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Shrinkage of alkali-activated slag-fly ash concrete cured at ambient temperature

Skurcz betonu z aktywowanym alkalicznie spoiwem żużlowo-popiołowym pielęgnowanego w temperaturze otoczenia

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Abstract. The paper summarizes the results of a study intended to characterize alkali-activated slag/fly ash concretes concerning their volume changes, freeze-thaw resistance, scaling resistance, and alkali-aggregate reactivity. The manifestation of early-age microcracking in the hardened alkali-activated paste phase of these concretes calls for attention. It is related to significant autogenous shrinkage, although it does not appear to agree with the other shrinkage measurements performed in the experimental program. Smaller pores and high sodium ion concentration result in higher internal pressure during the process of self-desiccation and could be the main causes for the very high autogenous shrinkage values recorded.

Keywords: alkali-activated materials; fly ash; shrinkage; slag.

Streszczenie. W artykule przedstawiono wyniki badań betonu z alkalicznym spoiwem żużlowo-popiołowym. Oznaczono zmianę objętości, odporność na cykle zamrażania-rozmrażania, w tym na złuszczenie, oraz reaktywność alkaliczno-krzemianową. Zwrócono uwagę na występowanie mikropęknięć w stwardniałym zaczynie we wczesnym wieku. Wysunięto hipotezę, że jest to związane ze znacznym skurczem autogenicznym, jakkolwiek inne pomiary skurczu, przeprowadzone w programie badawczym, nie potwierdzają tego mechanizmu. Małe pory i duże stężenie jonów sodu powodują wysokie ciśnienie wewnętrzne podczas wysychania i mogą być głównymi przyczynami dużych wartości skurczu autogenicznego zarejestrowanych w badaniach.

Słowa kluczowe: materiały aktywowane alkalicznie; popiół lotny; skurcz; żużel.

Significant attention has been drawn by alkali-activated systems AAS for environmental considerations [1] but also for their appealing engineering properties, such as mechanical strength [2 – 3]. Still, there are some concerns regarding the durability and stability of these materials. In particular, reported data on AAS have shown that shrinkage may be more significant in these systems than in conventional OPC systems [4]. It needs proper consideration since it can lead to substantial cracking. Parameters such as precursor proportion (slag vs. fly ash), activator type (mostly sodium content) and added water content can have a significant impact on porosity (volume and pore size distribution) and shrinkage. As part of a project devoted to an in-depth durability assessment of alkali-activated slag/fly ash systems, the study reported herein aims to identify the main parameters influencing

desiccation shrinkage as well as evaluate the respective contributions of chemical, autogenous and drying shrinkage [4 – 5].

Experimental Program

Materials. Two precursors were used in this study: a ground granulated blast furnace slag from Southern Ontario (Canada) and a class F fly ash from Alberta (Canada). The Blaine fineness values for the slag, fly ash and portland cement are 479, 334 and 403 m²/kg, respectively, and their fractions of particles retained on the 45- μ m sieve amount to 1.2, 26 and 4%. A 20-mm crushed granitic gneiss (Quebec, Canada) and natural sand derived from granite were used as coarse and fine aggregates, respectively. The alkaline activator was obtained by combining a sodium silicate solution (28.7% SiO₂, 9.0% Na₂O and 62.3% H₂O) and an 8M sodium hydroxide solution at a sodium silicate to sodium hydroxide ratio (Na₂SiO₃/NaOH) of 0.50.

Concrete and Paste Mixtures. In the experimental program, drying shrinkage tests were conducted on alkali-activated concretes. In contrast, chemical shrinkage,

autogenous shrinkage, and other tests were performed on neat pastes prepared with the same constituents and general proportions without aggregates. The variables in the mixtures were the binder's slag and fly ash proportions and the amount of added water in each composition. The detailed compositions of the concrete and paste mixtures are presented in Tables 1 to 3. All alkali-activated concrete mixtures were prepared with a binder content of 400 kg/m³ and an activator-to-binder ratio of 0.35 and had a minimum slump of 100 mm after 60 minutes and a minimum 3-d compressive strength of 20 MPa. The total w/b ratios ranged from 0.37 to 0.41.

