystals.^{13,14} Accordingly, there may be a lack of the binder phase interconnecting the aggregate grains in a sample. The results of the microstructure study support these assumptions. Changing the morphology of tobermorite is probably significant, as is the amount of tobermorite. Interestingly, the samples with a fineness of 6100 cm²/g of the siliceous raw material contain much more tobermorite than the samples with a fineness of 3000 cm²/g, but this does not affect the resulting mechanical properties as expected. Nor does the morphology of tobermorite. Chucholowski et al.¹⁶ show that thicker crystals exhibit lower strengths than the crystals with the house-of-cards morphology. On the other hand, samples with well-developed tobermorite crystals achieve a higher compressive strength.

Regarding the effect of the specific surface area, it was found that finer raw materials support the formation of tobermorite with respect to both the quantity and morphology. Smaller grains of silica were probably more easily soluble and more involved in the reaction of the resulting formation of CSH phases. On the other hand, it consumed the portion of the filler that is essential for the

resulting strength of the sample, causing a decrease in the compressive strength.

5 CONCLUSIONS

The paper deals with the influence of ground glass on the properties of a lime-silicate composite and, at the same time, it investigates the influence of the specific surface area of the raw material.

From the acquired knowledge, the following can be determined:

The presence of ground glass promotes the formation of tobermorite, especially its amount in a sample; however, at the same time, it reduces the compressive strength of the sample.

25 % is considered the maximum sand replacement. This substitution resulted in the lowest compressive strength of the sample. In the future, it would be interesting to verify the levels of substitution from 0 % to 25 %.

The presence of crystalline SiO₂ was found to be important for the filler function. Nevertheless, it is possible to completely substitute the crystalline raw material with glass, but only if the lower compressive strengths are satisfactory.

Increasing the specific surface area from 3000 cm²/g to 6100 cm²/g resulted in a significant increase in the amount of tobermorite in the sample. At the same time, the compressive strength, which was constant, was reduced and the glass substitution had no effect. This finding leads to the conclusion that a high fineness of the raw material is desirable if tobermorite is to be synthesized. In the case of the physical/mechanical properties of a calcium silicate composite, this appears to be unprofitable.

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