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ADEZIVI PE BAZĂ DE LIANȚI CU ACTIVARE ALCALINĂ PENTRU BETOANE ȘI PLACAJE CERAMICE
ALKALINE ALUMINOSILICATE-BASED ADHESIVES FOR CONCRETE AND CERAMIC TILES

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At present, a tendency to substitute hazardous organic adhesives in the majority of building materials is clearly observed. This is connected with the more strict than before requirements for health safety, fire safety and durability. The most important task is substitution of organic binders, traditionally used as adhesives for gluing concrete, brick and ceramics with non-hazardous inorganic binders. To solve this problem an adhesive for concrete, brick and ceramics based on ecologically friendly alkaline aluminosilicate binder (geocement) has been developed. This binder is itself an inorganic polymer, which combines properties of inorganic substances (high strength and frost resistance) and those of organic substances (elasticity, adhesion to various materials etc.) and is analogue to alkaline aluminosilicate materials occurring in nature: zeolites, feldspathoids, etc. Bonding strength of the geocement-based adhesives to various surfaces is higher than 1 MPa. With taking into account high pH of the geocement stone a proper choice of fillera and additives is important. The purpose of the study was to reveal influence of the geocement-based adhesive composition on properties and, accordingly, on structure of the interfacial transition zones: "concrete−concrete", "concrete−ceramics", "ceramics−ceramics".

Keywords: *aluminosilicate structures, geocement-based adhesives, metakaolin, mica, feldspathoid, quartz sand, zeolite formation*

1. Introduction

Joint work of individual building elements, the elements adjacent to each other and structures is important aspect of integrity and durability. Strong bonds should be provided between the hardened concrete and new cast-in-situ concrete, or between two concrete elements in structures made from precast reinforced concrete. In the first case, when a building is erected by layer-after-layer technique, a strong adhesion of new concrete to old one should be provided. In the second case, a strong adhesion of two old concretes should be provided.

The scientists of the SRIBM have developed alkaline aluminosilicate-based adhesives for gluing concrete and ceramics.

These binders (geocements), according to a classification given in [1], may be referred to the first class of alkaline (alkali- activated) cements, the basic composition of hydration products of which is represented by alkaline aluminosilicate hydrates - analogues to natural minerals of the zeolite and feldspathoid types [2, 3]. They are themselves inorganic polymers with a three-fold dimensional frame structure [4]. They are basic structure-forming elements, which add to a material a set of properties typical for inorganic materials such as high strength, non-toxicity, heat resistance, and organic ones (high adhesion). Such materials are capable to undergo polycondensation and to rapidly accept the required shape at low temperature (20 °C) [5].

Principles of polycondensation of aluminosilicate structures resulted in the formation of analogues to natural minerals (zeolites and feldspathoids) in the hydration products have been taken as a base in the creation of a geocement-based artificial stone. In character of the compositional build-up of main structure forming elements, natural zeolites may be referred to inorganic polymers, which, on the one hand, are similar to organic ones, and on the other hand, due to inorganic nature, are ecologically friendly materials. Researches held on target synthesis of analogues to natural minerals using clays of various structural types and alkali metal compounds [2, 3] as well as practical results of introduction of these materials in different sectors of building industry have been taken as theoretical base for creation of geocements of polymeric structure.

The purpose of this study was to evaluate the effect of mineral fillers and additives in the

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geocement-based adhesives on properties in various exposure conditions.

2. Raw materials

A system Me_2O-Me_2O_3-SiO_2-H_2O was taken as an object of study. The geocements were prepared using a metakaolin as a aluminosilicate component with a fineness expressed by a specific surface of 300-350 m^2/kg (by Blaine) that had been produced from a kaolin dehydrated at 800 °C and a mixture of soluble glass (silicate modulus Ms=2.8 and density ρ=1400 kg/m^3) and caustic alkalis as alkaline activator.

Fillers and additives were selected from the following materials: quartz sand with a grading factor of 1.42 and mica (“Mica 40”, commercial product of the company "Kemira", Finland), portland cement (strength class 50 MPa) and blast- furnace slag (modulus of basicity M_b = 1.09, fineness (specific surface by Blaine) = 430 m^2/kg).