Testing program. Chemical shrinkage of four neat alkali-activated slag/fly ash paste mixtures and a reference 0.50 w/c neat Portland cement paste mixture were evaluated according to ASTM C1608. Autogenous shrinkage of five neat alkali-activated slag/fly ash paste mixtures and a reference 0.50 w/c neat Portland cement paste mixture were evaluated according to ASTM C1698. Moist curing volume change and drying shrinkage of four alkali-activated slag/fly ash concrete

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Table 1. Alkali-activated slag/fly ash concrete mixtures

Tabela 1. Mieszanki betonowe z aktywowanymi alkalicznie spoiwami żuźlowo-popiołowymi

Mixture	Slag/FA [%]	Sand [kg/m ³]	Coarse aggregate [kg/m ³]			NaOH [kg/m ³]	Na ₂ SiO ₃ [kg/m ³]	Added water/binder (by wgt.)
			5 – 10	10 – 14	14 – 20			
C1	80/20	670	312	312	416	94	47	0.13
C2	60/40							0.13
C3	60/40							0.14
C4	80/20							0.14

Table 2. Alkali-activated slag/fly ash paste mixtures tested for autogenous shrinkage

Tabela 2. Aktywowane alkalicznie zaczyny żuźlowo-popiołowe do badania skurczu autogenicznego

Mixture	Slag/FA [%]	Activator/Binder (by wgt.)	Na ₂ SiO ₃ /NaOH (by wgt.)	Added water/binder (by wgt.)
aP1	80/20	0.35	0.50	0.16
aP2	80/20			0.14
aP3	80/20			0.12
aP4	70/30			0.14
aP5	60/40			0.14

Table 3. Alkali-activated slag/fly ash paste mixtures tested for chemical shrinkage

Tabela 3. Aktywowane alkalicznie zaczyny żuźlowo-popiołowe do badania skurczu chemicznego

Mixture	Slag/FA [%]	Activator/Binder (by wgt.)	Na ₂ SiO ₃ /NaOH (by wgt.)	Added water/binder (by wgt.)
cP1	80/20	0.35	0.50	0.13
cP2	60/40			0.13
cP3	60/40			0.14
cP4	80/20			0.14

te were evaluated according to ASTM C157. The porosity of the alkali-activated and OPC pastes was characterized using mercury intrusion porosimetry. Pore solution was extracted from the alkali-activated slag/fly ash paste specimens and the control OPC paste specimens using a high-pressure triaxial confining steel cell, loaded on a universal testing machine up to a maximum applied load of 200 kN. The Na, K and Ca contents were evaluated through atomic absorption spectroscopy.

Test Results

Chemical and Autogenous Shrinkage Experiments. Figure 1 a) presents paste specimens' chemical shrinkage test

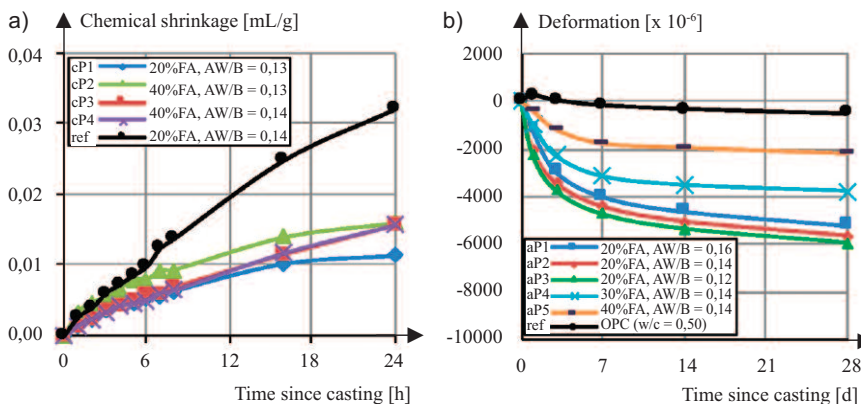


Fig. 1. Chemical shrinkage (a) and ASTM C1698 autogenous shrinkage (b) of alkali-activated paste mixtures prepared with different fly ash and water contents

Rys. 1. Skurcz chemiczny (a) i skurcz autogeniczny według ASTM C1698 (b) zaczynów aktywowanych alkalicznie z różną zawartością popiołu lotnego i wody

results through the first 24 h after initial contact between the precursors and the liquid constituents (activator and added water). At the age of 24 h, the chemical shrinkage recorded for the four tested alkali-activated slag/fly ash pastes ranged from 33 to 50% of that recorded for the control OPC paste specimen. In addition, the curves of the alkali-activated paste mixtures are flattening out much more rapidly than that of the OPC control.

