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EFFECT OF A COMBINATION OF FLY ASH AND SHRINKAGE-REDUCING ADDITIVES ON THE PROPERTIES OF ALKALI-ACTIVATED SLAG-BASED MORTARS

VPLIV KOMBINACIJE LETEČEGA PEPELA IN DODATKA ZA ZMANJŠANJE KRČENJA NA LASTNOSTI MALTE IZ Z ALKALIJAMI AKTIVIRANE ŽLINDRE

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This study is aimed at reducing the drying shrinkage of alkali-activated slag (AAS) through the use of low-calcium fly ash (FA) and commercially available shrinkage-reducing additives (SRAs) originally developed for OPC-based binders, since there are no such admixtures tailored for AAS systems. Generally, all the SRAs tested are based on modified alcohols. All the mortars were based on slag activated by waterglass, with the water-to-slag ratio equal to 0.40 and the sand-to-binder ratio 2:1. In the first step, the effect of the partial replacement of slag by FA (25, 50 and 75) % of mass fractions on the drying shrinkage and compressive strength was investigated. On the basis of the obtained results a mortar with 50 % FA in the binder was chosen for subsequent experiments, where the influence of three types of SRAs on the drying-shrinkage behaviour was examined. It was observed that while 25 % of the FA did not affect the drying shrinkage significantly, 50 % and 75 % of FA in the binder decreased the drying shrinkage by 57 % and 78 %, respectively. However, with an increasing content of FA, the compressive strength markedly decreased. All the tested SRAs had a similar effect on the drying shrinkage of the slag/fly ash (50/50) mortar: at a dose of 0.50 % (by mass of slag) the shrinkage was reduced only slightly, whereas 1.0–3.0 % of SRA resulted in a decrease by 49–66 %. Also, the drying shrinkage rate during the first days of drying was modified. However, all the SRAs reduced the compressive strength as compared to the neat slag-FA mortar, especially when the doses were higher than 0.50 %.

Keywords: alkali-activated slag, fly ash, shrinkage reducing additives, shrinkage, strength

Namen študije je zmanjšanje krčenja pri sušenju z alkalijami aktivirane žlindre (AAS) z uporabo letečega pepela (FA), z majhno vsebnostjo kalcija in komercialno dostopnega dodatka za zmanjšanje krčenja pri sušenju (SRA), originalno razvitega za veziva na osnovi OPC, ker do sedaj ni bilo takega dodatka primernega za AAS sisteme. Na splošno so vsi preizkušeni SRA temeljili na modificiranih alkoholih. Vse malte so bile iz žlindre, aktivirane z vodnim steklom, z razmerjem voda:žlindra (0,40) in pesek:vezivo v razmerju 2:1. Na prvi stopnji je bil preiskovan vpliv delne nadomestitive žlindre s FA (25, 50 in 75) % masnih odstotkov, na krčenje pri sušenju in na tlačno trdnost. Na osnovi dobljenih rezultatov je bila za nadaljevanje preizkusov izbrana malta s 50 % FA v vezivu, kjer se je preiskoval vpliv treh vrst SRA na skrček pri sušenju. Opaženo je bilo, da medtem ko 25 % FA ni vplivalo pomembno na skrček pri sušenju, je 50 % in 75 % FA v vezivu, zmanjšalo skrček pri sušenju za 57 % oziroma 78 %. Vendar pa se je z naraščajočim deležem FA tlačna trdnost opazno zmanjšala. Vse preizkušene SRA so imele podoben vpliv na krčenje pri sušenju malte, z razmerjem žlindra:leteči pepel (50:50), pri količini 0,50 % (masa:žlindra) se je skrček zmanjšal samo delno, medtem ko se je pri 1,0–3,0 % SRA skrček zmanjšal za 49–66 %. V prvih dneh se je spremenila tudi hitrost krčenja pri sušenju. Vendar pa je SRA zmanjšala tlačno trdnost, v primerjavi z maltami iz žlindre in FA, še posebno, če sta bila njuna deleža večja od 0,5 %.

