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## Comparison of two alkali-activated systems: mechanically activated fly ash and fly ash-blast furnace slag blends

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### Abstract

Poor reactivity of fly ash (FA) in alkali activation process can be improved either by mechanical activation of fly ash or by blending fly ash with more reactive material, such as blast furnace slag (BFS). Both options were explored in this paper and comparison was performed. Mechanical activation of fly ash was conducted in a planetary ball mill, while blends of fly ash and blast furnace slag were prepared with different ratios (FA/(FA+BFS) = 1; 0.75; 0.50; 0.25; 0). Alkali activation was carried out at 95 °C by use of sodium silicate solution as an activator. In both cases significant increase of geopolymer strength was observed in respect to the geopolymer based on the initial fly ash. Optimal geopolymer strength was correlated with the chemical composition of the binding gel. Empirical values of optimal gel composition could serve as a basis for tailoring properties of alkali-activated binders based on different precursors. Both alkali-activated systems represent promising routes for geopolymer technology development.

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*Keywords:* fly ash; blast furnace slag; alkali activation; geopolymers; compressive strength; microstructure

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### 1. Introduction

Fly ash is generated as an industrial waste material in the process of coal combustion in thermal power plants (TPP). There is an ongoing demand worldwide for the use of large quantities of FA as an aluminosilicate raw material. Over the last few decades, a new group of binding materials, geopolymers, has emerged as a result of

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alkaline activation of aluminosilicate materials such as FA. Geopolymers represent quite attractive binding material, known for high compressive strength, good durability in aggressive environments, low shrinkage and good thermal resistivity [1]. However, the limiting factor for wider use of FA in the synthesis of geopolymers is its low reactivity and consequent low strength gain when cured at room temperature [2]. The reactivity of initial FA (IFA) in the reaction of alkali activation can be improved by the appropriate choice of the reaction conditions [1], by mechanical activation of FA [3] and by blending with BFS [4]. The main advantage of using mechanically activated FA (MAFA) in the synthesis of geopolymers is the possibility of in-bulk utilization of FA. On the other hand, blending FA with BFS, a byproduct of pig iron production in steel plants, is also quite attractive possibility since it implies utilization of different industrial wastes.

In this work the reactivity of FA was addressed by mechanical activation and by blending with BFS. The effects of both options on the compressive strength and microstructure of the resulting alkali-activated binders were investigated.

## 2. Experimental

### 2.1. Materials

In the experimental work, the following materials were used:

1. FA TENT A, TPP “Nikola Tesla”, Unit A, Obrenovac, Serbia
2. FA TENT B, TPP “Nikola Tesla”, Unit B, Obrenovac, Serbia
3. FA Kostolac, TPP Kostolac B<sub>1</sub>, Kostolac
4. FA Svilajnac, TPP “Morava” – Svilajnac, Serbia
5. BFS from “Železara Smederevo” d.o.o. – Smederevo, Serbia
6. Sodium silicate solution was used as alkaline activator. Modulus (n) of sodium silicate solution ( $\text{SiO}_2/\text{Na}_2\text{O}$  ratio) was adjusted by adding NaOH (VWR, Germany, p.a. 99%).

### 2.2. Experiment design

#### 2.2.1. Mechanical activation of FA

Mechanical activation of FA (TENT A, TENT B and Kostolac) was carried out in planetary ball mill (Fritch Pulverisette type 05 102, Germany). The diameter size of stainless steel balls was 13 mm. FA to ball mass ratio was 1:20. FA samples were mechanically activated in an air atmosphere for 15 minutes, at maximum speed of 380 rev/min.

#### 2.2.2. FA-BFS blends

Blends with different FA-BFS mass ratios were prepared from FA Svilajnac and BFS as follows: FA/(FA+BFS) = 1; 0.75; 0.50; 0.25; 0. Appropriate blend denotations are FA/(FA+BFS) 1; FA/(FA+BFS) 0.75; FA/(FA+BFS) 0.50; FA/(FA+BFS) 0.25; FA/(FA+BFS) 0, respectively.

### 2.3. Synthesis of alkali-activated binders

The samples of IFA/MAFA and FA-BFS blends were alkali-activated by use of sodium silicate solution whereby the concentration of the activator was 10%  $\text{Na}_2\text{O}$  with respect to the mass of IFA/MAFA or FA-BFS blends, according to data presented in the Table 1. Given values of activator modulus and concentration were selected as optimum, based on the results given elsewhere [5-7].

