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Genesis of Structure and Properties of the Zeolite-Like Cement Matrices of the System Na(K)-Al₂O₃-SiO₂-H₂O within a Temperature Range of 20–1200°C

Pavel Krivenko and Volodymyr Kyrychok

Abstract

The chapter deals with a genesis of structure and properties of the zeolite-like cement matrices of the Na(K)-Al₂O₃-SiO₂-H₂O system within a temperature range of 20–1200°C. Due to the fact that zeolite-like structures and their characteristics vary within wide ranges, materials with high-performance properties can be obtained through regulation of the structure formation processes. This can be provided by a proper choice of type of an aluminosilicate component, cation of an alkaline component and additives, including Ca-containing ones, and curing conditions. When the cement matrix formation process is appropriately directed, the zeolite-like products (hydrosodalite, analcime, chabasite, faujasite etc.) dominate in the microstructure that is formed. The ability of some zeolites to recrystallize with temperature increase into stable feldspar-like aluminosilicates without destroying the basic skeleton opens a pathway that is worth to explore in the production of materials similar to low temperature ceramics, intumescent coatings, high temperature and corrosion resistant structures, etc. The examples are given on how to use the above cement matrices for making some of the above listed materials.

Keywords: alkali, aluminosilicate, cation, fly ash, metakaolin, phase transformation, pore, strength, thermal shrinkage, zeolite phases

1. Introduction

Technical advances in building industry in association with progress in knowledge collected on the chemistry of cementitious materials, requirements of global sustainable development serve as a moving force in further development of the alkali-activated materials [1–3].

Earlier, according to traditional views, free alkalis and compounds of alkali metals were excluded from traditional hydraulic cement compositions because of their high solubility which resulted in the worse durability and properties.

However, the studies held on ancient cements and concretes showed that their excellent durability could be attributed to the presence of aluminosilicates of alkali metals – analogs of natural zeolites – in their hydration products. Alkalis play an

important role in mutual transformations of minerals in the Earth's crust. It should be also mentioned that aluminosilicates of alkali metals (first of all, feldspars) are known to be more stable and durable compared to those of calcium [1].

In 1957 Viktor Glukhovskiy made an attempt to model natural processes of formation of the aluminosilicates of alkali metals at different temperatures and made an assumption that the compounds of alkali metals (Li, Na, K, Rb, Cs) – the elements of Group 1 of the periodic table of elements, exhibited hydraulic binding properties similar to compounds of the alkaline earth metals (Mg, Ca, Sr, Ba) – the elements of Group 2 [4].

An important conclusion was also made that the increase of temperature promoted a smooth dehydration process and subsequent re-crystallization of the hydration products into stable anhydrous aluminosilicates of alkali metals. This conclusion was later confirmed [5–7]. Unique service properties of materials predetermine its application for development of a wide area of modern composite materials for the building industry such as protective coatings, inorganic glues, heat-insulating materials, thermo resistance composites, etc. [8–14].

Extensive works carried out have allowed to revise views of regularities of exhibiting binding properties by mineral substances and to prove that, in parallel with the compounds formed by the elements of Group 2 (alkaline earth elements) of the periodic table of elements together with complex-formers of Groups 3, 4, 5 or 6, the compounds formed by elements of the main Subgroup of Group 1 together with twin complex-formers of the Groups 3 and 4 (aluminosilicates) possess binding properties. Such products can be formed through a combination of other amphoteric and acid compounds [4, 8, 9].

The established regularities governing the formation of a mineral-like cement matrix based on the compounds of alkali metals taken alone and in combination with the compounds of alkaline earth metals were established and studied in details (hardening processes, principles of compositional structure and prediction of their properties) and used for development of a new class of hydraulic binders known nowadays under a name of alkali-activated cements or alkali-activated aluminosilicate cements [10–17].

The idea behind the alkali activated cements is modeling of the minerals of the Earth's crust in the system of $\text{Me}_2\text{O}-\text{Me}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ ($\text{Me}_2\text{O}-\text{Li}_2\text{O}, \text{Na}_2\text{O}, \text{K}_2\text{O}, \text{Rb}_2\text{O}, \text{Cs}_2\text{O}; \text{MeO}-\text{CaO}, \text{MgO}; \text{Me}_2\text{O}_3-\text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3, \text{Cr}_2\text{O}_3$). For example, aluminosilicate rocks of feldspar composition are broken up by chemical wind erosion to a dispersion state or to clay minerals. These transformations are accompanied by hydration of anhydrous minerals composed from the compounds of alkali metals, the decrease of alkali content in hydrated new formations; the replacement of alkalis by hydrogenous ions or H_3O^+ -groups; the transition of aluminium from IV-coordination to VI-one; the partial removal of silicic acid, i.e. by processes occurring under hydration and hardening of building cements. Gel-like silicate and aluminosilicate substances are formed as a result of chemical erosion of feldspars in an erosion crust, in the zones of hydrothermal metamorphism proceeding at relatively low temperatures and pressures. These substances react with compounds of alkali metals brought by circulating superheated aqueous solutions. As a result, aluminosilicate hydrates of alkali metals of zeolite type are formed. These minerals have a very low water solubility despite the fact that their composition includes strongly soluble compounds of alkali metals [5–8].

In particular, analcime ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) is formed at 303 K (29.85°C) at the sea bed through a coagulation of silica and alumina sols with their concurrent adsorption of ions of alkali metals from environment.

Geological data suggest that on numerous occasions aluminosilicates of alkali metals of zeolite type or sodalite, feldspathoid, feldspar types (these minerals are

structurally analogous to zeolites) which are the rock-forming minerals, were formed at the expense of chemical interaction between a clayey substance and compounds of alkali metals in an erosion burst. But these processes in nature proceed very slowly, during geological periods. The presence of an alkaline medium is the determining factor for the progress of these processes.

The processes in natural or compositionally analogous to natural, artificial aluminosilicates of alkali metals can be accelerated to limits wherein aluminosilicates can be used as hydraulic binders. Similar to the production of Portland cement clinker, it is possible through the conversion of these substances from the stable crystalline state into a more active metastable one, including a glassy state, or through the external introduction of compounds of alkali metals [5].

Extensive experimental studies confirmed the proposed theoretical bases and allowed to prove that caustic alkalis; salts of alkali metals and weak acids; silicates, aluminates and aluminosilicates reacting in the presence of alkalis under condition that their concentration in the system is sufficient react with natural clay minerals or undead burnt ones; with natural and artificial aluminosilicate glasses, among them metallurgical slags, fuel ashes and slags. The processes can take place in natural conditions and under steam curing and a water-resistant stone with the hydration products that are analogous to natural minerals of zeolite type is formed [3, 4, 8, 9].

Main criteria to be applicable to a choice of starting materials for the zeolite-like cement matrices are: high contents of silica and alumina in them which promote a synthesis of the zeolite-like phases of the $(\text{Na}, \text{K})_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ system and some content of calcium oxide which will serve as an inhibitor of the process of zeolite synthesis [7–9]. The most appropriate for these goals are natural clays in natural and dehydrated state, volcanic rocks or industrial by-products like fuel ashes and slags, metallurgical slags, red muds etc. [3, 4, 9, 17, 18].

Large differences can be observed between microstructures of these cement matrices. A microstructure of the metakaolin derived cement stone, for example, was investigated by systematic variation of activator composition and related to mechanical strength [18–31]. The most important factors affecting a phase composition and, correspondingly, properties of the material are: curing conditions and type and concentration of the alkaline activator solution (that is, the ratios between main oxides $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ and $\text{SiO}_2/\text{Al}_2\text{O}_3$) as well as a water to solid (W/S) ratio [4, 9, 11, 18–23, 30, 31]. It was observed that with the Si/Al ratio increase, a porosity of the microstructure changed from large pores to more homogenous structure with small pores. This observation was linked to a strong correlation with the Young's modulus and mechanical strength increase [22].

