POTENTIAL MODIFICATION OF HYDRATION OF ALKALI ACTIVATED MIXTURES FROM GRANULATED BLAST FURNACE SLAG AND FLY ASH

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Alkali activated binders (AAB) and composites from suitable latent hydraulic raw materials represent an alternative to materials based on Portland cements. The paper deals with possibilities to influence functional parameters of AAB by setting the mixtures of GBFS and fly ash to the selected chemical composition or by fly ash reactivity change effected by milling. In this way course of hydration process is modified, the alkali activation products phase composition is changed as well as their final characteristic. The amorphous character of the hydration products limits the evaluation of the composition during the massing phase. Part of the study is the search for possibilities of identifying the differences in composition and properties of specially drafted mixtures of original raw materials after their alkali activation.

INTRODUCTION

Research on the chemical processes of suitable alkali activated latent hydraulic materials and the subsequent evaluation of properties of such systems is a topical subject of the research into materials. The targets and objectives in this area can be summarized as follows:

- To utilize of binder substitutions or alternatives to the Portland cements and subsequent proposal of binders which fulfill (or even exceed) the properties of Portland cements. Such alternatives reduce the production of cement clinker, CO_2 emissions originating from lime decomposition and burning processes during clinker production. Consumption of natural materials are decreased leading to the conservation of the environment.
- To prepare of cement free binders predominantly on a by-products basis. Using alkali activation, preparation of binders and composites with comparable or better properties than those of ordinarily used building materials and by-products.
- To ensure better value of by-products and solve questions of their production and disposal.

Raw materials utilized in the production of alkali activation binders (AAB) are classified as pozzolans or latent hydraulic binders. Their processing has been known since ancient times [1]. Substances which are designated to be latent hydraulic (LHL) cannot undergo direct setting and hardening during their reaction with water. Their hydraulicity needs to be activated in a suitable way, for example using $Ca(OH)_2$ or a solution of soluble alkaline compounds [2]. A range of LHL (pozzolans) can be found to be naturally occurring in nature, however some artificial pozzolans are also known. Several classification systems for pozzolans have been designed and the common classification which is often published can be seen here. [1] (Figure 1).

Artificial pozzolans are divided into two categories according to their origin – 'industrial by-products' and 'burnt materials'. Blast furnace slag, fly ash, silica fume, copper slag and nickel slag are typical industrial by-products of the iron industry, power generating plants as well as copper and nickel production respectively. 'Burnt materials' refer to those that have pozzolanic reactivity only after calcination: burnt clay, burnt shale, burnt rice husks and burnt bauxite are examples [1].

All pozzolans are raw materials with significant amounts of SiO_2 and Al_2O_3 and higher proportions of CaO are also found. One condition for their utilization as a binder is the presence of basic oxides SiO_2 and Al_2O_3 in an amorphous and preferably vitreous, therefore reactive form [2], [3], [4].

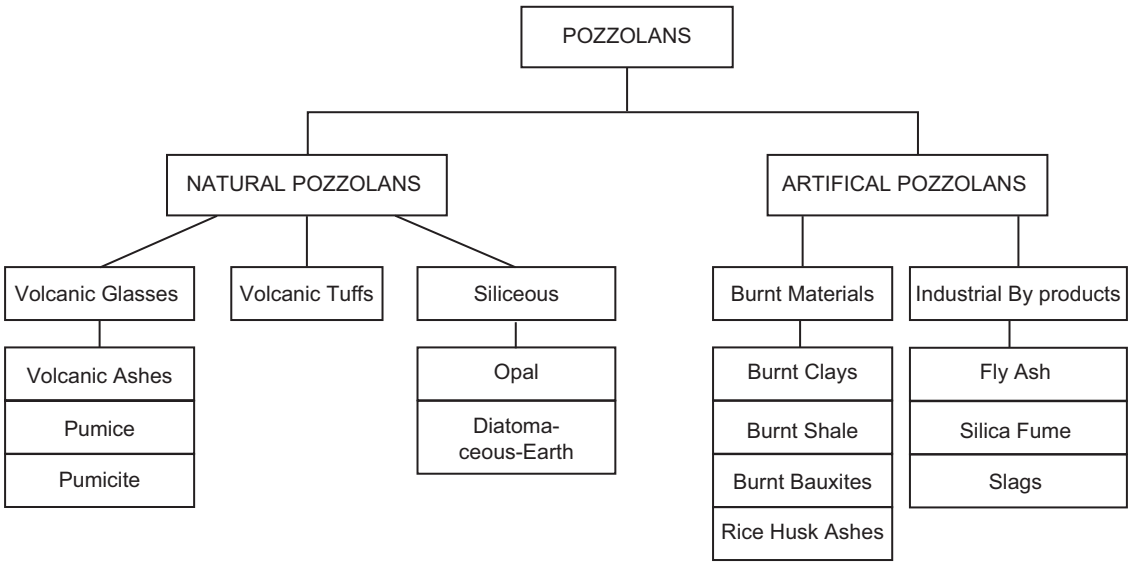

Figure 1. Classisification of pozzolans [1].

