



## Development of geopolymer binders

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**Abstract.** The scale of consumption of raw materials is large, and to a greater extent, it is the building materials industry that has a detrimental effect on the environment, thereby disturbing the pristine appearance and landscape of nature. Production volumes of Portland cement clinker have exceeded the mark of 5 billion tons per year. But the key dilemma lies in the emission of greenhouse gases, because during the high-temperature processing of raw materials to produce clinker, carbon dioxide, methane and nitrous oxide are released into the atmosphere.

At the same time, slag-alkali and geopolymer binders can be considered as an alternative to resource-intensive Portland cement; they have found practical application in many developed countries of the world. A large backlog of research has allowed the authors of the work to model materials of both technogenic and natural origin “technogenic reaction powder – natural component – alkaline activator” in one binder system. Microanalysis confirmed the effectiveness of the integrated use of sodium silicofluoride and finely dispersed bentonite additives in the binder system, which had a beneficial effect on the pore structure of the stone and the properties of the cement stone.

Using a properly designed binder composition “aspiration dust – finely dispersed bentonite – sodium silicofluoride – alkaline binder”, it is possible to obtain high-quality and durable composites with a low carbon footprint, thereby solving many environmental problems.

**Keywords:** geopolymer, aspiration dust, alkaline activator, binder system, composites, structure formation, composite clinkerless mineral binders

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## 1. INTRODUCTION

The construction materials industry is the most material and resource-intensive human activity. Throughout the existence of mankind, billions of tons of natural resources are extracted from the natural environment to produce demanded construction products. Of course, unlike in the chemical, petrochemical and metallurgical industries, construction does not emit toxic and life-threatening emissions. But the scale of resource consumption is such that the construction materials industry has a detrimental effect on the environment, thus disrupting the pristine appearance and landscape of nature [1-3].

Only the burning of Portland clinker to produce cement, indispensable at present in construction material, has passed the mark of 5 billion tons per year. The raw material is extracted from the ecological system in undolomite carbonate rocks with a stored calcium and carbon dioxide stock, and in kaolinite clay with balanced silica, alumina and iron oxide content. To produce 1 ton of clinker, you need to prepare up to 1.65 tons of designated raw material. But the key dilemma is in the emissions of greenhouse gases, because high-temperature processing releases carbon dioxide, methane and nitrous oxide into the lower atmosphere. It is known that when one ton of clinker is fired, approximately 0.72 tons of anthropogenic gases are released into the atmosphere as a result of the decarbonization of calcium carbonate and during combustion of fuel at other technological stages of cement production [4-5].

At the same time, the SC and GPC can be considered as an alternative to resource-intensive Portland cement, they have found practical application in many developed countries of the world. Thanks to the alkaline closure of fine-grained powders of aluminosilicate nature, it is possible to obtain a high quality and durable material with low carbon footprint, avoiding the above mentioned problems of environmental order [6-8].

The physico-chemical transformation in complex system «aluminosilicate solid phase - alkaline liquid phase» takes place consecutively and parallel with formation of a lasting crystallization. The alkaline medium leads to the dispersion and destruction of the aluminosilicate oxygen chains, with subsequent formation of colloidal solutions. The primary formed neoplasms of alkaline aluminums and siliciums as a result of the transformations are converted into larger aggregates. Cation exchange  $2\text{Na}^+ \leftrightarrow \text{Ca}^{2+}$  promotes the development of new and recrystallization of existing structures, with the emergence of condensation-crystalline formations [9, 11].

The revealed patterns of formation of structure of the binding system «aluminosilicate solid phase – alkaline liquid phase» confirm the identity with nature-like processes of synthesis of ceolites in the earth's crust. When modelling the composition of the alkaline composite, it is necessary to vary the formulation and process parameters, the concentration of components of the binding system, the conditions of the physical-chemical interaction and hardness, that will subsequently allow to purposefully manage the structure and properties of an artificial conglomerate [12-13].

Practical experience of the introduction of the clinker-free technology, confirms the uniqueness of alkaline activation of powders of man-made and natural origin with the presence of aluminosilicate phase, high results achieved in the field of production of fast-setting, acid-resistant, cellular, Heat-resistant, low exothermic and high strength concrete. Development of this area is currently relevant and will allow to expand the raw material base, opening up new opportunities for the cement industry [14, 15].

