

Study of the influence of the secondary raw materials on microstructure and properties of calcium silicate composite

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Abstract. Calcium silicate composites are a widely used building material, especially autoclaved aerated concrete or sand-lime bricks. The physico-mechanical properties of these materials depend on their microstructure. Microstructure is characterized by the content of crystalline calcium silicate compounds that arise during autoclaving. This is in particular the tobermorite mineral, which carries the mechanical strength of the composite. This paper focuses on the influence of secondary raw materials on properties and microstructure of the calcium silicate composite. Secondary raw materials were selected as slag from the combustion of lignite and ground glass. Mixtures of composites were selected with respect to the required C/S molar ratio of 0.73. The hydrothermal treatment was carried out at a temperature of 190 °C and a residence time of 4, 8 and 16 hours. The microstructure of calcium silicate composites and autoclaved aerated concrete was studied. The use of slag resulted in an increase in the intensity of the diffraction line of tobermorite by X-ray diffraction analysis as well as the use of glass. The difference was particularly evident in the shape of the tobermorite crystals. Long strong crystals were detected in the sample with slag, while the sample with glass exhibited low tobermorite leaves. Porous structure of autoclaved aerated concrete with slag was uniform, unlike samples with glass. Both materials have a positive effect on the increase in compressive strengths of the samples.

Keywords: calcium silicate composite, secondary raw materials, tobermorite, slag, glass.

Introduction

In the long-term ecological development, the question of the usability of low-value materials in autoclaved aerated concrete production technology has been studied and discussed for many years, as well as in other construction sectors. So far, the greatest attention has been paid to the replacement of primary raw materials in the field of cement composites. However, these composites are generally susceptible to unstable chemical composition of secondary raw materials, or to the presence of substances harmful to cement composites. Autoclaved aerated concrete (AAC) offers a higher degree of tolerance to more diverse raw materials, or raw materials that have not proven so much in cementitious composites. These include, for example, slag produced by burning brown coal (hereinafter referred to as slag) or ground glass. It is precisely these materials that are discussed in this article.

During the high-temperature combustion of brown coal, a glassy black material with gravel-like granometry is formed in the boiler bed. It is a slag. This slag is characterized by high inhomogeneity. Usually, it contains higher amounts of CaO than black coal slag. Furthermore, the slag contains mulite, silica, iron oxide, anortite, melilite, burnt clay clays, magnetite and gypsum (Dobeš, 2013). Furthermore, it may contain unburned coal residues and sulfur compounds. These residues are considered to be harmful to the use in cement composites (Smarzewski & Barnat-Hunek, 2016). However, for AAC technology, sulfur compounds could have a positive impact on the formation of tobermorite, as Chucholowski, Holger and Thienel (2018). They detected tobermorite in a morphology called “house of cards”. At the same time, they are of the opinion that this morphology contributes to higher compressive strengths than needle-shaped morphology, which is generally considered to be stronger.

Another almost unexplored material used in the field of AAC production technology is ground container glass. It is a highly reactive material which has been investigated primarily as an admixture in cementitious composites. As far as cement composites are concerned, the focus is on the grain size of the recycled material. Since it is an amorphous SiO₂, there is a risk of alkali-silica reaction. To avoid this, the glass should have a maximum grain size of 0.3 mm. On the contrary, ground glass helps to suppress the alkali-silica reaction because finely ground glass exhibits pozzolanic reaction, consumes portlandite to form calcium hydro silicate (CSH) phases that envelop the reaction edge of glass grains, and reduces monosulfate levels (Zheng, 2016; Lee, Hanif, Usaman, Sim, & Oh, 2018). In the case of AAC, this

condition also applies. As AAC is exposed to moist and warm environments during hydrothermal treatment, conditions are ideal for an undesirable alkali-silica reaction. The influence of the addition of ground container glass was examined by Walczak, Małolepszy, Reben, Szymański, and Rzepa (2015) who observed changes in the AAC microstructure. When replacing the quartz sand with glass, the morphology was changed from plate-like to fibrous. Furthermore, their research shows that the ideal glass replacement limit for silica sand is 8%. At higher replacement, the compressive strength AAC was reduced.