The majority of researchers [32–34] made a conclusion that the structure formation processes in the alkali activated aluminosilicate systems were determined by a required constitutional composition and flowed step-by-step with the formation, depending on a temperature, of the amorphous, glassy or crystalline zeolite-like cement matrices.

For example, reaction products of the interaction of clay minerals with NaOH at 100–300°C are hydronephelines with a structure of sodalite, and those of the interaction with KOH – caliophilites containing zeolitic and adsorbed water.

Hydronepheline and caliophilite themselves can act in a ceramic matrix as structure forming binders.

Low-temperature ceramics produced from them is characteristic of the enhanced resistance to alkalis. With further curing temperature increase of the mineral system to be synthesized the process will flow under a dehydration-condensation scheme. Hydrates that are formed at low temperatures start to dehydrate, their crystal lattices destroy and the substance becomes amorphous. Further

transformations of the dehydration products are attributed, in case of the sodium compounds, to their transformation at 100–800°C into nepheline, at 800–1100°C into albite under condition of required amount of silica available in the system, in case of the potassium compounds – first, into anhydrous calicophilite, afterwards – into orthoclase. The formation of a hydrate phase as a result of the interaction of minerals of unfired clays with salts of alkali metals in normal conditions is rather difficult to identify. However, being subjected to heating, they transform into anhydrous minerals of nepheline, leucite, afterwards – into albite and orthoclase. Their synthesis is preceded by the processes of dehydration of the clay minerals and thermal dissociation of the alkali metal salts.

A character and temperature at which the products are synthesized is determined by a structural type of a clay mineral, type of compound of alkali metal, and nature of siliceous component.

The phases composed from aluminosilicates of alkali metals of the albite and orthoclase type are the most intensively crystallized in the compositions which contain bentonite, and with the lowest intensity in the compositions which contain kaolin. The additives of mineralizers, amorphous silica, α -cristobalite and preliminary dehydration of the clays render an intensifying action on crystallization of these phases.

In the mixed binding systems of the $\text{Na}_2\text{O}(\text{CaO})\text{-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ composition the structure formation processes are determined by crystallization of the phases which are analogs to natural plagioclases.

A purpose of the paper is to make a systematic analysis of transformation of phase and properties of the zeolite-like cement matrices of the system $\text{Na}(\text{K})\text{-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ in relation to various factors, the most important of them are: temperature of curing, reactive silica content ($\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio), initial alkalinity ($\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio), cation type (Na or K, and Ca), type of aluminosilicate component (metakaolin or fuel ash (fly ash)).

2. Experimental

The cement compositions used in the study were formulated from an aluminosilicate component selected from a typical metakaolin and two type F fly ashes (380m²/kg by Blaine) (Table 1) and soluble sodium silicates (M = 2.8 and density = 1400 kg/m³) as an alkaline component. In some cases sodium hydroxide and silica fume were added as supplementary components. In the experiments on thermal behaviour exclusively in the tests held at high temperatures, a ground chamotte with a specific surface area = 410 m²/kg by Blaine was used as filler. After curing in an air tight mould at 80°C until solidification, the specimens were then were subjected for 6 hr- curing: in autoclave at 174°C, in steam curing chamber at 80°C, and in drying chamber at 80, 150, and 220°C. The structure formation processes at

Constituent	Chemical composition (% by mass)											In total
	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	CaO	R ₂ O	P ₂ O ₅	LOI	
Metakaolin	55.76	0.00	35.86	4.33	0.00	0.00	0.93	3.05	0.00	0.00	0.07	100.00
Fly ash 1	50.64	1.21	23.73	9.67	0.71	0.15	1.76	2.32	3.26	0.45	6.10	100.00
Fly ash 2	48.25	0.89	19.67	4.50	3.15	0.11	1.36	2.18	3.82	0.02	16.04	100.00
Silica fume	87.58	0.00	0.20	0.14	0.00	0.00	0.50	2.10	4.76	0.00	4.71	100.00

Table 1.
Chemical composition of raw materials.

high temperatures were studied on the specimens that then additionally cured for 4 hrs within a temperature interval of 600–1200°C. An interrelation between mechanical properties determined on the specimens of size 2 × 2 × 2 cm and the results of examination of a phase composition studied by means of XRD, DTA, and SEM techniques was established.

On the contrary to a traditional approach, under which changes in a pH-value and an aluminosilicate component to alkaline solution ratio were taken as variables, an approach applied in this study was based on a ratio between the main constituent oxides in a reacting mix (mainly, SiO₂/Al₂O₃); it makes more easier to understand the structure formation processes with regard to peculiarities of a synthesized microstructure.

3. Results

3.1 The structure formation processes in the cement of the R₂O-Al₂O₃-SiO₂-H₂O system

3.1.1 Influence of curing conditions

Ten cement compositions were chosen for this study (**Table 2**). Each cement composition was cured using one out of five curing regimes mentioned above. The XRD and DTA results allowed identifying the fields of crystallization of the aluminosilicate-based hydration products (**Figure 1**).

Thus, the phase compositions of the reaction products of the metakaolin- and fly ash-based cements are similar. The phase composition of the reaction products of the autoclaved fly ash-based cements is represented mainly by analcime, zeolite-P and zeolite-R. These conclusions coincide well the data obtained on the model systems and reported in [5, 6] and those obtained with the metakaolin-based cements [12].

A synthesis of hydroxysodalite which is formed due to high contents of Na-cation in the steam cured fly ash-based cement compositions with SiO₂/Al₂O₃ = 4 and those after drying correlates well with the data obtained on similar systems with high alkali concentrations and after curing in normal conditions [5, 6, 35–37]. When using the low-alkali cement compositions with SiO₂/Al₂O₃ = 6–8

Aluminosilicate component	Mix No	Molar ratio		
		Na ₂ O/Al ₂ O ₃	SiO ₂ /Al ₂ O ₃	H ₂ O/Al ₂ O ₃
Metakaolin	1	1.0	2.0	9.5
	2	1.0	4.0	10.0
	3	1.0	6.0	15.0
	4	1.0	8.0	20.0
Fly ash 1	5	1.0	4.0	7.0
	6	1.0	6.0	10.5
	7	1.0	8.0	16.5
Fly ash 2	8	1.0	4.0	10.0
	9	1.0	6.0	11.5
	10	1.0	8.0	17.0

Table 2.
Ratio of the components in a cement matrix.

Figure 1.
Type of hydration products vs. aluminosilicate component of the cements.

Figure 2.
The ²⁷Al MAS-NMR spectra of (a) typical metakaolin, (b) metakaolin-based Na-geopolymer from metakaolin with Si/Al ratio of 2.15, (c) typical fly ash, and (d) Na-geopolymer from NaOH activation of fly ash (20 hours, 85 °C) [38].

simultaneously with a low-temperature curing such as steam curing or drying, the accepted exposition time is not enough for the zeolite crystallization.

A speed of the mineral (in our case, zeolite) formation is usually measured by a height of the XRD peaks. These peaks in case of the fly ash-based cements are much more higher compared to those in case of the metakaolin-based cements.

This also follows from the Si MAS-NMR and the Al MAS-NMR spectra (**Figures 2 and 3**) [38–46].

Figure 3. The ^{29}Si MAS-NMR spectra of (a) typical metakaolin, (b) metakaolin-based Na-geopolymer with Si/Al ratio of 1.65, (c) typical fly ash, and (d) fly ash-based Na-geopolymer (20 hours, 85°C) [39].