The development of a low carbon binding alkali closure, using appropriate, available and if possible technologically advanced raw materials is a key research objective. Production of SC and concrete binders for the North Caucasus republics is economically unprofitable, since waste from metallurgical plants is a scarce and logistically unjustifiable raw material, which is demonstrated for visual perception in Fig. 1.

Therefore, the development of geopolymer binders is the most preferred option for low-carbon development. The qualitative and quantitative content of the binder compositions is presented in the classification of alkaline materials (Table 1) [16].

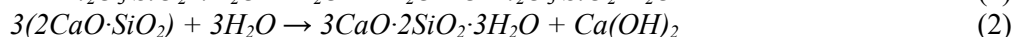
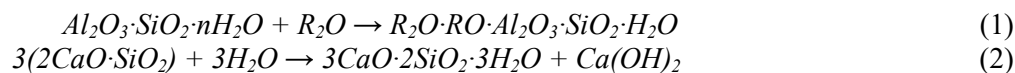


Fig. 1. Transport accessibility of waste from metallurgical plants.

Table 1. Classification of alkaline materials.

Binding type	Phase composition	Content Alkaline oxides	Products of hydration
Alkaline cement: -slag -zole	slag + R <sub>2</sub> O zole + R <sub>2</sub> O	2 – 8 % 5 – 10 %	R <sub>2</sub> O·RO· Al <sub>2</sub> O <sub>3</sub> ·SiO <sub>2</sub> ·H <sub>2</sub> O
Geopolymer Cement: -High-Dispersion Aluminosilicate Powders	Al <sub>2</sub> O <sub>3</sub> ·SiO <sub>2</sub> ·nH <sub>2</sub> O + R <sub>2</sub> O RO·SiO <sub>2</sub> + R <sub>2</sub> O	10 – 15 %	RO·SiO <sub>2</sub> ·nH <sub>2</sub> O

According to the given classification, the production of geopolymer composites is based on the chemical interaction of aluminosilicate, silicate components with alkali and alkaline earth metal cations:



The availability of a suitable phase composition can be ensured by combining sediment rocks: clay, otroc, gudgeon, cement production wastes and others. The large amount of studies carried out allowed the authors of the work to model in one binding system both materials and techno-, and natural genesis «techno-reaction powder – natural component – alkaline activator».

## 2. METHODS AND MATERIALS

As a man-made reaction component, clinker dust aspiration was investigated, this product is unsuitable for return to the process, is removed from the dedusting system and stored in nearby areas, as accumulation is used in the mountain range of the republic, violating the natural environment. Finding the application of this in principle to a chemical and mineralogical composition product is an important national and economic task. It should be noted that aspirating dust has positive features, first, it does not need to be subjected to mechanoactivation, in the natural state, the specific surface is on average 220-230 m<sup>2</sup>/ kg (PCH-12); secondly, it is a product of heat, at 400-500°C clay minerals kaolinite and montmorillonite lose their crystallization direction, become hydrated water and convert to active kaolinite an idrury – methaolithine (Al<sub>2</sub>O<sub>3</sub> 2SiO<sub>2</sub>). The hydraulic activity of the powder was confirmed by samples obtained from water-filled aspiration dust and was 3.36 MPa. For the activation of the aspirate dust, a low sodium liquid glass solution with density 1.42 g/cm<sup>3</sup> and silicate module 2.8 (in the conversion to Na<sub>2</sub>O - 6.2%) was used. The hydrogen level of the alkaline capping indicator was determined by a special pH meter (measuring accuracy up to 0.01 units of pH) and the numerical value of the pH of the alkaline medium was 12.6.

The aspirating dust as mentioned earlier, product of a ready carefully selected raw material mixture, for clinker roasting, the percentage of acid oxides is about 20-25%, so to increase the aluminosilicate phase, in the studies used natural bentonite  $Al_2[Si_4O_{10}] \cdot (OH)_2 \cdot nH_2O$  – clay with a predominance of Montmorillonite in the composition (Fig. 2). Bentonite was investigated in its natural form, after drying it was ground in a roller mill for 5 minutes, the specific surface area was  $550 \text{ m}^2/\text{kg}$ . To improve the process of forming structure and precipitating the catalyst of the curing gel of silicon acid, the binder composition was added  $Na_2SiF_6$  silica sodium.

