

# Dry Mix Slag—High-Calcium Fly Ash Binder. Part One: Hydration and Mechanical Properties

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## Abstract

High-calcium fly ash (HCFA)—a residue of high-temperature coal combustion at thermal power plants, in combination with sodium carbonate presents an effective hardening activator of ground granulated blast-furnace slag (GGBFS). Substitution of 10% - 30% of GGBFS by HCFA and premixing of 1% - 3%  $\text{Na}_2\text{CO}_3$  to this dry binary binder was discovered to give mortar compression strength of 10 - 30 to 30 - 45 MPa at 7 and 28 days when moist cured at ambient temperature. High-calcium fly ash produced from low-temperature combustion of fuel, like in circulating fluidized bed technology, reacts with water readily and is itself a good hardening activator for GGBFS, so introduction of  $\text{Na}_2\text{CO}_3$  into such mix has no noticeable effect on the mortar strength. However, low-temperature HCFA has higher water demand, and the strength of mortar is compromised by this factor. As of today, our research is still ongoing, and we expect to publish more data on different aspects of durability of proposed GGBFS-HCFA binder later.

## Keywords

Ground Granulated Blast-Furnace Slag, Blast-Furnace Slag Activation, High-Calcium Fly-Ash, Sodium Carbonate, Blast-Furnace Slag Binder

## 1. Introduction

In studies on the hydration of binders based on ground granulated blast-furnace slag (GGBFS) alkali silicates and hydroxides are preferred as hardening activators, since they let achieve the highest strength characteristics [1] [2] [3] [4] but in fact these activators come with several disadvantages, which have a restraining effect on practical implementation of such approach. These disadvantages include, for example, industrial safety problems associated with the high alkalinity

of activators and significant shrinkage of GGBFS geopolymer.

Another important note is that these activators, in general, are utilized in form of concentrated aqueous solutions, since solid sodium and potassium silicates, which are readily soluble at ambient temperature, are quite expensive materials. Due to this reason the solid batch of the GGBFS binder and the liquid activator must be stored and supplied to the consumer separately and mixed in-situ right before application. It seems that for a successful wide-spread commercial implementation of the GGBFS-based binders it is important that the way they are processed would not differ significantly from traditional concrete or mortar practices. This means, before all, that the binder should come in the form of a “one-pack” dry mix, which includes all the necessary activators premixed with binder in one bag [1] [5], and the product must have a reasonable shelf time.

Compared to alkali silicates, sodium and potassium carbonates are not considered to provide high early strength, but at the same time they do not have the abovementioned drawbacks, since they are safe to handle, they come in a bulk solid form, have high solubility in water, and, not the least one, are quite cheap [4] [6]. Shrinkage of geopolymer during hardening of slag binders with alkali carbonate activators is 3 - 6 times lower compared to systems with alkali silicate activators [6].

The main difficulty of exploiting sodium or potassium carbonates as the GGBFS-activators is that the initial pH of their aqueous solutions is of the order of 11, which is insufficient to promote required rate of dissolution of slag glass. With time the pH of the pore liquid increases gradually due to slow binding of carbonate ions with  $\text{Ca}^{2+}$  coming from glass dissolution, and the release of an equivalent amount of hydroxyl [2] [6]. The combination of carbonates with alkaline silicates and hydroxides increases the rate of strength development, but at the same time brings back the previously identified problems.

It is possible to increase the efficiency of carbonate activators, like  $\text{Na}_2\text{CO}_3$ , by exploiting their ability to engage into exchange reactions with substances capable of releasing  $\text{Ca}^{2+}$  more readily than slag when the binder is mixed with water. One example of such compound is  $\text{Ca}(\text{OH})_2$ . Among the industrial materials available as a source of  $\text{Ca}(\text{OH})_2$ , high-calcium fly ash (HCFA), a product of combustion of brown coal or oil shale may be of interest as an activator of GGBFS. This type of fly ash is a widely known, yet underutilized resource for binder technology [7] [8]. High-calcium fly ash contains free  $\text{CaO}$ ,  $\text{CaSO}_4$ ,  $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ , which all can react with water. In addition, a significant part of the HCFA represents glass phase that is capable of hydration in an alkaline environment to precipitate as a C-S-H gel. The main hydration products of crystalline part of HCFA are  $\text{Ca}(\text{OH})_2$ , gypsum, and ettringite. The pH of a water suspension of HCFA almost immediately reaches values above 11.

As an activator of slag, HCFA is good enough by itself, but the effect can be much greater when HCFA is used together with carbonates due to exchange reactions between them, which raises the pH even further. In combination with  $\text{Na}_2\text{CO}_3$ , pH of an aqueous suspension of HCFA reaches values of 13 and above

due to interaction between  $\text{Na}_2\text{CO}_3$  and  $\text{Ca}(\text{OH})_2$  to form  $\text{NaOH}$  and  $\text{CaCO}_3$  precipitate. The promoted alkaline environment stimulates both slag and fly ash hydration, so an additional amount of C-S-H is formed in process.

In current world practice, beside “traditional” high-temperature flame combustion process of solid pulverized fuel at thermal power plants, a circulating fluidized bed technology is also utilized, which is characterized by a relatively low temperature in combustion zone, typically below  $900^\circ\text{C}$ . The ash produced so is rich in free  $\text{CaO}$  which quenches quickly in contact with water and thus does not cause delayed expansion and cracks in geopolymer [7].

Considering different properties and behavior of high and low-temperature HCFAs, authors sought to compare their effectiveness as both standalone activators of GGBFS and when sodium carbonate is additionally introduced into slag-ash system.

## 2. Objects and Methods

The goal of this research was to study hydration of no-clinker mixes of GGBFS with two different types of HCFA obtained from: 1) high-temperature pulverized fuel combustion in conventional furnace (brown coal-fired *Nazarovskaya* power plant, Russia, thereafter “HCFA-H”), and 2) low-temperature circulating fluidized bed combustion (oil shale-fired *Auvere* power plant, Estonia, “HCFA-L”).

The GGBFSs of two manufacturers were used: 1) PAO “*Severstal*” (GGBFS-1) and 2) PAO “*NLMK*” (GGBFS-2). A chemically pure sodium carbonate was used as activator, sodium gluconate as retarding agent and powdered sodium lignosulfonate as plasticizer.

Phase composition of the studied materials was determined by XRD (Rigaku SmartLab 3 diffractometer,  $\text{Cu}_{K\alpha}$  radiation). SEM EDS was used for studying of chemical composition (TESCAN VEGA 3 SBH with INCA x-act 51-ADD0007 analyzer, Oxford instruments). Particle size distribution was determined by means of LDA (Shimadzu SALD-7500 nano) with ultrasonic dispersion in ethanol media. Specific surface area of the materials was estimated by Blaine test (TESTING 1.0297). Free  $\text{CaO}$  content in HCFAs was determined by well-known ethanol-glycerin method. Loss on ignition (LOI) for HCFAs was carried out at  $1000^\circ\text{C}$  in a laboratory electric muffle furnace.