The greater intensity of the peaks at 93 and 98 ppm in the fly ash-based cement compared to the signal at 84.6 and 89 ppm in the metakaolin-based cement is an indication that the aluminosilicate gel that is formed (N-A-S-H) in the fly-ash based cement has a higher silica content.

After drying of both metakaolin- and fly ash-based cements, a minor phase was fixed at first as a “phase Z” [18], but further studies on carbonation finally showed that these peaks could be identified as a trona mineral ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$). After steam curing, another minor phase with main peaks (0.276, 0.237 nm) was identified [18]. These peaks can be an evidence of formation of another sodium carbonate, $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ (due to carbonation process). These two phases may sometimes co-exist, however, their formation takes place under a different mechanism: the higher W/S ratios, the higher amounts of the trona are formed. A synthesis of the sodium carbonate hydrate takes place only at low W/S ratios and high alkalinity under hydrothermal conditions (steam curing, curing in an air tight mould).

In order to study a phase composition of dehydration products the cement specimens (**Table 2**) were, after pre-curing, subjected to high temperature curing (800°C). On the contrary to the phase composition after hydration, which is dependent, above all, on a mode of pre-curing, the phase composition after dehydration depends only on the cement composition and does not depend on the mode of pre-curing. So, in the cements with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 4$ a phase composition of the reaction product is represented by nepheline (**Figure 4**). The degree of crystallization does not depend on the mode of pre-curing, and depends on a type of the aluminosilicate component: a maximal degree of crystallization was observed in case of the metakaolin compared to the fly ashes. This can be attributed to the fact that the metakaolin is the most chemically pure component. The impurities from the fly ashes resulted in the reduced contents of the anhydrous aluminosilicates and in the formation of additional amount of hematite.

Figure 4.

The XRD scans of the metakaolin-based cements with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 4$ after high temperature curing at 800°C . Aluminosilicate component: Metakaolin (1–3), fly ash 1 (4–6), fly ash 2 (7–9). Pre-curing mode: Steam curing (1, 4, 7), drying (2, 5, 8), without pre-curing (3, 6, 9) N – Nepheline, Ab – Albite, Kr – Cristobalite, F – Hematite, FA – Residue of unreacted fly ash.

3.1.2 The role of type of the aluminosilicate component and $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio

Figures 5 and 6 demonstrate XRD scans and SEM images of the microstructure of a cleaved fragment of the artificial stone depending on the ratio $\text{SiO}_2/\text{Al}_2\text{O}_3 = 2:7$ in the original composition of the zeolite-like cement matrices after drying at 80°C (under condition that $\text{K}_2\text{O}/\text{R}_2\text{O} = 0.15$ and $(\text{Na}_2\text{O} + \text{K}_2\text{O})/\text{Al}_2\text{O}_3 = 1$).

A phase composition of the hydration products at low of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios (2:3) after drying at 80°C is represented by zeolite-Na-A ($d/n = 0.699; 0.365; 0.336; 0.293$ nm), natrolite ($d/n = 0.287; 0.243; 0.138$ nm), ussingite ($d/n = 0.492; 0.347; 0.295$ nm). Amorphous phases of the metakaolin-based cement and particles of the non-reacted metakaolin can be clearly seen in the SEM images (**Figure 6**).

The alkali-activated aluminosilicate cements with the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios = 4:5 have the zeolite-like hydration products of the following type: zeolite-Na-A ($d/n = 0.699; 0.365; 0.336; 0.293$ nm), heulandite-Na ($d/n = 0.509; 0.392; 0.296$ nm), heulandite-K ($d/n = 0.342; 0.281; 0.273$ nm), and phillipsite-Na-K ($d/n = 0.498; 0.408; 0.269$ nm).

As it follows from **Figures 7 and 8**, with the temperature increase the degree of crystallinity increases as well.

The 3D-polymeric crystalline or semi-crystalline aluminosilicates of alkali metals are main hydration products of the cements under study at low temperatures (usually below 200°C). Correspondingly, they refer to “zeolites” or “zeolite pre-cursors”. Thermal stability of these phases depends on their structure: some zeolite structures are known to be resistant to heating, and some of them decompose in the process of heating. Among various zeolites able to crystallize in the cement matrix,

Figure 5.
The XRD scans of the metakaolin-based cements after drying at 80°C ($K_2O/R_2O = 0.15$ and SiO_2/Al_2O_3 , respectively: a – 2; b – 3; c – 4; d – 5; e – 6; f – 7. Q – Quartz; N – Natrolite; a – Zeolite-Na-a; U – Ussingite; P' – Phillipsite-Na-K; H – Heulandite-Na; H' – Heulandite-K.

Figure 6.
The SEM images of the metakaolin-based cements after drying at 80°C ($K_2O/R_2O = 0.15$ and SiO_2/Al_2O_3 , respectively: a – 2; b – 3; c – 4; d – 5; e – 6; f – 7 ($\times 2500$)).

only certain zeolites remain their structure until 700–800°C. Thermally stable structures are: sodalite network (hydroxysodalite), analcime, chabazite structures (zeolite-R, herchelite), faujasite family (zeolites-Na-X and Na-Y), mordenite [5–7].

Figure 7.
The XRD scans of the metakaolin-based cement ($K_2O/R_2O = 0.15$ and $SiO_2/Al_2O_3 = 5$) after drying at temperatures, °C: a – 20; b – 40; c – 60; d – 80. Legend: Q – Quartz; A – Zeolite Na-A; P' – Phillipsite-Na-K; H – Heulandite-Na; H' – Heulandite-K.

Figure 8.
The SEM images of the microstructure of the metakaolin-based cement ($K_2O/R_2O = 0.15$ and $SiO_2/Al_2O_3 = 5$) after drying at temperatures, °C: a – 20; b – 40; c – 60; d – 80 ($\times 2500$).

Once these phases (or N-A-S-H gels of similar structure) are synthesized in the cement matrix, they slightly improve their crystallinity during heating until 200–400°C, and then keep their structure up to approx. 800°C and after this re-crystallize with the formation of structurally similar nepheline or albite. Other zeolitic structures, for example, zeolites-Na-A or P, decompose at temperatures within the range of 120–300°C, making impossible to use them in the materials that are resistant at high temperatures.

In studying the influence of the cement composition on the phase composition after heating above the temperature of dehydration, a conclusion was drawn on a correlation between the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio in the initial cement compositions and their dehydration products (**Table 3**). With increase of the ratio from 2 to 8, the reaction products transform in the following direction: nepheline ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) – albite ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$) – α -cristobalite (SiO_2) (**Figure 4**). This tendency in general coincides well with the data obtained on the model systems of the alkali-activated aluminosilicate cements [18, 47]. So, a feldspathoid nepheline ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 2$ in the aluminosilicate framework) appears in a phase composition of the cements with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 2\text{--}4$, irrespectively of a type of the aluminosilicate component used. A maximum XRD- measured quantity of nepheline was found in case when a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio was 2. The increase of the ratio up to 6–8 resulted in the additional formation of α -cristobalite ($d = 0.411; 0.252; 0.206; 0.163 \text{ nm}$). The higher contents of amorphous silica, the higher speed of α -cristobalite formation.

In the fly ash-based cements with the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio = 6, the reaction products are represented by high-silica albite and some amounts of nepheline (**Table 3**). Differences in a phase composition of the metakaolin-based and fly-ash-based cements can be attributed to high contents of main oxides in a non-active form such as quartz and mullite which reduce a real stoichiometric ratio in these two cements.