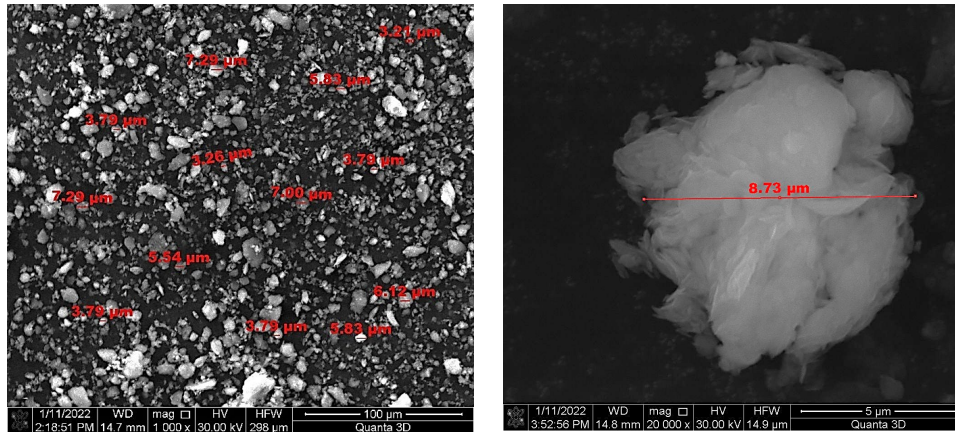
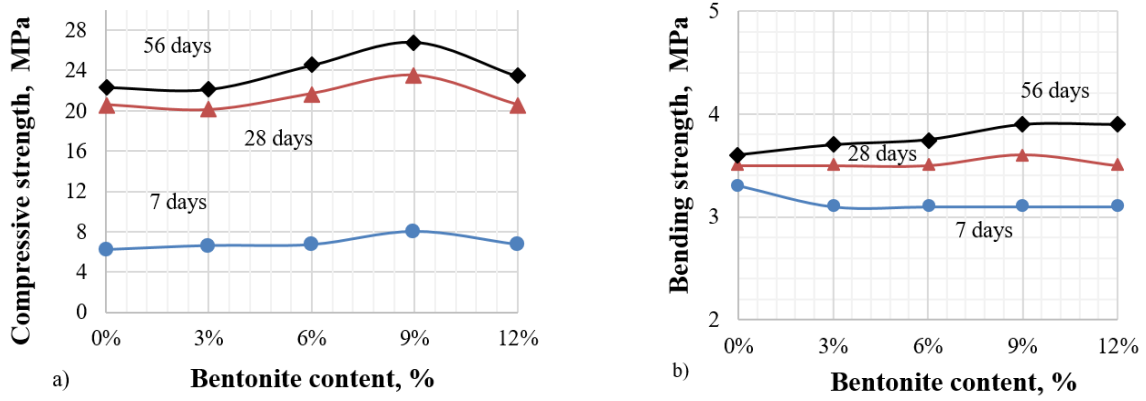


Fig. 2. Bentonite.

Using marked materials and quartz sand from the Chervenskoye quarry, made samples-beams, which before being melted in normal humidity conditions, and after and before the test stored in a dry room, but heated in a drying cabinet for 2-2,5 o'clock. The tests of the obtained samples were carried out according to GOST 310.4-81 Cements. Methods for determining the bending and compression strength of the Testometric FS150AT hydraulic machine. The investigation of physico-chemical processes occurring when concrete samples are heated at high temperatures was carried out by thermal analysis using the synchronous thermal analyzer STA6000 from Perkin Elmer. The X-ray phase analysis was performed on a SHIMADZU XRD-6000 diffractometer using the software complex of powder diffractograms database PDF-2 and the Crystallographica Search-Match package integrated into the device hardware and software complex. Conditions of the survey – anode copper, wavelength of copper radiation  $K\alpha$  lines is  $1.54051 \text{ \AA}$ , 40kV, 30mA, angle range 10-160 degrees, speed of the survey 1 degree/ min.

