

EXPERIMENTAL STUDY OF AUTOCLAVED AERATED CONCRETE USING CIRCULATING FLUIDIZED-BED COMBUSTION FLY ASH

EKSPERIMENTALNA ŠTUDIJA V AVTOKLAVU PREZRAČENEGA BETONA IN UPORABE Z ZGOREVANJEM V VRTINČASTI PLASTI NASTALEGA DIMNIŠKEGA PEPELA

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The research deals with the possibility of maximum utilization of FBC fly ash in AAC technology and its impact on the properties of AAC. In the research, fly ash was used as a partial substitute for binder components in the AAC formulation. The amount of fly ash substitution was chosen on a scale of 10 % to 100 %. Physical-mechanical properties such as compressive strength and bulk density were determined on autoclaved samples. XRD analysis, SEM/EDX analysis were performed. Using these analyses, the change in the microstructure of autoclaved aerated concrete was monitored with increasing amount of FBC fly ash used. EDX microstructural tests have confirmed the incorporation of aluminum ions into the crystalline CSH. Further, an amount of crystalline tobermorite in the samples was observed which was almost constant up to 50 % of the FBC substitution. Compressive strength also began to decline significantly when the 50 % FBC fly ash substitution threshold was exceeded. The results thus show that the maximum FBC fly ash substitution is possible up to 50 %.

Keywords: AAC, FBC fly ash, tobermorite, emission reduction

Uporaba dimniškega pepela, nastalega med zgorevanjem premogovega prahu v vrtinčasti plasti (CFBC) v izdelkih za gradbeništvo, je zahtevna zaradi njegove visoke vsebnosti žvepla. Mikrostruktura v avtoklavih prezračene betona (AAC) pa se spremeni v hidrotermalnih pogojih in tvorijo se kristalinični kalcij-silikatni hidrati (CSH). Ti so sposobni vezati v svojo strukturo kalcijev sulfat, ki ga vsebuje CFBC dimniški pepel. V raziskavi avtorji ugotavljajo kakšna je še maksimalna možna količina dodanega CFBC dimniškega pepela v beton, izdelan z AAC tehnologijo in njen vpliv na lastnosti tako izdelanega AAC. V raziskavi so avtorji nadomeščali živo apno z dimniškim pepelom v skladu z AAC receptom. Nato so iz izdelanega betona naredili preizkušance in določili njegove fizikalno-mehanske lastnosti, kot sta: tlačna trdnost in volumska gostota. Rezultati raziskave jasno kažejo možnost uporabe nadomestka v obliki dimniškega pepela v količini do 50 %. Nadalje so izvedli še XRD- in SEM/EDX-analize, ki so potrdile spremembe mikrostrukture prezračene betona zaradi uporabe povečane količine CFBC dimniškega pepela. EDX mikrostrukturne analize so potrdile vgradnjo aluminijevih ionov v kristalinični CSH.

Ključne besede: v avtoklavih prezračeni beton (AAC), zgorevanje premoga v vrtinčasti plasti (CFBC), dimniški pepel, tobermorit, zmanjšanje emisij

1 INTRODUCTION

The reduction of CO₂ emissions is the major current world issue. With the use of fossil fuels, the concentration of CO₂ in the atmosphere increases. Today, the CO₂ concentration in the atmosphere is 400 min⁻¹, which is 40 % more than in the pre-industrial period and continues to rise by 1–2 min⁻¹/year.¹ One of the major sources of CO₂ emissions in the construction industry is the production of Portland cement and lime.^{2–4} These basic binder raw materials are used in the production of AAC. Replacement-binder raw materials used in the autoclaved-aerated-concrete (AAC) production have not been determined so far. One of the possible solutions for replacing cement and lime can be the use of fluidized-bed combustion fly ash (FBC fly ash). FBC fly ash has pozzolanic properties. FBC fly-ash solidifies and hard-

ens due to the reaction of active pozzolanic components with calcium hydroxide.⁵ The literature describes the use of FBC fly ash as a substitute for Portland cement in cement composites, where its pozzolanic properties are used.⁶ However, the use of FBC ash in cement composites is limited due to the high content of SO₃ and free lime.^{7–9} FBC fly ash contains SO₃ in the form of calcium sulfate (II-anhydrite). This form of calcium sulfate reacts with water to produce much larger reaction products, which cause cracks in the material. Finally, calcium sulfate reacts with alumina hydroxide and calcium hydroxide to form ettringite, which increases its volume by up to 125 %.^{6,10–12} These negative properties of FBC fly ash can be eliminated with an autoclaving process.¹²

