

Dry Mix Slag—High-Calcium Fly Ash Binder. Part Two: Durability

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Abstract

This work investigates durability of cement-free mortars with a binder comprised of ground granulated blast furnace slag (GGBFS) activated by high-calcium fly ash (HCFA) and sodium carbonate (Na_2CO_3): the soundness, sulfate resistance, alkali-silica reactivity and efflorescence factors are considered. Results of tests show that such mortars are resistant to alkali-silica expansion. Mortars are also sulfate-resistant when the amount of HCFA in the complex binder is within a limit of 10 wt%. The fineness of fly ash determines its' ability to activate GGBFS hydration, and influence soundness of the binder, early strength development, sulfate resistance and efflorescence behavior. The present article is a continuation of authors' work, previously published in MSA, Vol. 14, 240-254.

Keywords

Ground Granulated Blast-Furnace Slag, High-Calcium Fly-Ash, Sodium Carbonate, Blast-Furnace Slag Binder, Durability, ASR, Sulfate Attack, Soundness, Efflorescence

1. Introduction

Clinker-free binders based on ground granulated blast-furnace slag (GGBFS) are considered as materials suitable for the industrial-scale production of structural concrete along with Portland cement [1]. Since GGBFS has a mediocre hydraulic activity, the composition of clinker-free binders typically includes components that promote GGBFS hydration, and thus accelerate the hardening of cement-free mortars and concretes. Alkali and alkaline earth silicates, hydroxides, carbonates, and sulfates often serve as such activators.

An essential problem in the field today is the insufficient knowledge of dura-

bility of concretes with alkali activated slag binders, *i.e.* the stability of their properties under the influence of external environmental or intrinsic factors [2] [3] [4] [5]. Published studies demonstrate possibility of producing mortars and concretes based on alkali-activated GGBFSs that meet criteria of sulfate resistance, resistance to alkali-silica reactions, exposure to chlorides, and frost resistance. At the same time, certain disadvantages, such as efflorescence and shrinkage, are more common for some types of alkali-activated slag binders than for ordinary Portland cement materials [6] [7] [8]. However, all these characteristics are determined by quite a few parameters including binder composition, type of aggregate, water-to-binder ratio and others. The significance of those is yet to be established.

This work is a continuation of the study of alkali-activated GGBFS binders with a complex chemical activator based on high-calcium fly-ash (HCFA) and sodium carbonate; their hardening patterns and technical capabilities were already considered in [9]. This article presents data regarding the soundness, sulfate resistance, the shrinkage deformations, alkali-silicate reactivity, efflorescence, as well as the influence of fly ash fineness on some of the properties of the binder.

2. Materials and Methods

As in the first part of this research [9], the GGBFSs from two manufacturers were used:

- 1) PAO “Severstal” (Slag-1) and 2) PAO “NLMK” (Slag-2).

The HCFAs of two power plants of Krasnoyarsk region (Russia), *Nazarovskaya* (Ash-N) and *Berezovskaya* (Ash-B), in combination with sodium carbonate (chemically pure Na_2CO_3) were used as GGBFS-hardening activators. Sodium gluconate and powdered sodium lignosulfonate were utilized as plasticizer agent. Gluconate also has a pronounced setting retarding properties in formulations with HCFA.

Chemical and phase composition, as well as granulometric data on both Slags and Ash-N were presented in [9]; sample preparation and analysis of Ash-B were carried in the same manner. Data on both Ashes are shown in **Table 1**, **Figure 1** and **Figure 2**.

Between two Ashes, the Ash-B is of less fineness and has larger average particle size. According to results of XRD, both Ashes contain CaO, CaSO_4 , C_4AF , and C_3A . The content of free lime is about (15%wt - 20%wt), both show traces of

Table 1. Oxide composition and fineness of HCFAs.

	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	MgO	Na ₂ O + K ₂ O	Free lime, %wt	Blaine, cm ² /g	Mean particle size, μm
Ash-B	62.2	8.4	4.1	5.3	9.4	6.3	0.9	21.5	2190	18
Ash-N	44.1	14.7	9.6	14.6	11.0	4.4	1.1	15.2	2860	7