The process of alkali activation of LHL starts with the disruption of binders in the amorphous structure of raw materials occurring in the presence of an activator with a high pH. Residual released ions interact and subsequently, their connection into a new three-dimensional matrix occurs [4], [5].

Calcium-silicate hydrates, i.e. C–S–H in phase with specific portions of bound Al^{3+} and absorbed ions, are the main products in the presence of a sufficient amount of CaO [2]. These phases ensure a gradual increase in strength in the setting system. In the case of a CaO shortage, gel-like aluminosilicate hydrates are formed. Silica and alumina are predominantly in the tetrahedral coordination with oxygen. This results in a three dimensional microstructure with both types of randomly ordered tetrahedral linked with shared oxygens [2], [3], [5]. The negative charge of the alumina tetrahedral is balanced with electrostaticly bound ions inside the structure cavities. Polycondenzates of such a type were prepared, applying the alkali activated solutions to the metakaoline Davidovits [6]. He called products of this process "geopolymers". There are being distinguished several basic fragments – polysialates, which differ with the Si:Al ratio. All geopolymer structures are largely disordered which corresponds to the Barbosy model [7]. Currently, the term 'alkali activated binders' is widely used, whereas the term 'geopolymers' should be used only when referring to the zeolites with amorphous or semi crystalline characteristics [5].

The hydration process, phase composition, morphology, and the level of functional properties of strengthened alkali activated systems are dependent on a number of factors: the chemical composition, phase composition and granulometry of raw materials, the type and amount of alkali activator, the processes during the mixing procedure, temperature and conditions and treatment of masses during hydrating etc. [3-5], [8-11].

A number of studies have been devoted to the description of the connections between the creation of different hydration products and type of raw materials and alkali activators.

Criado and others [12] have discussed the activation of fly ash and the detection of hydration products hydroxysodalite and herschlite using XRD analysis. Shi and coworkers [13], studying the alkali activation of GBFS at a temperature 150 °C, describe the formation of C–S–H and xonotlite. Wang and Schrivener [14] have proved that C–S–H gel is the main reaction product of alkali activation of GBFS with low C/S ratios. This is probably caused by the increased pH of the solution with low Ca concentrations and high Si concentration. These authors describe the formation of hydrotalcite any time the alkali solution was formed by using NaOH alone or its mixture with *water glass*. They did not find any zeolites or mica containing alkali cations. Palomo et. al [15] did not identify any new crystalline phases apart from the ones already existing in the original fly ash. These authors describe that when the activator is formed from *water glass* and NaOH, the Si/Al ratio is doubled even though the Na/Al ratio remains the same. As for hydration products, the following molar ratios are used: Si/Al = 2,8; Na/Al = 0,46 for activators NaOH and Si/Al = 5,2; Na/Al = 0,46 for activators composed of NaOH and *water glass* mixture.

It was proved that geopolymers display a microporous structure. Their size is derived by the nature of alkali cations present during activation. The study of fly ash geopolymer systems found that the presence of quartz and mullite particles which act as micro aggregates in the final matrix combined with glassy aluminosilicates which remained inert. The glassy part behaves as a source of aluminium and silicon used for gel formation [16].

An array of studies have been focused on composite systems of fly ash/granulated blast furnace slag. In most

cases, the analysis is restricted to phase analysis of XRD and compression strength determination. Due to the complexity of these systems the details of microstructure is unclear [16].

Geopolymers based on fly ash represent porous materials. In regards to nano range, the porosity of the geopolymers is very similar, regardless of preparation conditions. The strength of the geopolymers is considerably influenced by macro pores which are partially accountable for the hollow particles of fly ash. In the occurrence of Ca containing latent hydraulic matter (e.g. GBFS), the porosity decreases significantly due to the coexistence of the geopolymer and C–S–H phase. The maximum strength of the geopolymers is then achieved [17].

In the systems with high concentrations of Si, the condensation of products by formation of oligomer silicates [poly(sialate-siloxo) and poly(sialate-disiloxo)] of 3D solid polymer structures (stronger than poly(sialate) structures forming at low Si concentration) is achieved [18].