AAC consists of a microporous binder matrix and air macropores.¹³ The macropores give the AAC the heat-insulating property and they are formed due to the reaction of aluminum powder with calcium oxide and calcium hydroxide. This process takes place in a still

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uncured binder matrix. At this stage, it also begins to hydrate the cement to form amorphous calcium silicate hydrates (CSHs). After the binder matrix has hardened, the second stage of the AAC production takes place in an autoclave. At elevated temperature and pressure, AAC is exposed to hydrothermal conditions for the time necessary to form new crystalline phases, 1.1-nm tobermorites and well crystallized CSHs.^{14,15}

Our research examines the possibility of using FBC fly ash as the binder of AAC instead of lime and cement. The binder-component replacement is in a range of 10–100 %, increasing by 10 %. The tests were divided into two groups, testing the physical/mechanical properties of AAC and the microstructure of AAC.

2 EXPERIMENTAL PART

2.1 Materials

AAC consists of silica sand, lime, cement and aluminum powder. These raw materials are labeled as basic, which means that they are part of the reference mixture without FBC fly ash. These basic raw materials were mixed with water to form an aerated concrete suspension. Calcium sulfate is the raw material supporting the formation of a thixotropic structure and the crystallization of new phases. Instead of the natural calcium sulfate, calcium sulfate from thermal combustion was used here as it achieves high purity ($\text{CaSO}_4 < 95\%$). Quartz sand was chosen due to its high amount of silica ($\text{SiO}_2 < 98\%$).

The FBC-fly-ash substitution for lime and cement was experimentally tested during the research. The FBC fly ash was subjected to a chemical analysis and the results are shown in **Table 1**. FBC fly ash was selected due to its high content of free lime, which is necessary for hydrothermal reactions. The mineralogical composition of the fly ash included anhydride, quartz, calcite and lime.

2.2.1 Sample preparation

AAC samples had dimensions of (100×100×100) mm. The raw-material mixture consisted of 5 % lime, 8 % cement, 52 % silica sand, 0.05 % aluminum powder and 2 % calcium sulfate. The amount of water was constant and the water-cement ratio was determined to be 0.52. Fluid fly ash replaced the dry-binder component (cement, lime) in the range of 10–100 %.

Lime, cement and FBC fly ash were dry homogenized. A suspension was formed from the aluminum powder, degreasing additive and water. The next step was the production of a gypsum-sand suspension at a temperature of (40 ± 1) °C. A dry mixture was added to the gypsum-sand suspension, followed by an aluminum suspension. The mixture was poured into molds and after 24 h the samples were demolded. The samples were autoclaved in a laboratory autoclave in the environment of saturated water vapor. The hydrothermal time was set to 7 h and the temperature to 190 °C.

2.2 Methods

The compressive strength was determined on dried samples at (105 ± 5) °C. The test was performed according to standard ČSN EN 679 "Determination of the compressive strength of autoclaved aerated concrete". Each test specimen was placed in a press perpendicular to the mass growth and loaded at a constant rate of (0.1 ± 0.05) MPa/s. The size of the test specimens was $(100 \times 100 \times 100)$ mm). The bulk density was determined in line with standard ČSN EN 678 "Determination of the bulk density in the dry state of autoclaved aerated concrete". The compressive strength and bulk density were tested on six samples.

X-ray powder-diffraction data were collected using an Empyrean Panalitical diffractometer with Cu- $K_{\alpha 1}$ radiation, and $\lambda = 0.1540598$ nm. Angular reproducibility was $< 0.0002^\circ$. The cores were prepared from the samples and ground to a maximum size of 0.1 mm using a vibratory mill in the first stage of the sample preparation for the microstructure study. The ground sample was further milled in an isopropanol suspension with an addition of a standard (CaF_2) in a MC Microne mill to a grain size < 0.02 mm. The morphology and chemical composition of the synthesis products were analyzed with a TESCAN MIRA 3 XMU scanning electron microscope (SEM) at an accelerating voltage of 20 kV. Representative fragments of $(5 \times 5 \times 5)$ mm were selected for the microstructural study. The samples were, therefore, sputtered with a fine layer of gold to prevent electric charging during the measurement.