As mentioned above, a type of the aluminosilicate component used (metakaolin or fly ash) does not affect the differences: once heated to high temperatures (600–1200°C), a microstructure of the cements under study tends to transform into that with the phases resistant to high temperatures. In contrast to the OPC-based cements, no any instable phase was identified. However, metakaolin, a purer aluminosilicate component, gives the higher purity and higher content of the formed high-temperature phases formed. In case of the fly ash the lower quantities of the zeolite-like products, however, with a more variable composition due to small quantities of such oxides as Fe_2O_3 , MgO , CaO , TiO_2 etc. contained in the fly ash are formed.

Aluminosilicate component	SiO ₂ /Al ₂ O ₃ molar ratio	
	Initial cement	Main phase
Metakaolin	2	nepheline
	4	nepheline
	6	α-cristobalite , nepheline
	8	α-cristobalite , nepheline
Fly ash 1	4	nepheline
	6	α-cristobalite , nepheline
	8	α-cristobalite , nepheline

Remark: Dominating phases are given in bold.

Table 3.
The $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of the cements under study after high temperature curing (1200°C).

3.1.3 Role of initial alkalinity (Na₂O/Al₂O₃ ratio)

The alkalis in the alkali-activated aluminosilicate cements participate in all stages of structure formation. In particular, rate and degree of activation of the aluminosilicate component is determined by contents of alkalis [3, 31, 36]. A quantity of alkalis is to be chosen in view of formation of a required phase composition which determines the required properties. For example, the anhydrous aluminosilicates appear in small amounts in the systems with high content of alkali (Na₂O/Al₂O₃ = 1.0) at 600°C, whereas in the low-alkali compositions (Na₂O/Al₂O₃ = 0.5) the crystallization begins only at 1000°C (Table 4) [36, 37].

3.1.4 Role of a cation type and direction of phase transformations

Figures 9 and 10 demonstrate the XRD scans and SEM images of the microstructure of a cleaved fragment of the artificial stone (K₂O/R₂O = 0:0.3, (Na₂O + K₂O)/Al₂O₃ = 1 and SiO₂/Al₂O₃ = 5) after curing at 80°C. At the ratio SiO₂/Al₂O₃ = 5, a phase composition of the artificial stone is characterized by the zeolite-like hydration products of the heulandite and phillipsite types (Figure 9), and the

No	Main oxides, molar ratio			Phase composition after curing at			
	SiO ₂ /Al ₂ O ₃	Na ₂ O/Al ₂ O ₃	Na ₂ O (%)	600°C	800°C	1000°C	1200°C
1	4.0	0.5	6.5	—	N (low)	N, A	A
2	4.0	1.0	12.9	—	N	N	(g)
3	3.5	1.0	13.8	N, C	N	N	(g)

Remark: N – nepheline, A – albite, C – cristobalite, A – albite, (g) – glassy phase (destruction into a sintered phase).

Table 4.
Phase composition of the fly ash 1-based cements vs. quantity of Na₂O.

Figure 9.
The XRD scans of the metakaolin-based cements after drying at 80°C (SiO₂/Al₂O₃ = 5 and K₂O/R₂O, respectively: a – 0; b – 0.15; c – 0.3). Q – Quartz; N – Natrolite; A – Zeolite-Na-A; P' – Phillipsite-Na-K; H – Heulandite-Na; H' – Heulandite-K.

Figure 10.
 The SEM images of the microstructure of a cleaved fragment of the metakaolin-based cements after drying at 80°C ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 5$ and $\text{K}_2\text{O}/\text{R}_2\text{O}$, respectively: a – 0; b – 0.15; c – 0.3) ($\times 2500$).

microstructure of the cement matrix displays a large number of sub-crystal phases (Figure 10).

The phase composition of the alkali-activated aluminosilicate cements (at $\text{K}_2\text{O}/\text{R}_2\text{O} = 0$) is characterized by the zeolite-like hydration products of the following type: natrolite, zeolite-Na-A and heulandite-Na. When potassium ions are replaced by the sodium ions, other zeolite-like hydration products of the potassium heulandite and sodium-potassium phillipsite types appear as well. The presence of the natrolite phase is not observed, the crystallinity of the hydration products increases.

The cements made using sodium compounds (sodium-based cements) are the most widely used cements among the possible alkali-activated aluminosilicate cements due to the lowest price of the alkaline component. The potassium compounds show in some cases better results than the sodium compounds. In particular, potassium aluminosilicates are more thermally resistant compared to the sodium ones: for example, a temperature of thermal destruction (fusion) of orthoclase ($\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$) is 1170°C (against 1118°C of albite ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$)). A well-known fact is that the binary systems like the sodium/potassium system are significantly less thermally resistant compared to pure systems: eutectic solutions are formed in such systems and these mixed systems fuse at the significantly lower temperatures [37]. The same refers to other binary systems (Na/Ca or K/Ca) and a ternary system (Na/K/Ca). It is important in view of wide application of the Ca-containing compounds as cement modifiers: this technology helps to solve a lot of problems associated with ordinary cements [20] but, being applied for making heat-resistant materials, the increased content of Ca may cause low temperature of sintering and high thermal shrinkage. It is to be noted that this rule is only in power at limited contents of CaO (approx. below 10%), because at the higher calcium contents the system begins revealing other behaviour and, in fact, is not itself the alkali-activated aluminosilicate cement.

Curing temperature, (°C)	Reaction products after curing		
	N-A-S-(H)	K-A-S-(H)	N-K-C-A-S-(H)
400–600	none	—	—
600–900	nepheline	mainly leucite, kaliophilite	—
> 900	albite		leucite, then plagioclase

Description: N – Na₂O; K – K₂O; C – CaO; A – Al₂O₃; S – SiO₂; H – H₂O.

Table 5.
Phase composition of the fly ash 1-based cements after high temperature curing vs. cation type.

Formation of the phases in case of the fly ash-based cement, depending upon a type of the cation and curing temperature is shown in **Table 5**: the first phases which appear during heating (at approx. 600–900°C) are low-silica feldspathoids (nepheline in case of the sodium-based cements and leucite in case of the potassium-based ones), whereas high-silica feldspars appear at the higher temperatures (900–1200°C). Thus, the earlier collected data on alkaline activation of various clays [4, 28] showed that a phase composition of the synthesized aluminosilicates of alkali metals could also be regulated by changing a temperature of high-temperature curing. Nepheline is a main reaction product of the system composed of a clay activated by sodium compound after curing at 750–900°C, and albite – after curing at the higher temperatures (900–1000°C). When clays are activated by the potassium compounds, leucite is the main reaction product after high temperature curing [28].

Sodium and calcium compounds result in the synthesis of plagioclases (binary sodium-calcium feldspars such as labradorite). Such results were obtained in the potassium (KOH)- and calcium (OPC clinker)-modified cements [20, 21, 27, 29, 30], in which leucite (a potassium feldspathoid) and labradorite (a sodium-calcium feldspar) are the main phases after high- temperature curing (**Figure 11**). This composition, N-K-C-A-S-H, has an amorphous structure after curing at high temperature (800°C). With temperature increase up to 900°C, according to DTA examination (**Figure 12**), this amorphous phase begins to crystallize. After curing at 1000°C, according to XRD examination, leucite and labradorite occur.

After 1200°C, redistribution of shares of the above listed reaction products begins and, in accordance with their thermodynamic stability at this temperature, a quantity of labradorite increases, whereas that of leucite decreases.

Concluding the above, the formation of a microstructure of the alkali-activated aluminosilicate cements may be expressed by the following scheme:

3.2 Properties of the alkali-activated aluminosilicate cement-based materials

Formation of properties of the materials made using the zeolite-like cement matrices depends upon a cement composition and curing parameters applied to these materials.