Puertas at al. [19] who studied mixtures of fly ash and GBFS, state that C–S–H gel is the main product of the reaction. They also detected hydrotalcite ($Mg_6Al_2CO_3(OH)_{16}.4H_2O$), pirssonite, and calcite but found no aluminosilicate phases.

Krivenko and Kovalchuk [20] describe the formation of analcime and hydrosodalite- like zeolites with high molar ratios of SiO_2/Al_2O_3 = 4,5 ~ 5,0 for alkali activation of fly ash with NaOH and *water glass*.

Other authors [21] studied the activation of GBFS with solutions of NaOH that led to a reaction of products with Al/Si molar ratio higher (0,4) rather than using activators from NaOH and *water glass* (ratio; Al/Si = 0,2 ~ 0,3). Their explanation lies in the substitution of Si with Al present in the tetrahedral positions in the silicate chains.

Wang and coworkers indicate [8] that the character of activators influences mechanical strengths of alkali activated slag mortars and that the optimal amount of Na_2O varies between 3,0 ~ 5,5 % of slag weight. Simultaneously, they indicate that alkali activators with silicate modulus M_S = 1.0 ~ 1.5 lead to the highest mechanical strengths. Likewise, authors [22] found out that optimal amount of activators varies between 3 ~ 5 % of Na_2O of the slag weight. Higher amounts of Na_2O, apart from the higher price, causes trouble with efflorescence. Authors [23] indicate that activation of blast furnace slag with activators based on *water glass* with M_S = 1.0 ~ 1.5 leads to higher mechanical strengths. However, the highest strengths were reached using a batch of 8 wt. % of Na_2O. Xu and Deventer [24] proved that usage of *water glass* escalates the dissolution of primary raw materials. The same authors [25] found out, while studying the dissolution of some minerals, that raising the amount of Na leads to an increased solubility of SiO_2 and Al_2O_3. Lee and Deventer write in [26] that dissolution of raw materials in the excess of alkalis also leads to the enhanced alumino-silicate gel formation in the initial period of hydration which decreases mechanical strengths of alkali activation products.

It can be concluded that reaction products are dependent on both activators and raw materials. The main reaction product is C–S–H gel for systems with dominance of (Si + Ca), for systems with (Si + Al), the reaction products are polymer like zeolites [5].

According to Temuujin et al. [27], mechanical activation does not represent any changes in the phase composition of fly ash, and in the proportions of crystalline and amorphous parts. Only the portion of hematite and magnetite is slightly increased, apparently as a result of iron oxidation originally bonded in the amorphous phase.

The principal effect of grinding lies in the reduction of particle size - e.g expressed by the median size, and means the increase of specific surface values. Subsequently, this is represented by quicker setting during alkali activation as a result of faster FA dissolution in the alkali solution. The result is also an increased polymerization and hardening of gel phases resulting in a rise in compressive strengths [27].

Higher reactivity of mechanically activated FA may be due to a combined effect of smaller particles and creation of angled fragments, structural defects, and surface changes of the particles [11], [28]. The paper evaluates, with the aid of SEM, the morphology of the geopolymers obtained by the alkali activation of variously milled fly ashes.

EXPERIMENTAL

Materials

Basic raw materials used for processing of alkali activated non-clinker binders, were:

- Granulated blast furnace slag (GBFS), produced in a standard quality at ArcelorMittal Ostrava, a.s. Based on chemical analysis XRFA (energy dispersive fluorescence spectrometer SPECTRO XEPOS equipped with 50 W Pd X-ray tube) (Table 1), slag is moderately acidic, well granulated, and based on XRD analysis (difractometr Bruker D8 Advance using a $Co_{K\alpha}$ radiation, scanning rate 2°/min from 5° to 70° 2θ) mostly vitreous with the presence of a small portion of melilite, calcite and akermanite (Figure 5). GBFS was industrially ground to the specific surface area of 380 $m^2.kg^{-1}$ (Blaine, ČSN EN 196-6).
- Fly ash (FA) type F – by-product from ČEZ Dětmarovice, a.s. power station. Chemical composition is within the standard of this type of raw material (Table 1), based on XRD analysis, fly ash contains mullite, quartz, and a significant portion in a vitreous phase (Figure 5).

We assume that both raw materials contain SiO_2 and Al_2O_3 mostly in the vitreous state and are therefore latent hydraulic materials suitable for the alkali activation.