As AAC and its microstructure are mentioned in the previous paragraphs, the characteristics of this material need to be further specified. AAC is defined as lime silicate composite with a porous structure. The basic raw materials for the production of AAC include lime and quartz sand, followed by cement, gypsum and aluminum powder. Aluminum powder represents the function of pore formation. Al^{3+} ions react with calcium hydroxide resulting from the reaction of lime and water. During this reaction, hydrogen is released to loosen the mass. The lightweight mass that is created is exposed to the hydrothermal conditions in the autoclave, where the necessary reactions take place to form a solid microstructure. The AAC microstructure is based on the presence of crystalline SiO_2 , which partially functions as a filler, and partially provides the necessary Si^{4+} ions to form CSH. CSH phases are crystalline in the case of AAC and act as a binder. The most important CSH phase is then the tobermorite mineral. This determines the mechanical strength of the final product (Wang, Peng, Tang, Zeng, & Lan, 2014; Youssef, Ibrahim, Komarneni, & Mackenzie, 2010; Hartmann, 2004; Chen, Chang, Lai, & Chou, 2017; Drochytka, 1999).

The paper deals with the basic research of the effect of slag and ground glass on the basic parameters of lime-silicate composite.

Materials and methods

First, primary raw materials and two alternative siliceous raw materials were selected to replace silica sand in calcium-silicate composites. The main criterion for selecting siliceous raw materials was the silica content. The chemical composition of the raw materials is shown in Table 1. Slag and glass were selected as alternative raw materials. The reason for choosing these raw materials was the effort to verify the so far less used alternative sources of silica in the production of AAC.

Table 1. Basic chemical composition of used materials

Oxide	Quartz sand	Slag	Glass	Lime
SiO_2 [%]	92.9	51.0	71.0	0.0
CaO [%]	0.2	4.4	10.4	95.6
Al_2O_3 [%]	2.5	22.4	1.7	0.0
Na_2O [%]	0.7	1.8	13.0	0.0
K_2O [%]	0.2	3.3	0.9	0.0
SO_3 [%]	0.0	1.11	0.0	0.1

Design of the mixtures

The compositions were calculated based on chemical composition to maintain a silica to calcium oxide molar ratio of 0.73. The raw material ratios used are shown in Table 2. The substitution of quartz sand by secondary raw materials was 100%.

In the second phase, aluminum powder was added in the production of samples at 0.1% of the total raw material. Aluminum powder reacts with Ca^{2+} ions and H_2O to form hydrogen to form pores. In this way, the AAC structure was simulated. The aim is to monitor the influence of alternative raw materials on the formation of pore structure.

Table 2. Materials ratio

Raw material	Quartz sand	Slag	Glass
Lime [%]	40.8	27.4	35.6
Silica material [%]	59.2	72.6	64.6

Preparing of samples

Sample preparation consisted in the homogenization of lime, silica and water. The lime silica component was first carefully homogenized in a dry state. Then, water was added to the mixture to form a consistency of the liquid slurry. The water coefficient ranged from 0.57 to 0.77. The slurry was poured into molds of $20 \times 20 \times 100$ mm. The molds were pre-treated with oil. After 24 hours, the samples were removed from the molds and dried in an oven.

Hydrothermal treatment of the samples was ensured by autoclaving capsules. These capsules consist of a steel casing and a Teflon liner. The samples are placed in a Teflon liner on a dyestuff pad. Then, the added amount of water 10% of the volume of the Teflon liner. The capsule is then sealed with a double screw-thread to prevent pressure leakage. The capsule is placed in an drying oven to provide the desired temperature. Samples were autoclaved at 190 °C for 4, 8 and 16 hours hydrothermal holding.