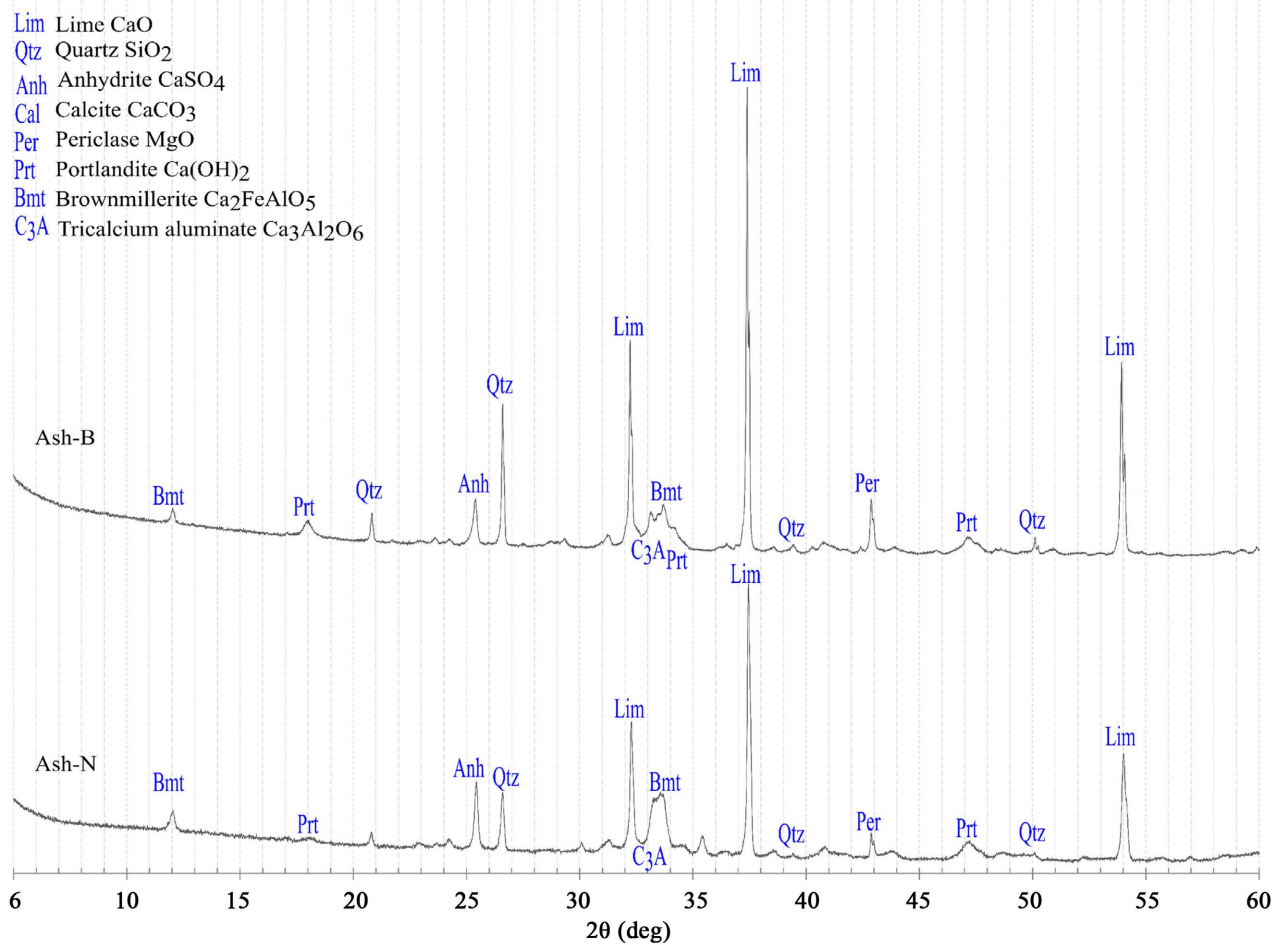


Figure 1. XRD patterns of fly ashes.

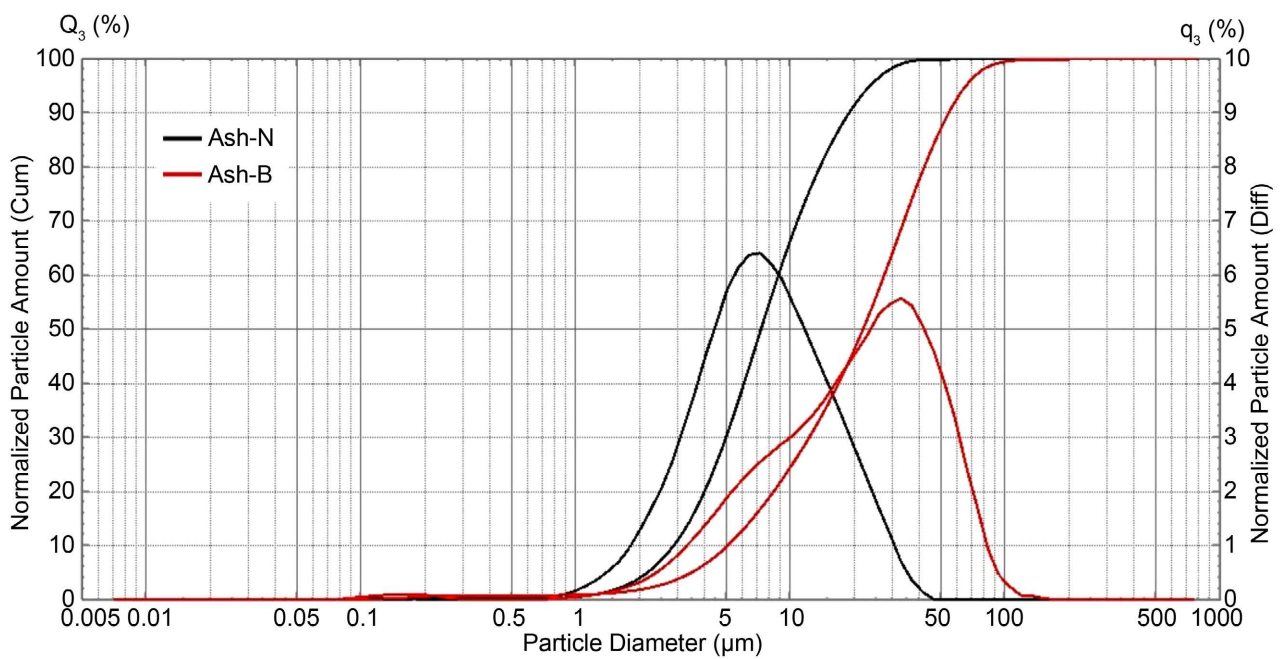


Figure 2. Particles size distribution of HCFA.

MgO and portlandite, the latter probably has been formed in-situ during storage or handling. Among water-inert crystalline components, quartz can be noted.

We carried out a comparative study of these HCFAs as constituents of cement-free binder that activate the hydration of GGBFSs. The Ash-B (coarser one) was put in formulations 1) as is, and 2) after additional dry (no liquid medium) grinding in a laboratory vibratory ball mill (3 mm ZrO₂ beads) for 4, 24 and 48 hours in an attempt to achieve specific surface area of about (4000 - 5000) cm²/g. Characteristics of Ash-B ground products are shown in **Table 2** and **Figure 3**.

