INFLUENCE OF CHEMICAL ADDITIVES AND CURING CONDITIONS ON THE MECHANICAL PROPERTIES AND CARBONATION RESISTANCE OF ALKALI-ACTIVATED SLAG COMPOSITES

VPLIV KEMIJSKIH DODATKOV IN POGOJEV SUŠENJA NA MEHANSKE LASTNOSTI IN ODPORNOST NA KARBONACIJO Z ALKALIJAMI AKTIVIRANIH KOMPOZITOV ŽLINDRE

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The main aim of the presented work is to investigate the effect of the addition of air-entraining (AEA) and shrinkage-reducing agents (SRA) on the mechanical properties and carbonation resistance of alkali-activated slag (AAS). The materials used for the sample preparation were blast-furnace slag activated using sodium silicate and AEA or SRA in various amounts. The samples were cured in various conditions (air curing under laboratory conditions and water curing at the same temperature) and the influence of these was also studied. The prepared samples (specimens with dimensions of 100 mm × 20 mm × 20 mm) were tested for compressive and bending strengths. The experimental results show that the addition of AEA did not have a significant influence on the mechanical properties, while the addition of SRA had a negative effect. However, the carbonation resistance markedly decreases with an increase of both agents. The same is true for air curing, as mechanical strengths are lower compared to those samples cured in water, and the ratio of the strength of the air-cured composite and that of the water-cured composite decreases with an increase in the content of SRA.

Keywords: alkali-activated slag, carbonation resistance, chemical additives, mechanical properties

Glavni namen tega dela je preiskava vpliva dodatka za zmanjšanje vsebnosti zraka (angl. AEA) in dodatka za zmanjšanje krčenja (angl. SRA) na mehanske lastnosti in odpornost na karbonacijo z alkalijami aktivirane žlindre (angl. AAS). Materiali za pripravo vzorcev so bili plavžna žlindra, aktivirana z natrijevim silikatom in različnim dodatkom AEA ali SRA. Vzorci so bili strjeni pri različnih pogojih (strjevanje na zraku v laboratorijskih pogojih in strjevanje v vodi pri enaki temperaturi) in študiran je bil njihov vpliv. Pripravljeni vzorci, z merami 100 mm × 20 mm × 20 mm, so bili preizkušeni na tlačno in upogibno trdnost. Rezultati preiskav kažejo, da dodatek AEA ni imel pomembnega vpliva na mehanske lastnosti, medtem ko je dodatek SRA nanje vplival negativno. Vendar pa se je odpornost na karbonacijo močno zmanjšala z večanjem vsebnosti obeh dodatkov. Enako velja za strjevanje na zraku, saj so mehanske lastnosti slabše v primerjavi z vzorci, strjenimi v vodi in se razmerje trdnosti vzorcev strjenih v vodi in razmerje trdnosti na zraku strjenih kompozitov, zmanjša s povečanjem vsebnosti SRA.

Ključne besede: z alkalijami aktivirana žlindra, odpornost na karbonacijo, kemijski dodatki, mechanske lastnosti

1 INTRODUCTION

AAS has received increasing attention as a potential alternative to Portland cement (PC) due to its high strength, durability and low environmental impact.[1–3] Many studies have been carried out on AAS to determine its microstructure characterization,[4,5] reaction kinetics,[6,7] and chemical resistance.[8,9] Additionally, the thermodynamic modelling of AAS cements[10] and the phenomenon of AAS composite shrinkage[11–14] have been studied. The latter has a negative effect on AAS properties, especially in terms of mechanical strength.[15,16] Therefore, many chemical and mineral admixtures have recently been introduced to this area.

