RESEARCH ARTICLE

The effect of hydrodynamic cavitation on performance of the alkaline aluminosilicate coatings for metal structures

Sergii GUZII, Pavel KRIVENKO
Scientific Research Institute for Binders and Materials, Kyiv National University of Construction and Architecture, Kyiv, Ukraine

Abstract: Load-bearing metal structures working in atmospheric conditions are exposed to corrosion. Known-in-the art paint-and-lacquer protective coatings can provide protection of metal for rather short period of time (5…10 years). These structures can be effectively protected by more advanced coatings of new generation, namely: alkaline aluminosilicate binder-based coatings of barrier type. These binders differ from the known-in-the-art binding materials by formation in their hydration products of zeolite-like minerals and feldspathoids. The paper discusses principles laid down in formulating the binder composition in the (xK, yNa)2OAl2O3nSiO2mH2O system, target synthesis of hydration products of the binder matrix under influence of dynamic of the binder matrix in cavitation, optimal parameter order to synthesis of cavitation treatment aimed at nanostructuring of zeolite-like and hydromica phases after solidification. These coatings exhibit high corrosion resistance, high adhesion to metal substrate and durability results of restoration works that had been carried out in December 2010 of the Big Bell Tower of the Kiev Petchersk Lavra in order to protect corroded metal surfaces by applying the aluminosilicate binder-based coatings, the major constituent (binder) of which was represented by (0.72Na2O+0.28K2O)1.5Al2O3(4.56)SiO217.5H2O are discussed in details. In 2016, after 6 years of service in high humidity conditions and other aggressive exposures, the coated metal structures were examined and no sign of corrosion of metal substrate and damage of the applied coating was found.

Keywords: alkaline aluminosilicate binder; hydrodynamic cavitation; nanostructuring; zeolites

1. Introduction

Metal structures during service are subjected to moisture, ultraviolet radiation, temperature drops, contamination, the key factors of occurrence and development of corrosion of metal, which, according to various estimates, destroy from 10 to 12 % of metalwork produced worldwide. All above listed factors related to atmospheric corrosion have deleterious effect on metal structures of historical monuments as well. Corrosion of metal structures in atmospheric conditions occurs as a result of the action of short-circuited electrochemical cells. The difference of electrode potentials of the elements – the result of presence of various structural components and various concentrations of the potential – determining ions in different sites adjacent to the metal surface layer of electrolyte (an aqueous solution containing acid, alkali or salt). Visualized atmospheric corrosion products consist mainly of hydrated iron oxides (rust)[1–4]. Rate of electrochemical corrosion of metal may increase or decrease to zero, depending on availability of specific active substances on its surface. For example, presence of moisture is an important factor determining the speed of corrosion process in a free access to oxygen or the presence of corrosive ions. Humid atmosphere, particularly in the presence of sulfur dioxide and carbon dioxide, can be sufficiently aggressive environment.

The cause and type of corrosion and its development determine choice of appropriate methods for protection. The

doi: 10.18063/msacm.v2i2.696

choice of method is determined by its efficiency in each particular case, as well as economic feasibility. Protection from corrosion using coatings is based on their insulating, barrier, passivation or protective effect. Insulating coatings completely exclude possibility of penetration of aggressive agents to protected surface. According to[5,6], mechanically activated water glass-based coatings lose their abilities after a few years in service as a result of destructive processes (loss of adhesion, interruption of continuity of the protective coating due to its cracking followed by its peeling and flaking from the substrate).

In order to eliminate these shortcomings, preparation process of such compositions should be changed accordingly. To eliminate these drawbacks, it is necessary to change the preparation process of such compositions accordingly. This can be achieved by means of their nanostructuring due to cavitation processing. Implementation of this approach can be done by using cavitation devices for low-temperature synthesis of the compositions with required properties. Nanoscale cavitation, due to collapse of cavitation bubbles, affect physico-chemical properties of substances that deplete macromolecules and supramolecular structures, inactivated bacterial cells, and more[7–15].

A simplified principal scheme of cavitation process is shown in **Figure 1**[16].

According to the works reported in[17–22], synthesis of zeolite-like phases to ensure durability of the alkaline aluminosilicate binder-based coatings can be provided by short-time hydrodynamic cavitation.