Figure 4 depicts a comparison between conditions of particles of free lime in Ash-N and Ash-B. The former has CaO in a specific state where the single particle has an appearance of an agglomeration of sub-particles of much smaller scale. The lime in Ash-B lacks this feature completely.

A twofold increase in the specific surface area of Ash-B and twice the decrease in the average size of particles were achieved within four hours of dry grinding. A longer duration of comminution is at first promotes further increase in the specific surface area up to 5000 cm²/g along with reduction of the average particle size, but at some point a trend of decreasing of specific surface area arise,

Table 2. Results of grinding of Ash-B.

Grinding time, hrs.	Ash-B grinding time and properties			
	0 (no grinding)	4	24	48
Mean particle size, μm	18	9	7	8
Blaine fineness, cm ² /g	2190	4500	5040	4280

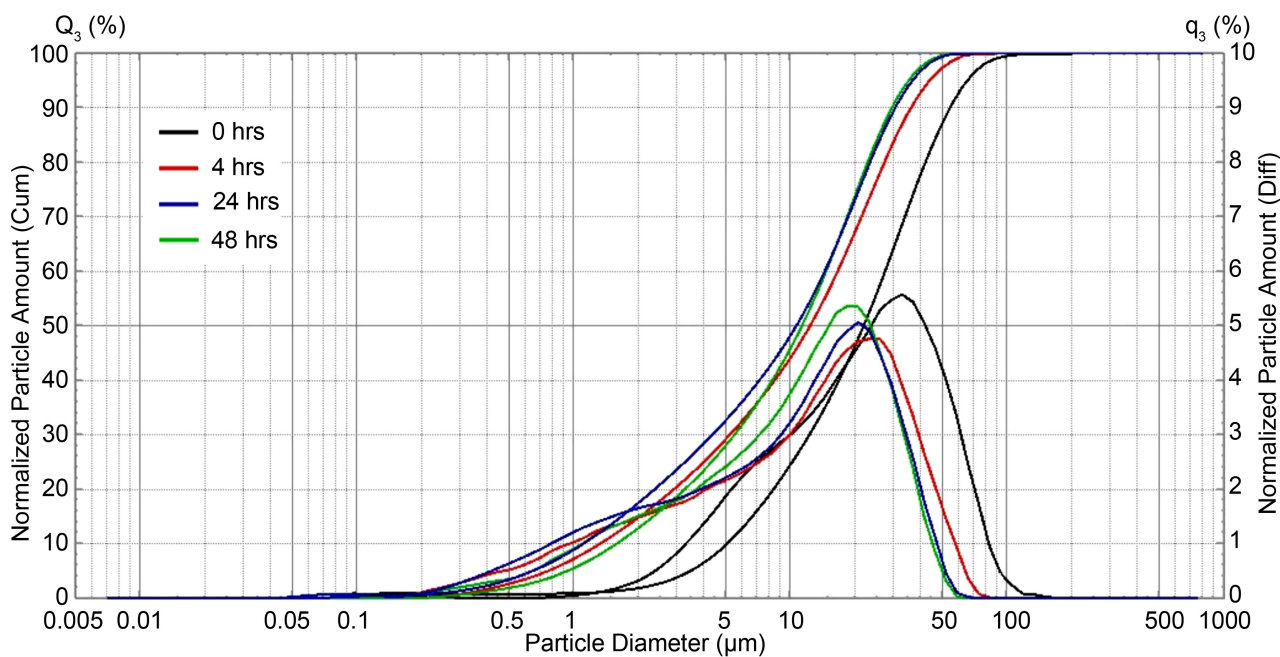


Figure 3. Particles size distribution of Ash-B vs grinding time.