Chemical additives, especially those that are organic based, have recently been added to PC concrete with positive results. In addition to the commonly known application of superplasticizers, shrinkage-reducing agents (SRA) and air-entraining agents (AEA) have recently been gaining interest. SRAs are able to decrease the surface tension of water in concrete pores, which decreases the capillary tension within the pore structure. This is why shrinkage is reduced when water evaporates. Such SRAs are primarily based on polypropylene glycol.[17] The main reason for introducing an AEA is to produce air bubbles dispersed throughout the concrete. This provides durability to the hardened concrete during frost-thaw cycling. The AEA is a surfactant with a structure consisting of hydrophilic and hydrophobic groups,[18] based on a soluble salt of an alkyl aryl sulphonate.[19,20] After adding AEA into a cement paste, AEA molecules are quickly adsorbed into the interface of the cement-water-air system. The adsorption of surfactant causes a significant reduction of the free energy from the system,

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thus making a large number of small, closed, uniform bubbles. As the cement particles are now separated, the frictional resistance among them is reduced, thus increasing the workability of the mixture. Conversely, a higher amount (generally more than 0.004 % of mass fractions) of AEA cannot improve the fluidity of the mixture because the free water content in the unit volume paste decreases, causing a workability loss.[18] SRAs and AEAs do not only influence the afore-mentioned properties, as most of these agents are primarily determined to be used in PC-based systems. These agents may increase the porosity[21] and thus influence the compressive and bending strengths. Another important issue is the carbonation of AAS composites. Together with various curing conditions, the final material behaviour may be completely different. The main aim of this work is to study the influence of additives and curing conditions on the mechanical properties and the ability to resist the carbonation of an AAS composite.

2 EXPERIMENTAL PART

2.1 Materials

Ground, granulated blast-furnace slag with a specific surface of 380 m^2 kg^{-1} was used as a raw material. A liquid sodium silicate was used as an alkaline activator. The activator consisted of 47 % of dry matter, i.e., 16.8 % of Na_2O and 30.2 % of SiO_2, thus providing an SiO_2/Na_2O molar ratio of 1.85. The phase composition of the slag was determined using a PANalytical Empyrean X-ray diffraction (XRD) spectrometer. The slag consists predominantly of an amorphous phase with a smaller amount of crystalline mellilite and merwinite. Granulo-metric measurements to determine the particle size distribution were performed with a Sympatec HELOS KR laser analyser with a measurement range between 0.1 μm and 1.500 μm. The particle-size distribution is shown in **Figure 1**. The median particle size is 8.45 μm.

Chryso®Air A was used as an AEA. It is a commercially available chemical agent based on sulphonic acids and coconut oil, with the reaction products diethanolam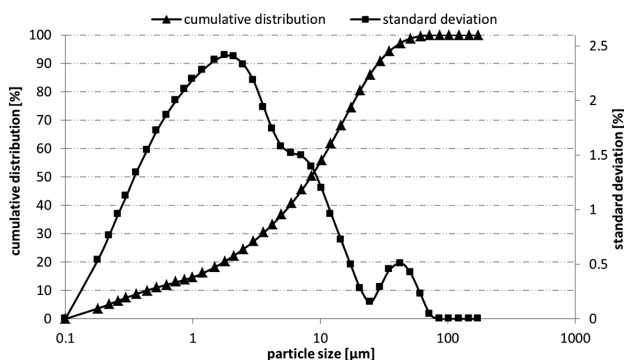ine and sodium thiocyanate. Chryso®Serenis was used as a shrinkage inhibitor (SRA). This additive is based on 2-methyl-2,4-pentanediol. Both are generally used for PC-based systems.

2.2 Composition of mortars and specimens preparation

Mortars were prepared by mixing the blast-furnace slag with an activating solution and sand. The amount of sodium silicate was 4.2 % by weight of slag. Standard fine sand as defined by CSN EN 196 1[22] was used as an aggregate. The slag-to-sand ratio and water-to-slag ratio of all the prepared mortars were 0.50 and 0.40, respectively. The mortars were subsequently modified by the addition of SRA in the amount of 0.25 %, 0.50 %, 1.00 % and 2.00 % by weight of slag. Finally, two mixtures were also modified with AEA in the amounts of 0.10 % and 0.50 % by mass of slag. The mortars were then cast into steel molds, demolded after 24 h, submerged in water for 3 d and then stored in air under ambient conditions until the 28th day. They were then tested. The other samples (with the same composition) were cured and submerged in water for the entire time. These were then compared with those cured in air.