The most important characteristics of these materials are mechanical strength (usually evaluated by a residual strength after high-temperature exposure) and stability of volume (evaluated by a thermal shrinkage). Other characteristics that are also important in some cases are resistance against crack formation, thermal resistance and a temperature of deformations under load.

Figure 11.
The XRD scans of the metakaolin-based cement with 10% OPC clinker by mass after curing at 800°C (1), 1000°C (2) and 1200°C (3). (Chamotte (Ch) as a filler)).

Figure 12.
The TGA, DTG and TG of the hydrated metakaolin-based cements. (Chamotte as a filler): 1 – Without OPC clinker; 2 – With 10% OPC clinker by mass.

Compressive strength and thermal shrinkage change with the temperature increase. When thermally stable zeolite-like phases are the main reaction products of the cement matrices, compressive strength and thermal shrinkage change slowly within a temperature range of 200–800°C. Above 800°C, a liquid phase starts to appear. As a result, the strength increases and the shrinkage also increases too (**Figure 13**). Once the thermal shrinkage reaches the values of 1–2%, the materials lose their functionality because of crack formation, instability of volume, etc., despite still high values of compressive strength. A temperature at which a limit value of thermal shrinkage is reached is a maximum use temperature for a material. The use temperature depends chiefly upon alkalinity and a cation type of the alkali compound. The best heat resistant alkali-activated aluminosilicate cement-based materials may withstand temperatures up to 1000°C).

Heat-resistant materials require a stability of volume changes within a wide temperature range. The shrinkage/expansion processes during exposure to temperatures can be regulated by a choice of an optimal cement composition and appropriate heat-resistant fillers, for example, chamotte [48]. The study of interrelation between a cement composition, curing parameters, phase composition of the reaction products and properties of the cement-based materials was carried out on the compositions: cement: chamotte = 1:1 by mass (**Figure 14**). Also, an interrelation between a relative intensity of the crystalline phase formation and the above properties was studied. In this experiment, a maximum height of the peak in the XRD patterns (fixed for the analcime main peak at 0.343 nm in the XRD pattern of the autoclaved fly ash 1 – based cement with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 4$) was taken as 100% (**Figure 15**).

The study of interrelation between cement composition, curing conditions, phase composition of the microstructure and properties of the artificial stone was carried out on the compositions (cement:chamotte = 1:1). It was also found that the 1:1 ratio for the composition “fly ash-based cement – chamotte” was optimal for meeting the requirements with regard to workability retention of the mix and

Figure 13. Compressive strength (a) and thermal shrinkage (b) of the alkali-activated aluminosilicate cement-based materials vs. curing temperature.

Figure 14. Compressive strength (a), residual strength (b), and shrinkage (c) after high-temperature curing at 800 °C (c) molar ratio $\text{Al}_2\text{O}_3/\text{SiO}_2 = 2, 4, 6, 8$ of the cements and mode of pre-curing. (A – Autoclave curing at 174 °C, S – Steam curing at 80 °C, none – Without pre-curing).

compressive strength of the materials both at normal and high temperatures. The higher contents of chamotte the worse are these properties, however, in this case high contents of chamotte help to control shrinkage at high temperatures.

A material made using the alkali-activated aluminosilicate cements with crystalline phases is less inclined to sharp changes in plastic deformations. A crystallization in a ceramic matrix of the compound of the $\text{R}_2\text{O} \cdot \text{Al}_2\text{O}_3 \times (2 \div 6) \text{SiO}_2$ composition, which is analogous to natural nepheline, caliphilite, albite, and orthoclase, is sufficient to produce the materials with properties of ceramics.

Facing materials can be produced using mixed alkali-alkaline earth-activated aluminosilicates of the $\text{mNa}_2\text{O} \cdot (1-m) \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_2$ composition. A conclusion was made that with the increase in the content of the phase of the albite composition ($m \rightarrow 1$) in the reaction products the materials with properties similar to those of facade tiles (water absorption below 10%), and with the increase of the phase of the anorthite composition ($m \rightarrow 0$) – with the properties similar to those of wall ceramics can be produced.

High intensity of crystal formation (higher than 10%) in the compositions after autoclave pre-curing side by side with insufficient degree of crystallization

Figure 15. Relationship between the relative intensity of crystallization and properties of the cement –chamotte compositions: Density, compressive strength after normal temperature curing, residual strength and thermal shrinkage after curing at 800°C.

results in sharp deterioration of the performance properties. In case of low degree of crystallization the structure is characteristic of a weak crystalline framework.

Cement composition		Filler
Aluminosilicate component	SiO ₂ /Al ₂ O ₃	
Metakaolin	4.0	Fly ash 1
Metakaolin	4.0	Fly ash 2
Fly ash 1	4.5	Chamotte
Fly ash 2	5.0	Chamotte

Table 6.
Optimal mixes of the heat resistant composite alkali-activated aluminosilicate cement-based materials.

Taking into consideration the higher reaction ability of metakaolin compared to the fly ash at initial stages of interaction, two systems of heat resistant composite materials were proposed (**Table 6**). These optimized compositions have the initial setting time at 80°C – up to 4 hours, compressive strength – up to 89 MPa, residual strength after high-temperature curing – up to 245% and thermal shrinkage – up to 4.2%. The developed compositions were used for making heat-resistant composite materials for high use temperatures without pre-treatment.

3.3 Experience of application of the alkali-activated aluminosilicate cements

The developed alkali-activated aluminosilicate cement-based materials were used for making a wide range of composite materials [13, 18, 20, 23, 25, 35–37, 44, 47–55] for the use in normal conditions and at high temperatures.

Some examples of production and application of the materials based on the alkali-activated aluminosilicate cements are given below.

3.3.1 Heat insulating materials

- **fibre-reinforced materials (mineral wool, superfine, thin and thickened basalt fibres).** Density of these materials is 90–400 kg/m³, binder content – 2–30% by mass, heat conductivity at 25°C – 0.044–0.056 W/(m·K), compressibility (at P = 0.002 MPa) – 2–35%, temperature resistance of the ready products – within a temperature range of 600–850°C, depending on a fibre type, contents of sorption moisture and water absorption, of the materials meet the Ukrainian standard-specified requirements.
- **with expanded rocks (perlite and vermiculite).** Inorganic nature of these materials and high temperature resistance determines their high fire resistance and fire safety. These materials have density – 150–300 kg/m³, compressive strength – 0.26–1.0 MPa, flexural strength – 0.15–0.3 MPa, heat conductivity – 0.062–0.09 W/(m·K).
- **with mullite-silica fibres** have mean density 310–420 kg/m³, flexural strength – up to 0.4 MPa, the lower heat conductivity at 600°C (0.18–0.22 W/(m·K)) compared to commercial products, the lower loss on ignition (0.01–1%), the increased content of Al₂O₃ + SiO₂ (97–98%) and possess the higher temperature resistance (1300°C).
- **gas concretes** exhibit compressive strength – 2–5 MPa, density – 400–550 kg/m³, much higher temperature resistance – up to 800°C compared to the traditional gas cement concretes. These materials can be recommended for the

use in not only in construction, but for the production of insulation of industrial equipment working at high temperatures.

