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Article

# Design Characterization and Incorporation of the Alkaline Alumino-Silicate Binder in Temperature Insulating Composites

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**Abstract:** The paper covers the development of formulations and technology for low energy building materials based on the alkaline alumino-silicate binder and appropriate for special purposes. The microstructure of the binder was investigated using scanning electron microscopy and atomic force microscopy. The identification of the phase compositions was done by means of X-ray diffraction. By leach rate measurement and chemical analysis of pore liquid, the linkage of the alkali metal ions in water-insoluble composites was researched. The dependence of structure formation on mix design and curing conditions was investigated. Specific examples of manufacture and application of binder-based glues and adhesives have been considered, incl. ones for low-temperature insulating composite materials, heat insulation perlite-based materials, heat insulation of industrial boilers, and the fire resistant heat insulating system. The advantages of the binder-based temperature insulating composites compared to traditionally used ones are shown.

**Keywords:** alkaline alumino-silicate binder; mix design; curing conditions; durability; linkage; structure formation; zeolite-like reaction product; material for special application

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## 1. Introduction

Considering the consequences of military actions, terrorism, and natural disasters, today puts forward increasingly high demands for the reliable protection of objects of critical military and civil infrastructure, including strategic purposes. Composite materials for the construction and protection of critical infrastructure facilities should be based on mineral binders that don't require complex manufacturing technologies, also to be environmentally friendly, have low energy consumption, and characterized by stable characteristics under the influence of various aggressive factors, primarily high temperatures and fire. Also important is to reduce energy consumption due to the higher efficiency of insulating composites used both in civil engineering and in industry.

A possibility to synthesize alkaline hydro-alumino-silicates, the analogues of natural zeolites, using a mixture of natural (clays) and artificial alumina-silicate with alkali metal compounds, under conditions of hydrothermal and low temperature thermal treatment under regimes used in the production of building materials, was established by Victor Glukhovsky [1]. This evidence was based on modeling studies of natural processes during the formation of alkaline zeolite-like alumino-silicates at different temperatures. An important conclusion was made, that increase of temperature promoted a smooth dehydration process and subsequent re-crystallization of the hydration products into stable anhydrous alumino-silicates of alkali metals, i.e. Li, Na, K, Rb, and Cs [2]. The alkali metals compounds act not only as activators of hardening but also are responsible for the formation of the main structural elements of the alkali-activated materials. Just these reaction products, analogs to

natural zeolites of the  $\text{Na}_2\text{O}(\text{K}_2\text{O})\cdot\text{Al}_2\text{O}_3\cdot(2\ldots 4)\text{SiO}_2\cdot\text{nH}_2\text{O}$  type, has been discovered in ancient concretes (Ancient Greece, Ancient Rome, Egypt, Syria) [3]. The durability of the ancient concretes and the similarity of their structure with that of the alkali-activated cement concretes allowed us to predict the high durability of the last ones. Thus, the effectiveness and high performance properties of alkali-activated materials, such as increased strength [4], heat resistance [5], corrosion resistance [6], and freeze-thaw resistance [7], have been confirmed by over 65 years experience of their service.

As it was later noted, the types of synthesized zeolite-like products are determined by the structural features of the alumino-silicate component (precursor), its composition, the conditions, intensity of chemical reaction, and the mix design of starting compositions [8–12]. The most appropriate for the mentioned goals are natural clays in a dehydrated state, volcanic rocks, industrial by-products like fuel ashes and slags, metallurgical slags, red mud, etc. [9, 13–19].

Conditionally, the alkali-activated materials can be divided into alkaline cements and geopolymers (geocements) [20]. Depending on the precursor, certain phase ratios are formed in the systems  $\text{CaO}\text{-}\text{Al}_2\text{O}_3\text{-}\text{SiO}_2\text{-}\text{H}_2\text{O}$ ,  $\text{R}_2\text{O}\text{-}\text{CaO}\text{-}\text{Al}_2\text{O}_3\text{-}\text{SiO}_2\text{-}\text{H}_2\text{O}$ , and  $\text{R}_2\text{O}\text{-}\text{Al}_2\text{O}_3\text{-}\text{SiO}_2\text{-}\text{H}_2\text{O}$ , where R – Na, K, Li [21]. The binder systems can be characterized as high-calcium, intermediate (hybrid), and low-calcium ones [22].

Currently, good experience has been accumulated in producing composite materials based on zeolite-like matrices of the low-calcium system  $\text{Na}_2\text{O}(\text{K}_2\text{O})\text{-}\text{Al}_2\text{O}_3\text{-}\text{SiO}_2\text{-}\text{H}_2\text{O}$ , i.e. the alkaline alumino-silicate binder [23, 24, 25, 26, 27].

An analysis of this experience showed that the use of zeolite-like binder systems for the production of building materials, for both general construction and special applications, makes it possible to solve the problems of durability, energy saving, and environmental protection more effectively compared to traditional binder systems [13, 23].

The principles of polymerization of silicate structures resulted in the formation within the reaction products, that are analogous to natural minerals (zeolites and feldspathoids), which have been taken for creating a zeolite-like artificial stone. By the compositional build-up of main structural elements, the natural zeolites may be referred to inorganic polymers, which, on the one hand, are analogous to organic ones (elasticity, corrosion resistance, and adhesion to various materials), and on the other hand, due to a mineral nature, are ecologically pure, heat- and fire-resistant [9, 13]. As the theoretical premises for the creation of alkali-activated materials with polymeric structure, there has been taken the researches aimed at the synthesis of the analogs to natural minerals, based on clays of various structural types and alkali metal compounds [3, 8, 26]. The practical results, concerning the application of these systems in different sectors of construction, were also used [28–38]. But, the next objective here is to create the low energy technology for obtaining water resistant composite at low temperatures.

The purpose of this paper was to propose an approach to mix design of the alkaline alumino-silicate binder's (further, the binder) structure formation under various curing conditions to obtain composite materials for special applications.

## 2. Raw materials and testing techniques

As the object of research, the binder of the system  $\text{Na}_2\text{O}(\text{K}_2\text{O})\text{-}\text{Al}_2\text{O}_3\text{-}\text{SiO}_2\text{-}\text{H}_2\text{O}$  with different ratios of oxides ( $\text{Na}_2\text{O}(\text{K}_2\text{O})/\text{Al}_2\text{O}_3$  and  $\text{SiO}_2/\text{Al}_2\text{O}_3$ ) was used. The binder was prepared using metakaolin (powder) as the main alumino-silicate component, as well as soluble glass and caustic alkalies as alkaline components.

Chemical composition of metakaolin, % by mass: 0.27 CaO; 54.08 SiO<sub>2</sub>; 43.61 Al<sub>2</sub>O<sub>3</sub>; 0.77 Fe<sub>2</sub>O<sub>3</sub>; 0.52 MgO; 0.25 K<sub>2</sub>O+Na<sub>2</sub>O.

The identification of the phase composition of the binder was done by means of X-ray diffraction (XRD), using a single-crystal X-ray diffractometer equipped with a copper anode and nickel filter at  $U = 30$  kV,  $I = 10\ldots 20$  mA and range of the registered angles ( $2\theta$ )  $8\ldots 60$  (rotation speed of the counter 2 degrees per minute by technique reported in [39]. The X-ray spectrums were identified according to the references [40, 41, 42].