Table 1. Mortar preparation conditions (recipe).

Sample	Sample mass (g)	Standard sand mass (g)	Alkali activation conditions		
			Sodium silicate modulus (SiO <sub>2</sub> /Na <sub>2</sub> O)	Sodium silicate concentration (% Na <sub>2</sub> O)	Water/binder ratio
IFA	TENT A	450	1350	1.5	0.85
	TENT B				0.80
	Kostolac				0.69
MAFA	TENT A	450	1350	1.0	0.37
	TENT B				
	Kostolac				
FA/(FA+BFS) 1	450	1350	1.5	10	0.46
FA/(FA+BFS) 0.75					0.43
FA/(FA+BFS) 0.50					0.39
FA/(FA+BFS) 0.25					0.37
FA/(FA+BFS) 0					0.37

Mortars were prepared by adding the activator solution to water and then mixing the solution with the IFA/MAFA or FA-BFS blend and standard sand (one part of IFA/MAFA or FA-BFS and three parts of standard sand, Table 1). Water was added in the amount to obtain equal consistency (determined by flow table test – the mortar flow measured on a flow table was  $125 \pm 5$  mm). The water/binder ratio was calculated so that the water stands for the the total amount of water in the system (the water from the activator solution + the water added for the proper consistency) and binder represents the sum of the IFA/MAFA or FA-BFS blend mass and the solid part of the activator solution. For the compressive strength measurements mortars were cast into three mortar prisms (40 mm × 40 mm × 160 mm). The molds with mortar prisms were sealed into plastic bags in order to prevent the moisture loss during curing. The curing of alkali-activated mortars was conducted at the temperature of 95 °C. Mortars based on alkali-activated IFA/MAFA were cured for 4 h, while mortars of alkali-activated FA-BFS blends were cured for 24 h. After the specified time of curing was over, the molds were taken out of the bags and cooled down to the room temperature. Then the prisms were de-molded and subjected to strength measurements.

Pastes were prepared by mixing the IFA/MAFA or FA-BFS blends with the alkali activator solution (in the same proportion as in the preparation of mortars) and water. After curing, the specimens were cooled down to the room temperature. Alkali activation reaction was stopped by soaking and grinding the specimens in isopropyl alcohol, and then the specimens were dried at 50 °C.

#### 2.4. Methods

Compressive strength of the mortar samples was tested according to SRPS EN 196-1 (2008) standard which is in compliance with European EN 196-1 standard, using Controls model 65-L1300/P (Italy) device.

Microstructural characterization of the paste samples was conducted by scanning electron microscopy (SEM) method using VEGA TS 5130MM Tescan electron microscope. Energy dispersive X-ray spectroscopy (EDS) was done by INCAPentaFET-x3 (Oxford Instruments). Prior to EDS analysis the samples were polished and Au coated. SEM imaging and EDS analysis of all investigated samples were performed at accelerating voltage of 20 kV with no less than 20 acquisitions per sample.

### 3. Results

#### 3.1. FA particle size analysis

The results of FA particle size analysis are given in the Table 2.

Table 2. Characteristic particle diameters of FA samples (adapted from [6]).

Sample		Characteristic particle diameters ( $\mu\text{m}$ )		
		$d_{10}$	$d_{50}$	$d_{90}$
IFA	TENT A	4.16	33.40	140.60
	TENT B	13.26	79.95	252.30
	Kostolac	10.96	62.04	299.10
MAFA	TENT A	0.52	3.15	31.39
	TENT B	0.48	2.30	33.11
	Kostolac	0.58	3.08	102.29

As can be observed from the Table 2, mechanical activation of FA resulted in remarkable decrease in FA particle size. All MAFA samples showed a decrease in median particle size  $d_{50}$  for more than ten times compared to IFA samples. Despite the notable differences in IFA particle size distributions, after mechanical activation there were relatively small differences between FA samples regarding  $d_{10}$  and  $d_{50}$  values.

### 3.1. Compressive strength

Compressive strength of mortars of alkali-activated IFA/MAFA and FA-BFS samples is given in Fig. 1.