The purpose of this work was to develop technology (choose parameters) for the alkaline aluminosilicate binder-based coating preparation in the fields of hydrodynamic cavitation and to try them in real application.

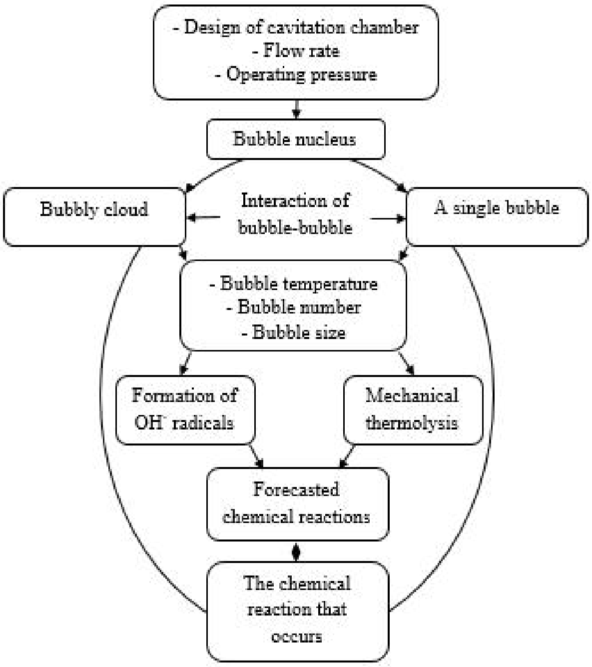

Figure 1. A simplified principal scheme of hydrodynamic cavitation

2. Materials and testing techniques

The following materials were used to prepare the alkaline aluminosilicate suspensions with the following formula: ($0.72Na_2O+0.28K_2O$: KM 60 metakaolin (Czech Republic); water glass with density of 1400 kg/m^3 and silicate modulus of 2.8 (SiO_2 – 33.1 %, Na_2O – 12.2 %); microsilica (SiO_2 – content higher than 85%); technical grade alumina (5% by weight of metakaolin). Chemical grade sodium and potassium hydroxides were used in the process of nanostructuring of the above suspensions.

Synthesis of the binder was performed in compliance with the polycondensation reaction:

$Al_2Si_2O_7+NaOH+KOH+nSiO_{2am}+H_2O \rightarrow (Na_2O+K_2O)\cdot1.5Al_2O_3\cdot nSiO_2\cdot mH_2O$.

According to the data of X-ray phase analysis, diffraction peaks were identified in metakaolin (Fig. 2, curve 1): β-SiO_2 (d=0.427; 0.336; 0.249; 0.212; 0.182; 0.166 nm), kaolinite γ-$Al_2O_3\cdot2SiO_2\cdot2H_2O$ (d=0.331; 0.287; 0.239; 0.235;

0.229; 0.213; 0.199; 0.194; 0.189; 0.179; 0.166; 0.162 nm) and dickite β-$Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$ (d=0.72; 0.50; 0.448; 0.418; 0.358; 0.259; 0.252; 0.235; 0.179 nm) as well as some halloysite $Al_2O_3{\cdot}2SiO_2{\cdot}4H_2O$ (d=0.44; 0.418; 0.393; 0.258; 0.249; 0.239; 0.202 nm); pyrophyllite $Al_2O_3{\cdot}4SiO_2{\cdot}H_2O$ (d=0.50; 0.41; 0.33; 0.290; 0.260; 0.240; 0.209; 0.200; 0.199 nm).

Three main phases of corundum were identified in the aluminium oxide (**Figure 2**, curve 2): α-Al_2O_3 (d=0.351; 0.256; 0.239; 0.209; 0.174; 0.160 nm), β-Al_2O_3 (d=0.570; 0.269; 0.252; 0.214; 0.204; 0.193; 0.155 nm); κ-Al_2O_3 (d=0.270; 0.257; 0.232; 0.210 nm) as well as small amounts of the following phases: γ-Al_2O_3 (d=0.239; 0.197 nm), η-Al_2O_3 (d=0.284; 0.197 nm), χ-Al_2O_3 (d=0.240; 0.211 nm).

Activation of the alkaline aluminosilicate dispersions was carried out in a high-speed cavitator and specific features of the alkaline aluminosilicate suspensions were examined using X-ray phase and differential-thermal analyses.