3.3.2 Constructive materials

- **with basalt rovings** have density 850–1000 kg/m³, surface density – 2.6–9.85 kg/m², binder content – 42–49% by mass, organic matters content of the final product 0–10% by mass, flexural strength – 28–30 MPa, maximum use temperature – 250–500°C. They have equal or considerably higher maximum use temperature (up to 500°C).
- **with glass- and basalt non-woven materials and fabrics** have density 900–1800 kg/m³, binder content – 21–38% by mass, contents of organic matters of the final product – 5–12% by mass, flexural strength – 94–130 MPa, maximum use temperature – 300–400°C, maximum temperature of short-time exposition to high temperatures – 400–500°C.
- **with mullite-siliceous fibres** have density 1600–1700 kg/m³, binder content – up to 25% by mass, flexural strength – up to 11 MPa, maximum use temperature – 1000°C.
- **with carbon fabrics** have density 2200 kg/m³, binder content – 50% by mass, organic matters content of the final product – 11% by mass, flexural strength – up to 110 MPa, maximum use temperature – 300°C.
- **with expanded rocks** have density 640–1600 kg/m³, binder content – up to 25% by mass, compressive strength 1.0–15.0 MPa, flexural strength 2.8–10.0 MPa. These materials possess high heat resistance (residual strength after firing at 800°C is up to 225%).
- **with organic fabrics (jute)** have density 1000–1250 kg/m³, flexural strength 30–45 MPa, Young's modulus – $2\text{--}14 \times 10^9$ Pa, temperature resistance – up to 105°C.

An example of industrial application of the constructive alkali-activated aluminosilicate cement-based materials is a body of a fire fighting bomb. The use of the developed constructive alkali-activated aluminosilicate cement-based materials and basalt fabrics allowed to replace a metallic body of the aerosol forming bomb in fire-fighting, which is heated in the process of blasting and is a source of secondary ignition. Field testing of the bomb showed its efficiency in fire-fighting. The material of the bomb body withstands mechanical and thermic loads occurring in the process of operation and is not a source of secondary ignition.

3.3.3 Abrasion resistant composite materials

The abrasion resistant composites with high thermo-mechanical characteristics and instruments from them were developed through modification of the alkali-activated aluminosilicate cement composition by a silicon carbide. The material of the instruments that were produced commercially in Ukraine had the following properties: compressive strength – 47–50 MPa, flexural strength – 23–25 MPa, breaking strength – 5–7 MPa, thermo-resistance – 25 heat cycles “800 °C – water”.

3.3.4 Glues for wood-based materials

The use of the alkali-activated aluminosilicate cements as a binding agent or adhesive in the production of wood-based materials permits not only to replace toxic organic resins, but to enhance considerably fire resistance.

One more example is the use of the alkali-activated aluminosilicate cements in the production of wood-based materials (chip wood aggregate concretes and wood particle boards).

The wood particle boards have densities from 500 to 1500 kg/m³, flexural strength – 8–20 MPa, swelling – less than 1% for 24 hours, the cement content in them – up to 40% by mass of the ready product.

3.3.5 Binders for metallurgical industry

High thermal resistance of the alkali-activated aluminosilicate cement-based materials allowed to develop a range of products for the needs of metallurgical industry: pipes for feeding metal melt, sieves for melt filtration, heat insulating feeders, etc. The use of these materials allows for to replace high-cost ceramics. Above all, the developed compositions for moulding and core sands to be used in the foundry permit to replace highly toxic organic adhesives. The developed materials are characteristic of high green strength (up to 0.25 MPa) and strength in a dry state – up to 7.5 MPa, required minimal strength of a moulding sand after metal is fed, high values of sand reclamation (80–90%), thus meeting the requirements applied to moulding sands.

Intumescent fireproofing and expanded heat insulating coatings based on the alkali-activated aluminosilicate cements have coefficient of volume increase – 15–23, compressive strength – up to 4.6 MPa, water absorption – below 10% by mass, adhesion to metal – 0.78–0.84 MPa and ceramics – 4.8–5.0 MPa. The expanded coatings are characteristic of coefficient of heat conductivity (λ)–0.041–0.065 W/m·°C. Fireproofing coatings for wood, wood-based materials and fibre-reinforced boards are characteristic of resistance in an open flame (800–1000°C) for 10–20 minutes. The tests and introduction at the enterprises of Ukraine showed their efficiency in replacing traditional compositions made using organic components.

Corrosion resistant coatings made with using the alkali-activated aluminosilicate cements have compressive strength after hardening within a temperature range of 20–150°C – 50–110 MPa, changes in mass and volume after boiling in 2% milk acid solution – 1.5–2.0%, whereas in 1–3% solutions of sulphuric acid – 2–2.5% with a coefficient of resistance 0.85–0.97 in organic mediums and 0.7–0.78 in sulphuric acid. The use of autoclave treatment allows to produce a material, which is able to withstand exposure 5–10% concentrations of these chemicals, coefficient of resistance after attacks of organic chemicals being 0.98–1.00, of sulphuric acid – 0.8–1.0 and volume changes – 2.0–2.5%. Adhesion between the coating and concrete – 3–8 MPa. The composites with the enhanced acid resistance were used in a two-layered coating of the external lining of a sewage waters disposal canal. The coatings can be recommended for service in the solutions of sulphuric acid (with concentrations below 5%), pickling solutions and solutions of heavy metal salts.

3.3.6 Glues for repairing and restoration

A variety of the alkali-activated aluminosilicate cement-based materials for repairing and restoration needs was developed: primers and putties etc.

Materials to be glued together	Ratio of summary areas in non-uniform breaking, %		
	Cohesion failure (in adhesive), no more than	Adhesion failure (Interaction zone “material-adhesive”), more than	Failure in fibre, not less than
Heat insulating board – paperboard	5	5	90
Paperboard – steel sheet	20	30	50
Heat insulating board – steel sheet	20	30	50
Heat insulating board – aluminium sheet	20	30	50

Table 7.
Properties of the adhesive joints made using the alkali-activated aluminosilicate cement.

3.3.7 Inorganic adhesives

One of the most effective application of the alkali-activated aluminosilicate cements is to use them as inorganic binders for anchoring application, for bonding together various materials: mineral fabrics, fibre-reinforced heat insulating articles and paper, concrete, brick and ceramics, wood with concrete and gypsum, for metal, expanded polystyrene, plastics etc. The adhesive joints exhibit strength in non-uniform pulling-out – 3–15 MPa, high freeze–thaw resistance (more than 100 cycles) and water resistance. Examples of the use of these adhesives are given in **Table 7**.

3.3.8 Acid resistant ceramic materials

Basing on the mixed albite-orthoclase compositions of the reaction products that are used as binders and silica sand as filler, the acid resistant ceramic materials with the properties of traditional acid resistant materials based on clays and those very

Characteristics	Materials based on alkali-activated aluminosilicate binders	Cast basalt	Ceramics based on clays
Water absorption, %	0.2–5.0	0.05	2–10
Volume mass, kg/m ³	2200–2400	3000	2000–2170
Strength, MPa			
compressive	110–200	250–300	30–90
flexural	25–40	50–65	10–20
tensile	12–20	30	6–10
Acid resistance, %	98.0–99.6	99.0–99.6	95.0–98.0
Thermal resistance, a number of heating-sharp cooling cycles	5–30	3–3	2–20
Wear abrasion, kg/m ²	0.30–0.50	0.15–0.25	0.60

Table 8.
Comparative physico-mechanical characteristics of the acid resistant ceramic materials.

close to cast basalt (**Table 8**) can be produced. A curing temperature is between 1150 and 1200°C.

Testing by boiling of the specimens in H₂SO₄, HCl, and HNO₃ for 700 hr. showed that with the longer duration the rate of degradation of the material tended to decrease, on the contrary to the acid resistant ceramics based on clays, the process of degradation of which in the same conditions became more intensive.

Water absorption, mechanical strength and acid resistance of the materials after storage for 12 months in H₂SO₄-solutions (98, 60, and 30% concentration), in HCl-solutions (30, 20, and 10% concentrations) and in HNO₃-solutions (60, 30, and 10% concentrations) suggested to conclude that corrosion of the acid resistant materials based on the alkali-activated aluminosilicate cements tended to decrease. Long-term testing showed high resistance of these materials not only in mineral acids, but in chlor-containing air media.