A microstructure of the binder was investigated using a scanning electron microscope (SEM) with the settings as follows: accelerating voltage – up to 35 kV; SEI mode resolution – 5 nm; magnification – from 10 to 250.000. The settings of the energy dispersive X-ray spectrometer were as follow: analyzed element range – from Na; energy resolution – 143 eV at MnK $\alpha$ ; energy range – up to 30 kV.

The microstructure of the binder was also investigated using atomic force microscope (AFM), designed by the V.A. Belii institute for mechanics of metal-polymer systems of the National academy of sciences of Belarus.

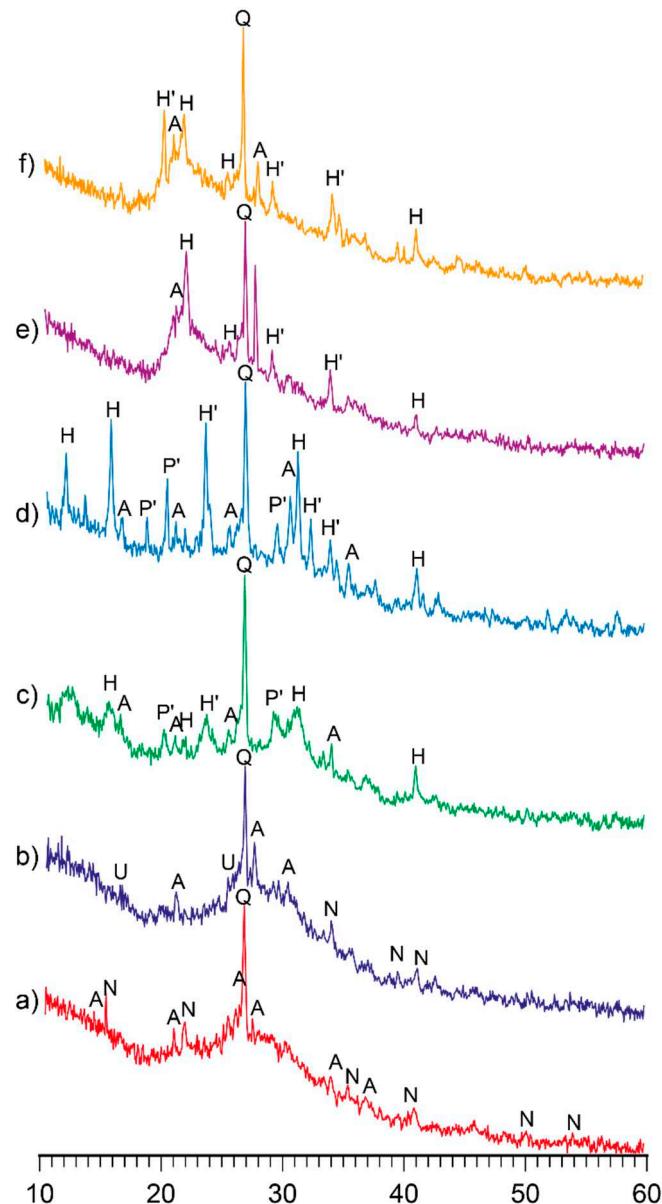
By various methods of the analysis (leaching of the hardened binder and chemical analysis of an interstitial liquid) the linkage of alkali metals ions in water-insoluble compounds was investigated [43].

### 3. Results and discussions

#### 3.1. Research in influence of initial composition and type of curing on structure formation of the alkaline alumino-silicate binder

##### 3.1.1. Influence of mix design

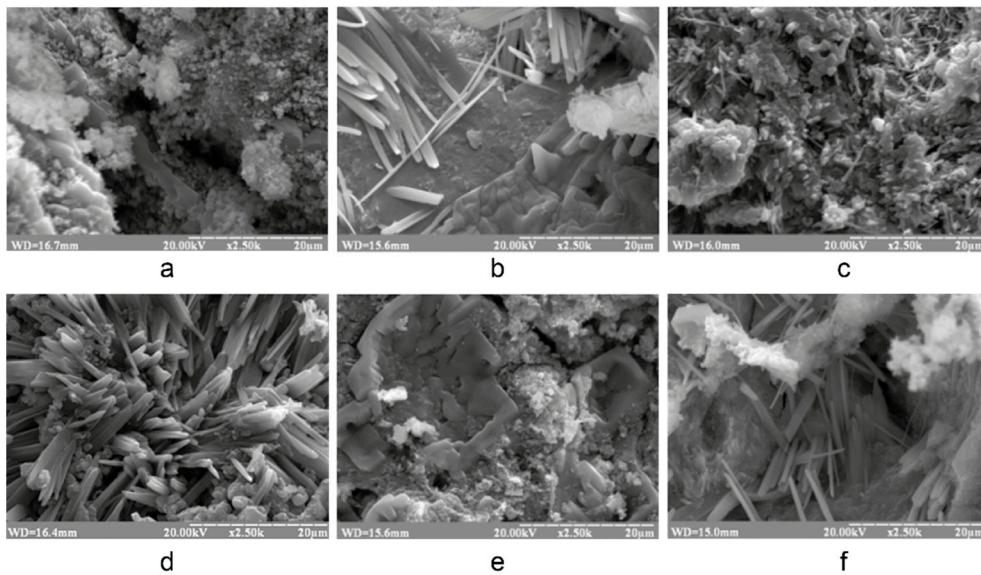
Figure 1, 2 demonstrate XRD patterns and SEM images of artificial stone, that was obtained depending on the ratio  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 2\dots 7$  in the original composition of alkaline hydro-alumino-silicate (at ratios  $\text{K}_2\text{O}/(\text{Na}_2\text{O}+\text{K}_2\text{O}) = 0.15$  and  $(\text{Na}_2\text{O}+\text{K}_2\text{O})/\text{Al}_2\text{O}_3 = 1$ ), and after hardening of the binder at  $t = 80^\circ\text{C}$ .



**Figure 1.** XRD patterns of the binder, obtained after its hardening at  $t = 80\text{ }^{\circ}\text{C}$  and at constant ratio  $\text{K}_2\text{O}/(\text{Na}_2\text{O}+\text{K}_2\text{O}) = 0.15$  and different ratios  $\text{SiO}_2/\text{Al}_2\text{O}_3$ : a – 2; b – 3; c – 4; d – 5; e – 6; f – 7.

Abbreviations: Q – quartz; N – natrolite; A – analcime; U – usingite; P' – Na-K phillipsite; H – Na-heulandite; H' – K-heulandite.

Phase composition of reaction products, at low ratios  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 2\ldots 3$ , is characterized by zeolite-like formations: analcime ( $d/n=0.699; 0.365; 0.336; 0.293\text{ nm}$ ), natrolite ( $d/n=0.287; 0.243; 0.138\text{ nm}$ ), usingite ( $d/n=0.492; 0.347; 0.295\text{ nm}$ ). The presence of amorphous phases, presented by alkaline hydro-alumino-silicates and particles of non-reacted metakaolin, was confirmed (Figure 2).