Hydration behavior of HCFAs was studied in pastes prepared by mixing 10 g of HCFA, 0.3 g of  $\text{Na}_2\text{CO}_3$  and 8 g of water; the pastes were cast in the shape of thin (2 - 3 mm) tablets, then cured in moist conditions at  $20^\circ\text{C}$ . On 7-th and 28-th day small fragments of the hardened pastes were taken from the tablets and soaked in ethanol for 1 - 2 days, then fully dried at  $40^\circ\text{C}$  -  $45^\circ\text{C}$ . In SEM studying freshly cleaved surface of these fragments of paste was analyzed. For an XRD these dried fragments were ground into fine powder.

The effect of HCFA on the hardening of GGBFS was tested on slag-sand mortar samples. The preparation of mortar samples and their strength determination, as well as soundness evaluation of the GGBFS-HCFA pastes were per-

formed by standard procedures (GOST 30744-2001). Mortar samples ( $40 \times 40 \times 160$  mm prisms) were demolded in 1 to 5 days or later, depending on their physical state at the time, and then stored in 100% RH conditions at  $20^\circ\text{C}$  until the moment of testing.

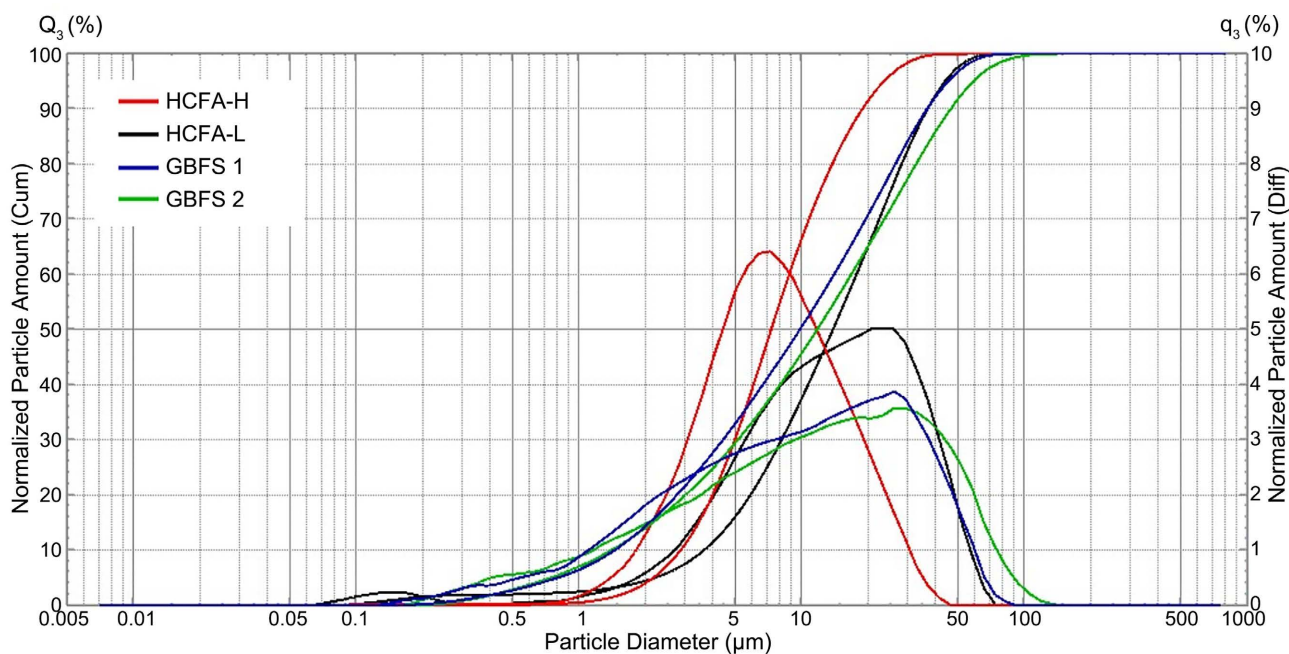
The setting time was determined on mortars using Vicat device and the standard needle, but the mass of the moving part of the device was 1000 g (NF P15-431 test).

After testing for compressive strength, fragments of about 5 - 10 mm were taken from the central part of the crushed mortar samples, stored submerged in ethanol for one day, and then dried at  $40^\circ\text{C}$  -  $45^\circ\text{C}$  for 6 - 8 hours. The surface of these mortar fragments was then studied by SEM.

Particle size distribution and mineral composition of dry GGBFSs and HCFAs are shown in **Figure 1** and **Table 1**, GGBFS phase composition is presented in **Figure 2**.

Both GGBFSs have very similar particle size distribution and specific surface area, as well as average particle size (**Figure 1**, **Table 1**). In the XRD patterns of both slags, there is a diffusive area in the range of  $25^\circ$  -  $35^\circ 2\theta$  specific to the glass (**Figure 2**). It appears that GGBFS-2 is in overall more crystalline than GGBFS-1. The main crystalline phase is an inert to water merwinite ( $3\text{CaO}\cdot\text{MgO}\cdot 2\text{SiO}_2$ ). Quartz peaks are present in diffraction patterns of both GGBFSs, it may probably be classified as a mechanical impurity of an unknown origin. The absence of peaks of any other crystalline constituents in pattern of the GGBFS-1 indicates a significant predominance of the glass phase in its composition.

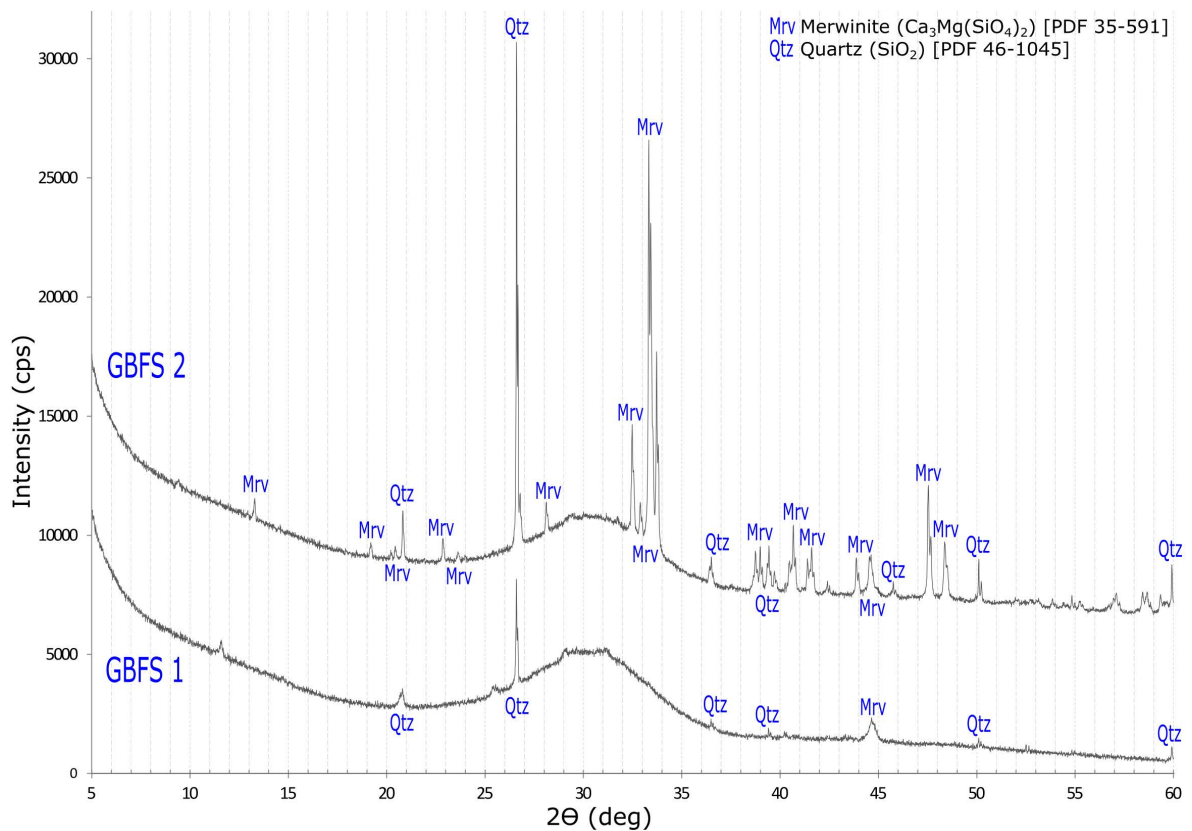
The HCFA-H is characterized by higher fineness and smaller average particle size, but the HCFA-L has a higher specific surface area. This can be explained by