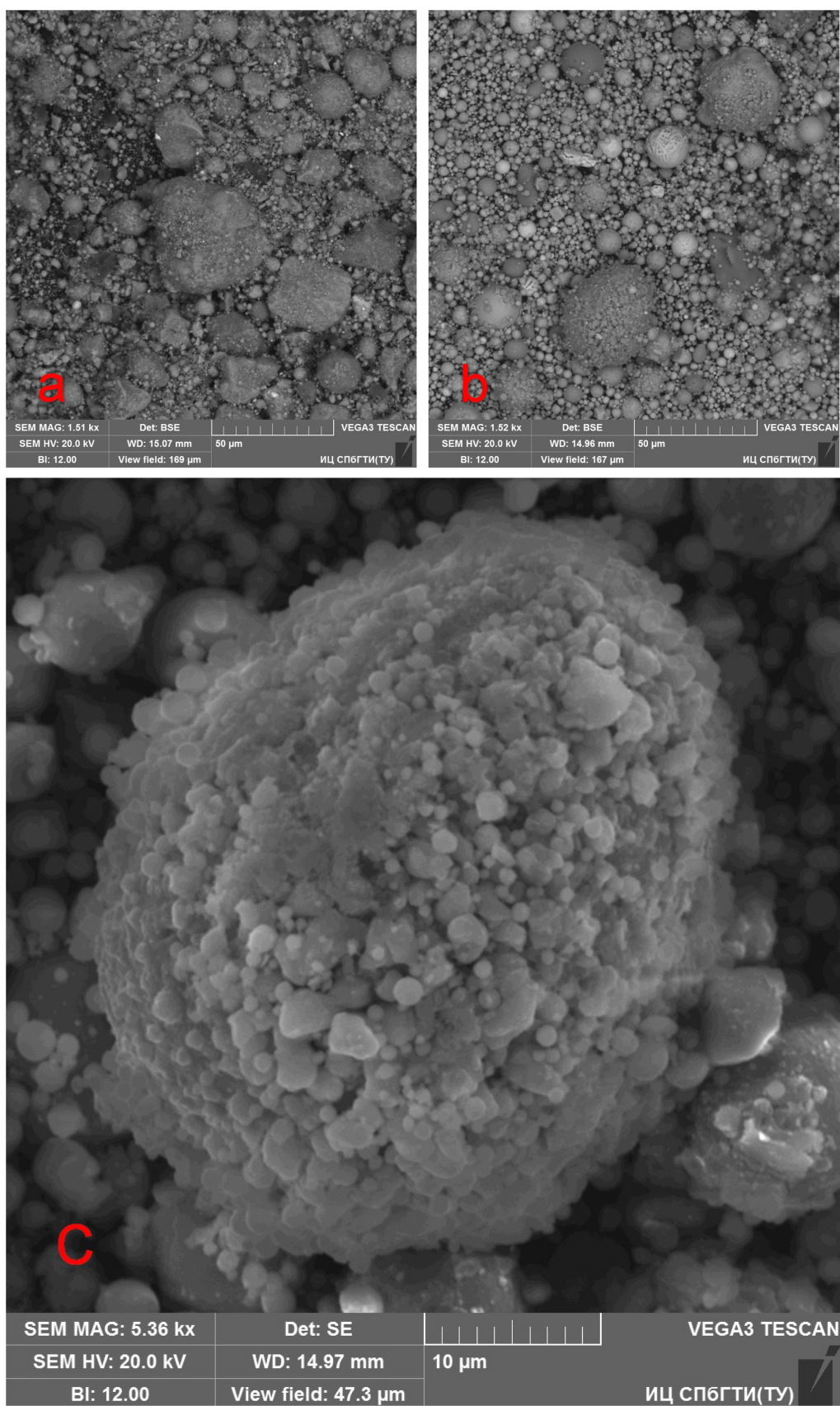


Figure 4. CaO particles in Ash-B (a) and Ash-N ((b), (c)).

which is likely due to an aggregation of fine particles; a slight increase in average particle size is also observed.

The effect of HCFA on hardening of GGBFS was assessed by measuring a gain in compressive strength of standard mortar samples over time. Preparation of samples and determination of their strength were carried out in the same manner as described in [9]. Demolding of mortar samples was performed within first (1 - 5) days, when samples obtain enough strength for safe handling. After demolding mortar samples have been stored in 95% RH, 20°C until the moment of testing.

The soundness test was performed via standard procedure in Le Chatelier molds on pastes made of GGBFSs, HCFAs, sodium carbonate and water.

Determination of sulfate resistance, shrinkage deformations of mortars on drying, and resistance to alkali-silica reaction tests were performed by measuring changes in length of mortar bars cured under appropriate conditions. Mortars were put into bar molds of (20 × 20 × 100) mm with stainless-steel anchor plates installed at both ends for subsequent measurement at a dial indicator stand.

3. Results and Discussion

3.1. Strength Development of Slag Binder Vs HCFA Fineness

The type and fineness of HCFA, the degree of slag substitution with ash, and the Na₂CO₃ content were varied in the experiment. A water-to-binder ratio (water-to-(slag + ash)) was in the range of 0.3 - 0.4 to achieve a reasonable workability (flowability). The formulations and properties of mortar samples we tested in this part are present in **Table 3**.

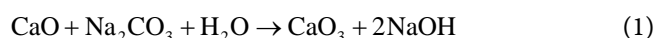
The Ash-B in its initial form, in contrast to Ash-N, has no effect on mortar hardening ratio: the demolding time and 7-day strength for composition 1 (reference) and composition 3 are practically the same. The 48 hours of grinding of ash lead to an increase in its' chemical activity. It is to be noted that the specific

Table 3. Compressive strength of mortars.

Sample	Mortar composition, g (+1350 g of standard sand)							Demolding time, d/hrs.	Compressive strength, MPa, at days	
	Slag-2	Ash-N	Ash-B (ground, hrs.)	Sodium carbonate	Sodium gluconate	Lignosulfonate	W/B ^a		7	28
1	450	-		13.5	-	2.25	0.38	5 d	0.8	24.9
2	405	45	-	13.5	0.9	-	0.31	3 d	16.1	35.1
3	405	-	45 (0)	13.5	0.9	-	0.31	4 d	0.7	24.9
4	405	-	45 (4)	4.5	0.45	-	0.36	1 d	1.0	-
5	405	-	45 (24)	13.5	0.45	-	0.36	4 hrs	13.5	23.4
6	405	-	45 (48)	13.5	0.45	-	0.36	4 hrs	12.7	21.7

a. W/B is Water-to-Binder ratio, where Binder is (slag + ash).

surface area of Ash-B ground products after 4 and 24 hours has somewhat comparable values, corresponding to double the initial specific surface area (**Table 2**). The 4 hours-ground ash is comparable in its properties to the original one (it does not show sufficient reactivity), while the use of 24 hours ground ash allows the samples to be demolded within a period of few hours and to achieve 7-day strength comparable to samples containing more potent Ash-N. This can be explained by the fact that the chemical activity of ash is determined by fineness of CaO crystals, which is of key importance for the mechanism of alkaline activation of GGBFS, where it's participating in the exchange reaction with sodium carbonate:



However, in our case sufficient fineness of CaO could only be achieved over a long-term grinding due to a relatively high hardness of lime.

3.2. Soundness of Slag Binder Vs HCFA Fineness

Results of soundness evaluation (Le-Chatelier test) are shown in **Table 4**.

When the content of Ash-N in binder composition is of (10%wt - 15%wt), the expansion (opening) of molds does not exceed 10 mm. This is within the limits of regulatory requirements, and we hence presume that no additional grinding of this ash is necessary.

Utilization of Ash-B in its original state can be associated with significant expansion of paste even at dosages of this ash up to only 10%, likely due to the presence of well-crystallized CaO and MgO in it. After short grinding (4 hrs.), the result is still unsatisfying, however long-term grinding of Ash-B makes it possible to reduce volumetric expansion to an acceptable level.