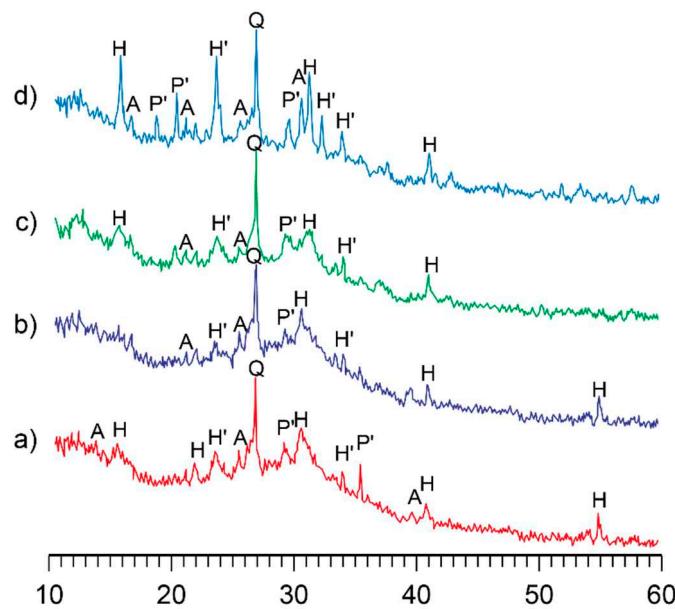
**Figure 2.** SEM images of the cleavage surface of the binder, obtained after its hardening at  $t= 80\text{ }^{\circ}\text{C}$  and at constant ratio  $\text{K}_2\text{O}/(\text{Na}_2\text{O}+\text{K}_2\text{O}) = 0.15$  and different ratios  $\text{SiO}_2/\text{Al}_2\text{O}_3$ : a – 2; b – 3; c – 4; d – 5; e – 6; f – 7 (magnification  $\times 2.5\text{K}$ ).

The hardened binder with the ratio  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 4\ldots 5$  is characterized by the presence of zeolite-like formations: analcime ( $d/n=0.699$ ; 0.365; 0.336; 0.293 nm), sodium heulandite ( $d/n = 0.509$ ; 0.392; 0.296 nm), potassium heulandite ( $d/n = 0.342$ ; 0.281; 0.273 nm) and sodium-potassium phillipsite ( $d/n = 0.498$ ; 0.408; 0.269 nm). The crystallinity of the structure is rather high, which follows from the intensity of diffraction bursts (Figure 1) and the microstructure of artificial stone (Figure 2).

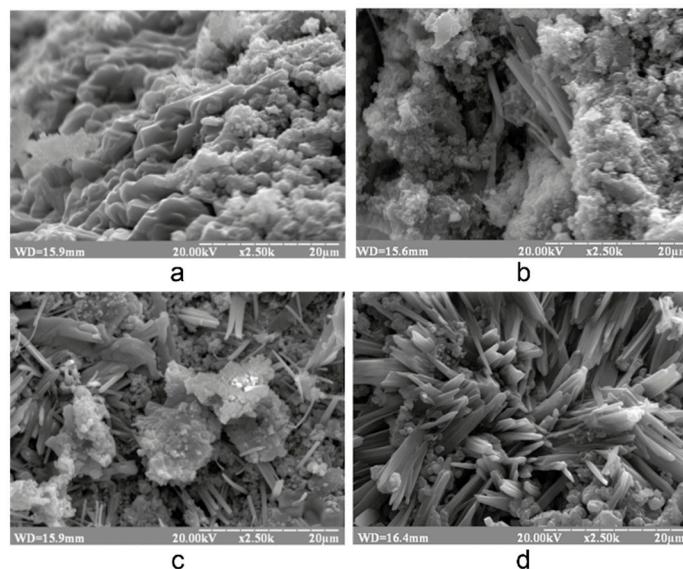
As it was previously noted, modification of the binder by Ca-containing additives caused the formation of zeolite-like reaction products of the hybrid type, specifically: calcium-sodium hydro-alumino-silicates and insignificant content of Na- and K-heulandites [44]. In this way, it was possible to accelerate the strength gain of artificial stone and to ensure its water resistance under the normal temperature of hardening ( $t= 20 \pm 2\text{ }^{\circ}\text{C}$ ). The examples of Ca-containing modifiers that were tested: Portland cement, ground granulated blast furnace slag,  $\text{Ca}(\text{OH})_2$ , and  $\text{CaCO}_3$ .

### 3.1.2. Influence of the curing conditions

The influence of temperature during the hardening of the binder on its phase composition of the binder was analyzed. It was defined that phase composition of alkaline hydro-alumino-silicate at the ratios of  $\text{K}_2\text{O}/(\text{Na}_2\text{O}+\text{K}_2\text{O}) = 0.15$  and  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 5$  is characterized by the presence of zeolite-like formations: analcime, potassium and sodium heulandite, as well as sodium-potassium phillipsite (Figure 3). Thus, the structure formation of artificial stone accelerates with rising temperature without affecting the phase composition, but the increasing crystallinity of the reaction products has been noted (Figure 4).

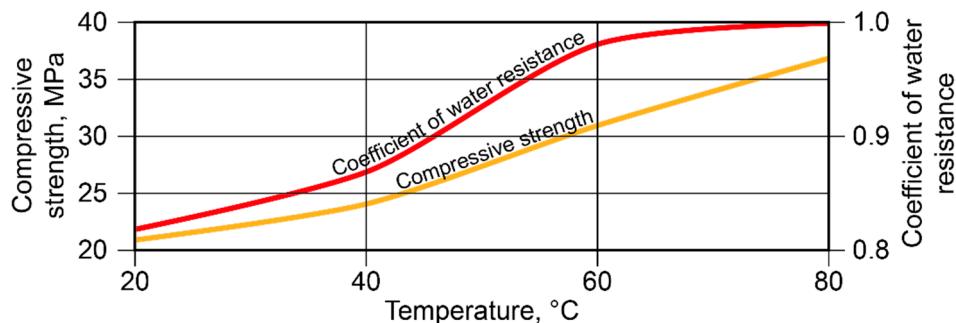


**Figure 3.** XRD patterns of the binder, obtained at constant ratios  $K_2O/(Na_2O+K_2O) = 0.15$  and  $SiO_2/Al_2O_3 = 5$ , after its hardening at temperatures,  $^{\circ}C$ : a – 20; b – 40; c – 60; d – 80.  
Abbreviations: Q – quartz; A – analcime; P' – Na-K phillipsite; H – Na heulandite; H' – K heulandite.



**Figure 4.** SEM images of the cleavage surface of the binder, obtained at constant ratios  $K_2O/(Na_2O+K_2O) = 0.15$  and  $SiO_2/Al_2O_3 = 5$ , after its hardening at temperatures,  $^{\circ}C$ : a – 20; b – 40; c – 60; d – 80 (magnification x2.50K).