**Figure 1.** Particle size distribution of GGBFSs and HCFAs.

**Table 1.** Oxide composition and properties of GBFA and HCFA.

Oxide/property	Material			
	HCFA-H	HCFA-L	GGBFS-1	GGBFS-2
CaO	44.1	53.8	34.2	38.6
SiO <sub>2</sub>	14.7	21.7	36.6	38.7
Al <sub>2</sub> O <sub>3</sub>	9.6	6.8	11.1	8.6
SO <sub>3</sub>	11.0	5.7	2.9	2.5
Fe <sub>2</sub> O <sub>3</sub>	14.6	4.3	1.5	1.7
K <sub>2</sub> O	0.1	4.0	0.5	0.5
MgO	4.4	2.7	10.7	9.2
TiO <sub>2</sub>	0.0	0.5	1.4	0.3
Na <sub>2</sub> O	1.0	0.0	0.5	0.0
MnO	0.2	0.0	0.5	0.0
CaO <sub>free</sub>	3.8	3.7	-	-
LOI, wt%	0.4	7.2	-	-
Blaine fineness, cm <sup>2</sup> /g	2860	6330	3270	3400
Mean particle size, μm	7	14	8	9

**Figure 2.** XRD patterns of ground granulated blast furnace slags 1 and 2.

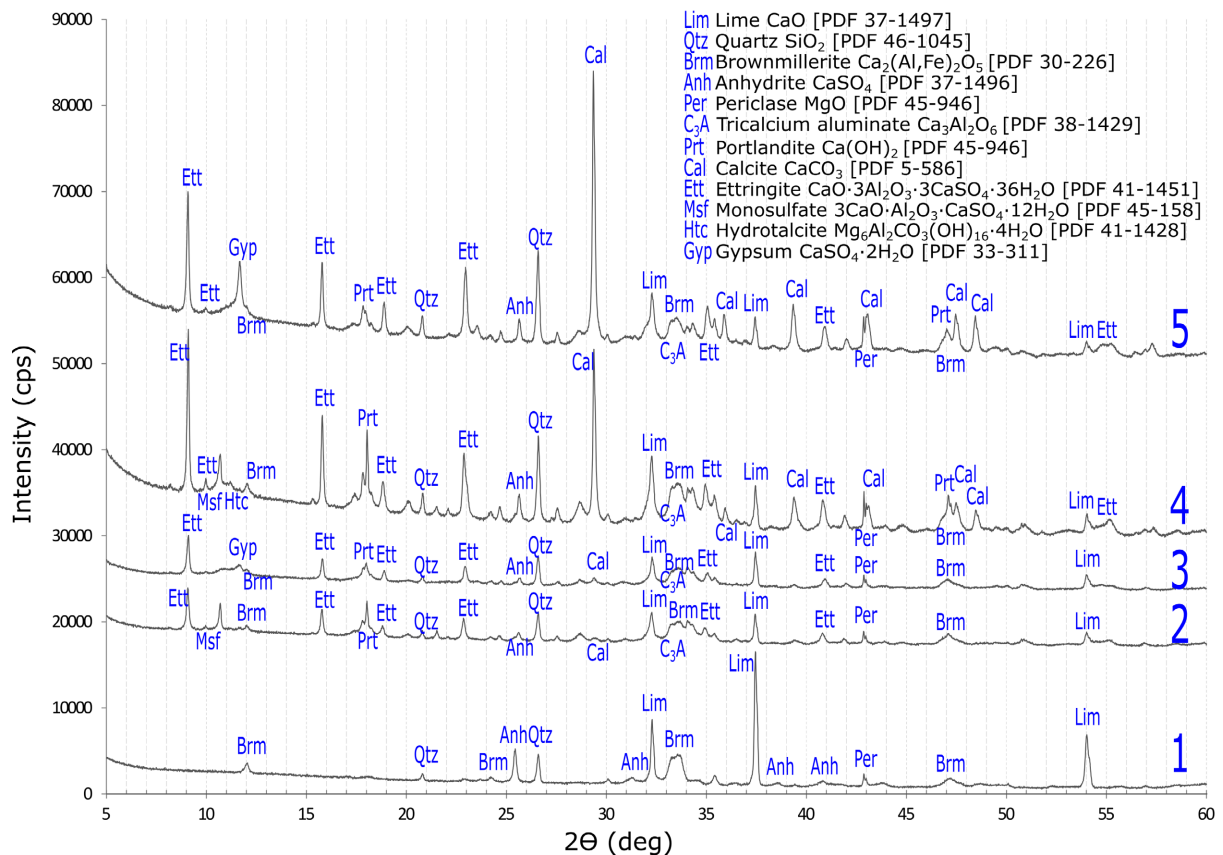
lower degree of vitrification and more developed particle morphology of HCFA-L, which is produced at lower temperature than HCFA-H. According to results of

XRD, free CaO, CaSO<sub>4</sub>, C<sub>4</sub>AF, and C<sub>3</sub>A phases are presented in both fly ashes (C<sub>3</sub>A can also originate from the glass). The CaO<sub>free</sub> content in both HCFAs is approximately the same (**Table 1**). Portlandite (Ca(OH)<sub>2</sub>) is observed in small amount, apparently formed in bulk of HCFAs during their shelf storage. Among inert to water constituents, quartz can be noted. The HCFA-H contains MgO, whereas in HCFA-L CaCO<sub>3</sub> is presented: relatively low temperature of combustion in the fluidized bed process ~850°C - 900°C does not ensure its' complete decomposition. Another possibility is that a certain amount of limestone is introduced in the combustion process to desulfurize SO<sub>3</sub> into CaSO<sub>4</sub> and then some of the limestone can co-deposit with the ash [7]. LOI value indicates the content of CaCO<sub>3</sub> in HCFA-H is about 15 wt%.