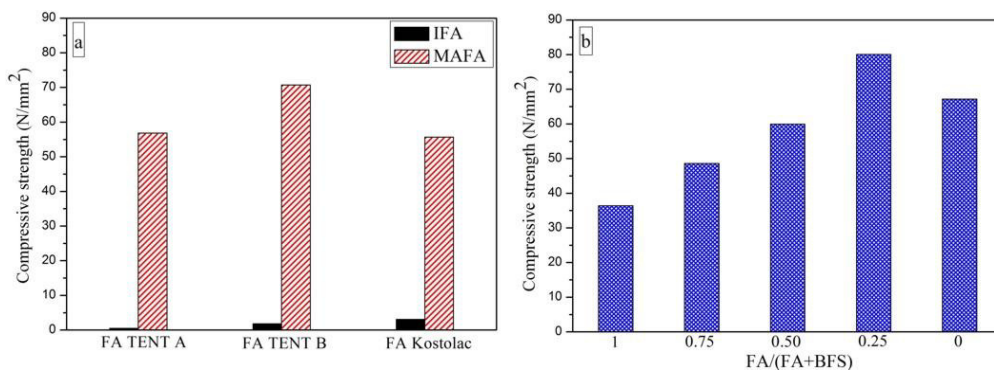


Fig. 1. Compressive strength of mortar samples: a) IFA/MAFA (adapted from [6]); b) FA-BFS blends (adapted from [7]).

The compressive strength of investigated mortars tended to increase both with the mechanical activation of FA and the increase of BFS content in the blend (Fig. 1). It is obvious that mechanical activation of FA resulted in drastic improvement of compressive strength. Compressive strength of mortars based on alkali-activated IFA, synthesized under given conditions, was extremely low in all investigated cases (Fig. 1a). In sharp contrast to that, the compressive strength of mortars based on alkali-activated MAFA exceeded the values of  $50 \text{ N/mm}^2$ , therefore it is clear that mechanical activation affected the drastic enhancement of FA reactivity in alkali activation reaction. The highest compressive strength was achieved by alkali-activated MAFA TENT B ( $70.72 \text{ N/mm}^2$ ).

In the case of alkali-activated FA-BFS blends, it is observable that the increase of BFS content in the blend was followed with the increase in compressive strength (Fig. 1b) under given experimental conditions. Compressive strength of FA/(FA+BFS) 0 mortar was higher than majority of investigated samples except for FA/(FA+BFS) 0.25 mortar. The compressive strength of this mortar was  $80.09 \text{ N/mm}^2$ , thus exceeding the strength of the FA/(FA+BFS) 0 mortar.

### 3.2. Microstructure (SEM/EDS)

Microstructure of alkali-activated binders based on IFA and MAFA TENT B is given in Fig. 2. Microstructure

of alkali-activated binders based on FA/(FA+BFS) 1 and FA/(FA+BFS) 0.25 is given in Fig. 3.

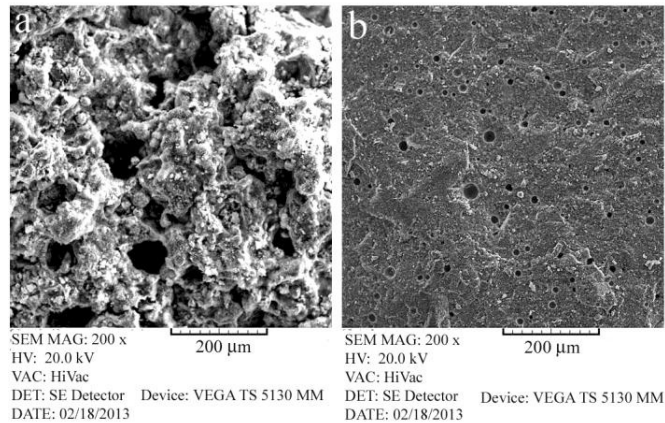


Fig. 2. Microstructure of alkali-activated binder based on FA TENT B: a) initial (IFA); b) mechanically activated (MAFA).

Morphological differences between the structure of alkali-activated binders based on IFA/MAFA TENT B are markedly visible (Fig. 2). Morphologically, alkali-activated IFA TENT B appears highly heterogeneous, with large cavities that dominate in the structure (Fig. 2a). On the contrary, alkali-activated binder derived from MAFA TENT B showed very dense and compact microstructure (Fig. 2b).