3.3. Shrinkage on Drying

To prepare mortars for this part of the testing, the components in the proportions

Table 4. Binder compositions and soundness (Le-Chatelier test).

Component	Content, %wt ^a										
Ash-N	10	15	30	10	30	-	-	-	-	-	-
Ash-B (grinding time, hrs.)	-	-	-	-	-	5	10	10	10	10	10
Slag-1	90	85	70	-	-	-	-	-	-	-	-
Slag-2	-	-	-	90	70	95	90	90	90	90	90
Na ₂ CO ₃	3	3	3	1	3	1	1	1	3	3	3
W/B	0.3	0.28	0.26	0.21	0.21	0.25	0.3	0.3	0.3	0.3	0.3
	Mold expansion, mm										
	3	2	18	6	63	2	48	67	31	9	0.5

a. Hereafter main binder constituents (slag + ash) amounts for 100%, the rest of components make for an extra amount.

indicated in **Table 5** were mixed with standard sand with sand-to-binder ratio of 3:1. Six samples of every given composition were made.

The molds were stored at (20°C - 22°C), 95% RH; when samples reach enough strength, typically at the age of (4 - 7) days, they are demolded and are kept under the same wet storage conditions. At 28th day zero measurements of lengths of samples were taken using a needle stand and a dial indicator, an average value then goes on plot.

To evaluate shrinkage deformations after initial length readings three samples of each composition were placed in open air at (20°C - 22°C) and RH of (15% - 20%). Another three samples for comparison were put under wet storage conditions at (20°C - 22°C), 95% RH. The length of samples was measured once every two weeks during the first month, then about once a month. The total duration of this test was 5 months. Under wet storage, no changes in length occurred for any of the compositions tested.

When samples are kept in open air, the highest value of shrinkage observed in the case of reference samples with OPC (**Figure 5**). Slag binder samples with about the same water-to-binder ratios show lower values of shrinkage, and, as the w/b ratio decrease, an even greater reduction in shrinkage is observed.

3.4. Sulfate Resistance

Sulfate resistance evaluation was performed by measuring the expansion of mortar bars of (20 × 20 × 100) mm cured under conditions that provoke sulfate attack—a delayed ettringite and thaumasite formation in mortar. The compositions of slag-ash binders for these tests are presented in **Table 5**. The OPC mortar bars were cast for reference purposes.

Table 5. Binder recipes for mortars in shrinkage, sulfate resistance and alkali-silica reaction tests.

Sample	Binder components, %wt							
	OPC	Slag-1	Slag-2	Ash-N	Ash-B (grinding time, hrs.)	Sodium carbonate	Sodium gluconate	W/B
1	100	-	-	-	-	-	-	0.40
2	-	90	-	10	-	3	0.2	0.36
3	-	90	-	10	-	3	0.2	0.40
4	-	70	-	30	-	3	0.2	0.36
5	-	-	90	10	-	3	0.2	0.40
6	-	-	90	10	-	3	0.2	0.30
7	-	90	-	-	10	3	0.2	0.36
8	-	90	-	-	10 (48)	3	0.2	0.36
9	-	70	-	-	30 (48)	3	0.2	0.36
10	-	90	-	-	10 (48)	3	0.2	0.40

After measuring the initial length of samples at the age of 28 days, bars were placed in a plastic container in threes and fully submerged in 5% Na_2SO_4 solution. Containers were sealed and stored at 5°C. During the first month the procedure of length measurement of samples and replacing of the sodium sulfate solution has been performed once every two weeks, then once a month. The total duration of the test was 1 year. Expansion curves are presented in **Figure 6**.

Upon completion of the test, small fragments (~5 mm in size) were taken from central part of mortar prisms, submerged in ethanol for 1 day and then dried at (40°C - 45°C) for (6 - 8) hours. These dewatered and dried fragments were taken for SEM examination to study microstructure of the stone.

The results indicate that linear deformations of mortar samples with no more than 10% HCFA in the binder composition stay within 0.02% expansion value at both room and low temperatures. With higher content of HCFA in the binder,

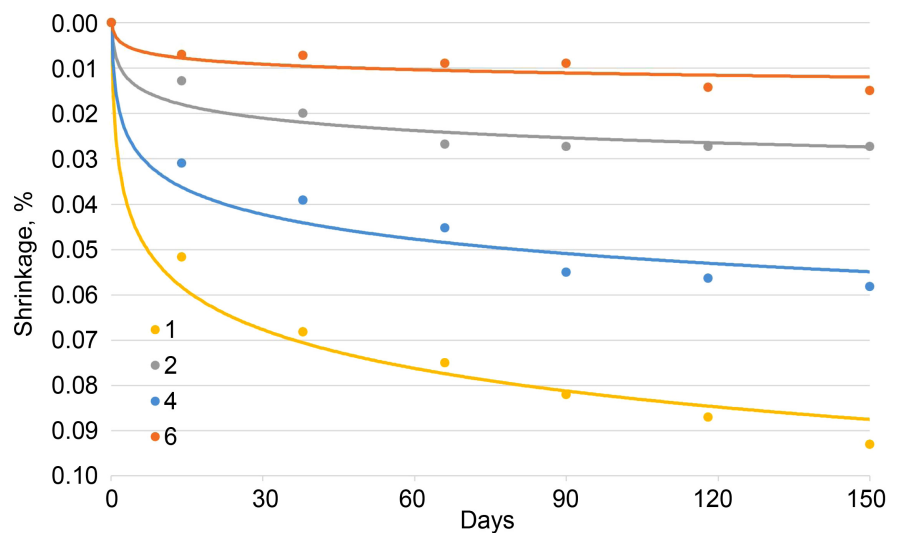


Figure 5. Shrinkage of mortars at low-humidity air storage.