### 3. Results and Discussion

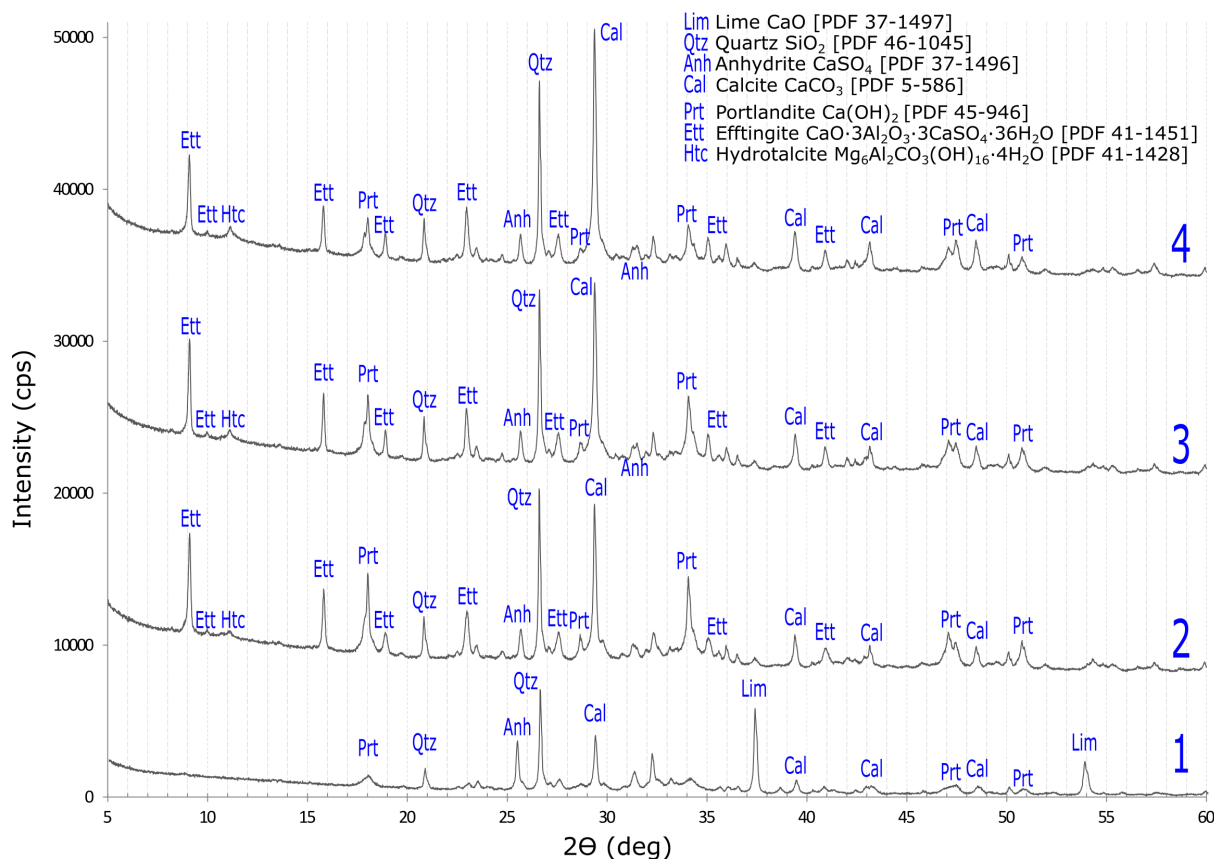
XRD patterns of HCFAs hydration products at the age of 7 and 28 days with and without Na<sub>2</sub>CO<sub>3</sub> are shown in the **Figure 3** and **Figure 4**. SEM data of these products at the age of 28 days are presented in the **Figure 5**.

In the XRD patterns of pastes of 7 days prepared from HCFA-L, CaO peaks can be hardly observed (**Figure 4**); by this time CaO had fully react to produce Ca(OH)<sub>2</sub>, CaCO<sub>3</sub>, and ettringite (corresponding reflexes rise in the pattern). In

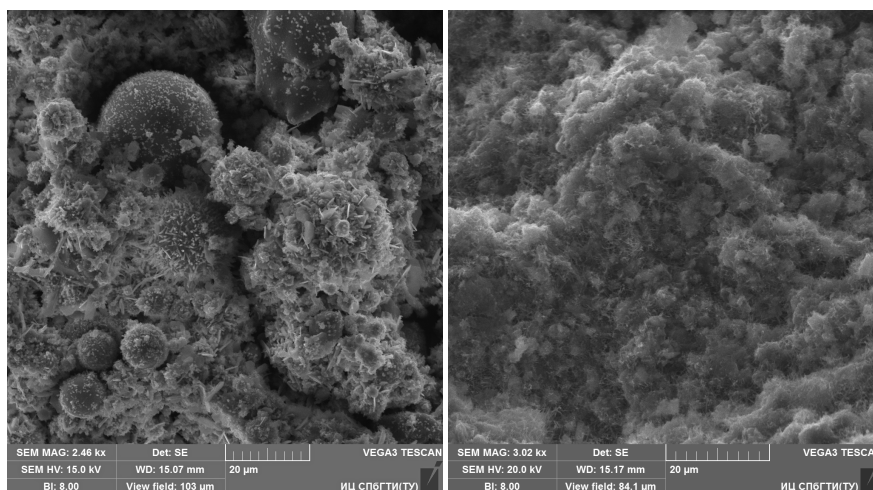


**Figure 3.** XRD patterns of dry (1) HCFA-H and hydrated for 7 days (2, 3) and 28 days (4, 5). Samples (3) and (5) contain 3 wt% of Na<sub>2</sub>CO<sub>3</sub>.





**Figure 4.** XRD patterns of dry (1) HCFA-L and hydrated for 7 days (2, 3) and 28 days (4). Samples (2) and (4) contain 3 wt% of Na<sub>2</sub>CO<sub>3</sub>.



**Figure 5.** SEM images (SE) of hydrated HCFA-H (left) and HCFA-L (right), 28 days.

paste with Na<sub>2</sub>CO<sub>3</sub>, the exchange reaction between Na<sub>2</sub>CO<sub>3</sub> and Ca(OH)<sub>2</sub> contributes to increase in intensity of CaCO<sub>3</sub> reflexes in addition to native effect of Ca(OH)<sub>2</sub> carbonization. The intensity of CaCO<sub>3</sub> reflexes continues to increase even past 7 days, while peaks of Ca(OH)<sub>2</sub> fade.

In hardened paste with HCFA-L some free CaO still remains after 7 days and

even after that (**Figure 3**);  $\text{CaCO}_3$  peaks in XRD patterns of 7-days samples is of a rather weak intensity, this may be due to weak crystallinity of the phase, but by the age of 28 days they increase.

The aluminoferrite in both types of ash remains inactive through the entire period of observation. Ettringite that is formed with the participation of CaO ( $\text{Ca}(\text{OH})_2$ ),  $\text{C}_3\text{A}$  and anhydrite, partially converts to calcium monosulfoaluminate over time. However, in pastes where  $\text{Na}_2\text{CO}_3$  was introduced, the high alkalinity of the environment stabilizes ettringite and prevents the conversion.

After 28 days, intact particles of ash are still discernable in the matrix of hydration products of HCFA-H, while the structure of HCFA-L sample has more homogeneous appearance (**Figure 5**).

When evaluating possibility of utilization of HCFA in formulations of a hydraulic binder—cement-based or clinker-free (alkali-slag)—it is important to consider the effect of free CaO, that disturbs uniform hardening of the binder/mortar and can cause volumetric deformations, cracks, or even complete failure of final product. Taking this into account, a standard soundness test (Le Chatelier molds) was performed on pastes prepared from mixes of GGBFS-HCFA- $\text{Na}_2\text{CO}_3$  with water. A maximum value of expansion is specified not to exceed 10 mm.

