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EFFECT OF THE BY-PASS CEMENT-KILN DUST AND FLUIDIZED-BED-COMBUSTION FLY ASH ON THE PROPERTIES OF FINE-GRAINED ALKALI-ACTIVATED SLAG-BASED COMPOSITES

VPLIV PRAHU IZ PEČI ZA CEMENT IN LETEČEGA PEPELA IZ VRTINČASTE PLASTI NA LASTNOSTI DROBNOZRNATEGA, Z ALKALIJAMI AKTIVIRANEGA KOMPOZITA NA OSNOVI ŽLINDRE

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The aim of this work is to investigate the influence of the by-pass cement-kiln dust (CKD) and two types of the fluidized-bed-combustion (FBC) fly ash on the workability, shrinkage and mechanical properties (compressive and flexural strengths) of the water-glass-activated slag. The utilization of CKD and FBC is very problematic. One of the main reasons for this is a high lime and sulfate content in these wastes, which can lead to the formation of expansive hydration products and, consequently, to the cracking of ordinary Portland-cement (OPC) materials. On the other hand, these products might act against the high shrinkage of the alkali-activated slag (AAS). In order to investigate this assumption and the influence of these admixtures on the other properties mentioned above, fine-grained AAS-based composites were prepared. A ground, granulated blast-furnace slag (the reference binder) was partially replaced (0–50 %) by one type of CKD and two types of the FBC fly ash. A significant reduction in the shrinkage was observed on the samples containing an even lower amount of fly ash, while the composites with CKD did not show any notable shrinkage reduction. When using higher dosages of these admixtures the mechanical properties were reduced, but lower dosages did not have such effects, especially as regards the compressive strength. The workability was also strongly dependent on the admixture dosage. Its improvement was observed especially in the case when slag was replaced by up to 30 % of CKD.

Keywords: alkali-activated slag, by-pass cement-kiln dust, FBC fly ash, workability, strength, shrinkage

Namen tega dela je preiskati vpliv prahu iz peči za cement (CKD) in dveh vrst letečega pepela (FBC) iz zgorevanja v vrtinčasti plasti na obdelovalnost, krčenje in mehanske lastnosti (tlačna in upogibna trdnost) žlindre, aktivirane z vodnim steklom. Uporaba CKD in FBC je zelo problematična. Eden od glavnih razlogov za to je visoka vsebnost apna in sulfatov v teh odpadkih, kar lahko povzroči nastanek ekspanzijskih hidracijskih produktov in posledično pokanje portlandskih cementnih materialov (OPC). Po drugi strani pa ti produkti lahko zavirajo veliko krčenje žlindre, aktivirane z alkalijami (AAS). Da bi preverili te predpostavke in vpliv teh dodatkov na druge, zgoraj omenjene lastnosti, so bili pripravljeni na osnovi AAS drobnozrnati kompoziti. Grobozrnata plavžna žlindra (referenčno vezivo) je bila delno nadomeščena (0–50 %) z eno vrsto CKD in dvema vrstama FBC letečega pepela. Opaženo je bilo občutno zmanjšanje krčenja pri vzorcih s celo majhnim deležem letečega pepela, medtem ko kompozit s CKD ni pokazal opaznega zmanjšanja krčenja. Pri uporabi večjih deležev obeh dodatkov so se poslabšale mehanske lastnosti, pri majhnem dodatku pa ni bilo takega vpliva na tlačno trdnost. Obdelovalnost je bila močno odvisna od količine dodatkov. Njeno izboljšanje je bilo posebno opazno v primeru, ko je bila žlindra nadomeščena z do 30 % CKD.

Ključne besede: z alkalijami aktivirana žlindra, prah iz peči za cement, FBC leteči pepel, obdelovalnost, trdnost, krčenje

1 INTRODUCTION

The binders based on AAS are considered as an ecological alternative to the OPC-based binders, which are most common in the concrete production. AAS, in comparison with Portland cement, can have a better durability, a lower hydration heat, a better resistance to elevated temperatures and an aggregate-matrix interphase and other benefits.[1] On the other hand, the main disadvantages of AAS are a very high shrinkage and a poor rheology, especially with respect to a relatively rapid setting in the case of a water-glass activation.[2]

CKD is a by-product of cement manufacturing with a highly variable composition, but it usually contains significant amounts of alkali, chloride, sulfate and free lime.[3] Several works investigating the CKD use in the mortar and concrete production were published. It is usually concluded that a replacement of OPC higher than 5–10 % has an adverse effect on the compressive and tensile strengths.[4] FBC technology has many advantages in comparison with pulverized coal combustion,[5] but the ashes from FBC are very porous and they contain high amounts of very reactive free lime and anhydrite, which lead, on the one hand, to their self-cementing properties, but, on the other hand, to the problems with the workability and volume stability due to the formation of expansive-hydration products.[6]