3 RESULTS

3.1 Physical/mechanical properties

The compressive strength and bulk density were analyzed for physical/mechanical properties (**Figure 1**).

Table 1: Chemical composition of raw materials

Raw materials	Chemical composition (%)											
	Al ₂ O ₃	CaO	SO ₃	Fe ₂ O ₃	FeO	K ₂ O	MgO	MnO	Na ₂ O	P ₂ O ₅	SiO ₂	TiO ₂
Quartz sand	2.53	0.23	0.02	0.84	0.19	1.53	0.16	0.01	0.70	0.01	92.91	0.14
Cement	5.40	64.25	2.66	3.06	0.22	3.32	2.02	0.10	0.36	0.16	19.67	0.31
Lime	–	95.62	0.07	–	–	–	0.79	–	–	–	–	–
FBC fly ash	14.2	35.67	26.6	6.76	–	1.19	2.16	0.08	0.38	–	26.6	0.78

The existing resources expect a decrease in the compressive strength with an increased content of FBC fly ash.^{10,11,16}

The compressive strength of the samples is the highest at a 10-% FBC fly-ash substitution. With an increased substitution, the strength is slightly decreased. The sample with a 30-% FBC fly-ash substitution achieves lower strengths than the reference sample. A gradual decrease in the strength continues up to the 50-% substitution of FBC fly ash. The 50-% FBC fly-ash substitution is the limit of maximum utilization. Up to 50 %, FBC fly ash can replace cement and lime due to its pozzolanic properties. This limit is surprisingly high. Within this limit, the formation of crystalline CSH phases is assumed, in parallel with the formation of amorphous CSH phases, which serve as the bonding matrix of silica-sand grains. Above the 50-% substitution of FBC fly ash, the strength of the samples decreases sharply and it is almost zero at 100 %. Thus, crystalline CSH phases are not expected to be formed above 50 %. The bulk density of the samples increases despite the decreasing strength. This trend indicates a higher bulk density of the non-crystalline CSH phases formed in the presence of FBC fly ash.¹⁶ Further explanation of the bulk density increase may be due to the loss of lime at higher FBC fly ash substitutions. The aluminum powder reacts to form a lower volume of hydrogen. This phenomenon will be studied in the next stage of the research.

3.2. Microstructure

The sample microstructure was monitored with SEM/EDX and XRD. The quality of the crystalline phases significantly affects the physico-mechanical properties of the AAC.¹⁷

The XRD analysis was carried out with respect to the intensity of the tobermorite diffraction line and its area below the diffraction line (Figure 2). The intensity of the tobermorite diffraction line is constant up to 40 % of the FBC fly-ash substitution and it only slightly decreases up to the 80-% substitution. These results indicate that FBC fly ash does not affect the crystallization of tobermorite.

The results are surprising in view of the decreasing strength of the samples and therefore do not show the dependence on the physical/mechanical properties.

Conversely, the area of the tobermorite diffraction line correlates with the compressive-strength results. Up to 50 % of the FBC fly-ash substitution, we can observe the same, or a slightly reduced, amount of tobermorite in the sample, but above 50 %, the amount of tobermorite decreases sharply. At 90 and 100 % of the FBC fly-ash substitution, tobermorite is not present in the sample. Thus, it is clear from the results that the amount of tobermorite is an important indicator of the AAC quality.

As mentioned before, the amount of tobermorite is almost constant up to 50 %. However, the uptake conditions change when the amorphous CSH phase is converted into the crystalline CSH phase. A reduction in the calcium oxide content indicates a decrease in the formation of crystalline phases. Therefore, FBC fly ash must sufficiently replace both the lime component (calcium hydroxide) and the cement component (clinker). The calcium hydroxide content of fly ash is 14–38 %. Thus, with respect to the hydrothermal reaction, such an amount is sufficient for the formation of CSH phases. FBC fly ash can substitute cement due to its pozzolanic activity.