Information in **Table 2** point out that results of this test are determined not only by the type of HCFA but also dependent on type of GGBFS. With a content of 10 - 15 wt% HCFA-H in slag-ash binder, samples pass the soundness test, but higher content of this ash (30%) causes severe expansion. The HCFA-L does not cause such level of expansion even when its content in the binary binder is high. This is because components of HCFA L, namely the free CaO, react with water when the paste is still in plastic state. In ethanol-glycerol evaluation of free lime, the CaO content of HCFA-L was titrated much faster compared to that in HCFA-H.

Thus, the hydration activity of the HCFA, which affects, beside other properties, the soundness of the binder, seems to depend on fuel combustion temperature as well as on particle fineness and morphology of the resulting ash.

Introduction of HCFA into GGBFS-1 and GGBFS-2 mortars leads to a rather quick loss of their workability in both cases (**Table 3**). To counter this phenomenon, some 0.01 - 0.02 wt% of sodium gluconate admixed into binary binder acts as an effective regulator of setting time (**Table 3**); in some cases, it also provides a pronounced plasticizing effect. Thus, sodium gluconate was used in all formulations with HCFA in amount of 0.01% and 0.02%, depending on the content of  $\text{Na}_2\text{CO}_3$  (1% and 3%, respectively). For no HCFA binders the plasticizing agent was sodium lignosulfonate (0.5% by weight of the slag) since it proved inefficient in mortars with high-calcium ash.

Effect of HCFA and  $\text{Na}_2\text{CO}_3$  on hardening of GGBFS was evaluated by comparing compressive strength of slag-sand mortar samples in accordance with GOST 30744-2001 (40 × 40 × 160 mm mortar prisms). Mortar formulations have varied in proportion of components, type of slag and ash, the degree of



**Table 2.** Results of soundness test.

Component/property	Value							
GGBFS-1, wt%	90	85	70	-	-	-	-	-
GGBFS-2, wt%	-	-	-	90	70	90	90	70
HCFA-H, wt%	10	15	30	10	30	-	-	-
HCFA-L, wt%	-	-	-	-	-	10	10	30
Na <sub>2</sub> CO <sub>3</sub> , (wt% of GGBFS + HCFA)	3	3	3	1	3	1	3	1
Water-to-solid ratio	0.3	0.28	0.26	0.21	0.21	0.24	0.25	0.38
Le Chatelier mold expansion, mm	3	2	18 <sup>a</sup>	6	63	0	2	2

a. Fine comminution of HCFA and increase in its' Blaine fineness decrease expansion and improve HCFA ability to promote GGBFS hydration.

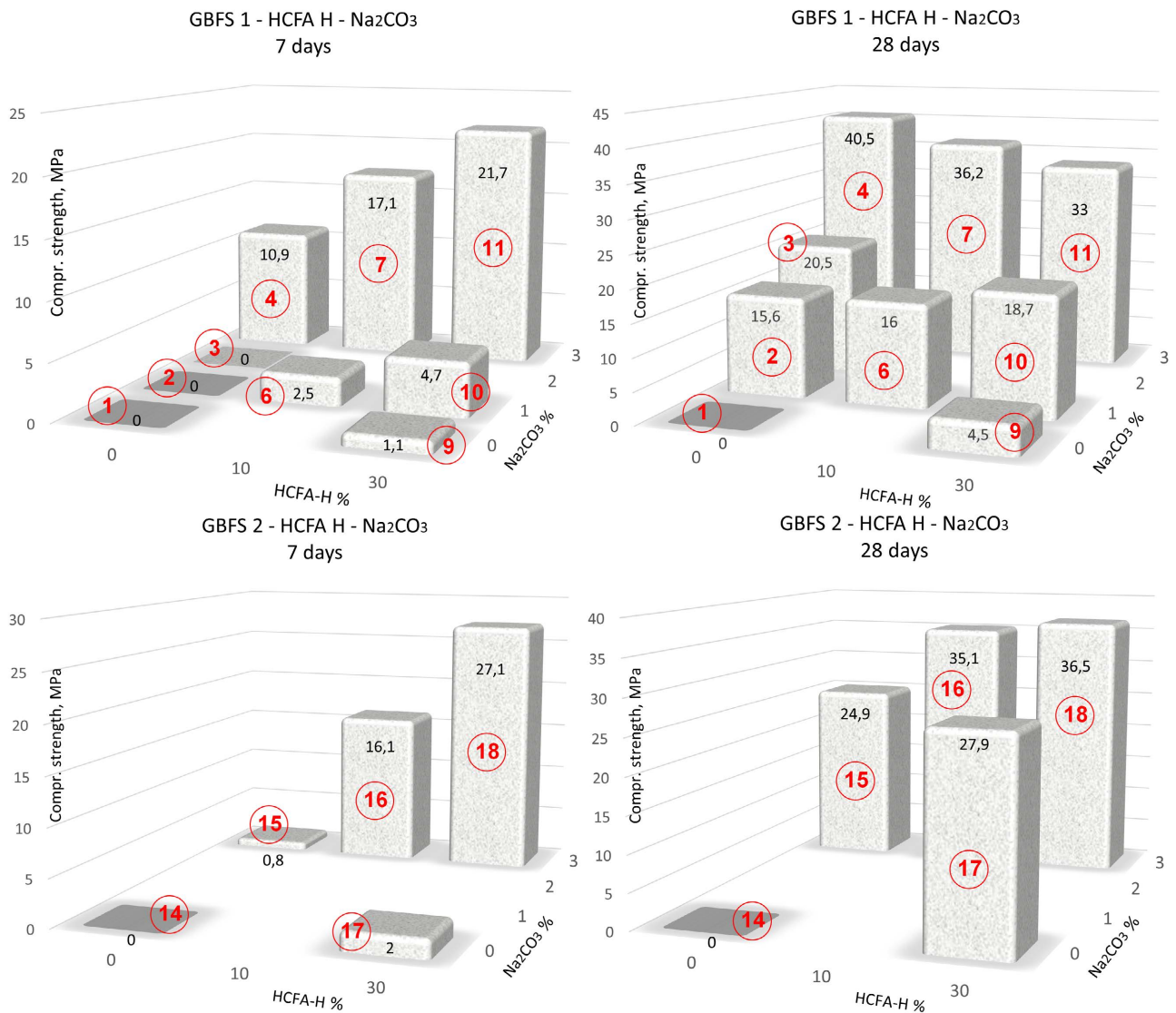
**Table 3.** Effect of sodium gluconate on setting time and workability of mortars.