SEM images of alkali-activated FA/(FA+BFS) 1 and FA/(FA+BFS) 0.25, given in Fig. 3, revealed unreacted or partially reacted particles of different dimensions and shapes incorporated within the matrix of the reaction products. FA particles are predominantly spherical (Fig. 3a), while BFS particles have noticeably irregular shape (Fig. 3b). In the case of alkali-activated FA/(FA+BFS) 0.25 very compact and dense matrix structure was observable, unlike the structure of alkali-activated FA/(FA+BFS) 1 which appeared more heterogeneous and more porous.

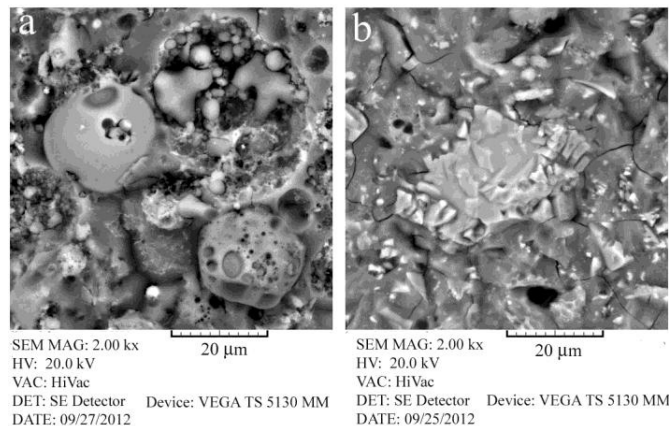


Fig. 3. Microstructure of alkali-activated binders: a) FA/(FA+BFS) 1; b) FA/(FA+BFS) 0.25.

The average content of main elements (atomic %) and their ratios in the matrix of alkali-activated binders based on IFA/MAFA and FA-BFS blends are given in the Table 3 and Table 4, respectively. Given that all samples were examined under the same experimental conditions (accelerating voltage and appreciable number of individual acquisitions per sample), the results given represent general trend in chemical composition of the reaction

products. It is possible that, at given accelerating voltage (20 kV), the migration of sodium atoms occurred in some extent, resulting in somewhat lower Na/Al ratio. However, it is highly unlikely that it significantly influenced the observed trends in chemical composition of the reaction products.

The results of EDS analysis showed that the reaction products of alkali activation of IFA/MAFA consist mainly of Si, Al and Na, which corresponds to sodium aluminosilicate gel or N-A-S-H gel ( $\text{N-Na}_2\text{O}$ ;  $\text{A-Al}_2\text{O}_3$ ;  $\text{S-SiO}_2$ ;  $\text{H-H}_2\text{O}$ ). In the gel composition of alkali-activated binders based on MAFA an increase of Al content and higher Al/Si ratio can be observed compared to alkali-activated binders based on IFA (Table 3). In the same time, there is a decrease in Na/Al ratio in the gel composition of alkali-activated binders based on MFA (compared to alkali-activated binders based on IFA). Higher Al content and Al/Si ratio indicate higher proportion of incorporated Al in the N-A-S-H gel of alkali-activated binders based on MAFA. Greater extent of Al incorporation can be related to the greater availability of this component during the alkali activation reaction. Greater availability of Al during the alkali activation reaction contributes to the formation of a more homogeneous and more cross-linked N-A-S-H gel, causing better strength development, as reported earlier [8].

Table 3. The average content of main elements (atomic %) and their ratios in the matrix of alkali-activated binders based on IFA/MAFA.

Sample		Si	Al	Na	Ca	Al/Si	Na/Si	Na/Al	Ca/Si
IFA	TENT A	14.71	5.25	4.90	2.95	0.33	0.36	1.11	0.24
	TENT B	17.61	5.53	5.89	1.90	0.31	0.33	1.10	0.10
	Kostolac	18.61	5.38	6.54	2.19	0.29	0.36	1.33	0.12
MAFA	TENT A	15.73	6.64	4.56	1.71	0.40	0.32	0.79	0.11
	TENT B	17.63	6.99	4.57	1.11	0.40	0.26	0.67	0.06
	Kostolac	18.48	7.21	4.23	0.35	0.39	0.23	0.63	0.02

From the results of EDS analysis presented in this investigation, it can be assumed that by mechanical activation a higher proportion of more evenly distributed Al from fly ash was enabled to dissolve and participate in N-A-S-H gel formation, most probably due to the breakage of large aluminosilicate spherical FA particles and release of the smaller ones usually contained inside. As a result, a N-A-S-H gel with more homogeneous and compact microstructure is formed during the alkali activation reaction.