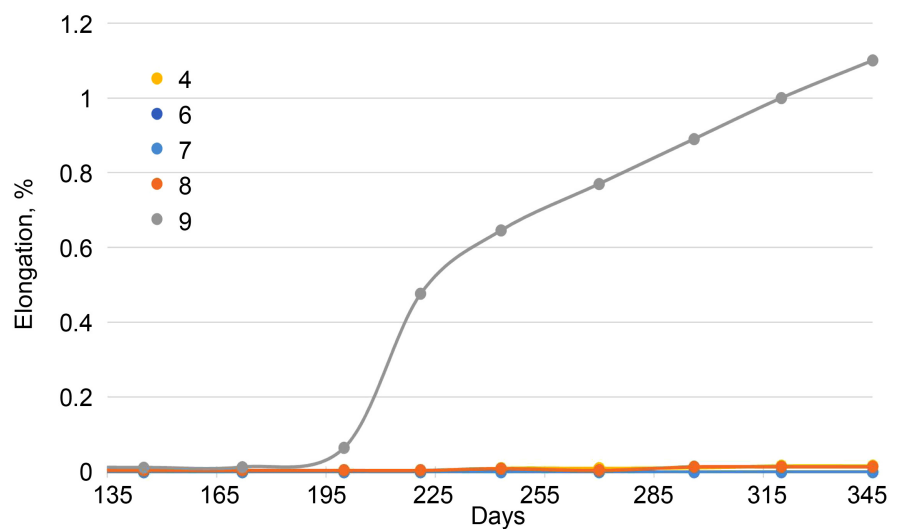


Figure 6. Expansion of mortars in 5% sodium sulfate solution at 5°C.

however, the results turned out to be ambiguous: when Ash-N content was increased up to 30% in the ash-slag binder, mortar samples do not manifest any significant expansive behavior (specimen 4), while 30% of Ash-B in binder result in a sudden onset of expansion of mortar few months into the run of the experiment (specimen 9).

SEM results (**Figure 7**) indicate that in the latter case the solid bulk of binder

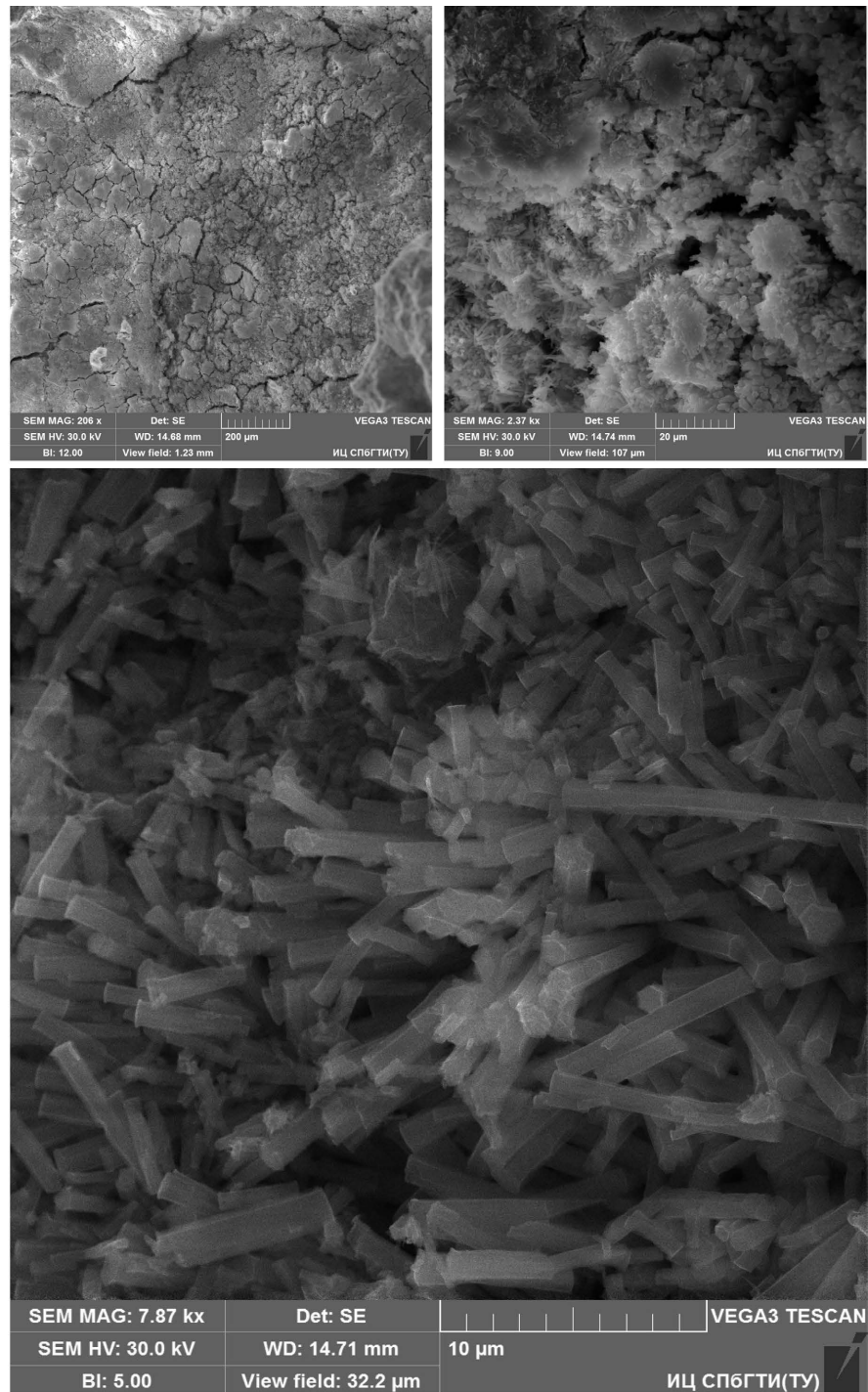


Figure 7. SEM images of sample 9 after one year of sulfate resistance test.

matrix turned into a loose agglomeration of crystalline product identified as hexagonal elongated prisms of Aft phases. There were no such negative changes observed in other samples.