### 3. RESULTS AND DISCUSSION

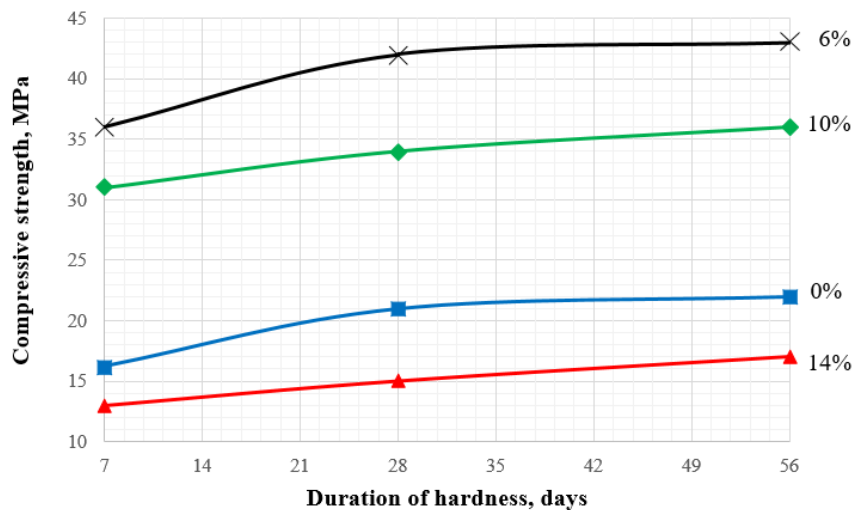
In modelling the binder system «aspiration dust – bentonite- alkali activator –  $Na_2SiF_6$ » the amounts of bentonite and sodium crepinyl were varied, as these components were introduced to enhance the properties of the composite and to prolong the bond binding time. Bentonite was added to the binding system after mechaonoactivation in a quantity of 3, 6, 9 and 12% of the total mass of dry matter. Sodium glass was used as a blocking agent ( $n = 2.8$ ;  $\rho = 1.42 \text{ g/cm}^3$ ). The results of the studies allowed to establish a relationship between compression and bending strength and bentonite content in the binder (Fig. 3). As a result, the optimum concentration of methane activated bentonite in the binder system was found, which amounted to 9% of the total dry matter mass.



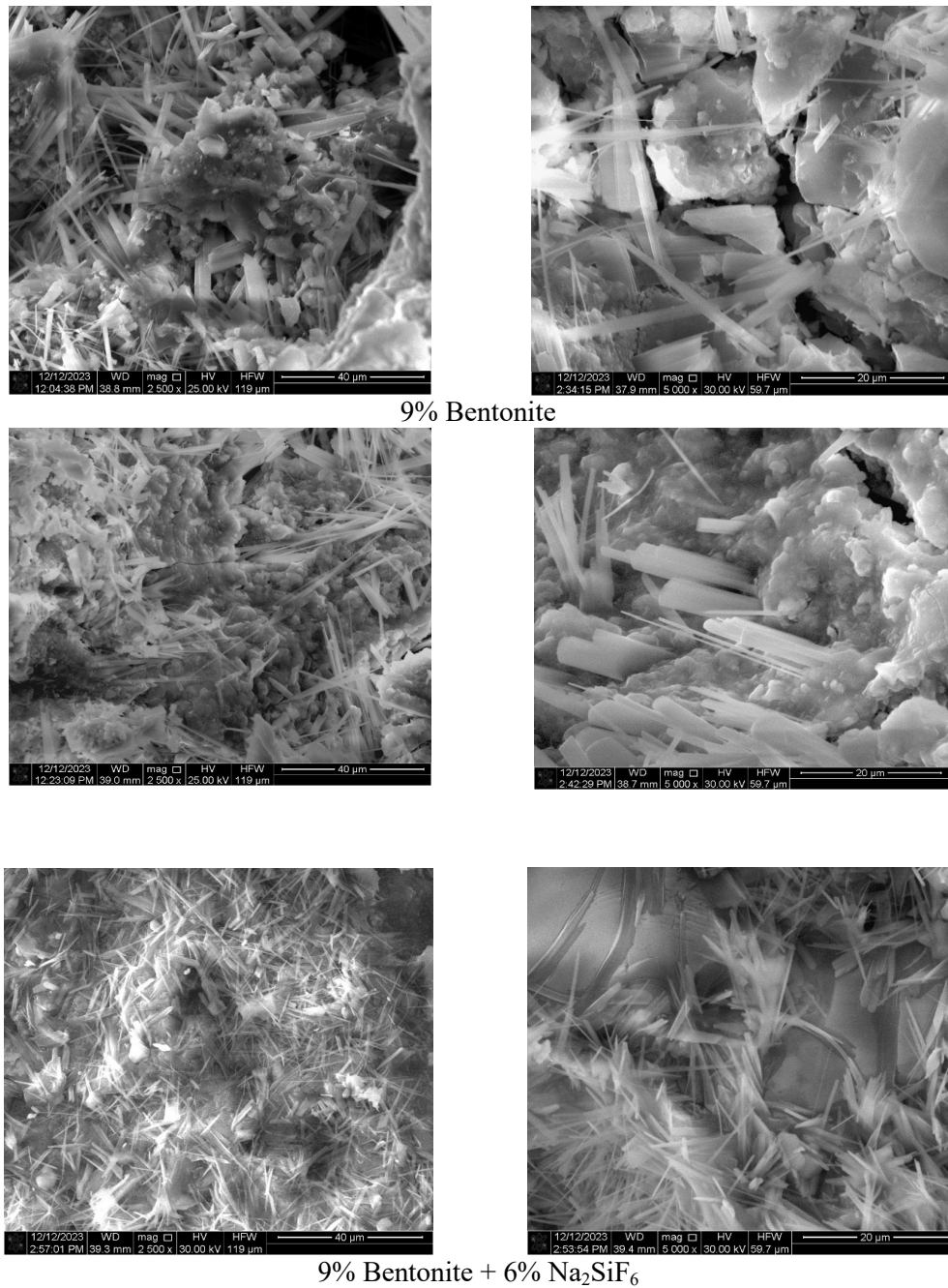
**Fig. 3.** Graph of the strength dependence on compression (a), bending (b) from the amount of bentonite.