Identification of the phase was done according to[23–26].

With consideration of[27–29] on the influence of cavitation treatment of the alkaline aluminosilicate suspensions the following binder with a structural formula $(0.72Na_2O+0.28K_2O){\cdot}1.5Al_2O_3\ 4.5SiO_2{\cdot}17.5H_2O$ was chosen for the study.

The study the results of which are presented in this paper was done in three steps: first, effect of cavitation treatment on structure formation processes in the alkaline aluminosilicate binders was studied; then, the alkaline aluminosilicate binder-based coatings were prepared and their properties were studied; and, at last, pilot trial of the alkaline aluminosilicate binder-based coatings was performed.

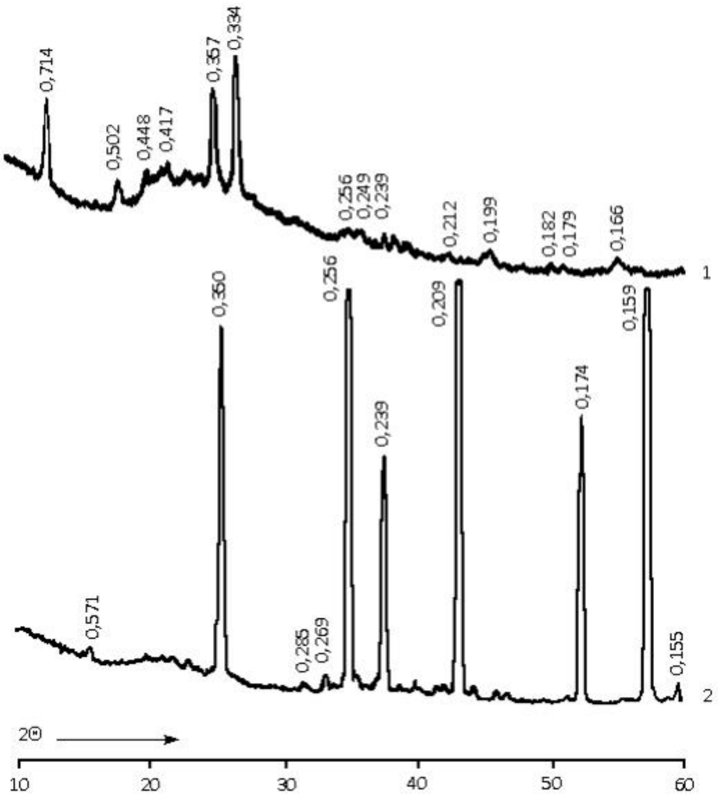

Figure 2. X-ray images of the constituent materials: 1 – metakaolin; 2 – aluminium oxide

3. Results and discussion

Analysis of the obtained data showed that pressure constituting 12.0 atm was measured on the second minute of cavitation treatment of the alkaline aluminosilicate dispersions. The pressure of 10 atm on the fifth minute and 8.0 atm on the sixth minute are indicative of the fact that the processes of dispergation of constituent components (aluminium oxide, metakaolin) occur in these dispersions. On the ninth minute, pressure (14 atm) and temperature (493K) reached maximal values (**Figure 3**), being characteristic of cavitation in hydrodynamic conditions and correlating well with the data given in[20,21,27,28].

After 28 day of hardening in natural conditions the hydration products of the alkaline aluminosilicate dispersion after cavitation treatment are characteristic of the following phases: $Al_2O_3\cdot 4SiO_2\cdot H_2O$ (beidellite) (d=0.260; 0.255; 0.239; 0.225; 0.214 nm); $Al_2O_3\cdot 2SiO_2\cdot H_2O$ (dickite) (d=0.487; 0.450; 0.433; 0.390; 0.351; 0.308; 0.276; 0.265; 0.255; 0.252; 0.238; 0.199; 0.166 nm); $Al_2Si_4O_{10}(OH)_2$ (pyrophillite) (d=0.433; 0.308; 0.255; 0.244; 0.215; 0.209 nm); $Al_2Si_2O_5(OH)_4$ (nacrite) (d=0.433; 0.390; 0.350; 0.243; 0.215; 0.204; 0.197; 0.177 nm); $NaAl_2(Si_3AlO_{10})(OH)_2$ (paragonite) (d=0.487; 0.430; 0.350; 0.320; 0.251; 0.244; 0.239; 0.215; 0.208; 0.222 nm) and $KalSi_3O_8\cdot H_2O$ (muscovite)(d=0.396; 0.300; 0.264; 0.252; 0.194 nm).