- As an alkali activator, solutions of *water glass* from an ordinary commercial source, whose main parameters are density ρ = 1390 kg m^{-3}, chemical composition (ČSN 653191:1987) – Table 1 defined by the silicate module $M_S = n_{SiO_2}/n_{Na_2O} = 3.29$, were used. This *water glass* was modified to $M_S = 1.00$ through 50% solution NaOH (optimal course of setting).
- Distilled water to an amount enabling a pasty consistency and the same workability, was added to the mixture.

Raw material mixture

Chemical composition of raw materials show Table 1.

One activator, prepared from the original *water glass* (VS) and the solution of 50% NaOH, was used in all mixtures.

Weight ratio of Na_2O in the activator A ($w_{Na_2O\,(A)}$) is:

$$w_{Na_2O(A)} = \frac{m_{Na_2O(A)}}{m_{VS} + m_{NaOH}} = \frac{m_{Na_2O(A)}}{V_{VS} \times \rho_{VS} + V_{NaOH} \times \rho_{NaOH}}$$

where V is volume of VS or NaOH and ρ is density.

Activator A was applicated in the batch of $m_A = 5.00$ wt. % Na_2O to 100 g of dry mix.

Weight ratio of SiO_2 in the activator A ($w_{SiO_2\,(A)}$) is:

$$w_{SiO_2(A)} = \frac{m_{SiO_2(A)}}{m_{VS} + m_{NaOH}}$$

where m is weight part of component in the mixture and w is weight ratio.

Into each 100 g of solid compounds, activator A introduces ($m_A \cdot w_{SiO_2\,(A)}$) of SiO_2 (g).

Chemical compositions of each raw material mixture (GBFS + activator) or (GBFS + FA + activator) is calculated additively from the representation and composition of each raw material. Chosen GBFS:FA ratios were 85:15 and 70:30.

For descriptions of experimental mixtures, contents of oxides taking part in the reaction of alkali activation were balanced, i.e. SiO_2, CaO, Al_2O_3 and Na_2O. Amounts of SiO_2 in each mixture can be calculated from a supply of solid components and activators, according to the general relation:

$$m_{SiO_2} = m_{GBFS} \cdot w_{SiO_2\,(GBFS)} + m_{FA} \cdot w_{SiO_2\,(FA)} + m_A \cdot w_{SiO_2\,(A)}$$

Likewise, amounts of Na_2O in each mixture are calculated. Chemical compounds CaO and Al_2O_3 are added only in the form of solid components.

A better formulation of the representation of listed oxides in each mixture can be calculated from their fictive 100% content. Such a calculation of mixture composition and its oxide content is given in Table 2.

Table 2 clearly documents changes in the chemical composition of the experimental system LHL with the same addition of alkali activator. This simplified expression outlines the following facts:

- Substitution of GBFS with FA changes the SiO_2 content in the mixture only slightly.
- Simultaneously, the CaO content in the mixture that will bind less SiO_2 into C–S–H phase, is decreasing.
- With substitution of part of the GBFS with fly ash, Al_2O_3 ratio in the mixture is increased leading to a significant increase in possible polysialate (geopolymers) formation,
- Na_2O content in the mixture is constant, whereas 5.0 wt. % is delivered with the activator and a small portion of Na_2O is bonded in GBFS and FA.

Proposed types of raw material mixtures of GBFS + FA are adjusted in a way that will be able, apart from the formation of C–S–H phase responsible for strength, to form aluminosilicates (precursors of zeolites) during alkali activation that will ensure additional advantageous utility properties of products.

Table 1. Chemical composition of raw materials.

Raw material	Compounds [wt.%]							
	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	Na_2O	K_2O
GBFS	37.74	12.09	41.86	5.74	0.21	0.18	1.06	0.35
FA	3.40	3.00	50.39	27.85	7.90	0.95	0.67	2.36
Original water glass	–	–	28.80	–	–	–	9.04	–

Table 2. Calculated composition of raw material mixture.

Mixture	Chemical composition [wt.%]				Composition ratio				
	SiO_2 (S)	CaO (C)	Al_2O_3 (A)	Na_2O (N)	C/S	S/C	A/S	S/A	S/N
GBFS	48.52	39.22	5.96	6.30	0.81	1.24	0.12	8.14	7.70
GBFS/FA = 85/15 (A)	50.17	34.08	9.48	6.27	0.68	1.47	0.19	5.29	8.00
GBFS/FA = 70/30 (B)	51.84	28.88	13.03	6.25	0.56	1.80	0.25	3.98	8.29

Mechanical activation of fly ash

Fly ash, produced during coal incineration, is a typical representative of a latent hydraulic compound substance suitable for the preparation of alkali activated materials.