Component/property	Value					
GGBFS-1, g	405	405	-	-	-	-
GGBFS-2, g	-	-	405	405	405	315
HCFA-H, g	45	45	45	45	45	135
Na <sub>2</sub> CO <sub>3</sub> , g	13.5	13.5	13.5	13.5	13.5	13.5
Sand, g	1350	1350	1350	1350	1350	1350
Water, g	140	140	140	140	140	140
Sodium gluconate, g	-	0.9	-	0.45	0.9	0.9
Slump, mm	100	100	107	-	117	115
Initial setting time, min	10	>390	15	90	>420	310
Final setting time, min/h	60 min	<21 h	390 min	165 min	<21 h	>390 min <21 h

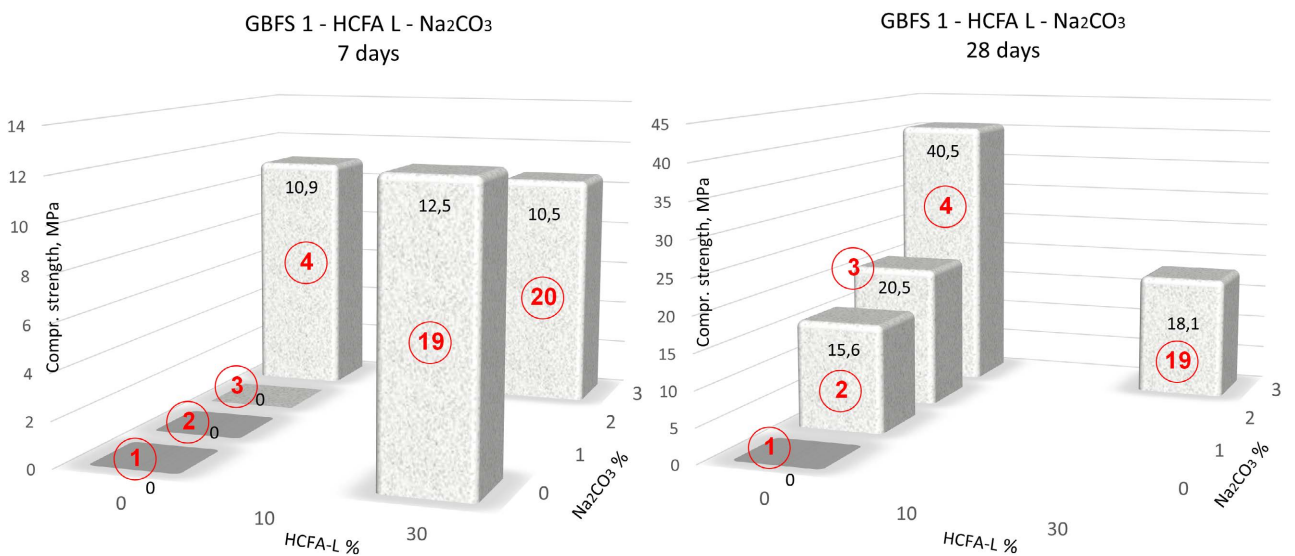
substitution of slag by fly ash in binary binder (0, 10, 30 wt%) and the content of Na<sub>2</sub>CO<sub>3</sub> (0, 1 and 3 wt% of the binder). Water-to-binder ratio was between 0.3 to 0.4 for mortars with HCFA-H, and 0.38 to 0.44 in mortars with HCFA-L due to a higher water demand of the latter one. The complete list of recipes checked in this work and mechanical properties of mortars are presented in **Table 4**. Results of compressive strength test of mortars at the age of 7 and 28 days are visualized in **Figure 6** and **Figure 7**. Workability values in **Table 3** and **Table 4** are evaluated as a diameter of slump of freshly prepared mortar spread from cone of Ø75/100, h = 50 after 15 strokes of the flow table.

“Pure” slag-sand mortars (no HCFA, nor Na<sub>2</sub>CO<sub>3</sub>) when moist cured at ambient temperature did not show any signs of gaining strength through the entire run of the experiment—*i.e.*, for at least three months.

Introduction of 3 wt% Na<sub>2</sub>CO<sub>3</sub> into slag mortars noticeably promoted early (7-day) strength. One distinguishing feature of GGBFS-1 samples was that they reach about 10 MPa at the age of 7 days, but strength of GGBFS-2 specimens of



**Figure 6.** Compressive strength of slag mortars with HCFA-H. Red indexing refer to sample numbers in **Table 4**.



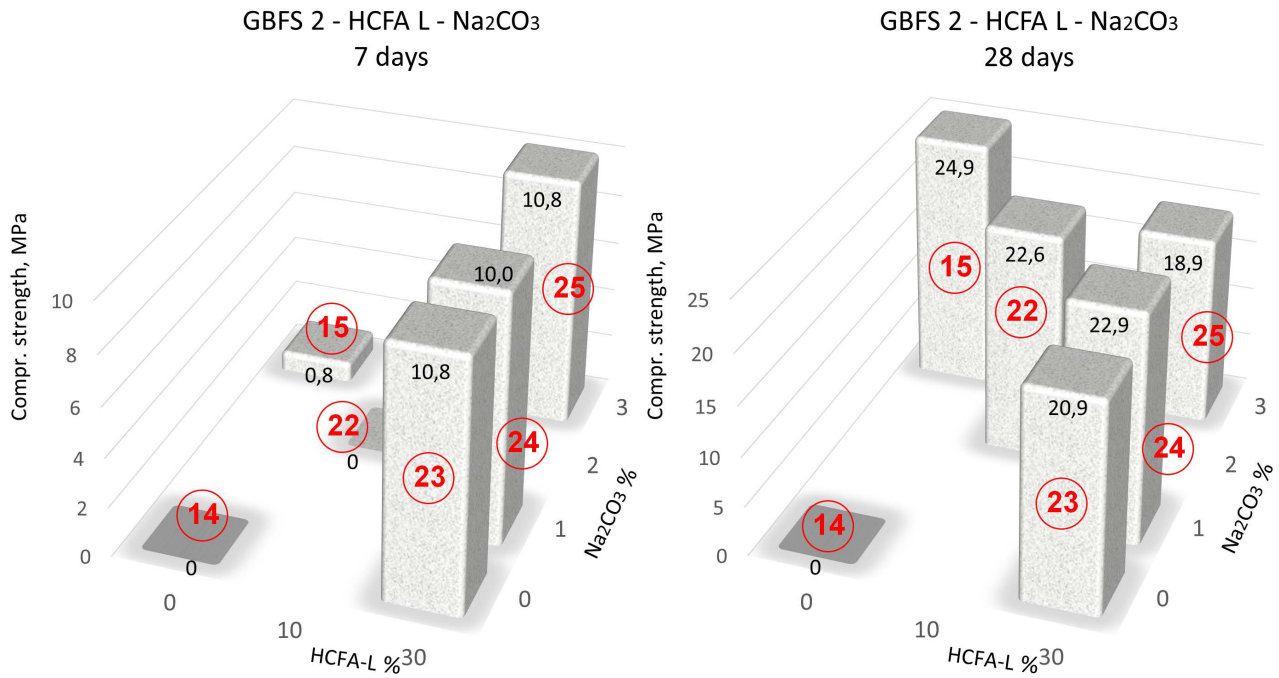


Figure 7. Compressive strength of slag mortars with HCFA-L. Red indexing refer to sample numbers in Table 4.

Table 4. Mortar formulations and mechanical properties.