2.3 Strength testing, carbonation and morphology

Compressive and bending strengths were tested on mortar specimens, with measurements of 20 mm × 20 mm × 100 mm, after 28 days. At least three samples of each composition were taken for a three-point bending test and the remaining parts of broken specimens were used for measurements of the compressive strength.

The depth of carbonation was determined on freshly broken specimens by spraying 1.0 % phenolphthalein solution on the fracture surface of the prism. The carbonation depth was measured and the sprayed cross-section surface photographed.

The microstructure of the selected AAS pastes was investigated using a ZEISS EVO LS 10 scanning electron microscope in the secondary-electron mode at a magnification of 1000× and an accelerating voltage of 10 kV. Gold sputter-coated fracture surfaces of air-cured Ref. and SRA1.00 pastes at the age of 28 d were examined using this technique.

3 RESULTS AND DISCUSSION

The flexural and compressive strengths of tested samples with various amounts of additives are shown in **Figure 2**. In **Figure 3**, the strengths are displayed relative to the strengths of the samples cured for 28 d submerged in water (samples submerged in water = 100 % strength, e.g. the reference water-cured mortar had approximately 121 MPa.[23] Generally, the curing of samples submerged in water led to higher values of compressive and bending strengths, which corresponds to the work of F. Collins and J. G. Sanjayan.[24] This is why the plotted values of air-cured samples are also
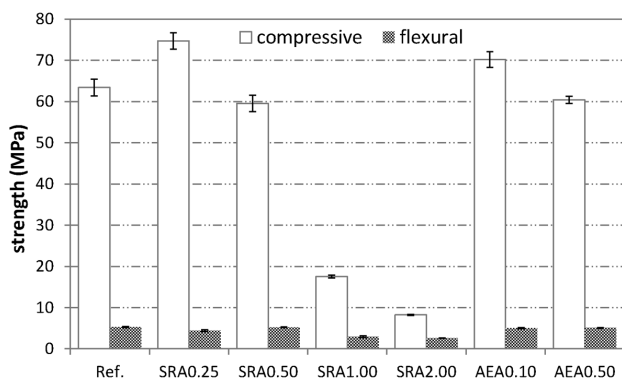
Figure 1: Particle size distribution of blast-furnace slag
Slika 1: Razporeditev velikosti delcev plavžne žlindre

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Figure 2: Compressive and flexural strengths of the prepared air-cured mortars
Slika 2: Tlačna in upogibna trdnost pripravljenih, na zraku sušenih malt

Figure 4: SEM picture of air-cured reference pastes
Slika 4: SEM-posnetek na zraku strjene referenčne paste

displayed relative to those cured in water. The curing of the specimens submerged in water permits their flexural and compressive strength development. It is also likely that surface cracking, which is often visible on AAS specimens, could serve as a crack initiator, leading to the propagation of major shrinkage cracks. Consequently, this significantly contributes to the decrease in flexural strengths.