Figure 1 b) presents the autogenous shrinkage test results through 28 d of testing. The tested alkali-activated slag/fly ash pastes exhibit significantly higher autogenous shrinkage values (4 to 13 times larger) than those recorded for the reference OPC paste. Increasing the added water dosage (AW/B of 0.12, 0.14 and 0.16) and fly ash content (20, 30 and 40% of precursor) both result in decreasing autogenous shrinkage values. Within the tested ranges of added water and fly ash contents, the latter has the strongest influence on reducing the final autogenous shrinkage. For a constant added water dosage, increasing the fly ash content from 20 to 40% led to a reduction in autogenous shrinkage of more than 60% at 28 d. Still, the tested alkali-

-activated blended slag/fly ash pastes show 28-d autogenous shrinkage values at least 4.3 times higher than the control OPC paste with a w/c ratio 0.50.

Volume Changes during Moist Curing and Drying. Figures 2 and 3 present the results of the length and mass change experiments conducted on the alkali-activated slag/fly ash concrete specimens immersed in lime-saturated wa-

ter and the alkali-activated slag/fly ash concrete specimens stored at 50% RH and 23°C, respectively. During the first 56 d of immersion, all tested concrete specimens exhibited a contraction going through a maximum of approximately 28 d. At the age of 28 d, the concrete specimens with the lowest tested added water content (52 kg/m³) show the highest shrinkage values, with 180 μm/m for mixture C2 (40%FA, AW/B = 0.13) and 110 μm/m for mixture C1 (20%FA, AW/B = 0.13). The 40% fly ash system led to higher shrinkage at 28 d for a given water content. It can be noticed in Fig. 2 b) that although the tested materials underwent a contraction in the early stage of the tests, they all gained mass during the same period, indicating that water was being absorbed. Furthermore, it can be observed that the rates of mass gain were relatively high at their highest level of the whole test duration. Shortly after 56 d, all tested concretes exhibited a net expansion, increasing at a low rate. Figure 3 presents the length change and mass change test (ASTM C157) results recorded for the alkali-activated slag/fly ash concrete mixtures stored at 50% RH and 23°C. The drying

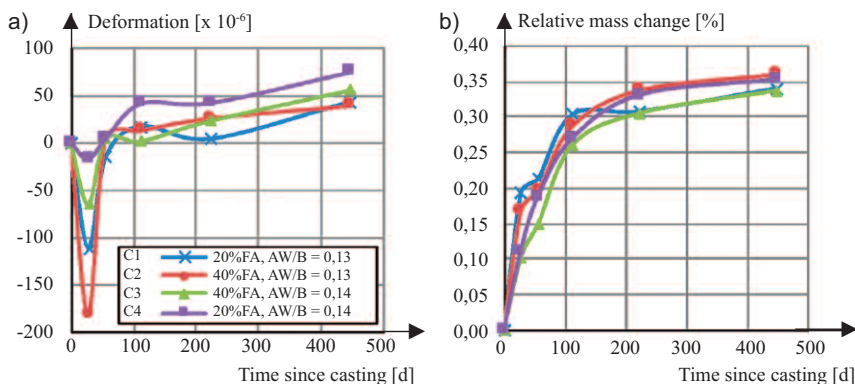


Fig. 2. Deformation (a) and relative mass change (b) of alkali-activated slag/fly ash concrete mixtures in saturated lime water at 23°C (including the 28-day curing period)

Rys. 2. Odkształcenie (a) i względna zmiana masy (b) mieszanek betonowych z aktywowanymi alkalicznie spoiwami żużlowo-popiołowymi w nasyconym roztworze wodorotlenku wapnia w 23°C (łącznie z 28-dniowym okresem utwardzania)