Sample	Mortar components, g (+standard sand 1350 g)								Slump, mm	Demolding time, days	Compressive strength, MPa	
	GBFS-1	GBFS-2	HCFA-H	HCFA-L	Na <sub>2</sub> CO <sub>3</sub>	NaGlu	LS	Water			7 days	28 days
1	450	-	-	-	-	-	2.25	180	100	-	0	0
2	450	-	-	-	4.5	-	2.25	180	121	>12	0	15.6
3	450	-	-	-	9.0	-	2.25	180	-	12	0	20.5
4	450	-	-	-	13.5	-	2.25	180	132	5	10.9	40.5
5	450	-	-	-	13.5	-	2.25	160	107	5	11.8	-
6	405	-	45	-	4.5	0.45	-	160	148	2	2.5	16.0
7	405	-	45	-	13.5	0.45	-	160	124	1	17.1	36.2
8	405	-	45	-	13.5	0.90	-	140	100	1	21.2	39.0
9	315	-	135	-	-	0.45	-	160	151	2	1.1	4.5
10	315	-	135	-	4.5	0.45	-	160	123	1	4.7	18.7
11	315	-	135	-	13.5	0.90	-	180	206	1	21.7	33.0
12	315	-	135	-	13.5	0.90	-	140	110	1	31.6	43.9 <sup>a</sup>
13	315	-	135	-	13.5	0.90	-	160	145	1	21.7	32.8
14	-	450	-	-	-	-	2.25	180	138	-	0	0
15	-	450	-	-	13.5	-	2.25	170	117	5	0.8	24.9
16	-	405	45	-	13.5	0.90	-	140	117	3	16.1	35.1
17	-	315	135	-	-	-	-	140	122	1	2.0	27.9
18	-	315	135	-	13.5	0.90	-	140	115	2	27.1	36.5

## Continued

19	315	-	-	135	-	0.45	-	200	-	3	12.5	-
20	315	-	-	135	13.5	0.90	-	200	-	3	10.5	18.1
21	-	315	-	135	4.5	0.45	-	190	114	7	0.5	20.8
22	-	405	-	45	9.0	0.90	-	170	133	12	0.0	22.6
23	-	315	-	135	-	0.45	-	200	113	5	10.8	20.9
24	-	315	-	135	4.5	0.45	-	200	118	5	10.8	22.9
25	-	315	-	135	13.5	0.90	-	200	155	4	10.8	18.9
26	-	315	-	135	13.5	0.90	-	180	104	2	10.4	18.8

a. By 90th day samples 4, 8, 12 reached 50 - 60 MPa; samples 7, 8, 11, 13—up to 35 - 40 MPa.

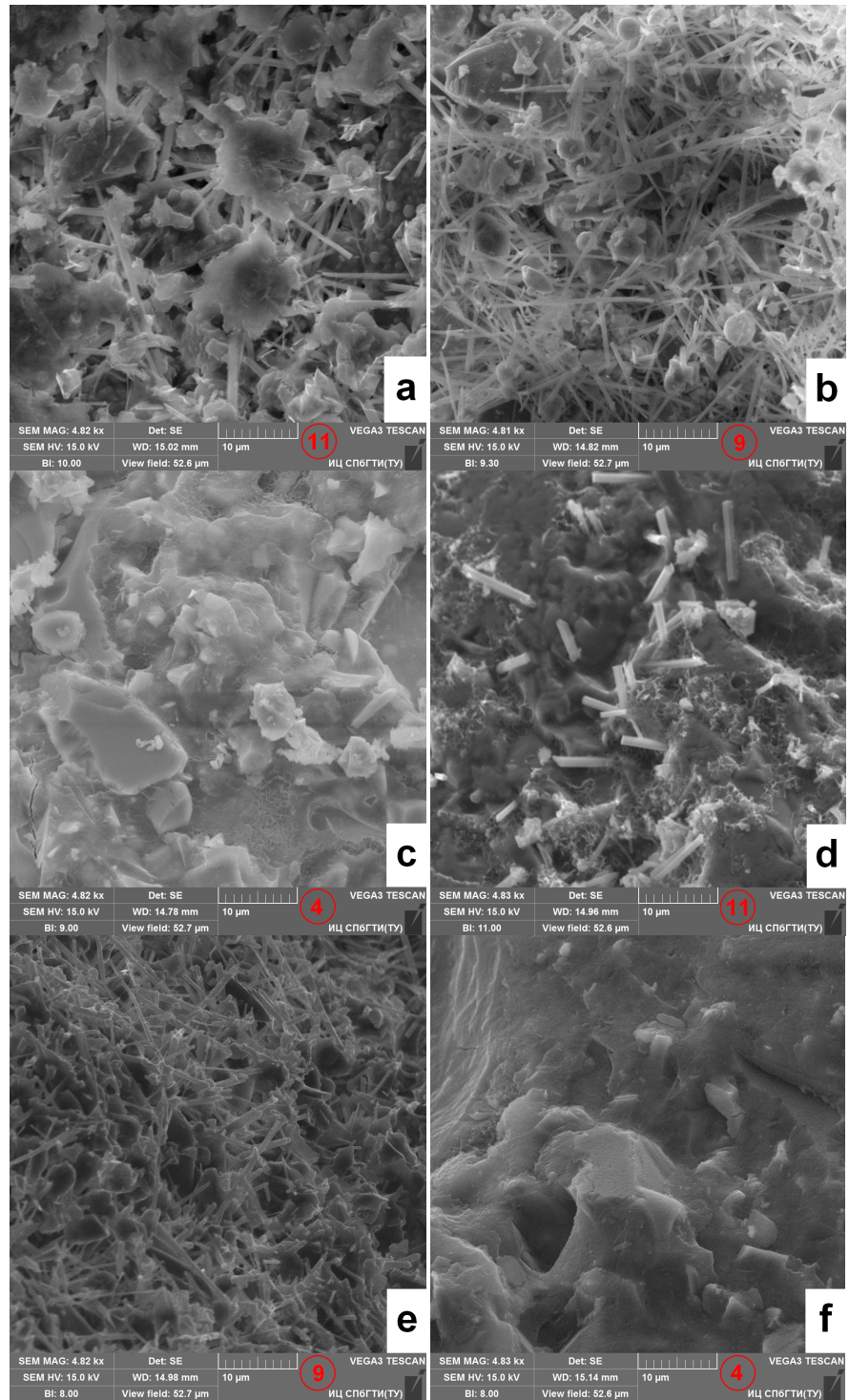
the same age don't exceed 1 MPa. In both cases, it was possible to demold samples no earlier than after 5 days of moist storage, and even at the age of 7 days the material had poor cohesion and crumbled easily, challenging the handling. These results indicate rather slow rates of slag hydration when  $\text{Na}_2\text{CO}_3$  is chosen as an activator; this observation agrees with the literature data [6].

Poor mechanical characteristics of mortars with no  $\text{Na}_2\text{CO}_3$  and 30% slag substituted by HCFA-H indicates that this high-temperature fly ash exhibit very weak hydraulic properties and does not have a stimulating effect on GGBFS. It is, however, the synergetic effect of sodium carbonate and HCFA-L that results in good strength development, this composition significantly outperform samples in which either HCFA-H or  $\text{Na}_2\text{CO}_3$  introduced individually. At the age of 7 days compressive strength of such samples reaches to 20 - 30 MPa and beyond with water-to-binder ratio decrease, besides, the unmolding time shortened to 1 - 2 days. The combined accelerating effect of  $\text{Na}_2\text{CO}_3$  and HCFA-H on slag mortars increase with an increase in their content in mortar, at least within the limits of formulations tested in the present work. The highest strength characteristics were obtained when the sodium carbonate dosage reaches up to 3% of GGBFS-HCFA-H binder.