4. Conclusions

The zeolite-like analogies to natural aluminosilicate minerals may be synthesized in the cement matrices of the Na(K)-Al₂O₃-SiO₂-H₂O system. Hydrous zeolites are formed in this system after 80 °C, after 600°C (within a temperature interval of 600–1200°C) they transform into anhydrous zeolites. The structure formation and properties of the alkali-activated aluminosilicate cement-based materials at low temperatures may be regulated by changing a cement composition, curing conditions, type and concentration of the alkaline activator solution as well as the solution to solid ratio. A directed regulation of the low-temperature structure formation process is a key instrument allowing to obtain a wide range of special materials using various types of the alkali-activated aluminosilicate cement and curing conditions. At high temperatures, the only significant factors affecting a phase composition and properties are an initial cement composition and a curing temperature. Regulation of the high-temperature structure formation is important in order to develop heat- and fire- as well as acid resistant materials. High durability of the alkali activated cement matrix can be attributed to a synthesis of the zeolite-like analogies to natural minerals. Excellent performance properties and high durability of the alkali-activated aluminosilicate cement-based materials for high temperature uses are provided due to smooth dehydration and subsequent re-crystallisation of the hydration products into stable anhydrous aluminosilicates of alkali metals.

Author details

Pavel Krivenko* and Volodymyr Kyrychok
Scientific Research Institute for Binders and Materials, Kyiv National University of Construction and Architecture, Kyiv, Ukraine

*Address all correspondence to: v.kyrychok@gmail.com

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References

- [1] Malinowski R. Concretes and mortars in ancient aqueducts. *Concrete International*. 1979; (1)1: 66–76.
- [2] Davidovits J. Design and Construction. *Concrete International*. 1987; (9)12: 23.
- [3] Krivenko P. Why alkali activation – 60 years of the theory and practice of alkali- activated materials. *Ceram. Sci. Technol*. 2017; 8(3): 3203–333. <https://doi.org/10.441/JCST2017-00042>
- [4] Glukhovskiy V. Durability of Concrete. In *Proceedings of the Intern. Seminar*. Göteborg; 1989. p. 53–62.
- [5] Breck D. *Zeolite Molecular Sieves*. J. Wiley & Sons: New York; 1974.
- [6] Barrer R. *Hydrothermal Chemistry of Zeolites*. Academic Press: London; 1982.
- [7] Dyer A. *An Introduction to Zeolite Molecular Sieves*. J. Wiley & Sons: New York; 1988.
- [8] Davidovits J. Geopolymer chemistry and properties. In *Proceedings of the 1st European Conf. on Soft Mineralurgy “Geopolymer’88”*; Saint-Quentin; 1988. p. 25–48.
- [9] Krivenko P. Alkaline cements: terminology, classification, aspects of durability. In *Proceedings of the Tenth International Congress on the Chemistry of Cement*; Göteborg; 1997. p. 4iv046-4iv050.
- [10] Sukhanovich M., Guzii S. The effect of technological factors on properties of alkali aluminosilicate systems used for preparation of fireproof coatings. *Refractories and Industrial Ceramics*. 2004; 45(3): 217–219. <https://doi.org/10.1023/B:REFR.0000036733.85631.f1>
- [11] Krivenko P., Pushkareva Y., Sukhanovich M., Guzii S. Fireproof coatings on the basis of alkaline aluminium silicate systems. *Ceramic Engineering and Science Proceedings*. 2009; 29(10): 129–142.
- [12] Krivenko P., Guzii S. Aluminosilicate coatings with enhanced heat- and corrosion resistance. *Applied Clay Science*. 2009; 73(1): 65–70. doi: 10.1016/j.clay.2012.10.010
- [13] Kovalchuk G., Krivenko P. Producing fire-and heat-resistant geopolymers. In: *Geopolymers: Structures, Processing, Properties and Industrial Applications*. Woodhead Publishing; 2009. p. 227–266
- [14] Kravchenko A., Guzii S. Determining the fire resistance properties of timber, protected by geocement-based coatings. *Eastern European Journal of Enterprise Technologies*. 2015; 1(5): 38–41. <https://doi.org/10.15587/1729-4061.2015.36843>
- [15] Kryvenko P., Tsapko J., Guzii S., Kravchenko A. Determination of the effect of fillers on the intumescent ability of the organic-inorganic coatings of building constructions. *Eastern European Journal of Enterprise Technologies*. 2016; 5(10–83): 26–31. <https://doi.org/10.15587/1729-4061.2016.79869>
- [16] Tsapko Y., Kyrycyok V., Tsapko A., Bondarenko O., Guzii S. Increase of fire resistance of coating wood with adding mineral fillers. *MATEC Web of Conferences*. 2018; 230: 20–34. doi: 10.1051/matecconf/201823002034
- [17] Xu H., Van Deventer J. In *Proceedings of the Second International Conf. on Geopolymers “Geopolymer’99”*; Saint-Quentin; 1999. p. 43–64.
- [18] Krivenko P., Skurchinskaya J. In *Proceedings of the Intern. Conf. on the*

Utilization of Fly Ash and other Coal Combustion By-Products. Shanghai. 1991. p. 64–1 – 64-7.

[19] Duan P, Yan C, Zhou W., Luo W. Thermal Behaviour of Portland Cement and Fly Ash-Metakaolin-Based Geopolymer Cement Pastes. *Arab. J. Sci. Eng.* 2015; 40: 2261–69. DOI 10.1007/s13369-015-1748-0

[20] Pangdaeng S., Phoo-ngernkham T., Sata V., Chindaprasit P. Influence of curing conditions on properties of high calcium fly ash geopolymer containing Portland cement as additive. *Materials & Design*. 2014; 53: 269–274. doi:10.1016/j.matdes.2013.07.018

[21] Bernal S, Rodríguez D, De Gutiérrez R, Gordillo M, Provis J. Mechanical and thermal characterisation of geopolymers based on silicate-activated metakaolin/slag blends. *Mater. Sci.* 2011; 46: 5477.

[22] Duxson P, Provis J, Lukey G, Mallicoat S, Kriven W, Van Deventer J. Understanding the relationship between geopolymer composition, microstructure and mechanical properties. *Colloids and Surfaces. Physicochem.* 2005; 269: 47–58. doi: 10.1016/j.colsurfa.2005.06.060

[23] Barbosa V F, MacKenzie K J. Thermal behaviour of inorganic geopolymers and composites derived from sodium polysialate. *Mater. Res. Bulletin*. 2003; 38: 319–31. doi:10.1016/S0025-5408(02)01022-X

[24] Saavedra W.G.V., De Gutierrez R. M. Performers of geopolymer concrete composed of fly ash after exposure to elevated temperatures. *Construction and Building materials*. 2017; 154: 229–235. <https://doi.org/10.1016/j.conbuildmat.2017.07.208>

[25] Lee N., Koh K., An G., Ryu G. Influence of binder composition on the gel structure in alkali activated fly ash/

slag pastes exposed to elevated temperatures. *Ceramics International*. 2017; (43)2: 2471–2480. doi:10.1016/j.ceramint.2016.11.042

[26] Rivera O., Long W., Weissjr C., Moser R., Williams B., Torres-Cacel K., Gore E., Allison P. Effect of elevated temperature on alkali-activated geopolymeric binders compared to Portland cement-based binders. *Cement and Concrete Research*. 2016; 90: 43–51. <https://doi.org/10.1016/j.cemconres.2016.09.013>