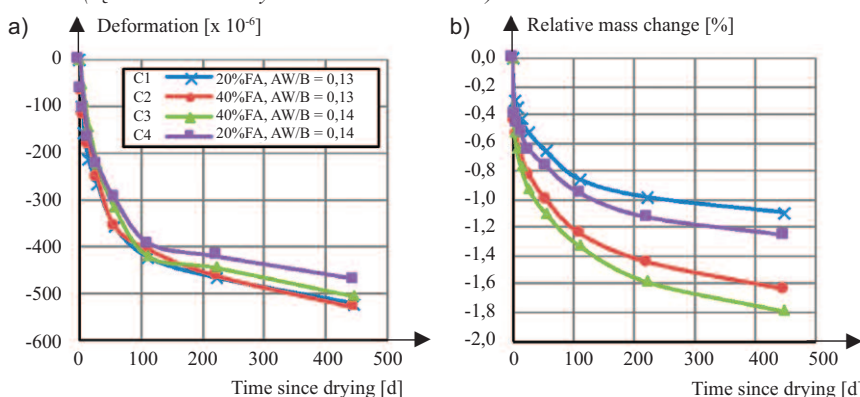


Fig. 3. Deformation (a) and relative mass change (b) of alkali-activated slag/fly ash concrete mixtures at 23°C and 50% RH (after 28-d moist curing)

Rys. 3. Odkształcenie (a) i względna zmiana masy (b) mieszanek betonowych z aktywowanymi alkalicznie spoiwami żużlowo-popiołowymi w 23°C i 50% wilgotności względnej (po 28-dniowym okresie utwardzania)

shrinkage data recorded for the four tested mixtures are very close, with average deformations at 448 d ranging from 470 to 530 $\mu\text{m}/\text{m}$, a large fraction of which (of the order of 80%) occurred within the first 100 d. Conversely, it can be observed that the mass loss results exhibit a significantly wider spread.

Porosity and Pore Solution Characterization. Table 4 presents the characteristics of the opened void system of the alkali-activated slag/fly ash paste specimens compared to that of a Portland cement paste specimen with a w/b ratio of 0.50. The average porosity values of the tested alkali-activated pastes are slightly lower than that of the reference OPC paste. Higher fly ash contents resulted in higher average porosity values, whereas the effect of added water (i.e. for the same FA content) was not found to be significant. All alkali-acti-

ated specimens showed higher average surface area values than that of the reference OPC mixture, which confirms the lower average pore radius of these systems as observed. The average pore radius of the OPC mixture is almost 2.5 times that estimated for the investigated alkali-activated mixtures.

Table 5 presents the sodium, potassium and calcium concentrations in the pore solutions of the alkali-activated paste mixtures tested for autogenous shrinkage. The sodium concentrations in the tested alkali-activated slag/fly ash paste mixtures after 28 d are between 4.8 and 6.6 times greater than in the OPC paste specimen (w/b of 0.50). It is observed to increase sharply as the fly ash content decreases from 40 to 30%, but much less with a further reduction. A similar pattern was observed for the potassium concentrations in the alkali-activated paste solutions. However, they were signi-

ficantly lower in alkali-activated pastes, reaching between 5.2 and 7.7% of the concentrations measured in OPC paste.

Discussion

Comparative Volume Changes. For all investigated alkali-activated systems, both chemical and drying shrinkage are significantly lower when compared to results obtained for the reference OPC-based systems. The chemical shrinkage recorded after 24 h for the various tested alkali-activated paste mixtures was at least 50% lower than that of the reference OPC paste specimens. The smaller average pore size recorded for alkali-activated systems could explain why the observed chemical shrinkage data does not match the trends observed in the case of autogenous shrinkage testing. A smaller average pore size implies that a potentially large fraction of pores is not being filled during the Le Chatelier contraction test (ASTM C1608), developed specifically for OPC systems, which would result in underestimating chemical shrinkage.

In the case of drying shrinkage, the alkali-activated concrete mixtures tested in the present study (aggregate-to-ce-

Table 4. Permeable pore characteristics of alkali-activated slag/fly ash paste mixtures
Tabela 4. Charakterystyka porów otwartych w aktywowanych alkalicznie zaczynach żużlowo-popiołowych

Mixture	Porosity [%]	Average pore surface area [m ² /g]	Average pore radius [nm]
cP1	23.82	78.42	3.55
cP2	27.13	95.82	3.50
cP3	29.17	104.96	3.50
cP4	22.16	75.79	3.40
OPC	30.31	47.17	8.25

Table 5. Alkali contents in the pore solutions of the alkali-activated paste
Tabela 5. Zawartość alkaliów w roztworach porowych zaczynów aktywowanych alkalicznie