The influence of the concentration of sodium creosote on the strength of the artificial stone was further investigated by introducing a curing catalyst in the prepared binding composition at dosages 6, 10 and 15% of the total dry matter mass. The results of the study are shown in figure 4. The addition of 6% N-cremiferyl contributed to maximum increase in compression strength (43.9 MPa) throughout the studies. For a more detailed study of the structure, samples were tested on the basis of the system «aspirative dust – bentonite (9%) – alkaline activator –  $\text{Na}_2\text{SiF}_6$  (6%)».

Microphotographs made on the Quanta 3D 200i microscope with integrated microanalysis system Genesis Apex 2 EDS from EDAX, allow to visually verify structural order changes in cement stone without adding sodium cementite and with 6%  $\text{Na}_2\text{SiF}_6$ . The use of a sodium cremiferyl modifier in this dosage has been beneficial for the pore structure of the stone, microcavities, cracks are completely permeated with needle and tubular crystallography of silicates and calcium aluminates, Calcium and sodium aluminosilicates of variable composition, which is confirmed by microphotographs at 2500 and 5000 crt magnifications (Fig. 5).



**Fig. 4.** Graph of strength versus additive concentration  $\text{Na}_2\text{SiF}_6$ .



**Fig. 5.** Microphotographs of cement stone with 2500 and 5000 crt magnification.

The studied samples were subjected to thermal analysis on an STA6000 device from PerkinElmer (Fig. 6), in air conditions at a temperature range of 30-1000 °C with a temperature rise rate of 10°C/min. The TGA results showed that all studied compositions of alkaline binder systems behave almost identically, the weight loss at all temperature intervals is the same, only at 950-1000 °C the “aspiration dust – alkaline activator” binder lost a larger percentage by weight. Micrographs of samples after TGA analysis (Fig. 7) make it possible to observe weight loss, in Fig. 7a, the structure of the cement stone is relatively weakened, there are voids and depressions. In samples using bentonite, the structure retains its integrity and dense structure.