3. Testing techniques

The adhesion of the geocement-based adhesives was determined by a method of uniform shearing of two glued samples “concrete−concrete”, “concrete − ceramics”, “ceramics − ceramics” using the developed adhesive of optimum composition after 14 days, 3, 6, 12 months after preparation. Compressive strength of concrete was 20 MPa and ceramic tiles − 30 MPa. The force was applied perpendicularly to the surfaces of the glued samples.

The shrinkage of the geocement-based adhesives was tested on prisms (40×40×160 mm) prepared from the adhesives that hardened at normal conditions (t = 20 °C and R.H. = 60%) after 14 days, 2, 6, and 12 months with the help of a need-type comparator.

The freeze-thaw resistance of the glued joints was determined using the following testing technique: "freezing−thawing" (2 hours of temperature decline to minus 18 °C, isothermal curing for 2 hours, thawing in water at t = 20 °C for 20 hours one cycle- one cycle). In the determination of freeze-thaw resistance the samples were tested for residual adhesion strength after each following 10 cycles of “freezing-thawing” (so-called “factor of frost resistance”).

The interaction processes between adhesives and various materials and study of the interfacial transition zones between glued materials were studied by electronic microscopy (magnification: X30− X6000).

An X-ray spectrum analysis (XRD) was carried out with the help of an X-ray diffractometer equipped with a copper tube and nickel filter at U = 30 kV, I = 10-20 mA and range of the registered angles of (20) 8-60 (rotation speed of the counter 2 degrees per minute) by a technique reported in [5], The X-ray spectra were identified according to the references [6, 7].

A complex **DIFFERENTIAL THERMAL ANALYSIS (DTA)** was carried out in the process of heating the samples up to 1000 °C (10 °C per minute) and the fired technical alumina was used as a reference material. The spectra have been identified as described in [6-8].

In order to accelerate formation of the hydration products, an accelerated curing procedure was applied (10-times autoclave treatment at pressure= 8 atm).

4. Discussion of results

4.1. Adhesion resistance in uniform shearing

Data given in Table 1 show that the values of adhesion resistance in uniform shearing of the glued materials “concrete−concrete”, “concrete−ceramics”, “ceramics−ceramics” with mica or quartz sand as fillers reach the values required by the standards, and increase during 12 months of storage by 1.1-1.65 times.

Table 1

Adhesion strength in uniform shearing of the glued materials

Characteristics of adhesive and glued materials				Adhesion strength, MPa, after				
No	Filler	Quantity, % by mass of geocement	Glued materials	14 days	3 months	6 months	12 months	24 hr (immersion in water)
1	–	-	concrete−concrete	1.28	1.30	1.31	1.31	1.00
2	mica	2	concrete−concrete	1.75	2.65	2.87	2.88	1.98
3	sand	50	concrete−concrete	1.35	1.38	1.38	1.38	0.82
4	-	-	concrete−ceramics	1.13	1.20	1.20	1.20	0.50
5	mica	2	concrete−ceramics	1.25	1.30	1.32	1.32	0.86
6	sand	50	concrete−ceramics	0.85	0.91	0.91	0.91	0.31
7	-	-	ceramics−ceramics	1.08	1.10	1.10	1.10	0.68
8	mica	2	ceramics−ceramics	1.25	1.30	1.29	1.30	0.71
9	sand	50	ceramics−ceramics	1.10	1.11	1.11	1.12	0.62

Table 2

Compressive strength of the geocements and linear shrinkage of the geocement-based adhesives

Filler/additive			Linear shrinkage, mm/m				Strength, MPa
			Age				
No	type	quantity, % by mass of geocement	14 days	2 months	6 months	12 months	
1	mica	5	1.42	3.98	5.92	5.92	38
2	mica	10	1.41	3.83	5.86	5.60	40
3	sand	100	0.91	2.42	3.23	3.23	70
4	sand	150	0.85	2.33	2.85	2.85	57
5	mixture: sand (90%) and slag (10%)	100	0.40	1.20	1.30	-	78
6	CaSO4	5	0.75	1.26	1.89	1.89	24
7	CaSO4	10	0.72	1.23	1.84	1.84	18
8	portland cement	10	1.34	1.89	6.51	6.52	35
9	portland cement	15	1.32	1.83	6.46	6.46	38

Visually observations showed that the glued materials (concrete and ceramic tiles) had failed and not the adhesives themselves testifying to the higher compressive strength of the adhesives compared to those of glued materials.