Ključne besede: z alkalijami aktivirana žlindra, leteči pepel, dodatki za zmanjšanje krčenja, skrček, trdnost

1 INTRODUCTION

Concretes based on Portland cement (PC) provide a very good mechanical performance for arelatively low cost. Besides some durability problems that may occur, PC production is connected with the significant emissions of greenhouse gases such as CO_2 and NO_x and a high energy consumption. It is estimated that the PC industry contributes 7 % to the global CO_2 emissions. The utilization of some industrial wastes or by-products such as blast-furnace slag (BFS) and fly ash (FA) may be a possible way to partially solving the above-mentioned problems. BFS and/or FA can be activated by an alkaline activator to formulate so-called alkaline cements with similar or even better properties than PC-based materials.[1]

Alkali-activated slag (AAS), especially when the activator is waterglass, shows similar mechanical properties to PC-based materials.[2] However, a high shrinkage, leading to cracking, usually occurs,[3] which is considered to be the most serious complication for the use of AAS in practice.[4] The fact that the drying shrinkage of AAS concrete is several times higher thana that of PC-based concrete is often associated with a higher mesopore volume in the AAS matrix, which results in substantial capillary tensile forces at the water-air meniscii and the material shrinks.[5]

One possible way to mitigate shrinkage is the use of shrinkage-reducing admixtures (SRAs). Generally, SRAs belong to the group of chemical substances called surfactants. The molecules of surfactants are composed of a polar head (ionic or non-ionic) and a non-polar tail. Considering the water-vapour interface, the polar head is attracted to the water phase, while the non-polar tail is oriented towards the gaseous phase, which means that surface tension is reduced and thus the capillary stresses decreas.[6] On the other hand, there are several doubts about the importance of surface tension and capillary stresses on shrinkage. For example, F. Wittmann[7] stated that even a significant reduction in the surface tension of the pore solution did not noticeably affect the shrinkage of a cementitious system and found the disjoining pressure to be more important. Also, M. J. Setzer[8] emphasized the role of the disjoining pressure and changes in the surface energy. Nevertheless, SRAs are successfully used in concrete production and a reduction in shrinkage of up to 50 % was reported.[6]

A limited number of studies concerning the use of SRAs in AAS are available. C. Bilim et al.[9] and also M. Palacios and F. Puertas[10] reported a reduction in shrinkage through the use of an SRA based on polypropylene glycol, especially in the case of moist curing. T. Bakharev et al.[11] achieved a lower shrinkage thanks to some non-standard SRA and also when using some air-entraining agent.

2 EXPERIMENTAL WORK

2.1 Materials and sample preparation

Ground granulated BFS with specific surface area of 400 m^2/kg was used as a reference binder and siliceous sand as a fine aggregate. The sand-to-binder ratio was 2:1. The BFS was activated by liquid sodium silicate with a SiO_2/Na_2O ratio of 1.85 at the doses of 4.2 % by binder mass. The water-to-binder ratio was 0.40.

In the first series the BFS was partially replaced by low-calcium FA. The weight ratios of the S/FA were 100/0 (marked as *S*), 75/25 (FA25), 50/50 (FA50) and 25/75 (FA75). The mortar FA50 was additionally modified using three commercially available SRAs in doses of 0.50, 1.0, 2.0 and 3.0 % by mass of BFS + FA. Based on the safety data sheets, these SRAs were generally a mixture of alcohols and glycols. The first one (A) was a mixture of 5-ethyl-1,3-dioxane-5-methanol, 2-ethylpropane-1,3-diol and 2-ethyl-2-(hydroxymethyl)propane-1,3-diol, the second one (B) was based on 2,2-dimethylpropane-1,3-diol and 2-butylaminoethanol and the third one (C) consisted mainly of 2-methoxymethylenoxy propanol and propane-1,2-diol.