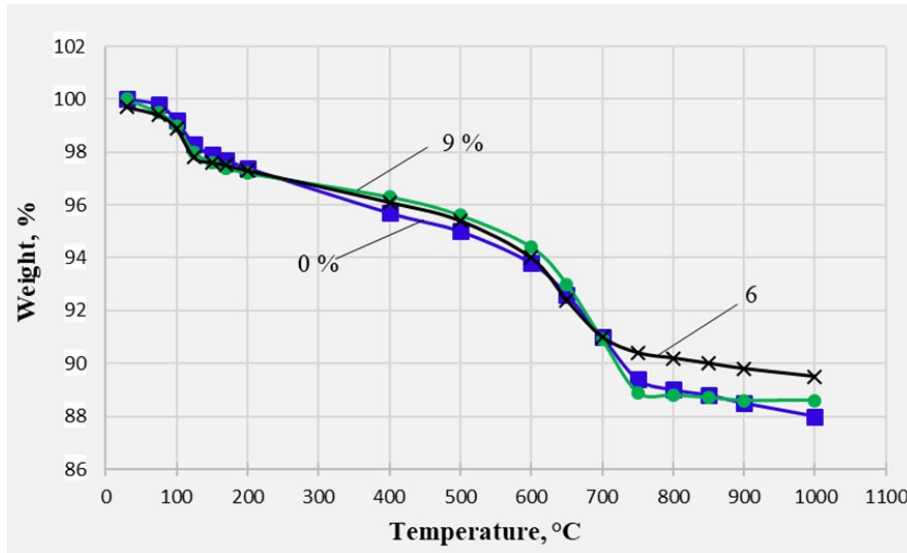


Fig. 6. Thermogravimetric analysis (TGA) curves.

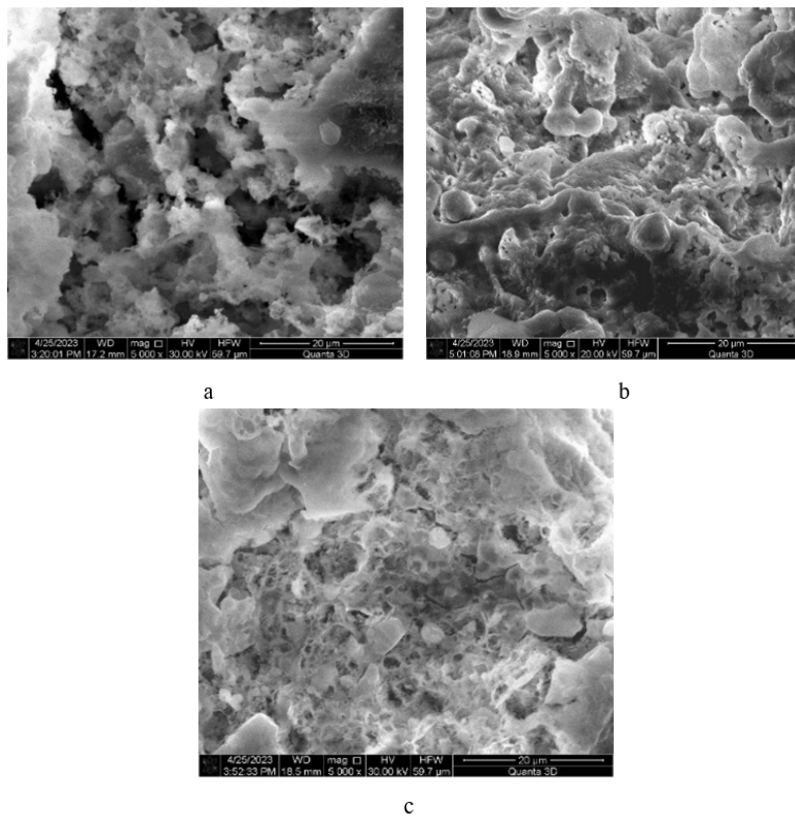
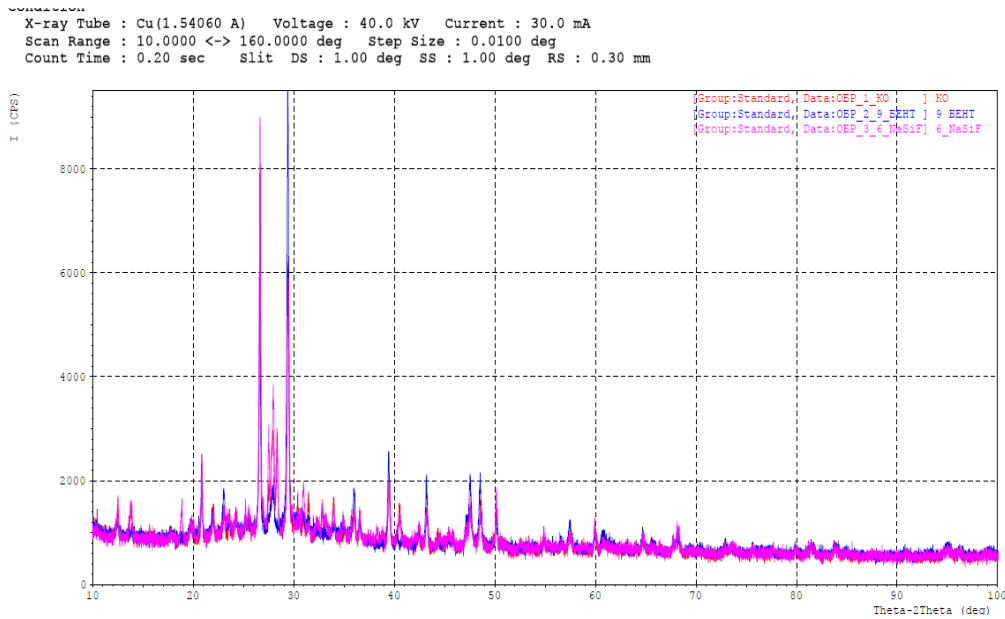