[27] Wang W-Ch, Wang H-Yu, Lo M-h. The engineering properties of alkali-activated slag pastes exposed to high temperatures. *Construction and Building materials*. 2014; 68: 409–415. <https://doi.org/10.1016/j.conbuildmat.2014.06.016>

[28] Hlaváček P, Šmilauer V, Škvára F, Kopecký L, Šulc R. Inorganic foams made from alkali-activated fly ash: Mechanical, chemical and physical properties. *Eur. Ceram. Soc.* 2015; 357: 03–09. doi:10.1016/j.jeurceramsoc.2014.08.024

[29] Zhang H, Kodur V, Qi S, Cao L, Wu B. Development of metakaolin–fly ash based geopolymers for fire resistance applications. *Constr. Build. Mater.* 2014; 55: 38–45. doi:10.1016/j.conbuildmat.2014.01.040

[30] Rovnaník P, Bayer P, Rovnaníková P. Characterization of alkali activated slag paste after exposure to high temperatures. *Constr. Build. Mater.* 2013; 47: 1479–87. DOI:10.1016/j.conbuildmat.2013.06.070

[31] Bakharev T. Thermal behaviour of geopolymers prepared using class F fly ash and elevated temperature curing. *Cem. Concr. Res.* 2006; 36: 1134–1147. doi:10.1016/j.cemconres.2006.03.022

[32] Sitarz M., Hager I., Kochanek J. Effect of High Temperature on

- Mechanical Properties of Geopolymer Mortar. In: Proceedings of the MATBUD'2018 – 8th Scientific-Technical Conference on Material Problems in Civil Engineering MATEC; 15 June 2018; MATBUD; 2018. doi: 10.1051/mateconf/201816306004
- [33] Su H., Xu J., Ren W. Mechanical properties of geopolymer concrete exposed to dynamic compression under elevated temperatures. *Ceramics International*; 2017; (43)2: 2471–2480. doi:10.1016/j.ceramint.2015.11.055
- [34] Zulkifly K., Young H.C., Abdullah M.M.A B., Ming L.Y., Panias D., Sakkas K. Review of Geopolymer Behaviour in Thermal Environment. In: Proceedings of the Int. Conf. on Innovative Research–ICIR EUROINVENT 2017; Materials and Engineering Vol. 209 (2017) Doi: 10.1088/1757-899X/209/1/01/2085
- [35] Sotiriadis K., Guzii S., Kumpová I., Mácová P., Viani A. The effect of firing temperature on the composition and microstructure of a geocement-based binder of sodium water-glass. *Solid State Phenomena*. 2017; 267: 58–62. doi: 10.4028/www.scientific.net/SSP.267.58
- [36] Sotiriadis K., Guzii S., Macova P., Viani A., Dvorak K., Drdacky M. Thermal Behaviour of an Intumescent Alkaline Aluminosilicate Composite Materials for Fire Protection of Structural Elements. *Mater. Civ. Eng.* 2019; 31(6): 04019058. Doi:10.1061/(ASCE)MT.1943-5533.0002702
- [37] Krivenko P., Guzii S., Bodnarova L., Valek J., Hela R., Zach J. Effect of thickness of the intumescent alkali aluminosilicate coating on temperature distribution in reinforced concrete. *Journal of Building Engineering*. 2016; 8: 14–19. doi:10.1016/j.jobbe.2016.09.003
- [38] Duxson P., Provis J., Lukey G., Separovic F., van Deventer J. ²⁹Si NMR study of structural ordering in aluminosilicate geopolymer gels. *Langmuir*. 2005; 21(7): 3028–3036.
- [39] Van Deventer J. S. J., Provis J. L., Duxson P., Lukey, G. C. Reaction mechanisms in the geopolymeric conversion of inorganic waste to useful products. *Journal of hazardous materials*. 2007; (139)3: 506–513.
- [40] Davidovits J. Geopolymeric Reaction in Archeological Cements and in Modern Blended Cements. In: Proceedings of the Geopolymer '88; 1988 Jun 1–3; Compiègne, France. p. 93–105.
- [41] Duxson P., Lukey G., Separovic F., Van Deventer J. Effect of alkali cations on aluminum incorporation in geopolymeric gels. *Industrial & Engineering Chemistry Research*. 2005; 44(4): 832–839.
- [42] Davidovits J. Geopolymers: inorganic polymeric new materials. *Journal of Thermal Analysis and calorimetry*. 1991; 37(8): 1633–1656.
- [43] Swaddle T., Salerno J., Tregloan P. Aqueous aluminates, silicates, and aluminosilicates. *Chemical Society Reviews*. 1994; 23(5): 319–325.
- [44] Petranek V., Krivenko P., Petropavlovskiy O., Guzii S. Perlite concrete based on alkali activated cements. *Advanced Materials Research*. 2014; 897: 280–283. doi:10.4028/www.scientific.net/AMR.897.280
- [45] Palomo Á., Alonso S., Fernandez-Jiménez A., Sobrados I., Sanz J. Alkaline activation of fly ashes: NMR study of the reaction products. *Journal of the American Ceramic Society*. 2004; 87(6): 1141–1145.
- [46] Fernández-Jiménez A., Palomo A., Sobrados I., Sanz J. The role played by the reactive alumina content in the alkaline activation of fly ashes. *Microporous and Mesoporous materials*. 2006; 91(1–3): 111–119.

- [47] Turker H., Alcikani M., Durmus I., Ozbay E., Erdemir M. Microstructural alteration of alkali activated slag mortars depend on exposed high temperature level. *Construction and Building materials*; 2014: 409–415. [https://doi:10.1016/j.conbuildmat.2015.12.070](https://doi.org/10.1016/j.conbuildmat.2015.12.070)
- [48] Rovnaník P., Šafránková K. Thermal Behaviour of Metakaolin/Fly Ash Geopolymers with Chamotte Aggregate. *Materials*. 2016; 9: 535. doi:10.3390/ma9070535 www.mdpi.com/journal/materials
- [49] Duxson P, Lukey G, van Deventer J. Physical evolution of Na-geopolymer derived from metakaolin up to 1000 C. *Mater. Sci.* 2007; 42: 3044–54.
- [50] Duxson P, Lukey G, Deventer J. Evolution of gel structure during thermal processing of Na-geopolymer gels *Langmuir*. 2006; 22: 8750–8757. DOI:10.1021/la0604026
- [51] Petránek V., Guziy S., Sotiriadis K., Nevřivová L. Study on the properties of geocement based thermal insulating materials for high temperature technical appliances. *Advanced Materials Research*. 2013; 734–737: 2356–2359. doi:10.4028/www.scientific.net/AMR.734-737.2356
- [52] Petránek V., Guzii S., Kryvenko P., Sotiriadis K., Kravchenko A. New thermal insulating material based on geocement. *Advanced Materials Research*. 2014; 838–841: 183–187. doi:10.4028/www.scientific.net/AMR.838-841.183
- [53] Petránek V., Nevřivová L., Zezulová D., Guziy S. Thermal Insulating Materials for Energy Storage Application. *Advanced Materials Research*. 2014; 911: 30–35. doi:10.4028/www.scientific.net/AMR.911.30
- [54] Petránek V., Guzii S., Kryvenko P., Sotiriadis K., Maňák J. Use of thermal insulating perlite composite materials based on geocement to protect technological equipment. *Advanced Materials Research*. 2014; 860–863: 1342–1345. doi:10.4028/www.scientific.net/AMR.860-863.1342
- [55] Krivenko P., Mokhort M., Petropavlovskii O. Industrial Uses of Geocement-based Materials in Construction and Other Industries. In the Proceedings of the Int. Conf. “Geopolymer” (2002).