The reduction of flexural strength is highest in the samples with 1 % and 2 % of SRA. The same is true for compressive strengths. With a lower content of SRA (0.25 % and 0.50 %), the reduction of strengths is lower than that of the reference sample without additives. In all the samples with SRA, the decrease of flexural strengths is lower compared to the compressive strengths, except for the sample with 0.25 % of SRA. This can be related to shrinkage. With a higher SRA content, the shrinkage and cracking during sample aging in air is reduced. However, a larger amount of SRA (in this study higher than 0.50 %) has a negative effect on the compressive strength. Therefore, sample SRA0.25 has a higher relative compressive strength than bending because the amount of SRA is such that it has no effect on the shrinkage and does not negatively influence the com-
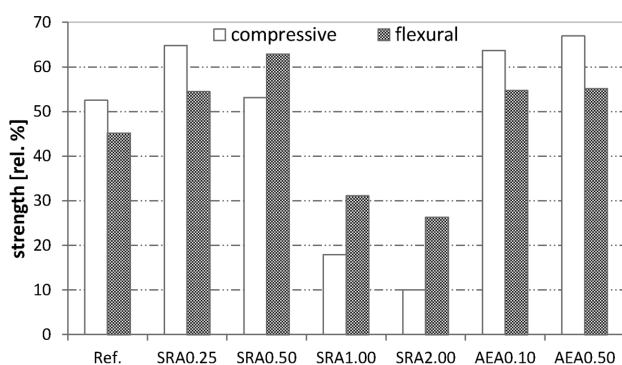
pressive strengths at the same time. The rapid reduction of strengths with the addition of SRA of 1 % and higher is further explained by the SEM images. **Figure 4** and **Figure 5** show the SEM picture of the fracture surface of the reference sample and the sample with 1 % of SRA, respectively. A dense matrix among the grains of slag is obvious in **Figure 4**, whereas in **Figure 5**, more porous matter among the grains of slag is observed. This also conforms to the study by V. Bílek et al.[23], where the authors investigated the influence of commercially available admixtures on the drying shrinkage of AAS in relation to the mechanical properties. Finally, the samples containing AEA had the highest relative compressive strengths (with AEA0.50 as the highest).

The carbonation depth reached 2.19 mm for SRA0.5 (**Figure 7a**) while SRA1.00 and SRA2.00 were completely carbonated (**Figure 7b**) after 28 d. Therefore the carbonation depths for SRA1.00 and SRA2.00 are not shown in **Figure 6**. According to V. Bílek et al.,[23] SRA likely acts as a hydration retardant. When the samples with a higher amount of SRA are cured in air, they lose significant amounts of water before they mature. Therefore, they contain a lower amount of binding phase, which is associated with higher porosity and

Figure 3: Relative compressive and flexural strengths (mortars cured in water = 100%)
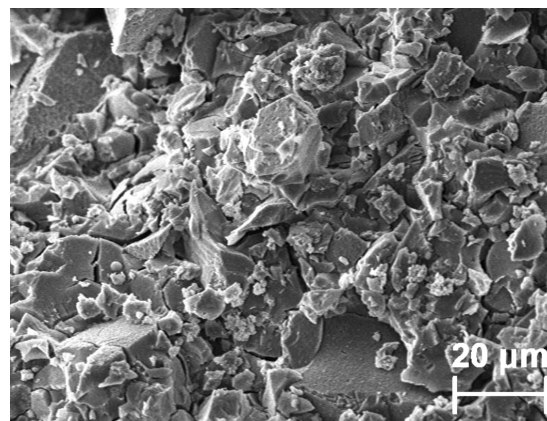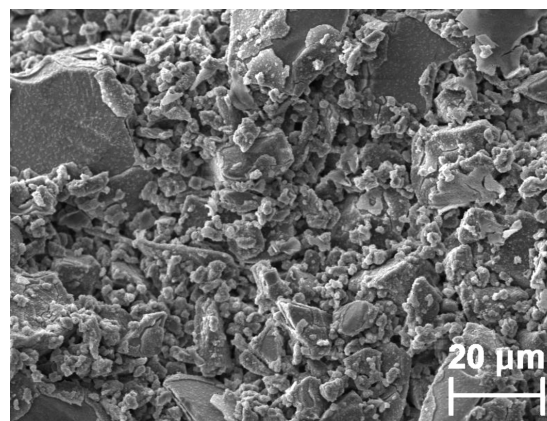**Slika 3:** Relativne tlačne in upogibne trdnosti (malta strjena v vodi =100 %)