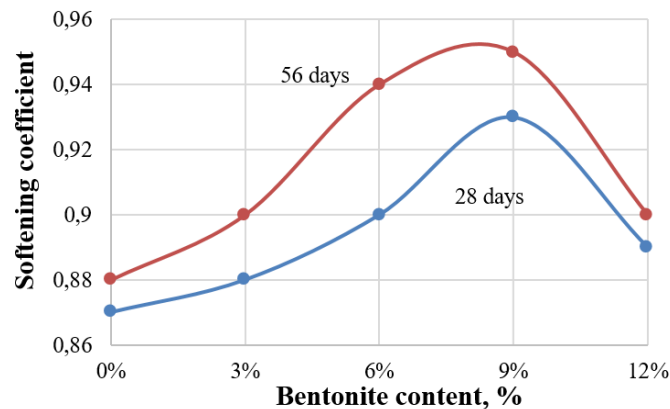
Fig. 7. Microimage of samples after TGA at 5000 crt magnification. a) control sample; b) 9% natural bentonite; c) 9% natural bentonite and 6%  $\text{Na}_2\text{SiF}_6$ .

X-ray phase analysis performed on a SHIMADZU XRD-6000 diffractometer (Fig. 8) confirmed the similarity of the mineralogical composition of the studied samples; the resulting peaks correspond to the following microphases: analcime, phillipsite, gismondite, garronite, fochagite, paragonite, larnite, albite, muscovite, potassium feldspar, etc.



**Fig. 8.** Sample X-ray phase analysis. a) control sample; b) 9% natural bentonite; c) 9% natural bentonite and 6%  $\text{Na}_2\text{SiF}_6$ .

The addition of finely dispersed bentonite (9% of the total dry matter mass) helps to compact the structure of the composite; microparticles of nanoclay – bentonite fill the pore space of the stone, due to the swelling effect of the montmorillonite mineral, and increasing the physical and mechanical properties of the binder. The softening coefficient of the studied binder systems confirmed the optimal degree of filling of the binder with bentonite 9% using sodium fluorosilicone 6% of the total dry matter weight. The maximum water resistance of the binder system is set to 0.95 (Fig. 9), which recommends this binder material for work in conditions of high humidity levels.



**Fig. 9.** Softening factor curve from the concentration of bentonite.

#### 4. CONCLUSIONS

The integrated use of cement production waste, the addition of bentonite, sodium silicofluoride, mixed with a sodium liquid glass solution in the binder system, had a beneficial effect on the processes of structure formation and strength gain, which is confirmed by the results of electron microscopy. Analyzing the research conducted, it can be stated that geopolymer binders can fully compete with energy-intensive and resource-intensive Portland cement in less critical construction areas. Using a properly designed binder composition, it is possible to obtain high-quality, durable composites with a low carbon footprint, thereby solving many environmental problems.

## 5. ACKNOWLEDGEMENTS

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