Fly ash, with its original granulometry characterized in Table 3, was ground using two types of laboratory mills:

- Laboratory vibrating mill (LVM) with two steel grinding segments inside the elementary grinding tub,
- Laboratory drum mill (LBM) with porcelain grinding balls,

and in

- Semi industrial steel drum mill (PBM) with steel grinding balls.

In all cases, grinding was performed in a dry state. In the first two cases, the load was 30 g. 2000 g of FA was ground at optimized conditions in PBM.

Table 3 summarizes granulometry (Fritsch particle sizer Analysette 22, medium alcohol) and specific surface (Blaine – ČSN EN 196-6:1993) data of FA samples applicated during the trial of alkali activation of GBFS and FA.

Sample preparation and testing

To the GBFS, or homogenized mixtures of GBFS and specific FA, liquid alkali activator was added to the amount equal to 5,0 wt. % Na_2O. Rheology properties of the mixtures were adjusted with the addition of distilled water maintaining the same plasticity using only visual controls of the mixture. Test samples were prepared in

Table 3. Granulometry and specific surface of FA.

Mill type	Time of grinding (min)	Granulometry criteria			Specific surface ($m^2\ kg^{-1}$)
		modus – d (0.5) (μm)	median (μm)	d (0.9) (μm)	
-	Original FA	32.4	70.9	134.0	365
LVM	2.5	8.9	7.8	35.8	491
	5.0	7.4	7.8	28.5	524
	7.5	7.4	7.8	23.0	529
LBM	10.0	6.6	6.1	42.9	501
	30.0	5.8	5.5	36.5	511
PBM	10.0	4.8	4.9	21.3	585
	30.0	4.3	4.5	18.2	623

Table 4. Volume densities ($kg.m^{-3}$) of alkali activated mixtures: GBFS/FA = 85/15 (A) a GBFS/FA = 70/30 (B).

Type of mixture	Type of mill	FA grinding time (min)	Time of hydration (days)				Designation of samples
			2	7	28	180	
A	LVM	0	1857	1910	1930	1974	A LVM 0
		2.5	1961	1972	2044	2053	A LVM 2.5
		5.0	1962	1990	2067	2072	A LVM 5.0
		7.5	1964	2004	2069	2075	A LVM 7.5
B	LVM	0	1952	1976	1989	1993	B LVM 0
		2.5	2038	2058	2097	2117	B LVM 2.5
		5.0	2053	2091	2153	2168	B LVM 5.0
		7.5	1962	1983	2052	2110	B LVM 7.5
A	LBM	10.0	1918	1928	2013	2052	A LBM 10
		30.0	1919	1933	1976	1989	A LBM 30
B	LBM	10.0	1913	1990	2016	2022	B LBM 10
		30.0	2002	2018	2036	2047	B LBM 30
B	PBM	10.0	2069	2083	2099	2133	B PBM 10
		30.0	2052	2085	2118	2154	B PBM 30
GBFS	-	-	2003	2004	2022	2030	GBFS

the moulds with a unit size of 20×20×20 mm. After 2 minutes of vibrating its content, the moulds were placed into boxes with a saturated aqueous vapour environment and laboratory temperature (20 ± 2 °C). The samples were demoulded (after 24 hours) and were kept under the identical conditions up to the further tests examination.

In selected terms (2, 7, 28, and 180 days), volume densities (Table 4) and compressive strengths (laboratory press Compact LLB1 fy BRIO Hranice, s.r.o. with continuous load 2400 $N.s^{-1}$) of selected samples (Table 5), or Figures 2-4, were determined. Selected samples were tested for chemical resistance.

Table 5. Compresive strength (MPa) of alkali activated mixtures: GBFS/FA = 85/15 (A) a GBFS/FA = 70/30 (B).

Type of mixture	Type of mill	FA grinding time (min)	Time of hydration (days)			
			2	7	28	180
A	LVM	0	49.3	66.2	68.8	76.1
		2.5	55.0	72.1	79.0	87.1
		5.0	50.3	71.3	99.2	110.4
		7.5	29.4	59.2	76.7	111.0
B	LVM	0	39.0	71.2	74.5	93.3
		2.5	25.0	56.7	76.3	112.7
		5.0	23.5	50.4	84.2	118.0
		7.5	21.9	47.7	68.0	110.8
A	LBM	10.0	28.4	68.6	83.7	88.1
		30.0	30.4	55.3	71.0	76.9
B	LBM	10.0	32.9	88.6	96.2	100.2
		30.0	27.7	55.0	78.9	102.5
B	PBM	10.0	33.4	88.5	115.4	121.2
		30.0	31.5	82.6	98.7	117.3
GBFS	-	-	45.2	79.7	114.4	120.6

RESULTS AND DISCUSSION

Volume densities of the samples show slight increases in hydration time, corresponding to the formation of the hydration products.