According to the data of differential - thermal analysis, endothermic effects at temperatures of 403, 433, 723 and 783K, which are characteristic of removal of physically bound and constitutional water from hydration products such as $Al(OH)_3$, potassium and sodium aluminosilicate hydrates. Above all, an exothermal effect at temperature of 648K, characteristic of the following transition: $\alpha\text{-}Al_2O_3 \rightarrow \beta\text{-}Al_2O_3$, was fixed. Losses of mass were 34 %.

The formulated alkaline aluminosilicate binder-based coatings were tried in practical conditions to protect portal frames in which the bells are hung of the Big Bell Tower of the Assumption Cathedral (VIII century) of the Kiev Petchersk Lavra in Kiev, Ukraine.

The binder was first activated by subjecting it to hydrodynamic cavitation treatment, then mixed with fillers[30–32].

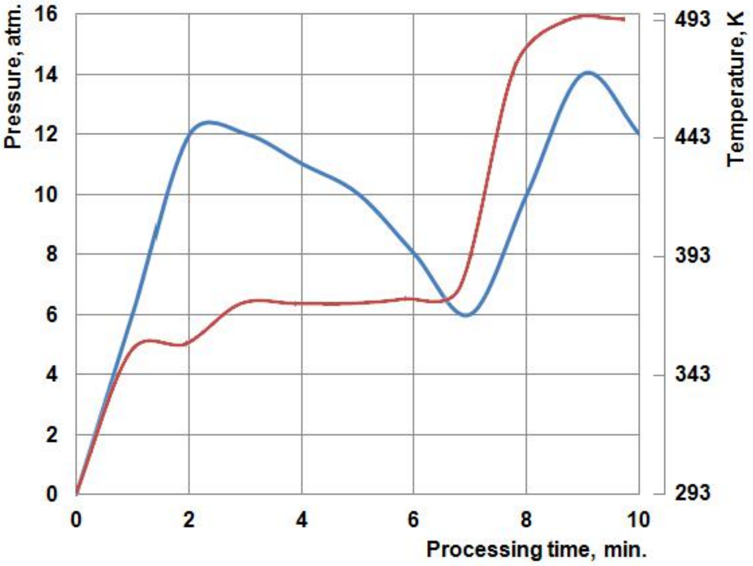

Figure 3. Pressure and temperature in the cavitator during cavitation treatment of the alkaline aluminosilicate dispersion of the following formula $(0.72Na_2O+0.28K_2O)\cdot 1.5Al_2O_3\ 4.5SiO_2\cdot 17.5H_2O$ vs. time of cavitation treatment

Physico-mechanical properties of the formulated coating are given below in Table 1.

Consumption of coating, kg/m², depending on type of substrate and coating thickness	**0.1…0.3**
Adhesion (pull-off strength), MPa	1.7…1.72
Coefficient of water resistance	1.05…1.15
Resistance to aggressive media:	
water and water vapor	excellent / good
diluted mineral acids (pH 3–5)	good
Lightfastness	excellent
Durability/coating life, years	Longer than 15

Table 1. Specifications of protective aluminosilicate-based coating

In 1968, the surfaces of these portal frames were painted using organo- mineral protective coating resistant to atmospheric corrosion. Between 1968 and 2010 no protection measures were taken with regard to metal structures. As a result of variations in temperature/humidity fields, centers of corrosion attack have occurred at a height of 35 m in the places where ends of the metal structures were embedded into load-bearing brick walls of the Bell Tower (**Figure 4**). The results of visual observation showed corrosion-induced damage of the metal beams (Figure 5) and a decision was taken as to restoration of metalwork to which the bells are hung.