It seems that there is a pronounced risk for such destructive processes to take place when a mortar with high content of HCFA is exposed to the sulfate environment.

3.5. Alkali-Silica Reaction in GGBFS-HCFA Mortars with Reactive Sand

A reactive aggregate for mortars tested for resistance to alkali-silica reaction (ASR) was prepared by mixing 98 wt% quartz sand (particle size composition, wt%: (1.25 - 2.5) mm - 27.5, (0.63 - 1.25) mm - 27.5, (0.315 - 0.63) mm - 27.5, (0.16 - 0.315) mm - 17.5)) and 2 wt% of crushed quartz glass of the same particles size composition.

Recipes for the binders are presented in **Table 5**. Mortars were prepared by mixing reactive aggregate with binder in a ratio of aggregate-to-binder of 2.25:1 and water-to-binder of 0.4. The (20 × 20 × 100) mm mortar bars were prepared in the same manner as for the sulfate resistance test. For each series 2 samples were made. The molds were kept at 20°C, 95% RH for 1 day in case of OPC mortars (references), and 14 days for GGBFS-HCFA samples—this time is sufficient for slag-ash mortar to acquire water resistance, because being cured for only a day make slag-ash samples partially wash out when put into hot water or NaOH solution as per test requirements.

After wet curing, the samples were demolded and put for 1 day in distilled water at 80°C. Then the samples were wrapped in polyethylene film and left to cool down to room temperature (~20°C), and their initial length was measured. After this zero reading the samples were placed in series in plastic containers in 1M NaOH solution for a subsequent storage at 80°C. The ratio of the volume of liquid to the volume of samples was approximately (2.5 ÷ 3) to 1, samples were horizontal inside containers. The elongation measurement of samples was performed on the stand with the dial indicator. Total duration of the exposure of samples to 1M NaOH was 12 days. Test results are presented in **Figure 8**.

It was only OPC samples that undergo the expansion, the value of their elongation by the end of the test exceeded 0.2%. The occurrence of the alkali-silica reaction in these samples is confirmed via SEM, by the presence of fragmented particles of quartz glass and alkali-silica hydrogel (**Figure 9**). These ASR-characteristic features are missing in the rest of the samples.

Inhibition of ASR in GGBFS-HCFA samples with reactive aggregate can be explained by the following two reasons:

- 1) insignificant, in comparison with OPC mortar, content of $\text{Ca}(\text{OH})_2$ in the hydration products of slag-ash binder; it is known that $\text{Ca}(\text{OH})_2$ enhances the expansive effect of alkali-silicate hydrogel;
- 2) a low permeability product of GGBFS hydration presumably shields reactive aggregate particles from the surrounding alkaline environment.

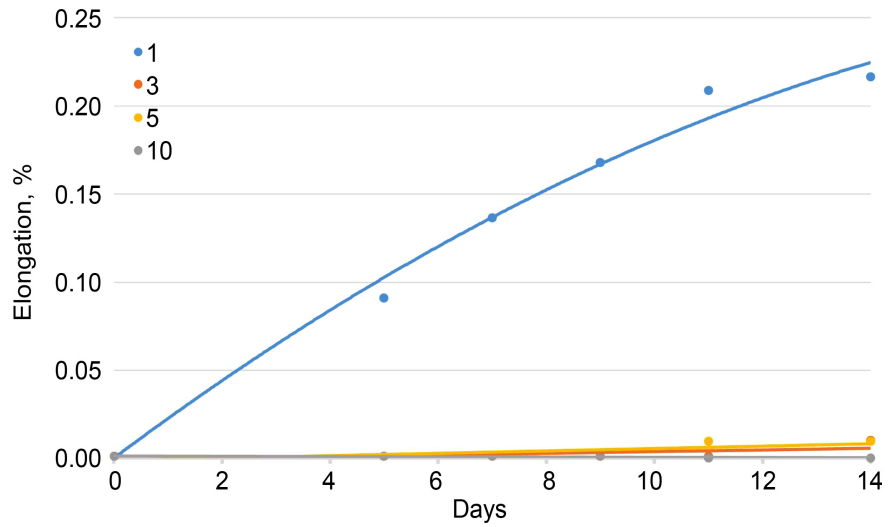


Figure 8. Expansion of OPC (1) and slag-ash binder (3, 5, 10) mortars under accelerated ASR test conditions.