Figures 2 to 4 document the tendency of increasing compressive strength of all samples to hydration time. Initial strengths are high after the application of ground fly ash that evidently serves as filler at the beginning. After 28 days of hydration, the strengths of the mixes with ground fly ashes exceed the strengths of the control mixtures A 0 or B 0. After 180 days of hydration, significantly high strengths of 110 MPa (the highest 118 MPa) were reached for mixtures B (70 GBFS/30 FA) with fly ash ground for 5 minutes.

Figure 4 summarizes data of the strength development of mixtures with fly ash ground in the laboratory drum mill (LBM) and the semi industrial drum mill (PBM). Mechanical activation of fly ash by grinding was clearly expressed by strength increase, the most effective was the grinding of fly ash in PBM with strengths of the mixtures B (70 / 30) reaching approximately 120 MPa.

All mixtures were activated using the same alkali activator – solution of *water glass* with $M_S = 1.0$, batch equal to 5 wt. % of Na_2O with respect to the solid compounds. It can be assumed, from the chemical composition of GBFS and FA, that when using GBFS, fundamental products of hydration will be C–S–H type phases that are main binding phases responsible for strength.

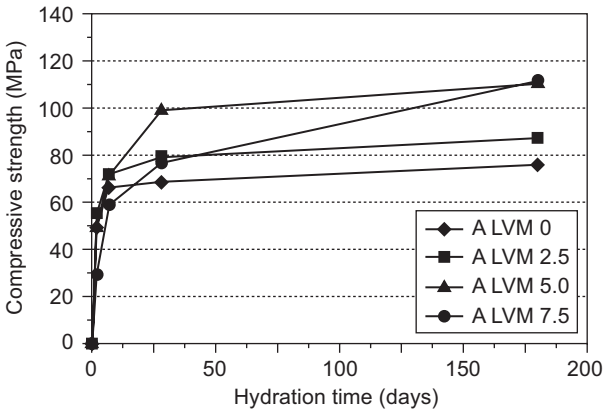

Figure 2. Compressive strengths (fly ash ground in the LVM).

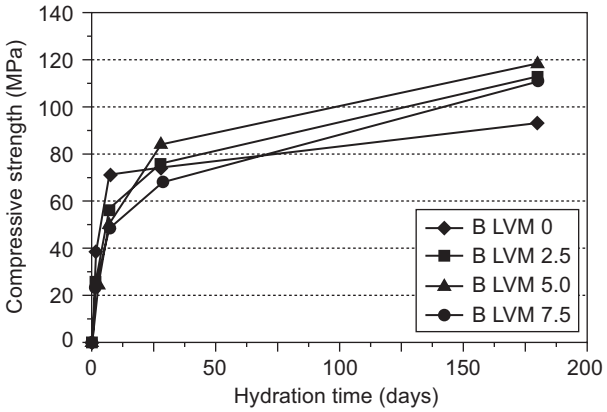

Figure 3. Compressive strengths (fly ash ground in the LVM)

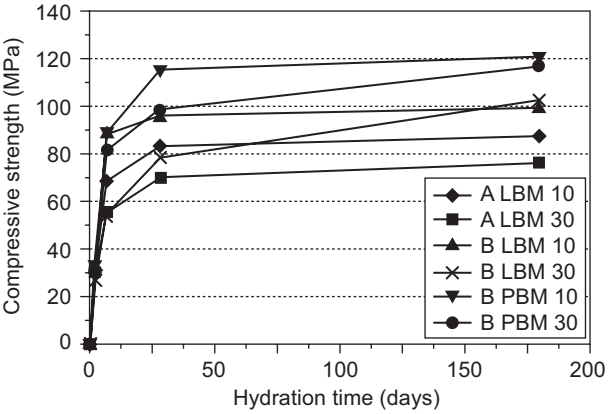

Figure 4. Compressive strengths (fly ash ground in the LBM and PBM)

With change of the chemical composition by substitution of part of the GBFS with fly ash in the mixtures, there are assumptions of modifications in the hydration process leading to the creation of not only C–S–H phases but also aluminosilicate hydrates containing Na^+ ions that can be specified as zeolite precursors. Their content in the hydrated samples does not contribute to the strength parameters of the products at the beginning. After a lengthy activation process, the presence of these phases, together with non-reactive portions of mullite and quartz, prove the function of a certain filler strengthening the C–S–H hydrates system and thereby increasing the strengths (Figures 2-4).