At the ratios  $SiO_2/Al_2O_3 = 5$  and  $K_2O/(Na_2O+K_2O) = 0.15$ , a substantial increase in strength occurs at  $t = 40...80$   $^{\circ}C$  (Figure 5). The highest values of water resistance for artificial stone can be obtained after the thermal treatment at  $t = 60...80$   $^{\circ}C$ .



**Figure 5.** Influence of temperature during the binder's hardening on its compressive strength and coefficient of water resistance at the ratios  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 5$  and  $\text{K}_2\text{O}/(\text{Na}_2\text{O}+\text{K}_2\text{O}) = 0.15$ .

For the binders with general structural formula  $(0.7\dots1.0\text{Na}_2\text{O}+0\dots0.3\text{K}_2\text{O})\cdot\text{Al}_2\text{O}_3\cdot2\dots7\text{SiO}_2\cdot\text{nH}_2\text{O}$  it was revealed that phase composition of artificial stone depends mainly on the ratio of oxides, and temperature, in the range of  $20\dots80$  °C, increases the rate of structure formation of zeolite-like hydro-alumino-silicates.

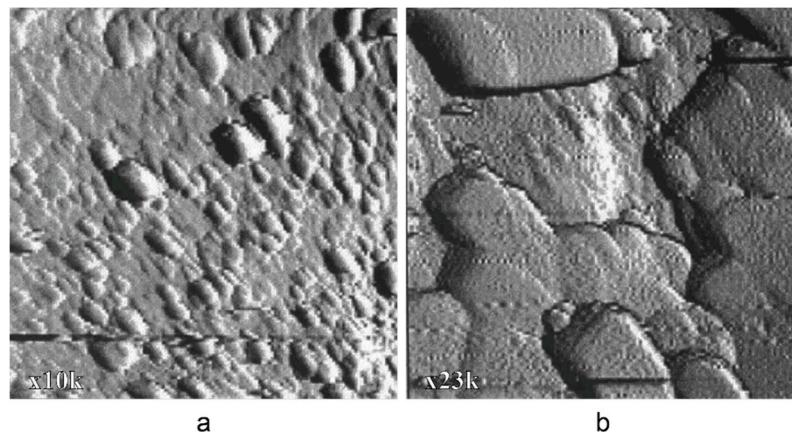
The main factor, determining the type of reaction products, is  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio; when it is increased, zeolite-like phases are formed with a larger amount of silica in the crystal lattice. At hardening of alkaline hydro-alumino-silicates of the above mentioned structural types under normal conditions, providing the highest degree of structure crystallinity, the ratio  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 4\dots5$  is optimal. The hardened binder with such a ratio of oxides is characterized also by the highest strength and water resistance.

The introduction of potassium ions into the composition of the binder helps to obtain zeolite-like reaction products and to increase the degree of crystallinity of the specified phases. To accelerate the formation of alkaline hydro-alumino-silicates under normal conditions, the addition of potassium oxide is required at  $\text{K}_2\text{O}/(\text{Na}_2\text{O}+\text{K}_2\text{O}) = 0.15\dots0.30$ . Potassium ions also contribute to the advanced water resistance and strength of artificial stone, regardless of the temperature at its hardening.

When the ambient temperature rises from  $20$  °C to  $80$  °C, the phase composition of the hardened binder does not practically change. However, this causes a higher rate of structure formation and crystallinity of artificial stone.

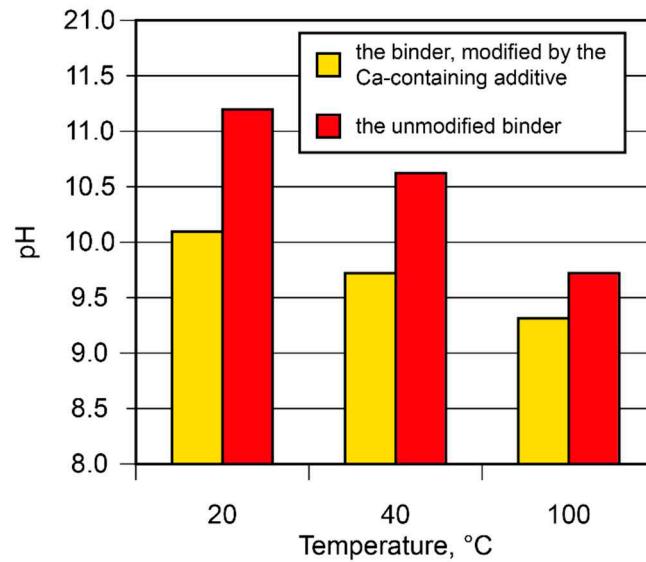
The microscopic research of the binder showed the presence of submicrocrystalline structure, characterized by microcrystals  $\leq 3.5$  microns in size, located in a amorphous matrix. A low roughness of the surface and continuous strong connection of submicrocrystalline and amorphous phases determine the strength and durability of such structure, which by virtue of its nature can fall under external destroying factors only in small measures. And as it was shown above, the structure of the hardened binder is mainly represented by crystals of hexagonal form, related to zeolite-like formations such as analcime, zeolite P (with a structure of garronite), zeolite G (with a structure of shabazite). These reaction products are present in various quantities, depending on the initial composition, and differ by crystallization degree (see Figure 1, Figure 2, Figure 3, and Figure 4). Changing the ratio of oxides  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  allowed to ensure the composition of reaction products and to control the structure formation of artificial stone and its resulting density. The density of zeolite-like reaction products can be arranged as follows: G (0.205-0.21 nm) < P (0.230 nm) < analcime (0.224 nm). It was noted that the maximum density of the artificial stone can be provided due to the formation of equal quantities of hydro-alumino-silicates like analcime and zeolite P types.

The represented results, obtained using atomic force microscopy (AFM), confirm the findings (Figure 6). Thus, the microstructure of the binder, prepared with a ratio of  $\text{H}_2\text{O}/\text{Al}_2\text{O}_3 = 12.5$ , is characterized by the presence of single microcrystals within  $0.1\dots0.5$  microns that are chaotically distributed in the amorphous phase, pointing out an inhomogeneity of the crystallization process. It allowed a conclusion about the absence of a clearly expressed stage in the formation of submicrocrystalline structure during the transformation of the amorphous state of the binder into a crystalline one. The nucleation of large crystals takes place during amorphous phase, resulting in significant retardation of crystallization and hardening processes.