At the beginning of the mixing procedure, all the liquid components were combined and the BFS + FA were added. After 30 s of mixing the sand was added. The total mixing procedure took 4 min. Then the fresh mortar was cast into the moulds. After 24 h of moist curing, the specimens were de-moulded and the strength or shrinkage testing followed.

2.2 Compressive strength testing

In the case of the first series (BFS partially replaced by FA), the compressive strength was tested on broken parts of the specimens (from the three-point bending test) with the dimensions 20 mm × 20 mm × 100 mm, while the influence of the different dosages of SRAs was studied on broken parts of the specimens with the dimensions 40 mm × 40 mm × 160 mm. All these tests were performed for 24 h, 7 d and 28 d after the mixing. After their de-moulding, all the specimens were submerged in water until the start of the test.

2.3 Shrinkage tests

The drying shrinkage was measured as length changes on the basis of the procedure described in ASTM C596. After the de-moulding the specimens were immersed in water, in which they were stored for 3 d. Then they were taken out to the laboratory conditions (approximately 50 % relative humidity and 23 °C), their surfaces were dried with a wet towel and measurements of their length changes began. Also, their mass changes during drying were measured and evaluated.

3 RESULTS

The results obtained for the first series, i.e., the influence of the partial replacement of BFS by FA on the compressive strength development, the drying shrinkage and the mass changes during drying, are presented in **Figures 1** to **3**, respectively. On the basis of these data, the mortar FA50 with a relatively low drying shrinkage and a concurrently satisfactory compressive strength was

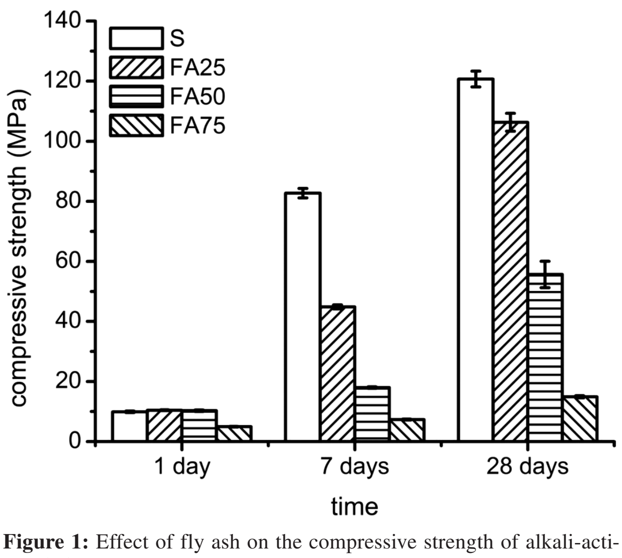

Figure 1: Effect of fly ash on the compressive strength of alkali-activated slag mortar

Slika 1: Vpliv letečega pepela na tlačno trdnost malte iz z alkalijami aktivirane žlindre

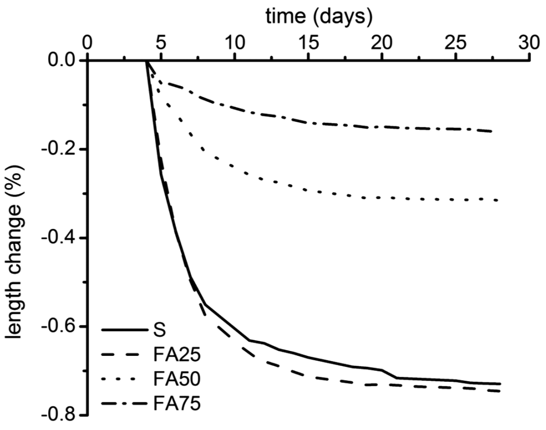

Figure 2: Effect of fly ash on the drying shrinkage of alkali-activated slag mortar
Slika 2: Vpliv letečega pepela na skrček pri sušenju malte iz z alkalijami aktivirane žlindre