After autoclaving, the samples were dried and subjected to physical-mechanical properties. Then the samples were stripped of the outer edges, which could contain undesirable impurities. A portion was left to study the microstructure by scanning electron microscopy (SEM) using a TESCAN MIRA3 XMU. The remaining sample cores were ground using a vibratory mill and then using a McCornie XRD mill to a maximum grain size of 20 µm. Microstructure was studied on the resulting powder by X-ray diffraction diagram obtained with the Empyrean Panalitical.

Results and discussion

Physical-mechanical properties

The sample weight was determined after the sample ČSN EN 12390-7 (European Committee for Standardization [CEN], 2009) and the compressive strength after the model ČSN EN 196-1 (CEN, 2016). These parameters were determined only for composites without pore structure. The main criterion under consideration is the microstructure of non-loosened composites, and the physical-mechanical properties serve as additional information. Physical-mechanical properties were determined on composites without pore structure. The porous structure composites exhibited low handling strengths and served only to monitor the pore structure.

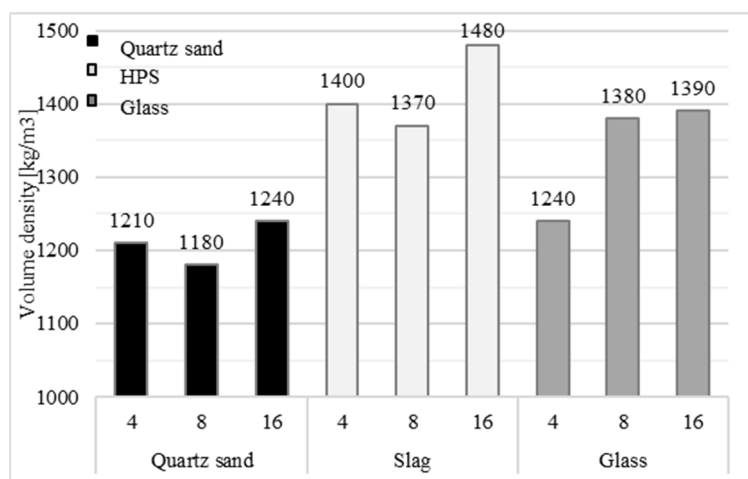


Figure 1. Volume density of composite samples

First, the volume density of the samples was monitored. When comparing the used alternative raw materials with the reference quartz sand (Figure 1), it can be seen that both raw materials resulted in an increase in volume density. The highest increase was observed in samples with slag, where the increase was almost 20%, regardless of the time of autoclaving. The lowest increase was recorded for the samples with glass autoclaved for 4 hours, when there was an increase in the order of tens of kg/m³. This increase can be considered insignificant. As for the effect of the autoclaving time, it is interesting that in the reference sample and the slag sample, the volume density decreased at 8 hours of autoclaving and the volume density increased at 16 hours. In contrast, a glass sample appears stable as early as 8 hours of autoclaving. Higher density could have a negative impact on the production of AAC. However, the porous structure plays a very important role in the production of AAC, thus giving rise to a higher volume density of the slag in the background.

When comparing the influence of alternative raw materials on the compressive strength of the samples, it can be seen that the sample with the slag does not have a significant positive effect on the increase in compressive strength (Figure 2). On the other hand, a glass specimen autoclaved for 8 hours, where a 40% increase in compressive strength compared to the reference sample, was found to be crucial. Based on this information, it can be assumed that the admixture of ground container glass in the AAC production technology could have a positive effect on the compressive strength of the resulting material. Regarding, the effect of autoclaving length, the time of 16 hours seems inappropriate. This autoclaving time has a negative impact on the compressive strength. This decrease is most evident in the glass sample. It is likely that fundamental changes occur in the sample microstructure, which have a negative progress to compressive strength. It can be a conversion of tobermorite into another, less stable CSH mineral.