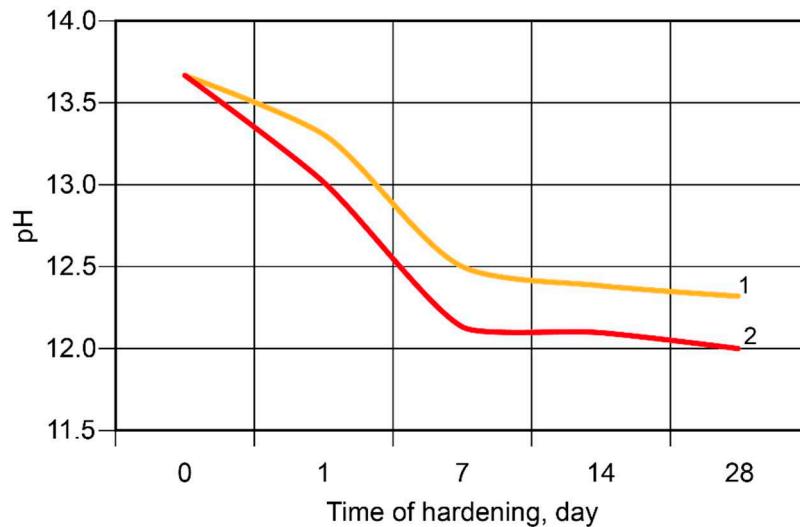
**Figure 6.** AFM microphotography of the binder  $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 4\text{SiO}_2\cdot 10\text{H}_2\text{O}$  that was modified by the Ca-containing additive and hardened within 28 d at  $t = 20 \pm 2$   $^{\circ}\text{C}$ : a - magnification  $\times 10\text{K}$ ; b - magnification  $\times 23\text{K}$ .

The linkage of the alkali metal ions in water-insoluble composites was researched. The linkage depends on the type of treatment and temperature, and most intensively this process passes at a microwave treatment (Figure 7). The rise of temperature from 20  $^{\circ}\text{C}$  up to 100  $^{\circ}\text{C}$  causes a lessening of pH values from 11.2 down to 9.7 of interstitial liquid. The introduction of Ca-containing additive reduces pH values from 10.1 to 9.3. It is possible to explain this phenomenon by resulting of this additive in the partial linkage of alkali in new formations, such as amicite ( $d = 0,564; 0,422; 0,314; 0,272$  nm), garronite ( $d = 0,710; 0,501; 0,410; 0,316; 0,267$  nm), and gismondine.



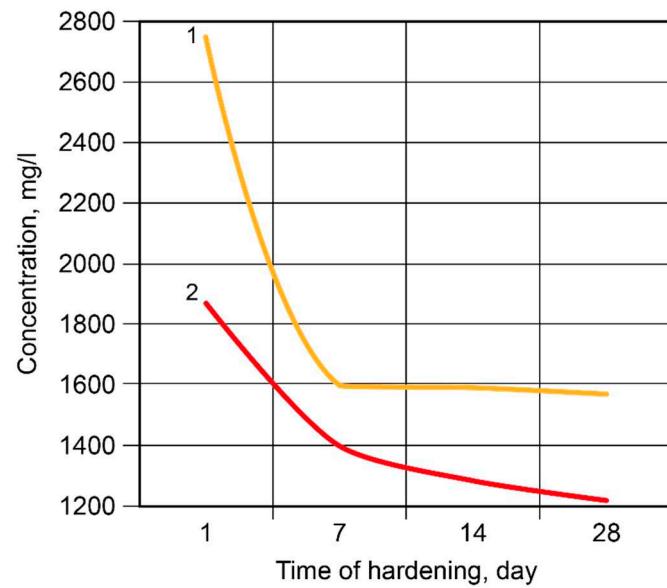
**Figure 7.** The pH values of interstitial liquid versus composition of the binder and its thermal processing.

During the hardening of the binder, the linkage of alkali metal ions takes place, and most intensively this process passes within the first 1...7 days (Figure 8). The Ca-containing additive accelerates the linkage of the ions in structure of insoluble reaction products.



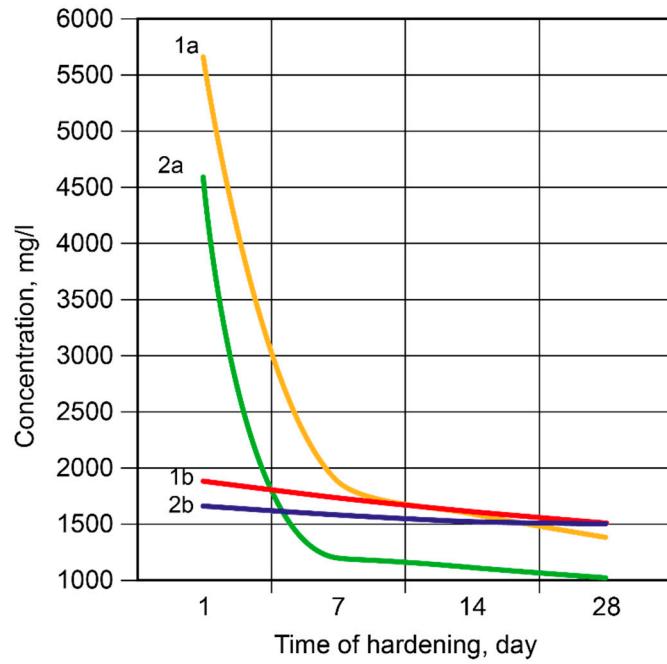
**Figure 8.** The pH values of interstitial liquid versus age at  $t = 20$  °C for: 1 – the unmodified binder; 2 – the binder, modified by Ca-containing additive.

Starting from initial concentrations, at the age of 2 d the samples were characterized by linkage of 84.99 % of free  $\text{Na}^+$ -ions in the case of the unmodified binder and 89.79 % when Ca-containing additive was used (Figure 9). At 7 d, accordingly, 91.26 % and 92.36 % of the ions were already bonded. Then, the linkage was considerably slowed down, especially in the case of unmodified binder. Thus, after 28 d the last one was characterized by the presence of 8.57 % of free  $\text{Na}^+$ -ions in interstitial liquid (from the total amount in the system), and the modified binder by only 1.2 %. The Ca-containing additive allows speeding up the linkage of  $\text{Na}^+$ -ions due to the formation of zeolites like amicite, garronite, and gismondine.



**Figure 9.** The concentration of  $\text{Na}^+$ -ions in interstitial liquid versus age: 1 – the unmodified binder; 2 – the binder, modified by Ca-containing additive.

Figure 10 represents the linkage of  $\text{K}^+$ -ions during the structure formation of the binder. Starting from initial concentrations, at 2 d the samples were characterized by linkage of 95 % of free  $\text{K}^+$ -ions in the case of the unmodified binder, and 96 % when the binder was modified by Ca-containing additive.