Figure 4. View of the Big Bell Tower (a) and its metal parts (b, c), which corroded as a result of exposure to high humidity atmosphere

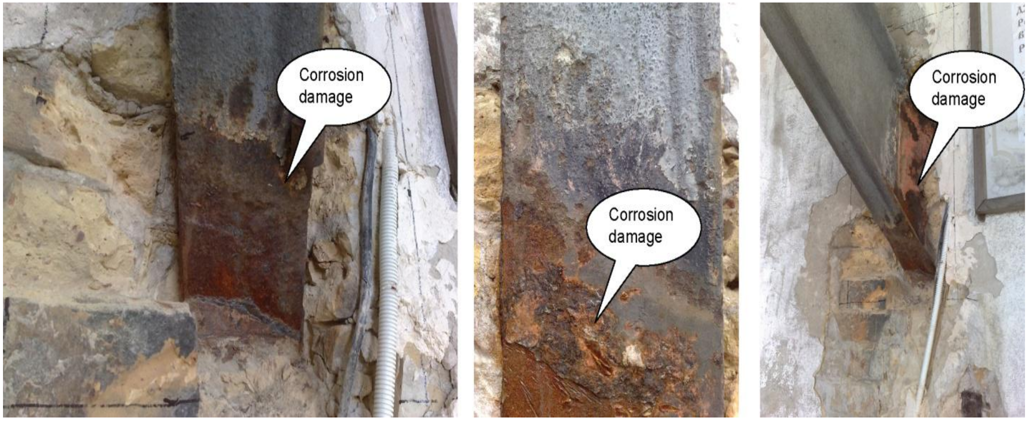

Figure 5. View of external ends of the metal substrate beneath plaster and brick masonry

The process of restoration work is shown in **Figure 6.**

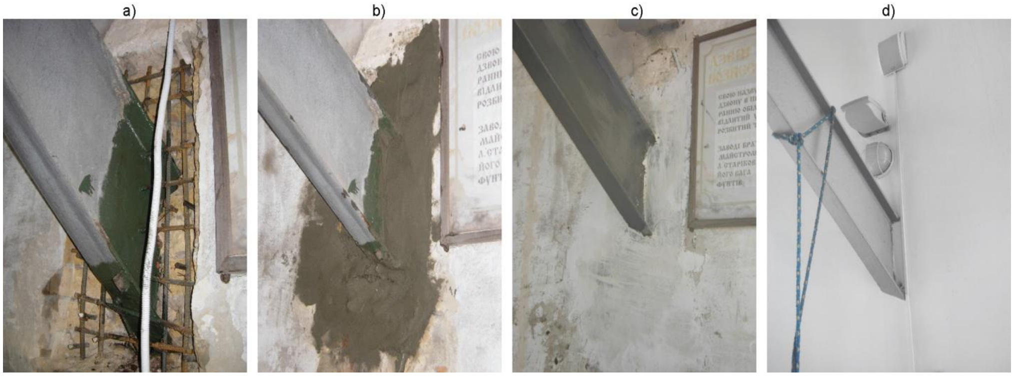

Figure 6. Application of the alkaline aluminosilicate binder-based coating (a), finishing works (b) (c), view of the metal beam after 6 years in service (d)

In the process of work the condition of the applied coating and metal substrate beneath this coating after 6 years in service in high humidity conditions and other aggressive exposures was studied.

Before the protective coating was applied the metal surfaces were properly cleansed. These preparatory works included:

removal of products of corrosion – layer of rust;

formation of profile and rough surface of the metal beams manually with the help of a grinding tool.

Examination of the condition of the metal substrate showed that:

steel surface, which began to corrode and started to worn due to abrasion, corresponded to corrosion grade B (as per ISO 8501-1);

after manual cleaning the rust was removed, and metal surface had grade of surface cleanliness Sa 1 (as per ISO 8503);

roughness group of the metal substrate was measured using a comparator: profile grading S – wave-like profile (corrugated), surface roughness group - medium-rough, Rz 125 mkm (as per ISO 8503). A given profile and roughness group are suitable for application of the alkaline aluminosilicate binder-based coating in thicknesses up to 150 mkm.

Determination of values of adhesion was carried out by forced detachment (pull-off strength). The formulated coating was applied manually with a brush to reference metal plates 70×150×3 mm in size. The plates with solidified coating were stored on horizontal surface of the flange beams in the conditions in which the frame itself was in service. Thickness of the alkaline aluminosilicate binder-based coatings was measured using a layer thickness meter TP-1, and the value of adhesion by a method of normal force detachment using a device for adhesion testing designed by the approved testing center for building structures of the Kiev National University of Construction and Architecture.