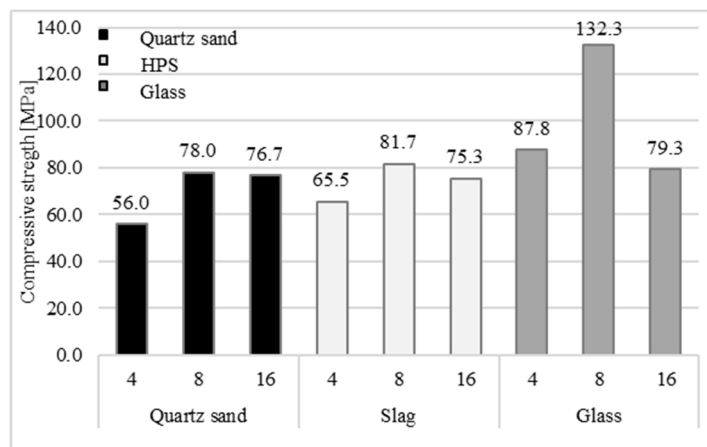


Figure 2. Compressive strength of samples

Microstructure

The greatest attention in this paper is devoted to microstructure. Respectively, the impact of secondary raw materials on the microstructure is taken as a priority in assessing the value of these raw materials.

Quartz and portlandite minerals were detected as major minerals in the sand samples using X-ray diffraction analysis (Figure 3). Furthermore, tobermorite ($\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$), was detected, with the dissolution of quartz dissolving in favor of tobermorite with increasing time of autoclaving.

According to X-ray diffraction analysis, the slag sample also contained quartz, tobermorite, and katoite in a weakly crystalline morphology. Anortite and hillebrandite were also detected at 190 °C for 16 hours. Anortite ($\text{CaAl}_2\text{SiO}_8$) is a mineral that occurs in granular, easily fissile aggregates. Hillebrandite ($\text{Ca}_2\text{SiO}_3(\text{OH})_2$) has rectangular plate-like crystals. The formation of anortite and hillebrandite was probably supported by the content of Al_2O_3 in the slag.

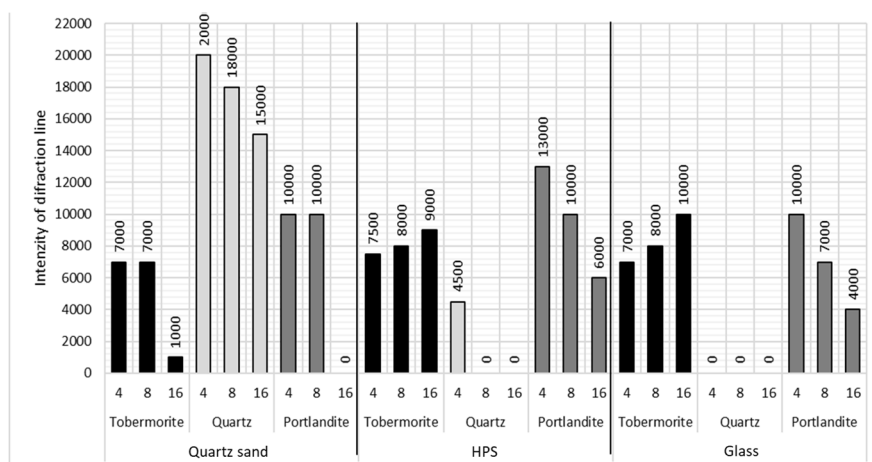


Figure 3. Intensity of diffraction lines according to X-ray diffraction analysis

The X-ray diffraction glass sample does not show the presence of crystalline SiO_2 . This is consistent with the phase composition of glass, which is entirely amorphous in nature. It was assumed that the presence of only amorphous SiO_2 should have a positive effect on the crystallization of tobermorite. This claim was confirmed in particular with a hydrothermal autoclave duration of 16 hours, where the intensity of the tobermorite diffraction line increased by 30%. Simultaneously with increasing length of hydrothermal endurance, the intensity of the diffraction line of portlandite decreased. Thus, $\text{Ca}(\text{OH})_2$ was probably dissolved in favor of tobermorite. It is interesting to note that in SEM images the tobermorite in the glass sample was not found to be needle-shaped with a developed crystal length. On the contrary, tobermorite was found in the form of relatively low leaflets (Figure 4). In contrast, tobermorite has been found to be a well-developed mineral in the form of long slats in the slag samples. If we admit a certain dependence of the compressive strength of the samples on the morphology of the tobermorite, then the low leaf-like morphology is probably more beneficial in terms of the microstructure quality of the samples. Indeed, Chucholowski et al. (2018) also claim the same in his research. At 16 hours of hydrothermal stamina, the intensity of the diffraction line was detected as high in the

glass sample and a significant decrease in strength was recorded. This finding can confirm the fact that when developing tobermorite on longer platelets and needles, compressive strength may decrease