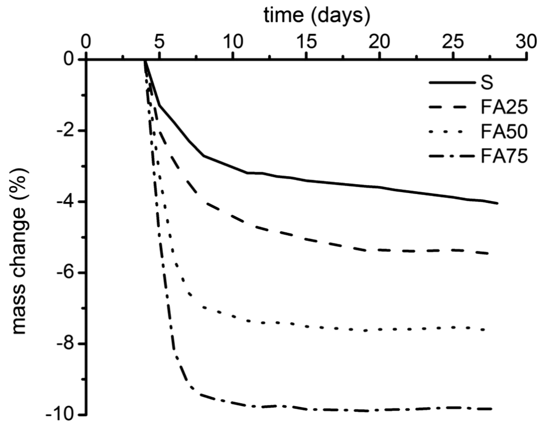

Figure 3: Effect of fly ash on the mass changes during drying of alkali-activated slag mortar
Slika 3: Vpliv letečega pepela na zmanjšanje mase med sušenjem malte iz z alkalijami aktivirane žlindre

chosen for further experiments, where the effect of different dosages of different SRAs on the compressive strength (**Table 1**), the drying shrinkage (**Figure 3**) and the mass loss during drying (**Figure 4**) was investigated. In order to compare the compressive strengths of the mortars containing SRAs with the reference mortar FA50 by using the specimens of the same dimensions, the FA50 mortar was prepared once more. Thus, the designation R for the FA50 mortar was used in the second part of this study.

4 DISCUSSION

As can be seen from **Figures 1** and **2**, the partial replacement of the BFS in the binder by FA led to a gradual decrease in the compressive strength, but also to a significant shrinkage reduction in the case of mortars with 50 % and 75 % of FA in the binder. These results correspond with those reported by M. Marjanović et al.[12], where the compressive strength of mortars with a predominant content of BFS in the binder were significantly higher than those with a predominant content of FA. Also, the slightly higher shrinkage of the mortar with a BFS/FA ratio of 75/25 than that of the 100/0 mortar was recorded in the same study. The increasing content of FA led to a substantial increase in the mass loss during the drying process under laboratory conditions, as can be seen from **Figure 3**. This could imply that a smaller quantity of hydration products was formed in the specimens with higher doses of FA, because the alkali activation of FA is generally favoured by an elevated temperature and a larger amount of Na_2O in the mixture.[12] Moreover, the main hydration product of FA activation, the N-A-S-(H) phase, does not chemically bind water,[13] which may also affect the mass changes during drying.

Table 1 shows the impact of SRAs on the compressive strength on the reference mortar R, whose composition was the same as the mortar FA50. The difference was only in the size of the specimens for compressive strength testing, as stated in Section 2.2. However, similar results for the compressive strength were obtained, when compared **Table 1** and **Figure 2**. Regardless of the type of SRA used, the compressive strength of the reference mortar was markedly reduced when SRAs were applied. Generally, the compressive strength decreased with the increasing dose of SRAs. The exception was the mortar with 3 % of SRA C, where a noticeably higher strength than that of the mortars with 1 % and 2 % of this additive were observed during the whole testing period.

The effect of SRAs on drying shrinkage of the reference mortar is shown in **Figure 4**. It is clear that all the SRAs tested modified the drying shrinkage development in a similar way. If only 0.5 % of SRA was used, the drying shrinkage slightly decreased, while a significant decrease in shrinkage was observed when the dose of SRA was raised from 0.5 % to 1.0 %. A further increase in the SRA dosage only led to a minor decrease in the drying shrinkage. A noticeably different situation was observed for the mass loss during the drying of these mortars (**Figure 5**), which exhibited a rather gradual

Table 1: Effect of SRAs (A, B, C) on the compressive strength development (in MPa) of alkali-activated BFS/FA 50/50 (*R*) mortar
Tabela 1: Vpliv SRA (A, B, C) na razvoj tlačne trdnosti malte BFS/FA 50/50 (R), aktivirane z alkalijami