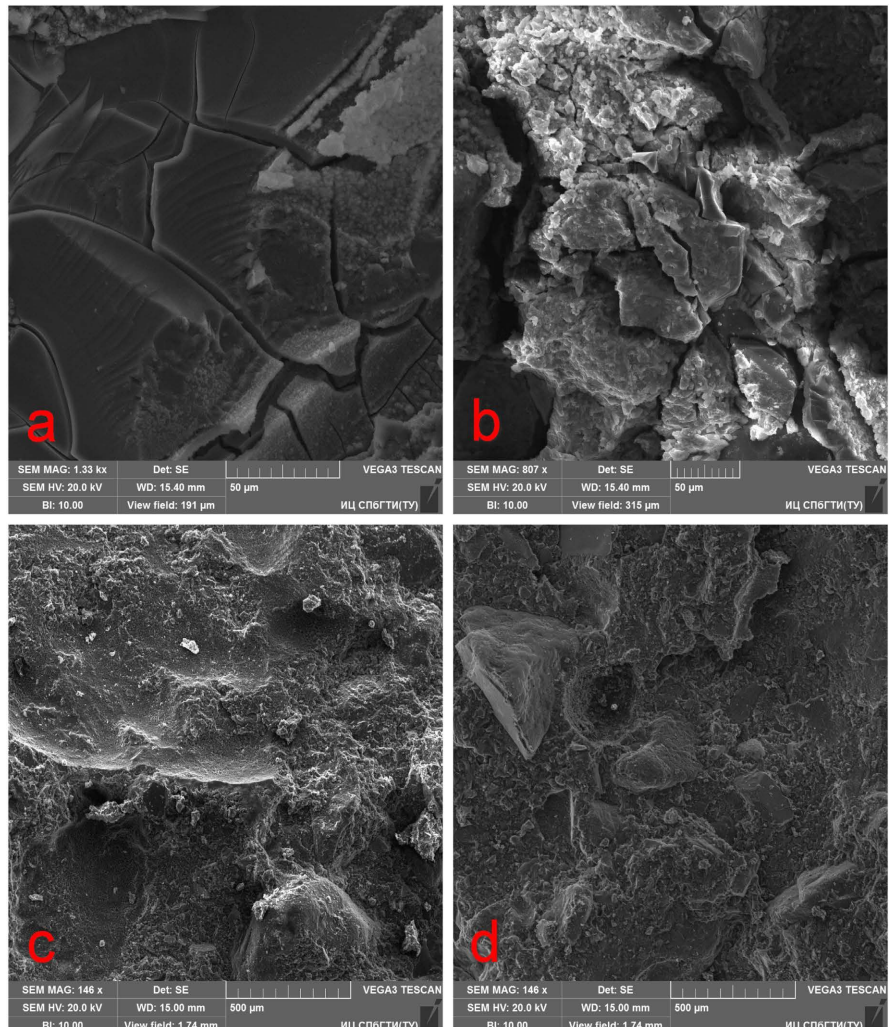


Figure 9. SEM images of samples after ASR test: (a) OPC mortar—glass particle, (b) OPC mortar—alkali-silica hydrogel, (c) and (d) slag-ash binder.

3.6. Resistance to Efflorescence

For efflorescence testing standard mortar prisms of (40 × 40 × 160) mm were made, recipes are given in **Table 6**; in [9], physical and mechanical tests were carried out for most of those samples. At the age of 90 days, after curing at 20 °C, 95% RH, mortar prisms were test-broken, and halves of the prisms were put vertically, cleavage up, in Petri dishes. Distilled water was poured into the dishes in such a quantity that the lower part of the samples was immersed to a depth of ~5 mm. The samples in dishes were kept in open air at 22 °C and RH ~(15% - 20%) for 10 days, during this period the distilled water was resupplied every other day to account for evaporation. After 10 days water addition is stopped and after full expense of water in dishes and drying of samples their surface was visually examined. The visual appearance of samples at this stage is shown in **Figure 10**.

In mortar recipes we varied the type of slag and ash, the content of ash and Na₂CO₃, and the water-to-binder ratio, meanwhile the efflorescence clearly manifested itself only in two cases. This can probably be attributed to an insufficient degree of hydration of GGBFS and the associated relatively high porosity of such mortars, which promote moisture migration (samples 9 and I). In sample 9, there was no Na₂CO₃ in composition. In the case of sample I the resulting efflorescence is likely due to utilization of Ash B instead of A, which, as noted before, has lower chemical activity. Sample II has the same Ash B in the recipe, but after

Table 6. Binder recipes for mortars in efflorescence test.

Sample	Mortar composition, g (+1350 g of standard sand)							
	Slag-1	Slag-2	Ash-N	Ash-B (grind time, hrs.)	Sodium carbonate	Sodium gluconate	Lignosulfonate	W/B
I	-	405	-	45	13.5	0.2	-	0.31
II	-	405	-	45 (24)	13.5	0.2	-	0.36
Recipes from [9]								
4	450	-	-	-	13.5	-	2.25	0.40
6	405	-	45	-	4.5	0.45	-	0.36
7	405	-	45	-	13.5	0.45	-	0.36
9	315	-	135	-	-	0.45	-	0.36
10	315	-	135	-	4.5	0.45	-	0.36
11	315	-	135	-	13.5	0.90	-	0.40
12	315	-	135	-	13.5	0.90	-	0.31
13	315	-	135	-	13.5	0.90	-	0.36
15	-	450	-	-	13.5	-	2.25	0.38
16	-	405	45	-	13.5	0.90	-	0.31
17	-	315	135	-	-	-	-	0.31
18	-	315	135	-	13.5	0.90	-	0.31



Figure 10. Appearance of samples after the efflorescence test.

the comminution, and there are no signs of efflorescence in this case. This indicates that fine grinding of HCFA (which increase its chemical activity) can reduce the risk of efflorescence formation.

4. Conclusions

- 1) The cement-free GGBFS-HCFA mortars, unlike PC-based, do not develop harmful behavior due to alkali-silica interaction when a reactive aggregate is present.
- 2) Such slag-ash materials are sulfate-resistant in general; however, the risk of developing of destructive reactions with formation of Aft phases cannot be avoided completely given the content of fly ash in the binder is high enough.
- 3) While at the same amount in the binder formulation, HCFAs of different nature can have different effects on soundness of the binder; however, the extent of the expansion can be minimized by increasing the fineness of high-calcium fly ash by additional fine comminution.
- 4) In general, an increase in fineness of HCFA, which originally shows poor chemical activity, significantly increases its' ability to activate hydration of GGBFS and results in a promotion in the early strength development, enhances soundness and prevents efflorescence.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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