Both types of new formations are amorphous, thus unidentifiable with XRD analysis.

Figure 5 shows XRD analysis of both, original raw materials (GBFS and FA) and chosen activated samples after 90 days of hydration (hydration stopped by water extraction with acetone). Diffraction maximums correspond with crystal phases in non reacted raw materials (silica, calcite, akermanite, gehlenite, merwinite); new crystal products were not found. Broad diffusion maximums in the range of 30 ° ~ 44 °/2θ proves the presence of amorphous phases.

To distinguish the presence of quasi zeolitic phases among CSH phases, an array of other experimental methods were used – infrared spectroscopy, MAS NMR analysis in solid phase and study of pH changes of hydrated mixtures suspensions. We would like to publish these extensive results in a separate paper.

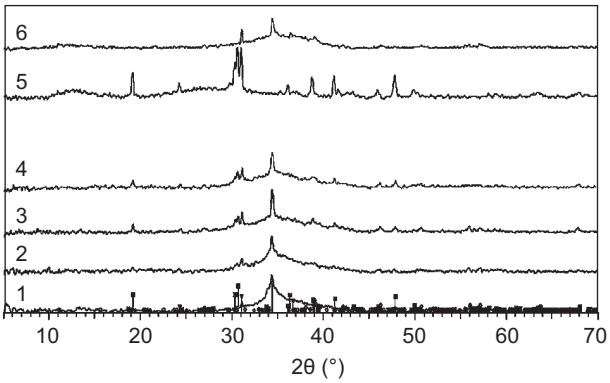

Figure 5. XRD analysis records of raw materials (5, 6) and chosen alkali activated samples (1-4): 1 – GBFS; 2 – mixture B LVM 2,5; 3 – mixture A LVM 7,5; 4 – mixture A LVM 2,5; 5 – FA; 6 – GBFS. (LVM = laboratory vibrating mill – Tab. 4).

Displayed here are two further methods that proved differences in the development of the characteristics of the alkali activated systems - intentionally drafted mixtures of GBFS + FA compared to GBFS itself:

a) Consideration of chemical resistance

We used experimental evaluation of differences in chemical resistance of mixtures in which phase composition is taken to be different based on the difference in their chemical composition. The principle of the test is evaluation of samples after 28 days of alkali hydration under standard conditions and a further 56 days exposed to the influence of a selected liquid medium, such as distilled water, that simulated the so called 'Hungry Water' (demineralized water) syndrome (degrading the concrete microstructure based on the portland cements) and further 0,5 % HCl solution, that primarily leaches out the CaO from hydrates.

Only after a short time of this influence by selected media (fresh media being replaced after each 2 weeks of usage) there are visible differences in strength of affected samples from GBFS or the mixtures GBFS + FA = 70 + 30 (type B). At the same time, differences in behaviour of systems with milled FA for a varying period in the laboratory vibrating mill were confirmed. A summary of the experiments is given in Table 6.

Compressive strength of samples GBFS + FA in distilled water increased by 10 ~ 30 %, at activated pure GBFS decreased the strength by 25 %. More visible are the differences in chemical impact of HCl solution: in samples of GBFS + FA mixtures decreased by 4 – 11 %, while samples from GBFS itself showed an average decrease in strength of 61 %.

Together with other test results, these differences are believed to be the consequence of the presence mostly of CSH phases in samples of alkali activated GBFS and systems of CSH phases and geopolymers of zeolitic characters in mixtures from GBFS + FA. This evaluation is based on a lot of data on different chemical resistance of CSH phases and zeolites and their precursors – e.g. [1], [4], [8], [23].

Table 6. Compressive strength of samples after 28 days hydration or 56 days of further chemical impact.

	Average compressive strengths				
	28 days	Distilled water		HCl of 0.5 wt.%	
Samples´ labels	of hydration (MPa)	Strength (MPa)	Relative strength (%)	Strength (MPa)	Relative strength (%)
B LVM 0	74.5	86.2	115.7	66.0	88.6
B LVM 2.5	76.3	87.3	114.4	72.8	95.4
B LVM 5	84.2	92.0	109.2	81.0	96.2
B LVM 7.5	68.0	87.5	128.7	62.2	91.5
GBFS	114.4	86.7	75.8	45.6	39.1

b) Gradual thermal dehydration

Samples of alkali activated GBFS and mixtures of GBFS/FA = 85/15 (A) and 70/30 (B) were gradually heated to temperatures of 100, 200 and 300 °C (heating rate 5 °.min^{-1}, maintain 2 hours at given temperature and followed by cooling back to achieving the ambient temperature). FA in the mixtures was used in 3 qualities – non milled, milled 10´ or 30´ in a laboratory drum mill. The determined weight changes were deduced by weighing samples, their average values are given in Table 7.