4.2. Water resistance

The samples of the glued materials were tested for water resistance (t= 20 °C; 24 hours immersion in water). The tests of water resistance show that developed adhesives maintained their strength after immersion in water. The greatest adhesion after immersion in water was characteristic of the adhesives containing mica as a filler. This can be attributed to acceleration of structure formation processes due to action of the mica as a crystallochemical intensifier of hardening.

4.3. Shrinkage deformations

In order to reduce shrinkage, the following mineral additives were introduced: portland cement, $CaSO_4$ and slag.

Compressive strength was determined on cube samples 20×20×20 mm after hardening in normal conditions (t = 20 °C and R.H. = 60%) for 6 months. The results are shown in Table 2.

The adhesives with slag and $CaSO_4$ (10% by mass) were characterized by the lowest shrinkage deformation after 12 months of storage (Nos 5 and 7). This may be attributed to the following: slag and $CaSO_4$ start to expand and can compensate the occurring shrinkage. However, the composition No 5 containing ground quartz sand and slag was characteristic of low plasticity. The adhesives containing portland cement (Nos 8 and 9) in their composition two months after preparation had a net of cracks, this may be attributed to stresses occurring in the glued materials. The compositions with mica (Nos 1 and 2) had smooth glossy surface without any visible cracks.

4.4. Freeze-thaw resistance

The results of freeze−thaw resistance of the glued materials “concrete-concrete”, “concrete−ceramics” and “ceramics−ceramics” are shown in Figure 1.

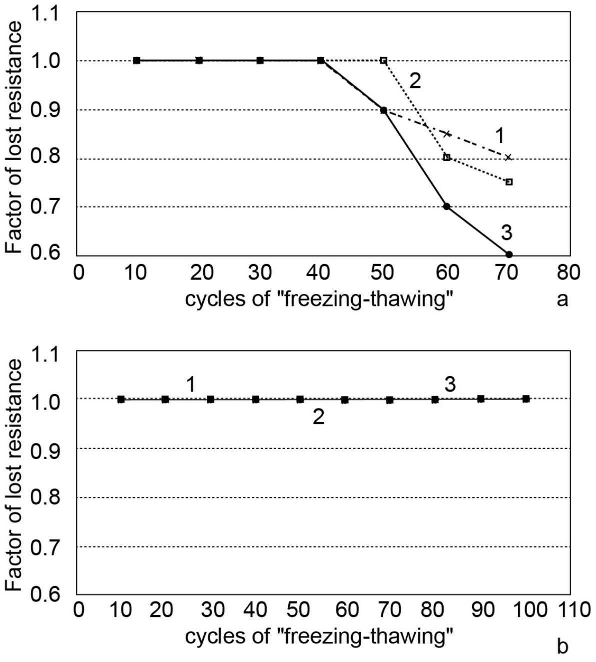

Fig. 1. - Freeze-thaw resistance of the glued materials (No 5, Table 2)(a − without filler/ additive; b − with filler/ additive): 1 − “concrete−concrete”, 2 − “concrete−ceramics”, 3 − “ceramics−ceramics”

As it follows from data shown in Figure 1a, freeze-thaw resistance of the glued materials: “concrete−ceramics”, “ceramics− ceramics” (in case of the adhesive compositions without filler and additive) starts to decrease after 40 cycles of freezing-thawing, and that of the glued materials “concrete− concrete” − after 50 cycles. This is demonstrated by the appearance of shrinkage-induced cracks on the surfaces of the glued materials. In the process of test, water starts to penetrate through these cracks and to expand when freezing is applied, thus the adhesives start to fail.