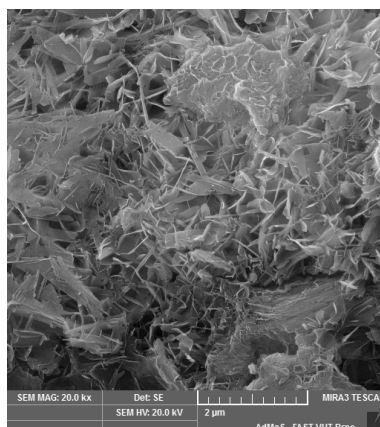


Figure 4. SEM image of the sample with glass autoclaved at 190 °C for 8 hours

Porous structure

This is an additional observation of the effect of the alternative raw material on the porous structure. Since a recipe was left where the sample consisted only of lime and silica, and aluminum was added for pore formation, it is not AAC in the true sense.

The effect of both siliceous raw materials on the porous structure is evident from the Figure 5. The quartz sand reference sample contains a relatively low zero phase representation in its structure. The pores are irregular in size up to 2 mm. The slag sample, on the other hand, has a relatively homogeneous pore distribution and a greater zero phase representation than the reference sample. Occasionally, pore agglomeration occurred in larger caverns, but the sample still had the nearest AAC structure. Finally, the glass sample contained the largest diameter pores. The pores are interconnected in 4 mm caverns. During the production of the sample with glass, a relatively strong aluminum-to-mass reaction occurred, and rapid evolution of hydrogen produced macropores. From these findings it can be concluded that the absence of silica in crystalline form has a negative impact on the porous structure, as is the case with the glass sample.

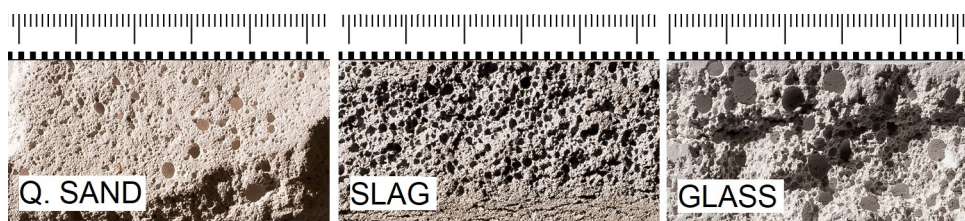


Figure 5. SEM images of samples with aluminum

Conclusions

The aim of this paper was to study the possibility of using secondary raw materials in AAC technology. It is a basic research that serves as a basis for further research phases. The effect of slag from brown coal combustion and the impact of ground glass was investigated. Based on the results obtained from samples of lime-silica composite, interesting findings were found. The slag samples showed a diffraction line intensity of the tobermorite according to X-ray diffraction analysis, while maintaining the compressive strength of the samples. The truth is that replacing sand with a slag has resulted in an increase in the bulk density of the sample, but on the other hand, a slag and porous pattern exhibited the most regular pore volume distribution. Replacing the sand with glass resulted in rather significant changes. Especially the changes in compressive strength values, when there was a significant increase compared to the sand sample. Furthermore, a change in morphology of tobermorite from needle-shaped to “house of cards” was noted. However, sand replacement with glass had a negative progression to the porous structure. So it can be said that both raw materials and slag and glass have the potential as a secondary raw material in AAC production technology. The slag can contribute positively to the formation of tobermorite and to the formation of a homogeneous pore structure. Glass can promote the compressive strength of the resulting AAC. In the future, it is necessary to verify different sand substitutes with these raw materials in real aerated concrete technology.

Acknowledgements

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