Table 4. The average content of main elements (atomic %) and their ratios in the matrix of alkali-activated binders based on FA-BFS blends.

Sample	Si	Al	Na	Ca	Al/Si	Na/Si	Na/Al	Ca/Si
FA/(FA+BFS) 1	18.14	6.31	5.54	2.20	0.35	0.31	0.95	0.12
FA/(FA+BFS) 0.75	16.31	6.58	4.67	2.07	0.40	0.31	0.95	0.13
FA/(FA+BFS) 0.50	14.87	3.72	5.56	4.73	0.25	0.37	1.55	0.32
FA/(FA+BFS) 0.25	14.57	2.95	4.31	5.80	0.20	0.29	1.49	0.40
FA/(FA+BFS) 0	12.12	1.59	6.27	8.09	0.13	0.52	4.04	0.67

In the case of alkali-activated binders based on FA-BFS blends, the situation is somewhat different. The average content of the main elements varied as a function of the blend composition (Table 4). The main difference between the binders based on IFA/MAFA and the binders based on FA-BFS blends is the amount of Ca in the reaction products. With the increase of BFS content in the blend, the amount of Ca noticeably increased, while the amount of Si and Al decreased. The atomic ratios of main elements also varied depending on the blend composition (Table 4). The differences in the content and ratios of the main elements as a function of the blend composition indicate the formation of reaction products with different composition and structure. In alkali-activated FA/(FA+BFS) 1 the formation of N-A-S-H gel took place, while the main reaction product of alkali-activated FA/(FA+BFS) 0 is calcium silicate hydrate with incorporated Al in the structure or C-A-S-H gel ( $\text{C-CaO}$ ;  $\text{A-Al}_2\text{O}_3$ ;  $\text{S-SiO}_2$ ;  $\text{H-H}_2\text{O}$ ). The reaction products of alkali-activated FA-BFS blends between two end members (FA/(FA+BFS) 1 and FA/(FA+BFS) 0) most probably consisted of coexisting N-A-S-H and C-A-S-H gels and/or a hybrid C-N-A-S-H gel as reported previously [9]. Remarkably high mortar compressive strength of FA/(FA+BFS) 0.25 sample most probably was the consequence of better compactness of the material, due to highly cross-linked structure of the reaction products caused by the presence of Al additionally supplied by FA [9].

### 3.3. Correlation of compressive strength and the gel composition

The correlation of mortar compressive strength of alkali-activated IFA/MAFA and the average values of Al/Si and Na/Al ratios in the N-A-S-H gel of corresponding paste samples (Table 3) is given in Fig. 4.

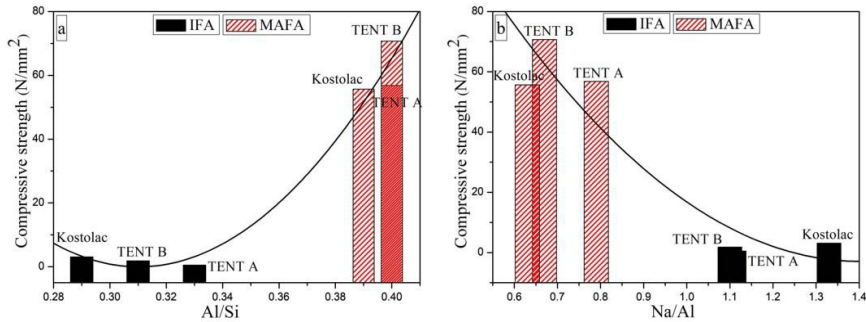


Fig. 4. Correlation of mortar compressive strength of alkali-activated IFA/MAFA and: a) Al/Si atomic ratio; b) Na/Al atomic ratio.