Mixture	*R*	A				B				C			
SRA dose (%)	0	0.5	1.0	2.0	3.0	0.5	1.0	2.0	3.0	0.5	1.0	2.0	3.0
1 d	8.1	4.4	5.0	–	–	4.7	3.0	–	–	4.1	3.8	1.2	5.7
7 d	16	9.9	9.1	2.7	1.5	11	5.7	2.4	1.9	7.9	5.7	4.0	11
28 d	54	40	16	3.6	2.8	44	19	2.2	2.2	40	7.6	4.2	14

increase in the mass loss with the increasing content of SRAs. The reason for such an increase in the mass loss is likely to be associated with some retardation effect of all the SRAs used on the hydration of alkali-activated BFS/FA mortars, which is indicated by its compressive strength development. The SRAs also modified the shrinkage rate during the first days of drying, where a significant reduction as compared with the reference mortar was observed. After this the period of most intensive shrinkage followed, while since approximately the 10th day of exposure to a dry climate, all the mortars had almost the same shrinkage profile.

Although its porosity was not measured, we can expect a significant decrease in the amount of hydration products of the mortars containing 1.0 % and more SRA and therefore a higher volume of larger pores filled with easily evaporable water before the start of the drying. This raises considerable doubts about the compatibility

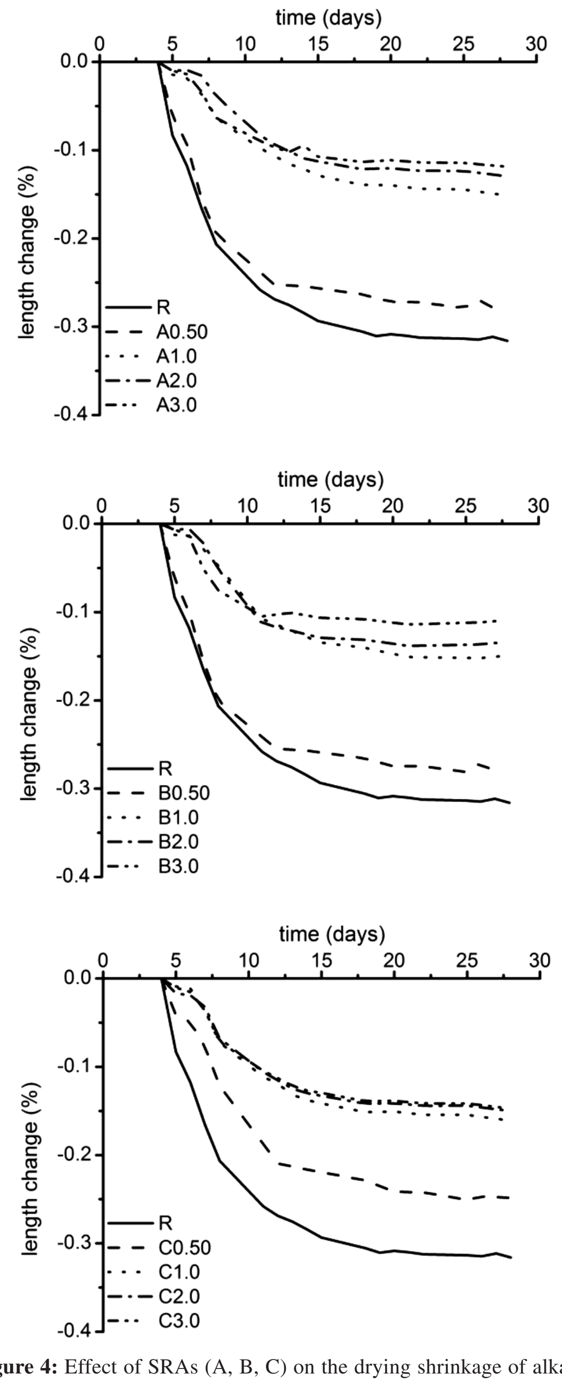

Figure 4: Effect of SRAs (A, B, C) on the drying shrinkage of alkali-activated BFS/FA 50/50 (R) mortar

Slika 4: Vpliv SRA (A, B, C) na krčenje pri sušenju malte BFS/FA 50/50 (R), aktivirane z alkalijami