Surface-element measurements were performed on tobermorite crystals (Figure 3). The two main indicators are the Ca/Si and Al/(Si+Al) molar ratios. As the FBC fly-ash admixture increases, we can see a reduction in the Ca/Si ratio. This result correlates with the expected result. Increasing the FBC fly-ash substitution decreases the calcium oxide content. In the absence of calcium oxide in the hydrothermal reaction, silicon-rich CSH phases are formed, thus reducing the Ca/Si molar ratio.¹⁵ In contrast, the Al/(Si+Al) molar ratio is higher with a higher FBC fly-ash substitution. This means that under hydrothermal conditions, tobermorite is formed, in which aluminum ions are bound. The resulting phases therefore arise from the hydration products of the pozzolanic reaction of the FBC fly ash. This result is consistent with the ones previously reported^{18–21}, confirming the possibility of binding aluminum ions to the structure of tobermorite. However, those articles only dealt with the

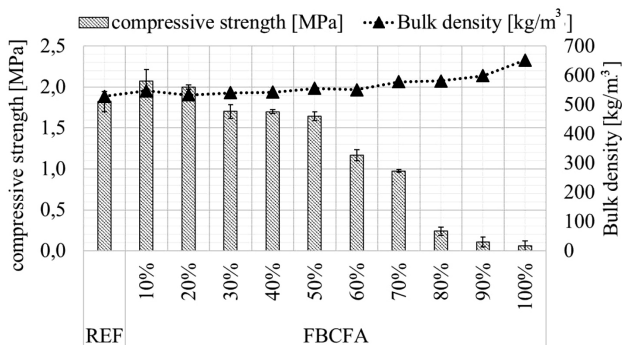


Figure 1: Compressive strength and bulk density of a sample with the FBC fly-ash substitution

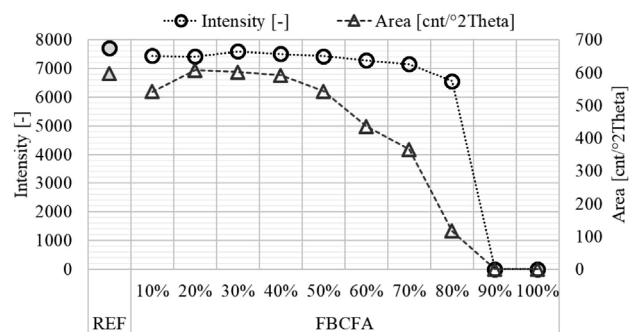


Figure 2: Intensity and area of the diffraction line of tobermorite for the samples with FBC fly ash

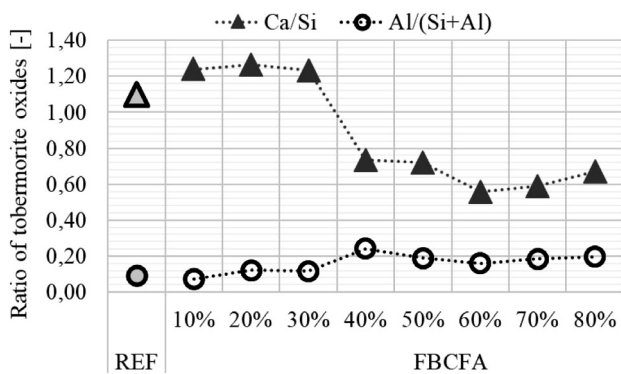


Figure 3: Molar ratio of tobermorite of the samples with the FBC fly-ash substitution

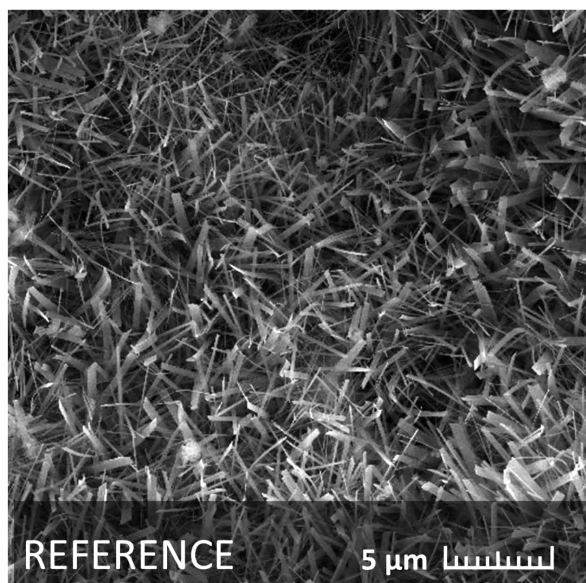


Figure 4: SEM image of the reference sample

replacement of silica oxide and thus our result may be helpful for further studies.