Compressive strength tends to increase with the increase of Al/Si ratio. (Fig. 4a). Mechanical activation of FA enabled more Al to be available in the alkali activation reaction. Under given experimental conditions, Al was quickly dissolved and more evenly distributed within the material. In the same time, there was enough Si (provided by the activator) available to take part in the reaction, so reactive Al and Si species condensed resulting in the formation of compact N-A-S-H gel with excellent mechanical properties. On the other hand, the increase of Na/Al over 1 negatively affected the compressive strength (Fig. 4b), presumably due to excess of Na which weakened the structure of N-A-S-H gel. It is known that optimal Na/Al ratio of alkali-activated binders based on FA should not exceed 1 in order to maintain good mechanical properties [10]. In the reaction of alkali activation of FA Na is mainly supplied by the activator solution. Optimal Na/Al ratio of 1 appropriates the amount of Na<sup>+</sup> cations needed for the compensation of Al<sup>3+</sup> in tetrahedral coordination. However, according to Provis et al [11] amorphous structures can be highly disordered which allows the deviations in tetrahedral geometry and ways of charge compensations other than strict association of each Al<sup>3+</sup> with single Na<sup>+</sup>. Given that, in this investigation, the concentration of Na supplied by the activator solution in the alkali activation reaction was the same for all samples (10%), it is possible that mechanical activation of FA resulted with the formation of N-A-S-H gel with highly disordered structure which allowed less Na<sup>+</sup> to be sufficient for charge compensation in MAFA samples. Optimal compressive strength shown by alkali-activated MAFA TENT B can be related to N-A-S-H gel with Al/Si ratio around 0.40 and Na/Al around 0.70.

The correlation of mortar compressive strength of alkali-activated FA-BFS blends and the average values of Ca/Si and Al/Si ratios in the reaction products of corresponding paste samples (Table 4) is given in Fig. 5.

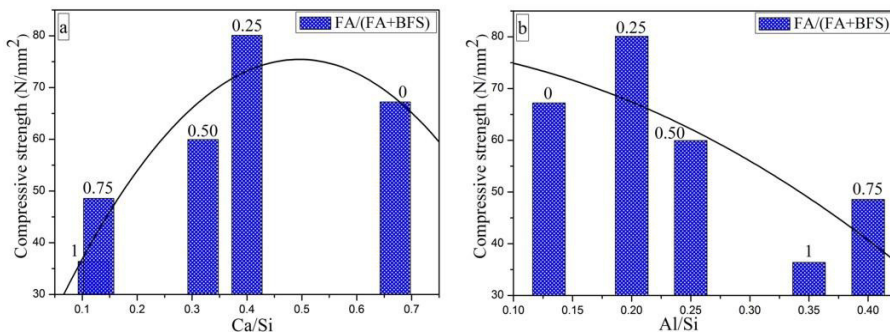


Fig. 5. Correlation of mortar compressive strength of alkali-activated FA-BFS blends and: a) Ca/Si atomic ratio; b) Al/Si atomic ratio (adapted from [7]).

The increase of Ca/Si ratio, i.e. the presence of larger amounts of C-A-S-H gel in the reaction products positively affected compressive strength (Fig. 5a), which is consistent with the increase of BFS content in the blend. With the increase of Al/Si ratio the compressive strength tended to decrease. Therefore, different types of the reaction products differently affected compressive strength. Optimal compressive strength for given alkali activation conditions, shown by alkali-activated FA/(FA+BFS) 0.25 blend, can be related to the binding gel of following composition: Ca/Si around 0.40 and Al/Si around 0.20.

#### 4. Conclusions

The reactivity of FA in the reaction of alkali activation was improved by mechanical activation of FA and by blending FA with BFS. The effects of both options on the compressive strength and microstructure of the resulting alkali-activated binders were investigated. The results obtained showed that both investigated options resulted in considerable increase of mortar compressive strength in respect to the mortar based on sole alkali-activated FA. Mechanical activation of FA resulted in a formation of more homogeneous and compact N-A-S-H gel with higher Al/Si ratio and lower Na/Al ratio compared to alkali-activated initial FA. Optimal compressive strength can be related to N-A-S-H gel with Al/Si ratio  $\sim 0.40$  and Na/Al  $\sim 0.70$ . In the case of alkali-activation of FA-BFS blends different reaction products were formed. The main reaction product of alkali-activated FA/(FA+BFS) 1 was N-A-S-H gel, while the main reaction product of alkali-activated FA/(FA+BFS) 0 was C-A-S-H gel. The reaction products of alkali-activated FA-BFS blends with the composition between two end members most probably consisted of coexisting N-A-S-H and C-A-S-H gels and/or a hybrid C-N-A-S-H gel. Optimal compressive strength most probably was the consequence of better compactness of the material, due to highly cross-linked structure of the reaction products and can be related to the binding gel of following composition: Ca/Si  $\sim 0.40$  and Al/Si  $\sim 0.20$ .

#### Acknowledgements

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