Figure 5: SEM picture of air-cured SRA1.00 paste
Slika 5: SEM-posnetek na zraku strjene SRA1.00 paste

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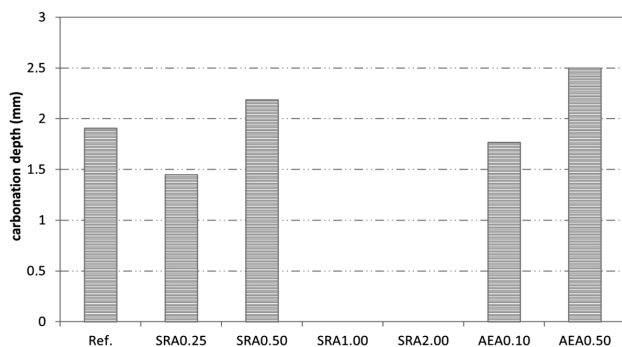P. BULEJKO, V. BÍLEK: INFLUENCE OF CHEMICAL ADDITIVES AND CURING CONDITIONS ...

Figure 6: Carbonation depth of the prepared mortars
Slika 6: Globina karbonacije pripravljenih malt

thus faster carbonation. This is another reason for their low strengths.

Some of the results obtained, especially those for carbonation resistance, are inconsistent with those reported earlier. C. Bilim et al.[25] did not observe a significant difference in the carbonation depth of the samples with and without SRA activated by solid sodium silicate. When C. Bilim et al.[26] used liquid sodium silicate, the carbonation resistance of AAS mortars was even better in the presence of SRA. These differences are caused by the different composition of the mixtures (particularly the SiO_2 to Na_2O ratio of the activator) and are most likely due to the different origins of the additives used. Bilim et al. used SRA based on polypropylene glycol in both aforementioned studies[25,26], while the SRA used in the present study was based on 2-methyl-2,4-pentanediol. This indicates a strong dependence in the behaviour of AAS on the composition of commercially

available SRAs originally developed for PC-based systems.

4 CONCLUSION

Based on the results above, the conclusions can be summarized as follows:

- It was confirmed that curing by submerging in water is better for AAS than air curing in ambient laboratory conditions. The compressive and flexural strengths significantly decreased in all samples.
- When the content of admixtures was low, the reduction in strengths was slightly lower compared to the reference sample with no additive, while with a higher amount of SRA, the reduction in strengths was significantly higher.
- The incorporation of more than 0.5 % of SRA led to a rapid carbonation of AAS, which is likely related to the negative effect of SRA on AAS hydration and the resulting porous matrix.

Acknowledgement

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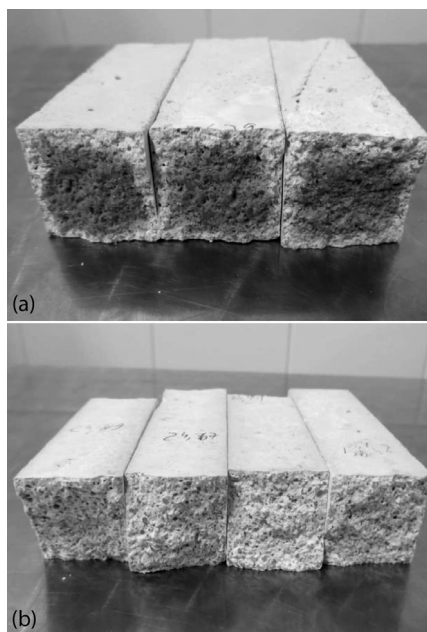

Figure 7: Carbonation of sample: a) SRA0.5 with carbonation depth of 2.19 mm and b) SRA1.0 completely carbonated
Slika 7: Karbonacija vzorcev: a) SRA0.5, z globino karbonacije 2,19 mm in b) SRA1.0 popolnoma karboniran

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