2 EXPERIMENTAL WORK

2.1 Materials and sample preparation

A ground, granulated blast-furnace slag with a specific surface of 380 m^2/kg was used as the reference binder (R). The slag was partially replaced (0–50 %) by one type of the by-pass CKD and two types of the FBC fly ash. The phase compositions of CKD and fly ashes were determined with X-ray diffraction (XRD). CKD mainly consisted of KCl, K_2SO_4, CaO and C_2S. The main phases found in both fly ashes were anhydrite, quartz, glassy phase, free lime, portlandite and calcite. The fly ash designed as P contained more anhydrite, quartz and free lime, while the fly ash designed as L contained a higher amount of the glassy phase. The water glass with the silicate modulus equal to 1.85 was used as the alkaline activator. The weight ratio of Na_2O/binder was kept constant at 0.042. The mass ratio of the Czech standard sand (three different fractions according to standard ČSN EN 196) to the binder was 2 : 1. The water-to-binder ratio (*w*/*b*) was kept constant at 0.40, only in the case of the mixtures with fly ash L, *w*/*b* had to be increased due to a very low workability. The binder compositions of the mortars prepared are shown in **Table 1**.

After approximately four minutes of mixing the workability of the mortar was measured using the flow-table spread test and then the mortar was cast into the molds. Prisms with the dimensions of 20 mm × 20 mm × 100 mm were prepared for the compressive- and flexural-strength tests and prisms with the dimensions of 25 mm × 25 mm × 285 mm and stainless-steel gauge studs in their front walls were prepared for the shrinkage tests.

2.2 Compressive- and flexural-strength testing

The prisms for the strength testing were demolded after 24 h and moist cured at a 99 % relative humidity and (23 ± 2) °C. Compressive strengths were tested at the ages of (1, 7 and 28) d. Three prisms were used for the flexural testing (three-point bending) of each mixture at each age and broken parts from these tests were used for the compressive-strength testing.

2.3 Shrinkage tests

The shrinkage tests were based on ASTM C596. After 24 h of moist curing the specimens were demolded, a comparator reading was taken and the specimens were immersed for three days in tap water. Then the bars were removed from the water, their surfaces were dried with a wet towel and a zero reading was performed. After that the bars were stored in laboratory conditions ((45 ± 5) % relative humidity, (23 ± 2) °C) for 56 d and their length changes were measured. These shrinkage tests were rather tentative because only two samples of each mixture were measured.

3 RESULTS AND DISCUSSION

The average values of compressive f_c and flexural strength f_f for different ages with the standard errors of the mean are listed in **Table 2**. There are also the results of the workability testing expressed as the average values of the diameters of the mortar spread *d* in the same table. The data for the mortars designed as P10, L30 and L50 are not included because these mortars did not harden even after three days.

Table 2: Flexural f_f and compressive f_c strength development, standard errors of the mean (in parenthesis) and workability of the prepared composites

Tabela 2: Spreminjanje upogibne f_f in tlačne f_c trdnosti, povprečje standardne napake (v oklepaju) in obdelovalnost pripravljenih kompozitov

Mortar	f_f/MPa			f_c/MPa			*d*/mm
	24 h	7 d	28 d	24 h	7 d	28 d	
R	2.5 (0.1)	7.3 (0.7)	11.7 (0.4)	10.0 (0.2)	72.7 (1.7)	107.4 (3.6)	190
CKD10	2.0 (0.1)	2.4 (0.3)	8.8 (0.1)	10.0 (0.2)	62.0 (1.0)	115.1 (2.8)	220
CKD20	1.3 (0.3)	4.1 (0.7)	7.6 (0.7)	6.0 (0.1)	46.5 (1.1)	99.4 (0.9)	240
CKD30	1.0 (0.0)	3.9 (0.4)	7.5 (0.4)	3.0 (0.1)	35.8 (0.6)	72.0 (2.9)	225
CKD40	1.0 (0.0)	3.9 (0.2)	5.9 (0.1)	2.6 (0.1)	33.9 (0.9)	50.2 (1.9)	170
CKD50	0.0 (0.0)	2.6 (0.4)	4.5 (0.2)	0.0 (0.0)	21.3 (0.4)	26.3 (1.8)	120
P2.5	1.6 (0.1)	6.1 (0.1)	8.4 (0.0)	6.6 (0.1)	67.6 (1.5)	104.3 (2.2)	155
P5	1.5 (0.0)	6.0 (0.2)	7.4 (0.3)	5.8 (0.1)	60.2 (1.7)	102.2 (1.1)	115
L10	1.2 (0.1)	2.4 (0.1)	7.4 (0.5)	4.8 (0.1)	11.1 (0.1)	66.3 (2.4)	215*

* *w*/*b* = 0.48

Except for some cases of the CKD10 mixtures, the highest strengths were observed for the reference mortar.