Macrostructure of the artificial stone was studied after preparation and hardening (solidification) (**Figure 7**, a) and after 6 years of service in high humidity conditions (**Figure 7**, b) using a digital microscope.

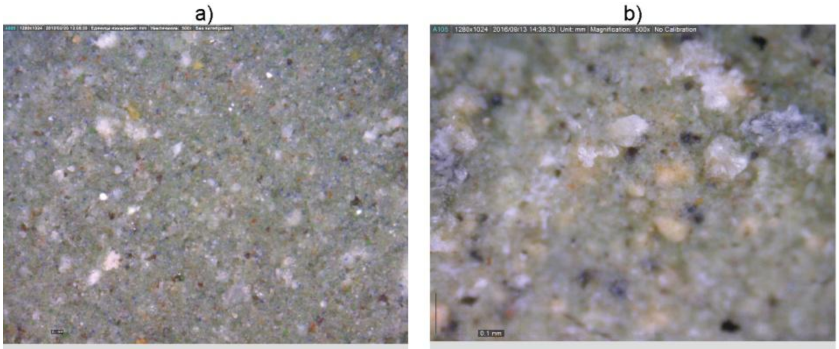

Figure 7. Macrostructure of the alkaline aluminosilicate binder-based coating after: (a) preparation and hardening (solidification); (b) 6 years of service in high humidity conditions. Magnification ×500 (a, b)

A conclusion was drawn that after 6 years in service in high humidity conditions, alternating temperatures (plus-minus) and atmosphere reagents the surfaces of the load-bearing walls of the Bell Tower and ends of the beams had no any sign of corrosion (Figure 6, d). According to visual observation of the coated reference specimens (metal plates) which were in service for the same period of time, no sign of cracks, swelling and flakes was observed. Values of adhesion of the coating immediately after preparation was 1.7 MPa, after 6 years in service – 1.72 MPa. Visual examination of the metal substrate of the beams and the reference metal plates beneath the coating showed no any sign of corrosion (Figure 6 d).

4. Conclusions

The results of work suggested to draw the following conclusions:

the application of hydrodynamic cavitation to the alkaline aluminosilicate binder affects positively zeolite phase formation in the hydration products in normal conditions; these zeolite-like phases are responsible for durability of the alkaline aluminosilicate binder-based coating;

the coated (using alkaline aluminosilicate binder-based coating) surfaces of the metal portal frames in which the bells are hung for a period of 6 years were not damaged, that is the applied coating was found to be resistant to atmospheric corrosion. No sign of cracks, swelling and flakes was observed, the value of adhesion of the alkaline aluminosilicate binder-based coating to metal substrate was 1.72 MPa, being by 2.9 times higher than the norm-specified value.

References

1. I Andreev. Corrosion of metals and their protection. Kazan, Tatar publishing house, 1979.
2. AA Gerasimenko. Protection against corrosion, aging and biodegradation of machinery, equipment and structure. Mashinostroyeniye, Moscow, 1987; 1.
3. GG Uhlig, RU Revie. Corrosion and fight against it. Leningrad, Khimiya, 1989.
4. VI Safronchik. Corrosion protection of building structures and technological equipment. Stroyizdat, Leningrad, 1988.
5. FN Suleymanov. Development activities and fireproof materials to ensure fire safety in the oil and gas facilities.