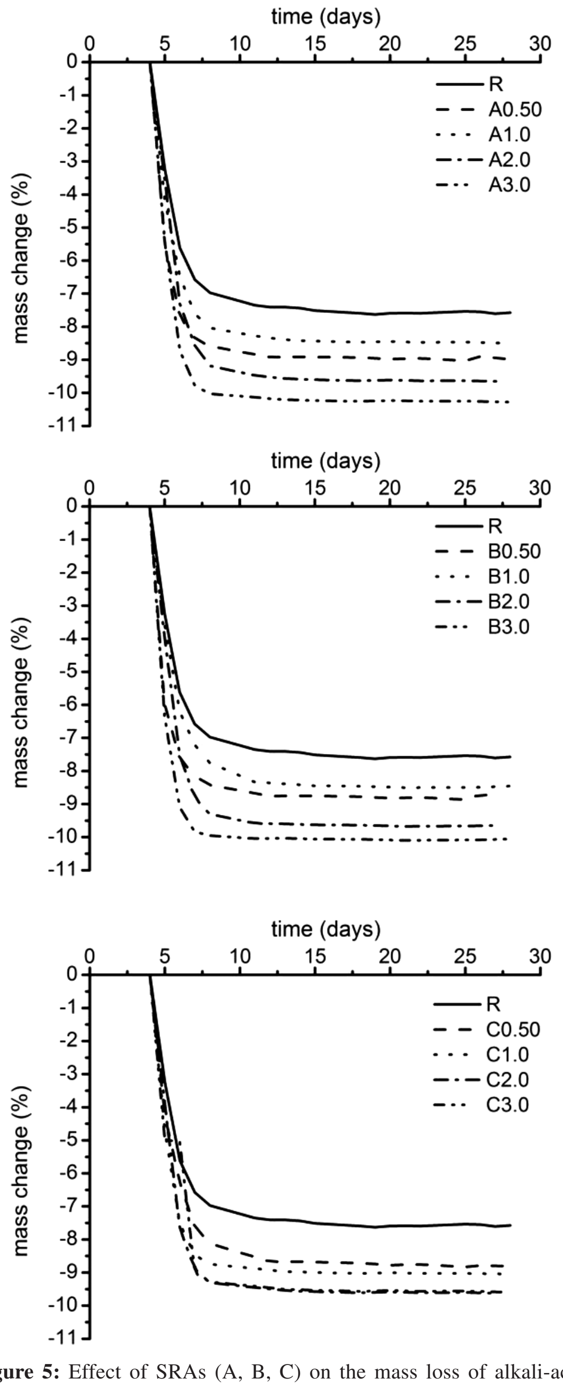

Figure 5: Effect of SRAs (A, B, C) on the mass loss of alkali-activated BFS/FA 50/50 (R) mortar during drying

Slika 5: Vpliv SRA (A, B, C) na zmanjšanje mase pri sušenju malte BFS/FA 50/50 (R), aktivirane z alkalijami of the tested SRAs with the studied alkali-activated system. Some of the authors mentioned in the introduction achieved a significant reduction of the drying shrinkage without any significant changes in the AAS hydration, but they used SRAs based on polypropylene glycol, while the SRAs used in this study mainly comprised low-molecular-weight diols.

5 CONCLUSIONS

This paper looks at the possibilities of drying-shrinkage reduction for mortars based on AAS by FA and SRAs. The compressive strength and mass changes during the drying were also evaluated. From the results obtained it can be concluded that despite a certain strength decrease the FA can be successfully used for the shrinkage reduction of AAS. Considering both the compressive strength and the drying shrinkage, the mortar with the ratio of BFS/FA 50/50 seems to be the most favourable FA. A further decrease in the shrinkage of this mortar was achieved through the application of commercial SRAs based mainly on diols and designed for Portland-cement-based systems. However, all these SRAs had a very negative impact on the compressive-strength development, which makes them unsuitable for the studied alkali-activated BFS/FA system.

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