Table 1: Binder compositions of the prepared composites in mass fractions, *w*/%

Tabela 1: Sestava veziv pripravljenih kompozitov v masnih deležih, *w*/%

Mixture designation	R	CKD10	CKD20	CKD30	CKD40	CKD50
Slag	100	90	80	70	60	50
Cement kiln dust	0	10	20	30	40	50
Mixture designation	P2.5	P5	P10	L10	L30	L50
Slag	97.5	95	90	90	70	50
FBC fly ash P	2.5	5	10	0	0	0
FBC fly ash L	0	0	0	10	30	50

However, a significant strength gain was observed between 24 h and 7 d and also between 7 d and 28 d in the case of replacing the slag with up to 40 % of CKD and up to 5–10 % of the FBC fly ash. Higher dosages of these admixtures had a fatal effect on the mechanical properties of AAS, especially in the case of the FBC fly ash.

Both compressive and flexural strengths gradually decreased with the increasing slag replacement at all the ages. The strength reduction was the most severe at the early ages and in the case of the flexural strength. The strength reduction in the presence of CKD could have been caused not only by the decrease in the slag content, but also by a possible formation of chloro and sulfoaluminate phases, leading to a softening and an increased porosity.[7] Another reason can be the increase in the real *w/b* ratio if taking into account the CKD composition, which can also be a reason for the workability improvement at the replacement levels of up to 30 %. When more than 30 % of CKD was used, the workability became reduced, which can be attributed to the fast setting. The setting time was not measured but it was observed that these mortars set very soon after the filling of the molds. A shortening of the setting time was also observed with the increasing FBC-fly-ash dosages. The reason for this can be the formation of the primary CSH through the reaction between $[SiO_4]^-$ from the water glass and Ca^{2+} released from the free lime present in the fly ash. The precipitation of portlandite is probably suppressed due to its higher solubility in comparison with CSH.[8] Anyway, the hydration of the alkali-activated slag in the presence of the FBC fly ash needs further investigation to explain the problems with the hardening of the mortars with the replacements of the slag by the FBC fly ash higher than 5–10 %. Perhaps most of $[SiO_4]^-$ from the activator is consumed during the first minutes to form some type of calcium silicate which is cannot contribute to the strength gain or which suppresses further hydration.

On the other hand, at the later ages, especially the compressive strength grew faster in the case of the appropriately blended composites in comparison with the reference composites. From this point of view, it could be interesting to study the strength development over a longer period. This strength increase might be associated with the C_2S hydration and the pozzolanic reactions of the slag in the presence of the lime contained in CKD. The strength increase of the L10 mortar at the later ages might be due to the pozzolanic reactions of its glassy phase.

The shrinkage development is outlined in **Table 3**. The highest shrinkage rate was observed during the first three days after taking the specimens out of the water. After 14 d, only slight length changes were recorded.

When using CKD at a different replacement level, no clear trend in the shrinkage development was observed. Some mortars showed a slightly lower shrinkage than the reference mortar, but the shrinkage values of the other mortars were higher. From the data obtained, CKD does not seem to affect the shrinkage reduction. However, the situation with both fly ashes is considerably different: in the case of a 2.5 % replacement of the slag by FBC fly ash P, the shrinkage of the reference mortar was reduced by more than 20 % and if 10 % of fly ash L was used, the shrinkage was reduced even by more than 70 %. Unfortunately, both P5 specimens were broken during demolding, so the data for them were not obtained. These preliminary results showed that the FBC fly ashes can be beneficial for the suppressing of the AAS shrinkage, but attention must be paid to the preservation of the other properties. Additional investigations through instrumental methods like scanning electron microscopy, calorimetry or XRD are planned for the future to clarify the role of the FBC fly ash in the AAS systems.

Table 3: Shrinkage development of the prepared composites
Tabela 3: Spreminjanje krčenja pripravljenih kompozitov

Composite	Days after water curing					
	1	3	7	14	28	56
R	0.52	0.74	0.81	0.83	0.85	0.86
CKD10	0.58	0.81	0.88	0.89	0.90	0.91
CKD20	0.52	0.84	0.84	0.84	0.84	0.84
CKD30	0.36	0.77	0.78	0.78	0.78	0.78
CKD40	0.40	0.75	0.81	0.81	0.81	0.81
CKD50	0.40	0.78	0.90	0.91	0.91	0.91
P2.5	0.32	0.55	0.61	0.66	0.67	0.67
L10	0.05	0.13	0.15	0.18	0.22	0.24

4 CONCLUSIONS

This pilot study investigated the effect of a partial replacement of the water-glass-activated blast-furnace slag with the CKD and FBC fly ashes on the workability, mechanical properties and the shrinkage. It was observed that CKD, in proper dosages, improved the workability, while the FBC fly ashes reduced it dramatically even at a low content. On the other hand, unlike CKD, the FBC fly ashes significantly reduced the shrinkage. Both these admixtures, at low replacement levels, had no or little adverse effect on the compressive strength, especially at later ages. In contrast, the flexural strength was affected more negatively. The FBC fly ashes at the dosages higher than 5–10 % had a fatal impact on the strength development.

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