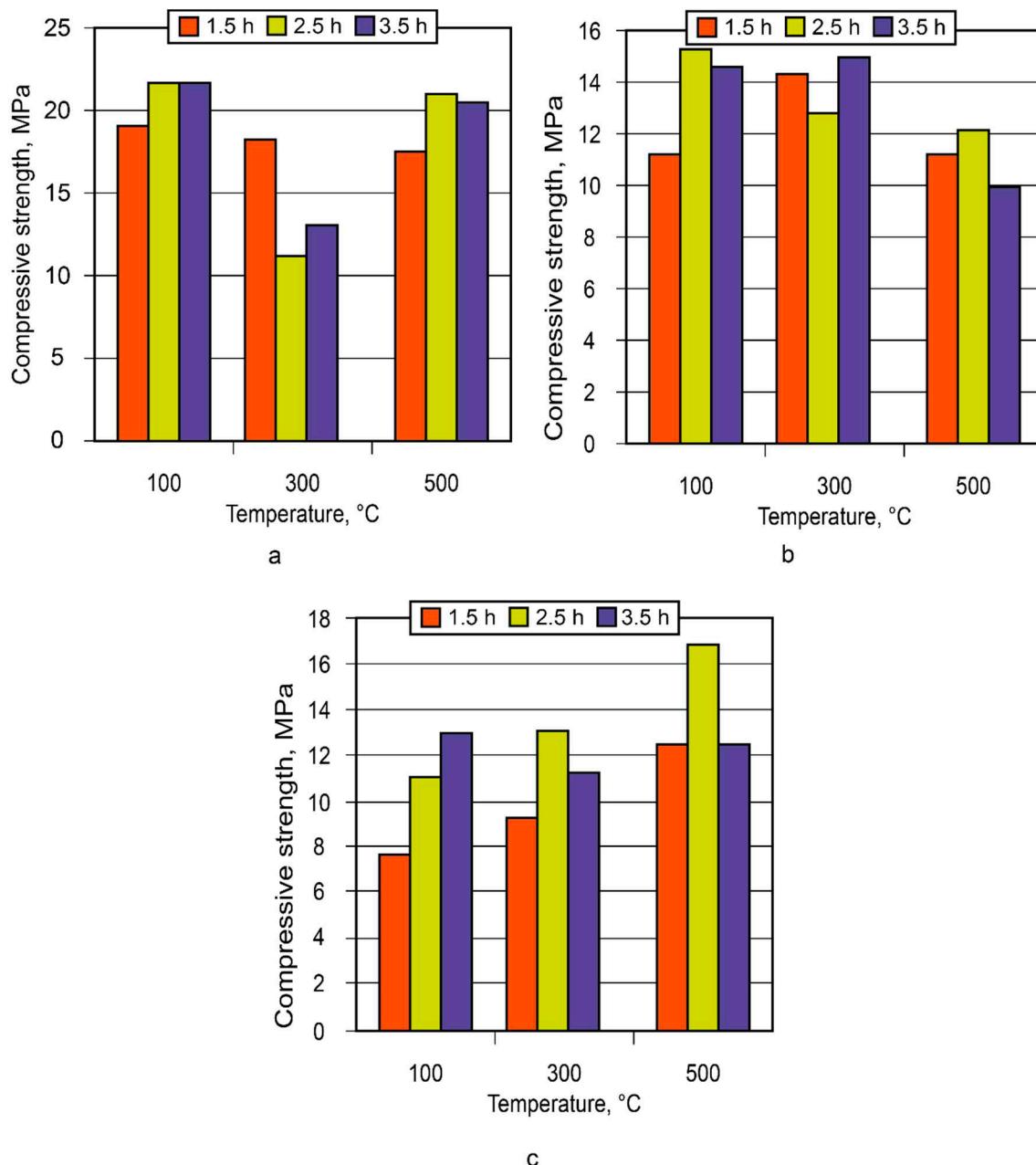


**Figure 10.** The concentration of  $K^+$ -ions (a) and soluble silica (b) in interstitial liquid versus time of hardening: 1 – the unmodified binder; 2 – the binder, modified by Ca-containing additive.

Within 7 d approximately 99 % of  $K^+$ -ions have been bonded in the hardened binder. Then the process of linkage considerably slowed down, in particular for the unmodified binder. So, the last one was characterized by the presence of 1.25 % of free  $K^+$ -ions (from the total in the system) after 28 d, and the modified analogue by only 0.85 %.

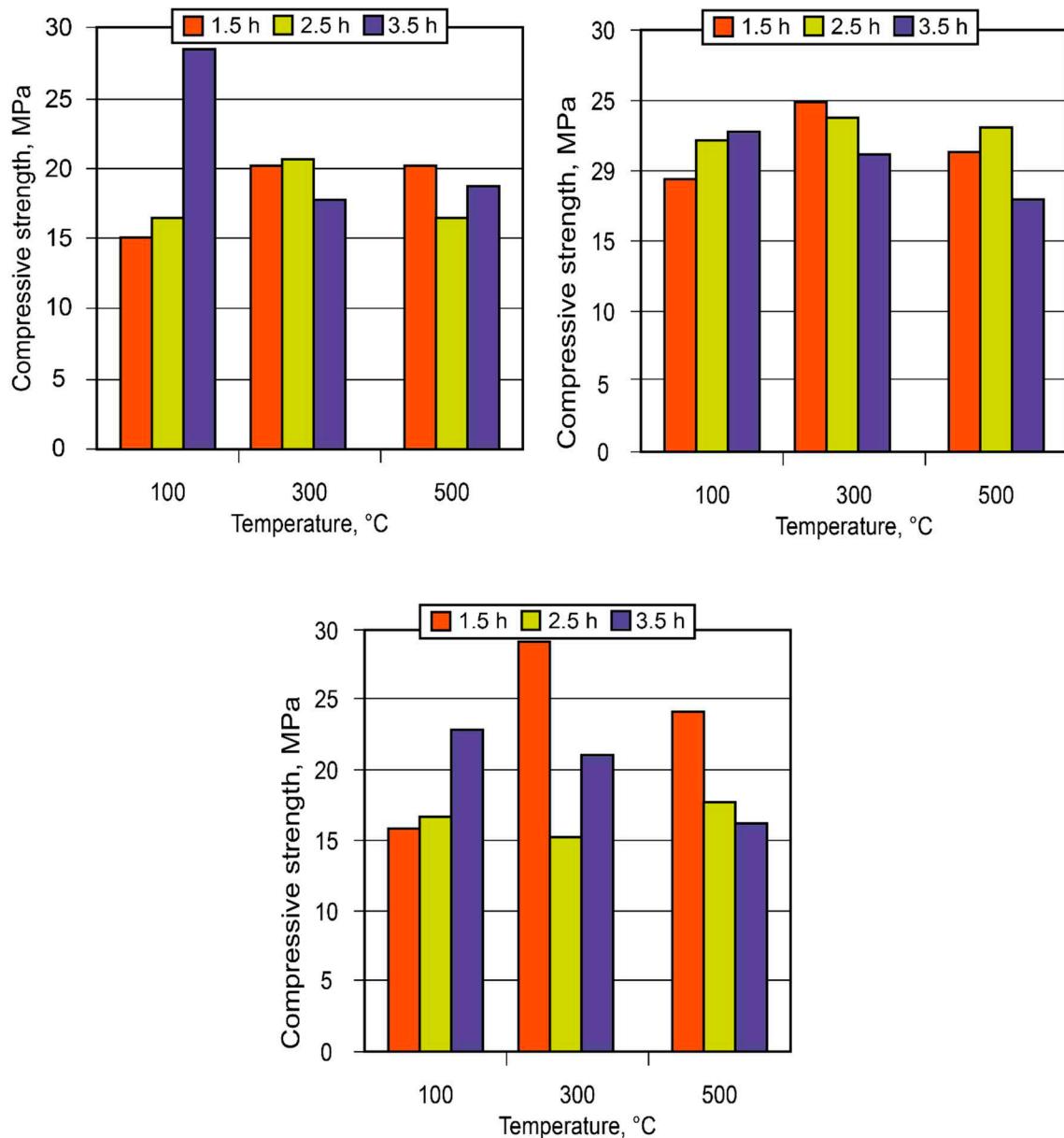
### 3.2. Manufacture and using of the alkaline alumino-silicate binder

To demonstrate practical application in the production of low-temperature insulating composite materials, the alkaline alumino-silicate composition of hydronepheline-analcime type with the structural formula  $Na_2O \cdot Al_2O_3 \cdot 3.5SiO_2(10.5; 12.5; 14.5)H_2O$  was chosen as the binder. The influence of the amount of water molecules in the binder, produced using kaolin and metakaolin, after conditioning (maturing) of the alumino-silicate compositions during 1.5...3.5 h and their further thermal treatment, on the strength of the resulted ceramic matrixes are represented below (Figure 11, Figure 12).