The use of sand in combination with slag (composition No 5, Table 2) in the adhesive composition was found to improve freeze-thaw resistance by two or more times (more than 100 cycles)(Fig. 1b). Sand was found to reduce also shrinkage of the adhesive and less water could penetrate into the adhesive defected areas, thus eliminating the overall destructive effect during freezing and thawing.

4.5. Structure formation processes

According to [9 – 11] a directed synthesis of zeolite-like hydration products of various composition and with a set of required properties takes place in the process of interaction of clay minerals with solutions of alkaline metals compounds. The properties are determined by a build-up of aluminosilicate framework, by an Al_2O_3 to SiO_2 ratio, nature and structural arrangement. Density and porosity of the hydration products are determining factors for strength, water resistance, and durability of the adhesives, that's why it is necessary to develop the adhesive compositions and process parameters to provide conditions for synthesis of the most dense zeolites, for example, zeolite P and analcime.

The X-ray spectra of hydration products of the geocements with a H_2O/Al_2O_3 ratio of 10 are shown in Figure 2.

When the adhesive containing mica (No 2) hardened at t=20 °C, its phase composition is represented by initial aluminosilicate phase that did not enter into reaction side by side with the X-ray amorphous phase (Fig. 2 curve 1), what is supported by single peaks corresponding to metakaolin (d/n= 0.425; 0.335; 0.325 nm). After long hardening of the adhesive at t=20 °C for 12 months (Fig. 2, curve 2) its hydration products are represented by single peaks of zeolite P (d/n=0.714; 0.335; 0.318 nm), and the peaks of initial phase of metakaolin have been detected. The intensification of crystallization processes with the help of 10-times autoclave treatment allowed to establish just the phase composition of the hydration products, which could be predicted after long hardening (Fig 2, curve 3). A phase composition was represented by zeolite P (d/n=0.716; 0.505; 0. 412; 0.365; 0.335; 0.319; 0.268 nm) and analcime (d/n= 0.561; 0.342; 0.293; 0.282; 0.252; 0.178; 0.172; 0158 nm).

In the thermograms of the samples under study (Fig. 3 curve 1) with X-ray amorphous phase, low-temperature endothermical effects at t = 50-250 °C have been detected which are caused by removal of the adsorption water. With increase in crystallization degree of the hydration products (Fig. 3, curve 2) the endothermical effect typical for zeolites was observed within the temperature interval of 50 …300 °C. With the higher intensity of peaks (Fig. 2, curve 3) the endothermical effect shifted to the area of the higher temperatures (Fig. 3, curve 3).

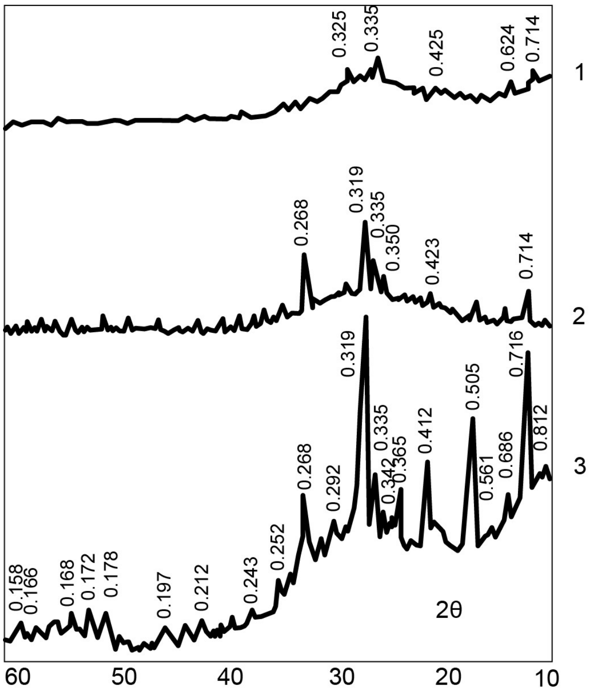

Fig. 2 - X-ray spectra of hydration products of the geocement-based adhesives: 1 – after hardening at t = 20 °C; 2 – after hardening for 12 months at t = 20 °C; 3 – after 10-times autoclave treatment (pressure = 8 atm).