**Figure 8** shows SEM images of freshly cleaved surface of mortar samples with GGBFS-1 at the age of 7 and 28 days. As **Figure 8(a)** indicates, a combined action of  $\text{Na}_2\text{CO}_3$  and HCFA-H results in geopolymer structure that resembles an agglomeration of hydration products of both crystalline and amorphous parts of HCFA and GGBFS—an ettringite and amorphous C-S-H gel. Hydration of the glass phase of slag and fly ash is promoted by alkaline environment created by reaction between  $\text{Na}_2\text{CO}_3$  and HCFA. In the absence of  $\text{Na}_2\text{CO}_3$  (**Figure 8(b)**), the C-S-H gel can be hardly found, and clusters of ettringite crystals do not have intergrown nodes.

In the absence of HCFA (**Figure 8(c)**), on the contrary, ettringite is missing, so that slag and aggregate particles are cemented only by an amorphous product. In a weakly alkaline medium this process develops rather slowly, because of this the stone remains loose for a long time due to the lack of strong contact between





**Figure 8.** SEM images (SE) of GBFS-1—HCFA-H mortar samples at 7 days (a, b, c) and 28 days (d, e, f). Red indexing refer to sample numbers in **Table 4**.

individual grains. What should be noted here, is that with 3 wt% of  $\text{Na}_2\text{CO}_3$  “pure” GGBFS-1 mortars at 28 days in some cases show even higher strength than HCFA-substituted (samples 4, 5 and 11 - 13, **Table 4**). One way to explain it would be that given enough time a denser product is formed (**Figure 8(f)**),



contrary to accelerated development of structure when slag is activated by the high-calcium fly ash (**Figure 8(d)**).

In contrast to HCFA-H, the low-temperature ash contributes to development of early (7 days) strength of mortars when its content in the binder is of 30 wt% (**Figure 7**). Firstly, this is due to the well-developed surface of the HCFA-L particles—they are less vitrified (smoothed out) in comparison with particles of high-temperature ash, higher surface area helps for faster conversion of  $C_3A$  and  $CaSO_4$  into ettringite and other products. The free CaO of HCFA-L is highly reactive and quickly interacts with water, raising pH to levels necessary to initiate a desired rate of hydration of glass phase of slag and fly ash itself. This could explain why slag mortars with low temperature fly ash don't benefit from admixing of another activator agent, and the strength of mortars of somewhat different formulations come out on pretty much the same level. We should note here that the main contribution to the strength of the mortar comes specifically from the reaction of the slag glass, since when the slag in our experiment was replaced by inert finely-ground quartz ( $d < 40 \mu m$ ), compressive strength of such samples with HCFA-L at the age of 7 days decrease by a factor of 4.

On the other hand, high specific surface area and high reactivity of CaO make for an increased water demand of HCFA-L, which in turn limits the achievable strength of the stone. Another limiting factor for low temperature ash may be the high content of hydraulically inert constituents, namely  $CaCO_3$  in this specific type of fly ash. For these reasons, the maximum strength of specimens with HCFA-L remain below strength levels of slag mortars with high-temperature ash and  $Na_2CO_3$ .

#### 4. Conclusions

1) The ability of HCFAs to activate hydration of GGBFS depends on specific conditions of the process they originate from. High-calcium fly ash formed during fuels combustion in circulating fluidized bed at temperatures below  $900^\circ C$  contains free CaO, which quickly quenches in water to produce  $Ca(OH)_2$  and ettringite. It creates an alkaline environment to activate hydration of the glass in slag and fly ash. This kind of ash exhibits binding properties itself and stimulates hydration of the slag. Also, it does not seem to cause expansion in matured geopolymer structure. Sodium carbonate as an additional activator does not contribute to its effectiveness in slag-ash mortars.

2) Hydration of HCFA originating from high-temperature flame combustion of solid fuels in traditional furnaces is activated by introduction of sodium carbonate into the slag-ash binder, and the higher the dosage of  $NaCO_3$ , the greater the effect observed. In this case required level of alkalinity emerges from the exchange reaction between sodium carbonate and fly ash, it promotes the hydration of crystalline and amorphous parts of fly ash and slag.

3) The maximum tolerable content of high-temperature fly ash in binary slag-ash binders should be determined by results of the soundness test to avoid

development of volumetric deformations of the geopolymer. For slags and high temperature ash particularly mentioned in this article the content of up to 15 wt% of HCFA in the binder was considered as “safe”.

4) Substitution of 10% - 30% of GGBFS by high temperature HCFA together with introduction of 1% - 3%  $\text{Na}_2\text{CO}_3$  by weight of the binary binder, at water-to-binder ratio of 0.30 - 0.45 made compressive strength of slag mortars reach about 10 - 30 to 30 - 45 MPa at the age of 7 and 28 days when moist cured at ambient temperature. Therefore, this combination of high-temperature high-calcium fly ash and sodium carbonate presents an effective dry activator of blast furnace slag-based binders.

5) With such combination of  $\text{Na}_2\text{CO}_3$  and HCFA-H to achieve high early strength of GGBFS binder it is sufficient for the slag to only have specific surface area of about 3000 - 3500  $\text{cm}^2/\text{g}$ , which means typical requirement of fine comminution of slag is not mandatory in this case.

## Conflicts of Interest

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

## References

- [1] Van Deventer, J.S.J. (2017) Progress in the Adoption of Geopolymer Cement. In: Nazari, A. and Sanjayan, J.G., Ed., *Handbook of Low Carbon Concrete*, Elsevier, 217-262. <https://doi.org/10.1016/B978-0-12-804524-4.00010-5>
- [2] Provis, J.L. and van Deventer, J.S.L. (2014) Alkali-Activated Materials. State of the Art Report, RILEM TC 224-AAM, Springer. <https://doi.org/10.1007/978-94-007-7672-2>
- [3] Zhang, P., Wang, K., Li, Q., Wang, J. and Ling Y. (2020) Fabrication and Engineering Properties of Concretes Based on Geopolymers/Alkali-Activated Binders—A Review. *Journal of Cleaner Production*, **258**, 120896. <https://doi.org/10.1016/j.jclepro.2020.120896>
- [4] Mendes, B., Pedroti, L., Vieira, C., *et al.* (2020) Application of Eco-Friendly Alternative Activators in Alkali-Activated Materials: A Review. *Journal of Building Engineering*, **35**, 102010. <https://doi.org/10.1016/j.jobbe.2020.102010>
- [5] Shi, C., Qu, B. and Provis, J. (2019) Recent Progress in Low-Carbon Binders. *Cement and Concrete Research*, **122**, 227-250. <https://doi.org/10.1016/j.cemconres.2019.05.009>
- [6] Yuan, B. (2017) Sodium Carbonate Activated Slag: Reaction Analysis, Microstructural Modification & Engineering Application. Ph.D. Thesis, Technische Universiteit Eindhoven, Eindhoven.
- [7] Brandstetr, J., Havlica, J. and Odler, I. (1997) Properties and Use of Solid Residue from Fluidized Bed Coal Combustion. In: Chandra, S., Ed., *Waste Materials Used in Concrete Manufacturing*, Norwich, Noyes Publications, 1-52. <https://doi.org/10.1016/B978-081551393-3.50004-1>
- [8] Sahin, M., Mahyar, M. and Erdogan, S.T. (2016) Mutual Activation of Blast Furnace Slag and a High-Calcium Fly Ash Rich in Free Lime and Sulfates. *Construction and Building Materials*, **126**, 466-475. <https://doi.org/10.1016/j.conbuildmat.2016.09.064>