**Figure 11.** Strength of the ceramic matrix based on kaolin versus time of conditioning of the alkaline alumino-silicate compositions and treatment temperature: a – system  $\text{Na}_2\text{OAl}_2\text{O}_33.5\text{SiO}_210.5\text{H}_2\text{O}$ ; b – system  $\text{Na}_2\text{OAl}_2\text{O}_33.5\text{SiO}_212.5\text{H}_2\text{O}$ ; c – system  $\text{Na}_2\text{OAl}_2\text{O}_33.5\text{SiO}_214.5\text{H}_2\text{O}$ .

The analysis of findings shows that the ceramic matrix (the alkaline alumino-silicate binder  $\text{Na}_2\text{OAl}_2\text{O}_33.5\text{SiO}_214.5\text{H}_2\text{O}$ , based on metakaolin, and obtained after conditioning during 1.5 h and thermal treatment at  $t=300\text{ }^\circ\text{C}$ ) demonstrates the highest strength among the other ones.



**Figure 12.** Strength of the ceramic matrix based on metakaolin versus time of conditioning of the alkaline alumino-silicate compositions and treatment temperature: a – system  $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot3.5\text{SiO}_2\cdot10.5\text{H}_2\text{O}$ ; b – system  $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot3.5\text{SiO}_2\cdot12.5\text{H}_2\text{O}$ ; c – system  $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot3.5\text{SiO}_2\cdot4.5\text{H}_2\text{O}$ .

Using the binder, the production of heat insulation perlite-based materials was organized (Figure 13).



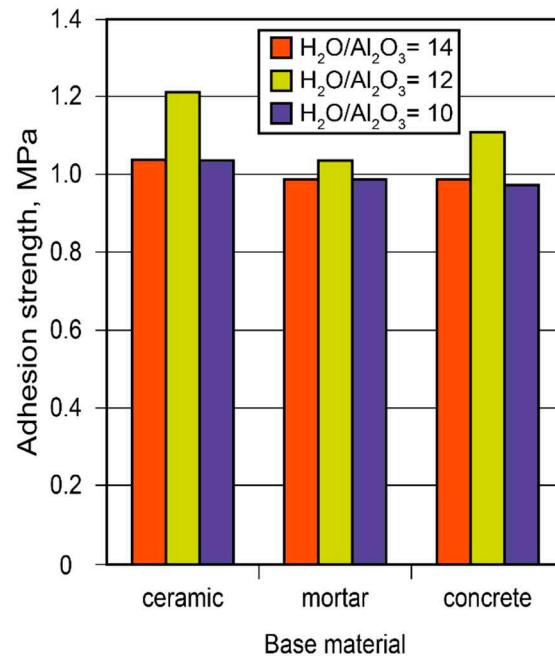
**Figure 13.** The pilot-scale production of heat insulating boards using expanded perlite.

The results of tests of the perlite-based concretes made using various cements are given in Table 1. It was concluded that the most effective for high temperature insulation application were the composites based on the alkaline alumino-silicate binder.

**Table 1.** Basic physico-mechanical characteristics of the perlite-based concretes based on the binder and OPC (for comparison).

Characteristic	Class by density, kg/m <sup>3</sup>			
	150	200	250	300
<i>Alkaline alumino-silicate binder</i>				
Binder content [% by volume]	3.0	6.0	8.0	10.0
Compressive strength [MPa]	0.25	0.30	0.35	0.45
Flexural strength [MPa]	0.15	0.15	0.20	0.30
Heat conductivity at 25 °C [W/(m·°C)]	0.062	0.068	0.076	0.082
<i>Ordinary portland cement (OPC)</i>				
Binder content [kg/m <sup>3</sup> ]	–	–	80	110
Compressive strength [MPa]	–	–	0.15	0.25
Flexural strength [MPa]	–	–	0.16	0.20
Heat conductivity at 25 °C [W/(m·°C)]	–	–	0.075	0.085

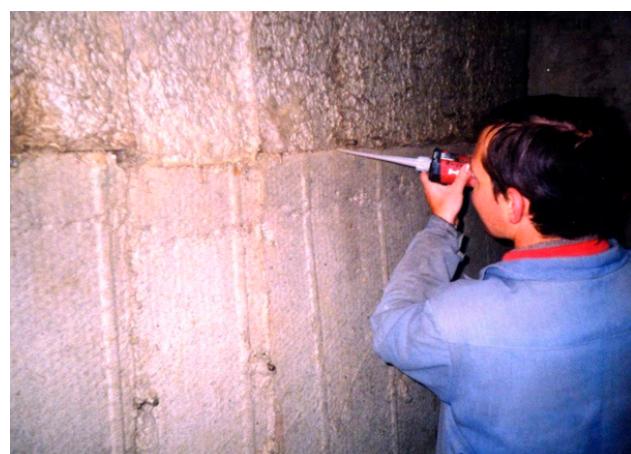
In conditions of permanent increase in energy consumption, the problem of heat conservation and saving becomes of first priority. Especially important is to save heat in high-temperature installations, since the relative cost of energy unit produced in the field of high temperatures (exceeding 500 °C) is considerably higher than that produced at the lower temperatures. A design of high-temperature heat insulation for boilers was proposed. The principles of how to choose and arrange insulating materials have been elaborated as well, based on the study's results of strength characteristics of the adhesive joints in (adhesion strength), the formulations of the alkaline alumino-silicate binder-based adhesives and mathematical model for the design of high- temperature heat insulating materials have been developed (Figure 14).



**Figure 14.** The 28 d adhesion strength of the adhesive joints between the glass crystalline plates and different base materials.

An industrial use of the investigated systems for the heat insulation of industrial boilers was done. Among the advantages of the alkaline alumino-silicate binder-based adhesives are as follows: ecological friendliness, incombustibility, absence of hazardous gases released under exposure to high temperatures, durability, and low cost. These materials are also characterized by simplicity of preparation and application: can be produced practically in any conditions, in any quantities with the use of simple mixing equipment such as an electric drill.