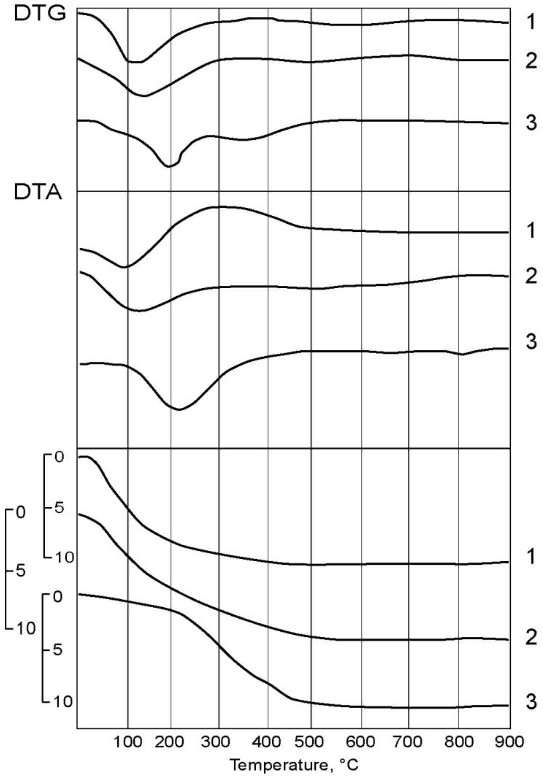

Fig. 3 - DTA-curves of hydration products of the geocement-based adhesives (No 2, Table 2): 1 – after hardening at t= 20 °C; 2 –after hardening for 12 months at t = 20 °C; 3 –after 10-times autoclave treatment (pressure = 8 atm).

The study of hydration products phase composition allowed to conclude that the products of interaction were represented by an amorphous gel of a cementing phase, composition and structure of which were determined by specific features of polymerized particles. First of all, the amorphous gel was formed in the system, which later transformed into sub-microstructure. This conclusion correlates well with the data reported in [7]. In compliance with the results of physical-chemical studies, the centres of crystallization were formed and increased not in a liquid phase, and, probably, by the mechanism of zeolites crystallization in a solid phase with regulation of the aluminosilicate structure. Noncrystalline structure was not identified using traditional methods (X-ray and Infra-red analyses), however it became possible using an atomic force microscope [12]. A conclusion was drawn that the process of hardening of the adhesives passes through stages of formation of aluminosilicate hydrates of amorphous, sub-microcrystalline and crystalline structure and is can be intensified by introduction of active fillers and additives.

The obtained results on the hydration products composition allowed to make a conclusion on a linkage of the alkaline ions in water-resistant structures of aluminosilicate hydrates of the zeolite P type of the garronite structure ($Na_2OAl_2O_3 \cdot$ (3.3-5.3)$SiO_2 \cdot$(4.3-5.7) H_2O) and analcime ($Na_2O \cdot Al_2O_34SiO_2 \cdot 2H_2O$).

5. Conclusions

According to results of physical-chemical studies of phase composition of the geocement-based adhesives, the process of hardening flows under a scheme of zeolite formation with the formation of amorphous sub-microcrystalline gel with polymeric structure, which crystallized to aluminosilicate hydrates of the zeolite P and analcite types.

The developed geocement-based adhesives with a set of properties (high adhesion, water- and freeze-thaw resistance, etc.), can be used for gluing together various materials like concrete, ceramics, etc.

Application techniques are simple-in-use. The geocement-based adhesives containing mica as a filler can be recommended for severe weather conditions for outdoor application. This can be attributed to acceleration of the structure formation processes by mica which acts, on the contrary to quartz sand, as a crystallochemical intensifier of hardening,

The geocement-based adhesives containing quartz sand as a filler with low shrinkage and low cost can be recommended for restoration of large defects on concrete surfaces. The geocement-based adhesives containing mica as a filler can be recommended for repair of concrete surfaces with deep cracks. The geocement-based adhesives with$CaSO_4$ as an additive with good plasticity and minimal shrinkage can be recommended for filling narrow deep cracks in concrete as well as large cracks. The geocement-based adhesives containing slag as an additive are advantageous because of shorter time required for hardening and the higher early strength.

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