PhD Thesis: 05.26.06. UGNTU, 2001.
6. NV Yeryomina. Flame retardant compositions based on liquid glass and mechanically activated oxides of aluminium and magnesium. PhD Thesis, 2007.
7. PG Komokhov. The sol-gel as concept of a cement composite nanotechnology, system structure and ways of its realization. J. Building Materials 2006; (9): 14–15. (in Russian).
8. H Schmidt. Inorganic-organic composites for optoelectronics. Springer US, on Sol-Gel Optics 1994; 451–481.
9. EI Yevtushenko. Activation processes in building materials technology. V.G. Shukhov State Technological University, 2003.
10. TM Vitenko. Mechanism and kinetics of intensifying action of hydrodynamic cavitation in chemical and technological processes. DSc (Eng) Thesis, 2008 (in Ukrainian).
11. GS Khodakov. Fine crushing physics: monograph. Nauka, 1972 (in Russian).
12. IM Fedotkin, IS Gulyi. Cavitation: cavitation engineering, their use in industry (theory, calculations and designs of cavitation devices). Poligrafknika, Part I, 1997.
13. IM Fedotkin, IS Gulyi. Cavitation: cavitation engineering, their use in industry (theory, calculations and designs of cavitation devices). OKO JSC, Part II, 2000 (in Russian).
14. IM Fedotkin, AF Nemchin. Application of cavitation in technological processes. Vysshaya Shkola Publishing House of the Kiev National University, 1984.
15. CJ Brinker, GW Scherer. Sol-gel science: The physics and chemistry of sol-gel processing. Academic Press, 1990.
16. HJ Abdullah Al Musa, SG Guzii. Process for receipt of geocement coatings in the fields of hydrodynamic cavitation. Proc. of the II International scientific and technical conference “Energy-efficient machinery and technology” 2015; 25 – 26 (in Russian).
17. PV Krivenko. Elaboration of physical and chemical grounds of targeted synthesis of inorganic binders in the system Na2O-Al2O3-SiO2-H2O for production of environmentally friendly intumescent materials. Stroitelstvo Ukrainy Journal (Construction of Ukraine). 1997; (2): 46–49 (in Ukrainian).
18. PV Krivenko. Fireproof coatings based on alkaline aluminium silicate systems. Developments in Strategic Materials. Ceramic Engineering and Science Proceedings 2009; 29(10).
19. SG Guzii, SA Terenchuk. Studies of the physical properties of alkali aluminosilicate suspensions after cavitation treatment. News NTU "KPI". Thematic issue "Chemistry and chemical technology in ecology", NTU "KPI" 2010; (65): 119–126 (in Russian).
20. PV Kryvenko, SG Guziy. Abdullah Al Musa J. Effect of Cavitational Treatment on Nanostructuring of Alkali Aluminosilicate Dispersions. VI Int. Conf. on Nano-Technology in Construction (NTC 2014), Cairo, Egypt. 2014; 52–64.
21. PV Krivenko. Influence of cavitation treatment at rheokinetic properties of alkali aluminosilicate dispersions. News ODABA. Zovnishreklamservis 2015; (57): 65–72 (in Russian).
22. P Krivenko, S Guziy, J Abdullah Al Musa. The Influence of Cavitation Treatment On Amorphization of Kaolinite in the Dispersion of the “Kaolin-Na2O.nSiO2.mH2O-NaOH-H2O” Composition”. Calcined Clays for Sustainable Concrete, RILEM Bookseries 2015; 387–394.
23. VN Semushin. X-ray detector of zeolites. Nauka Publishing House, 1986 (in Russian).
24. GI Ovcharenko. Zeolites in building materials. Altai State Technical University Publishing House, 2000 (in Russian).
25. DW Breck. Zeolite molecular sieves: Structure, chemistry and use. Wiley, 1973.
26. IA Belitsky. Thermographic study of zeolites. In Proceedings for Genetic and Experimental Mineralogy 1972; (7): 255–309 (in Russian).
27. SG Guziy. Features of processes of structuration of binders compositions in the system “xNa2O·yAl2O3·nSiO2·mH2O. On Proc. of XII symposium on science and Research in the Silicate chemistry, Chemistry of Non Silicate Binders and Technology Application SILICHEM, Brno 2007; 35–41.
28. SG Guziy. Research of a microstructure of an artificial stone of a binder composition in system xNa2OyAl2O3nSiO2mH2O. Non-traditional Cement&Concrete III. proc. of the Int. Symp., Brno University of Technology 2008; 312–319.
29. SG Guzii. Alkali aluminosilicate binding compositions based on soil silica: fundamentals of synthesis, technology for production and application. Scientific and Practical Conference “High-temperature materials and technologies in the 21st century”, D. Mendeleev University of Chemical Technology of Russia, November 2008.
30. PV Krivenko, SG Guziy, JHA Al Musa. Atmospheric Corrosion Protection of Metallic Structures Using Geocements-based Coatings. Solid State Phenomena 2015; (227): 239–242.
31. S Guzii, JHA Al Musa. Study adhesive properties on aluminosilicate-based coatings of barrier-type. Technology Audit and Production Reserves 2016; 4/4(30): 13–17.
32. P Krivenko, S Guziy. Aluminosilicate coatings with enhanced heat-and corrosion resistance. Applied Clay Science 2013; (73): 65–70.