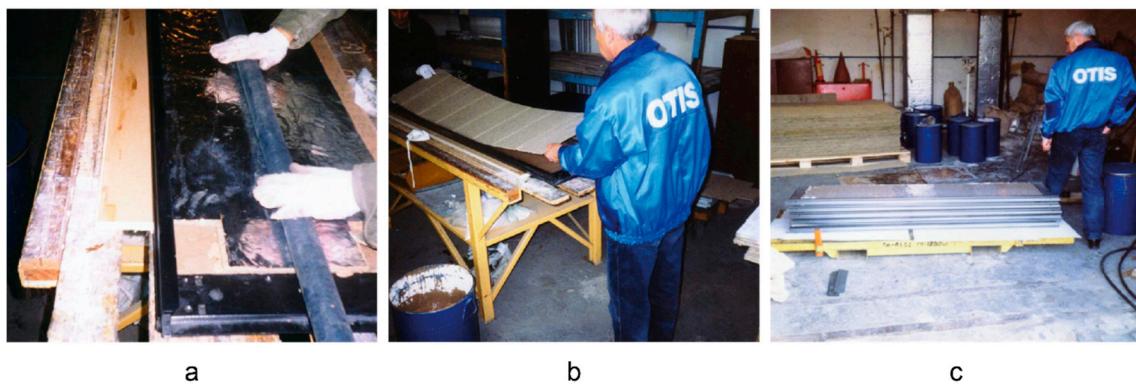
The adhesives, based on the alkaline alumino-silicate binder, can be used for bonding layers of heat insulation to each other, for heat insulation to structural elements of geometrically complicated shapes, for impregnating basalt-fiber cords intended for sealing holes in heat insulation, and for direct sealing of the holes. For these applications, the composition was designed, using ground sand as filler, and was applied with an injection pistol into the holes from 0 to 4 mm in width and also with a putty-knife into the holes from 4 to 20 mm in width (Figure 15). Shelf life of this composition was between 1 h and 6 h, solidification time – between 1 h and 8 h, time for strength gain – from 24 h to 48 h, depending on the ambient temperature.



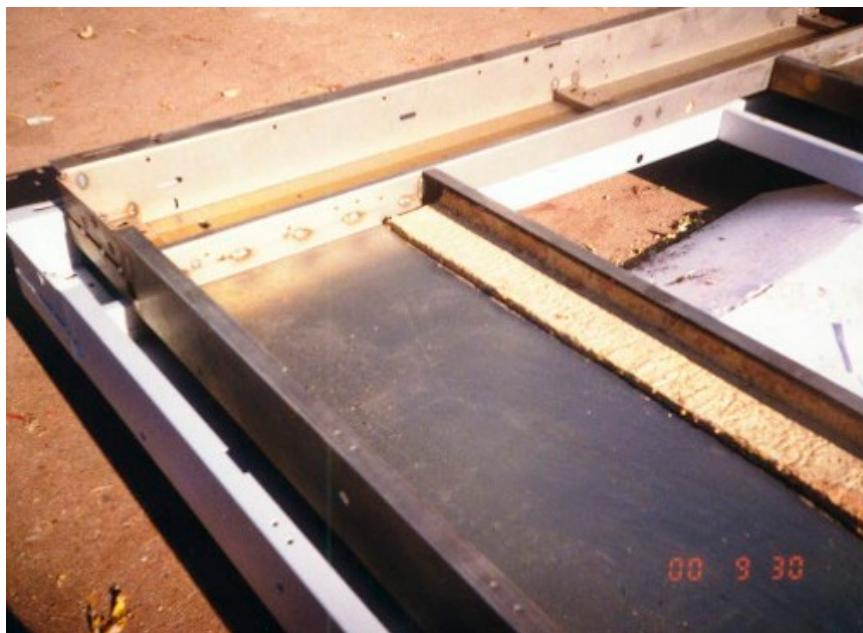
**Figure 15.** Sealing holes in the heat insulating layer using an injection pistol.

Building of multi-storey residential houses and offices requires an approach to the problem of how to secure health safety in case of catastrophes. One of the tasks is to ensure quick localization of fire. There is also the necessity for quick hoisting of the fire-fighting gang using lifts, and relatively low temperatures should be provided in lift shafts. The solution to this problem was proposed due to research, resulting in advanced types of doors for the shafts, which would provide fire resistance and heat insulation in case of fire.

The fire resistant heat insulating system from basalt fiber materials and inorganic the binder-based adhesive, which does not release hazardous gaseous substances at high temperatures, as well the design of fire resistant doors, since the all earlier used adhesives did not meet the requirements for fire-resistant doors of the lift shaft. Using the binder the manufacturing techniques of fire-resistant floor frames have been also developed. The production and commercial-scale use of the mentioned articles were launched by the Company OTIS (Figure 16, Figure 17).



**Figure 16.** Technological operations: a – gluing of an aluminium foil; b – gluing of basalt cardboard; c – storage of the ready products (doors).



**Figure 17.** Manufacture of floor frames.

Characteristics of gluing connections must be defined for reference specimen by type of destruction. The binder-based adhesives were tested for bonding structures from different materials: basalt cardboard, rigid heat insulating boards to each other and bonding them with steel and aluminium foil (Table 2).

**Table 2.** Characteristics of properties of gluing connections.

Glued Materials	Correlation of the total areas at a uniform tearing, %		
	Cohesive destruction (in glue), no more than	Adhesive destruction (contact zone material-glue), no more than	Destruction in fibrous layer, not less than
Plate – cardboard	5	5	90
Cardboard – steel	20	30	50
Plate – steel	20	30	50
Plate – aluminium foil	20	30	50

#### 4. Conclusions

1. The structure formation of alkaline alumino-silicate binder, represented by the ratios  $(\text{Na},\text{K})_2\text{O}/\text{Al}_2\text{O}_3 = 1$ ,  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 2\dots 7$ ,  $\text{H}_2\text{O}/\text{Al}_2\text{O}_3 = 10\dots 15$ , is due to reaction products, mainly composed of hydro-alumino-silicates like analcime, zeolite P, and garronite. The introduction of calcium to a reactionary mixture causes the formation of zeolite P and analcime as well as calcium hydro-silicates with structure of ksonotlite and girolite types. The additional quantity of  $\text{SiO}_2$  in the binder determines the dominance zeolite-like formations with increased contents of  $\text{SiO}_2$ , i.e. minerals of Na-shabasite-gmelenite, fogasite and mordenite types.
2. It was revealed that in the binder, described by  $\text{H}_2\text{O}/\text{Al}_2\text{O}_3$  ratio lower than 10, the hardening process passes through the formation of hydro-alumino-silicates at the following stages: amorphous, submicrocrystalline, and crystalline. In the case of the binder with  $\text{H}_2\text{O}/\text{Al}_2\text{O}_3 > 10$  the formation of submicrocrystalline structure is very poorly expressed. Thus, the nucleation of large crystals happens immediately in the amorphous phase, which results in significant retardation of hardening and crystallization processes, and also deterioration of the structure and properties of artificial stone.
3. The hardening of the binder within 28 days is accompanied by a linkage of 93...99 %  $\text{Na}^+$  and  $\text{K}^+$ -ions. The introduction of the Ca-containing additives allows to speed up the linkage of these ions due to the formation of zeolites like amicite, garronite, and gismondine.
4. The experience gained for the small- and large-scale industrial use of the binder showed high technical advantages of the insulating composites based on it, especially to protect critical infrastructure facilities from the action of high temperatures and fire.

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