At temperatures of 100 °C the free water starts to be released from the samples. Observed values of Δm are mutually very close in all mixture samples (from 1,27 g up to 1,32 g – when the weight of samples is about 16 g). The GBFS itself has an average Δm 1,37 g.

Other water proportions of all samples are bonded in hydration due to the previous 28 days of alkali hydration. At GBFS these are mainly CSH phases because the Al_2O_3 volume is low for general formation of aluminosilicate hydrated phases. Samples of hydrated GBFS + FA mixtures were evaluated by comparing real weight loss at given temperatures (Δm_S) and "theoretical" loss (Δm_t) – calculated for relevant GBFS portions in mixtures (i.e. 85 % or 70 %) against Δm_S of samples from GBFS itself. In cases where average $\Delta m_S > \Delta m_t$ also other hydration products are formed, most often those of zeolitic (geopolymer) nature, during heating to temperatures of 200 or 300°C.

The influence of FA presence in mixtures that contributes to the formation of other hydration products than CSH phases, increases with its increasing portion in mixtures. Mixture A where 15 % of FA is real weight loss is on average higher by 11,5 %, whereas mixture B (30 % FA) is Δm, higher by 32,8 % when compared to *CSH dehydration alone*. At the same time, the increase of Δm values in both mixtures is more considerable and so the geopolymer formation during the application of milled fly ashes is more extensive.

These results can be assumed to be further indirect evidence of different phase composition of alkali activated mixtures, drafted with the intent of their chemical composition modifications. With increasing FA portions, CaO volume in mixtures decreases and so the CSH phases formation decreases; on the contrary Al_2O_3 participation, which enables formation of zeolitic products, increases.

CONCLUSION

Development of alkali activated materials is focused on the systems that, based on their properties and origin, represent favourable alternatives to the Portland cements as the most utilized hydraulic binder so far. Results proved the hypothesis that increased SiO_2 / CaO ratio by addition of FA into the initial GBFS (with S/C = 1,1) show changes in the hydration processes monitored by the different compressive strength development. With a constant Na_2O / SiO_2 (~ 0,12) ratio, substitution of part of the GBFS with fly ash, hence the increased SiO_2 / CaO ratio, will result in the increase of long-term strengths of alkali activated mixtures to the compressive strength values of 110 ~ 120 MPa. Improved strengths were recorded during the application of FA ground alternatively in three types of mills, whereas the optimum grinding period for these mills was identified.

The usage of activators adjusted to M_S = 1.0 proved to be advantageous, mixtures showed suitable time behavior of setting and hardening. Batches of Na_2O = 5,0 wt. % is suitable for gaining high strengths and it does not result in the creation of *blooms*.

The effect of the chemical composition of mixtures and mechanical activation of FA was tested using the performed chemical resistance test of alkali activated systems in distilled water and solutions of 0,5 % HCl. Mixtures GBFS/FA showed significantly higher resistance than samples from GBFS. Differences may be explained by the presence of zeolite (geopolymer) phases in hydrated mixtures of GBFS/FA. The effect of mechanical activation of FA was also proved.

The study analysis of gradual weight changes of alkali activated samples during their heating to temperatures 100, 200 and 300 °C showed the influence of sampled raw material composition modifications on their hydration.

The increase of Al_2O_3 in mixtures enables the formation of geopolymer products at the expense of C–S–H phases. These equations correspond with other methods for assessment of hydrated amorphous systems and contribute to the monitoring of content of raw material component mixtures forming with resulting alkali activated mass properties.

Table 7. Comparison of the weight changes of alkali activated mixtures at temperature treatment to 200 and 300°C.

	Temperature of treatment	GBFS Δm_s	Δm_t mixtures	Non-grinded FA Δm_s		FA grinded 10´ Δm_s		FA grinded 30´ Δm_s	
Mixture	(°C)	(g)	(g)	(g)	Rel. value (%)	(g)	Rel. value (%)	(g)	Rel. value (%)
A	200	2.76	2.35	2.60	110.6	2.65	112.8	2.68	114.0
	300	3.39	2.88	3.21	111.5	3.19	110.7	3.18	110.4
B	200	2.76	1.93	2.54	131.6	2.75	142.5	2.67	138.3
	300	3.39	2.37	3.00	126.6	3.02	127.4	3.10	130.8

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