The SEM image of the reference sample predominantly contains acicular tobermorite (Figure 4). Further SEM images (Figure 5) show that with lower FBC fly-ash substitutions, thin tobermorites are formed, emerging from non-crystalline CSH phases. This trend can be observed up to a 20-% FBC fly-ash substitution. At 30 %, tobermorite leaves begin to form. With a 30-% FBC fly-ash substitution, small leaves without split tips are formed. A gradual cleavage of the tobermorite tips can be observed at higher FBC fly-ash substitutions. This phenomenon has not been reported for AAC using FBC fly ash. The cleavage is probably related to the decrease in the Ca/Si tobermorite molar ratio. At a 60-% FBC fly-ash substitution, most of the crystals with split peaks are already present. At 80 %, very long and thin tobermorite crystals are seen, which means that the crystals have already frayed. At 90 and 100-% FBC fly-ash substitutions, crystalline phases no longer form. Only the flocculation of unreacted fluidized fly ash that encircles sand grains can be seen.

4 CONCLUSIONS

The research dealt with the possibility of a lime and cement replacement, using FBC fly ash. Based on the results, the following conclusions can be drawn:

- It is possible to use up to 50 % of FBC fly-ash replacement of lime and cement in AAC.
- Up to the 50-% FBC fly-ash substitution, the same, or a slightly reduced, compressive strength is maintained, compared to the reference sample.
- Up to the 50-% FBC fly-ash substitution, the tobermorite content in AAC is maintained or only slightly reduced.
- As the FBC fly-ash substitution increases, the AAC bulk density increases.

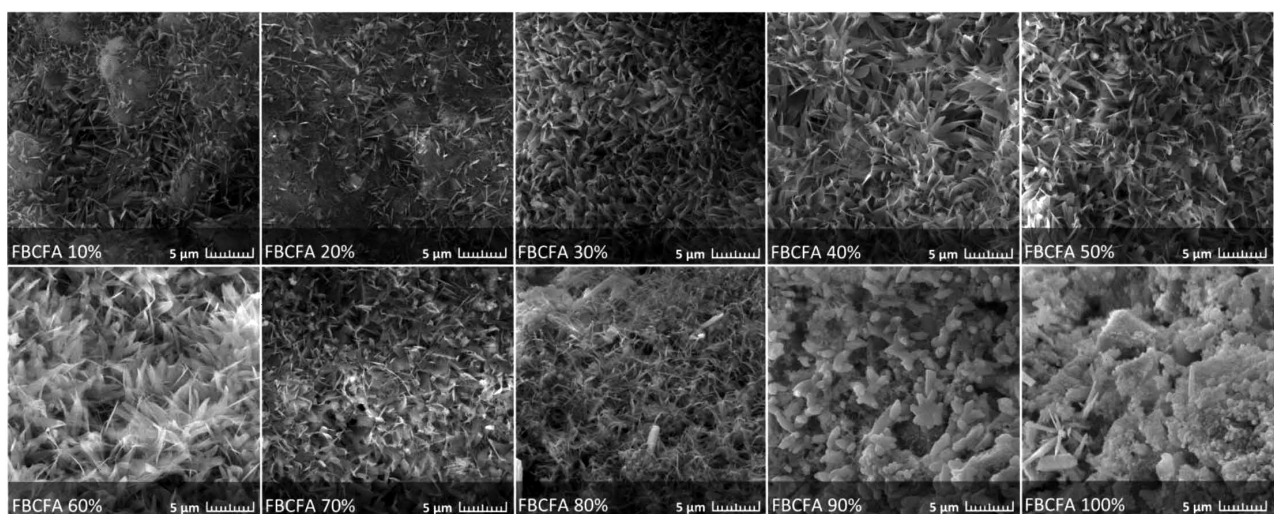


Figure 5: SEM images of the samples with a FBC fly-ash substitution

- As the FBC fly-ash substitution increases, the Ca/Si molar ratio of tobermorite decreases and the Si/(Si+Al) molar ratio of tobermorite increases.

The results showed a high potential of the use of FBC fly ash in AAC. The main aim of our research was to elucidate the behavior of fly ash as a substitute for the binder component. However, the issue of a binder replacement must be further studied.

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