Mixture	Contents [mg/L]		
	sodium	potassium	calcium
aP1	31 107	1 333	–
aP2	31 460	1 289	–
aP3	31 051	1 274	–
aP4	30 499	1 268	–
aP5	23 255	907	–
OPC	4 800	17 350	123

ment ratio of 2.6) exhibited lower drying shrinkage values than those typically reported for comparable OPC mixtures, with a maximum value exceeding slightly 500 $\mu\text{m}/\text{m}$ after 448 d (mixture C2 – Fig. 3a). On the contrary, the data presented previously (Fig. 1b) tend to show that autogenous shrinkage is much larger in alkali-activated slag/fly ash systems than in the case of an OPC system. The tests performed on paste specimens revealed autogenous shrinkage values of alkali-activated slag/fly ash paste ranging from 4.3 to 11.7 times greater than that recorded for a 0.50 w/b ratio OPC paste.

Physical and Chemical Factors of Influence. Pore size distribution significantly influences the mechanism of self-desiccation and thus, autogenous shrinkage. It is well established that the internal capillary stresses generated by water withdrawal from the pores are inversely proportional to the diameter of the pores involved, down to a specific size, meaning emptying smaller pores will induce higher internal stresses. This study's tested alkali-activated paste mixtures have shown average pore radius values that were at most 43% of the corresponding values for OPC paste specimens (w/b of 0.50) (Table 4). These findings suggest that pore size could be a parameter that influences the higher autogenous shrinkage values of alkali-activated systems compared to OPC systems. Increasing fly ash contents and, thus, the formation of N-A-S-H gels, which bind less water in their structure compared to C-A-S-H gels [7], explains the increasing porosity values (more water left after hydration to form capillary pores). Nevertheless, the very similar pore size amongst the four tested alkali-activated slag/fly ash pastes (3.40 to 3.55 μm – Table 4) can hardly explain the crucial differences observed in autogenous shrinkage. Gao et al. [8] found that increasing the activator modulus resulted in a refined pore structure due to increased silicate groups. Decreasing porosity values were also observed and attributed to the formation of reaction products at a small scale at later ages.

The pore solution's chemical composition also affects the extent of autogenous shrinkage of alkali-activated systems. Ballekere Kumarappa et al. [9] found that higher Na_2O content and silica

modulus result in higher surface tension in alkali-activated slag systems. Chemical analysis of the pore solution extracted from the alkali-activated slag/fly ash paste mixtures performed after 28 d of moist curing in the present study reveals sodium contents that are 4.8 to 6.6 times greater than what was observed in the OPC paste pore solution. Therefore, the surface tension in these alkali-activated slag/fly ash systems is high and could increase the magnitude of autogenous shrinkage. For constant added water-to-binder values (0.14 – Table 5), paste mixtures aP2, aP4 and aP5 have shown decreasing concentrations of Na and K in their pore solutions with increasing fly ash contents, which in turn correlates with a decreasing magnitude of autogenous shrinkage. In blended alkali-activated slag-fly ash systems, C-A-S-H, N-A-S-H, and hybrid N-C-A-S-H gels form [10], where the C-A-S-H gel forms from slag and N-A-S-H gel forms from fly ash. Silica from the activator is rapidly consumed by the reaction with slag, thus leaving an alkali-rich activating solution available to react with the fly ash [11]. Therefore, increasing the fly ash content leads to more N-A-S-H gel formation, binding more alkalis.

Previous work [12] on these systems can explain to some extent why less autogenous shrinkage is observed when increasing the added water and fly ash contents. Setting times are indications of the early progress of the paste hardening and its ability to resist deformation (stiffness). Therefore, longer setting times involve an extended time during which the paste can self-accommodate the chemical shrinkage it undergoes and have a tempering effect on self-desiccation shrinkage and associated cracking. The alkali activation of the binder containing fly ash at ambient temperature has been much slower [13] than that experienced in the case of slag presence, either solely or combined with fly ash.

Conclusion

This study aimed to identify the main contributing phenomena and factors responsible for the volume changes occurring at an early age in alkali-activated blended slag/fly ash systems. Based on the

testing carried out in this study, autogenous shrinkage appears to be the most significant component of early-age volumetric variations. Increasing the added water and fly ash contents can reduce this phenomenon. Self-desiccation is the main cause of early-age cracking of alkali-activated fly ash/slag mixtures. This situation could be explained by the high sodium concentrations in the pore solution and the small average pore size.

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