High-silica composite materials based on liquid glass binder modified with fluorine-containing additives

N. Klimenko, N. Mikhailenko, , N. Kakurkin,
M. Kopeikina, T. Shavshishvili

Abstract: *Development and investigation of the high-silica composite materials based on liquid glass binder were carried out. The effect of modifying functional additives on mechanical properties and biological resistance of the composite materials was determined. It is shown that all the proposed compositions are resistant to fungi and compositions, modified fluorine-containing additives possess fungicidal properties.*
Keywords: *liquid glass binder, biological resistance, high-silica composite materials*

INTRODUCTION

Multiple use of local raw materials, industrial waste, secondary raw materials are a promising direction in the development of building materials engineering. This provides resource and energy saving both in the construction period and during maintenance of the constructed buildings. Development of compositions and technological parameters production of effective non-fired materials from non-deficient and man-triggered materials is the actual problem in materials science, construction, technical, industrial, technological, economic and environmental aspects. In recent years, more and more attention is attracted to materials based on liquid glass binder due to their heightened ecological and energy efficiency [1].

Actual task is to increase the service properties of non-fired materials based on liquid glass binder which will enable expansion of their areas of application and increase the competitiveness compared to conventional building materials.

Longevity is one of the most important properties that determine the economic value and efficiency of materials. While in service materials and products undergo corrosion damage due to various environmental factors including microbial corrosion. Perspective direction is a study of biological resistance of materials and developing methods of their protection from biodegradation.

The purpose of this study was developing high-silica composite materials based on non-deficient local raw materials, industrial wastes and liquid glass as a binder, the study of opportunities to improve of service properties by modifying the raw mixtures, as well as the study and comparison of the biological stability of the synthesized compositions.

EXPERIMENTAL PART

The objects of the study were high-silica composite materials obtained from mechanically activated mineral placeholder and liquid glass as a binder modified fluorine-containing additives.

Silica sand, ground granulated blast furnace slag, sodium liquid glass and fluorine-containing additives were used as raw materials. The main mineral placeholder is quartz sand which according to the petrography consists of well-rounded grains of crystalline quartz some of which have amorphous surface and clay film. Content of quartz is approximately 98%. Ground granulated blast furnace slag, as calcium-silicate constituent, basically consists of a glassy mixture of large and small fractions of light-gray color. According to the petrography, the content of the glass phase in the sample is 99%. Sodium liquid glass with a module of three and a density of 1.48 g/cm^3 was used as an alkali binder.

Two series of samples were synthesized. Sodium silicofluoride (Na_2SiF_6) and waste of production of fluoride salts - silicon dioxide fluorine-containing (SDFC) were used to intensify the processes of curing and increase biological resistance of compositions. Sodium silicofluoride is a traditional curing agent for compositions based on liquid glass binder. According to [2] content Na_2SiF_6 normally is 15 – 20 % from the water glass. In this connection concentration of 2 and 5 wt. % Na_2SiF_6 have been selected. In order to improve the biological resistance of composites composition containing 10 wt. % Na_2SiF_6 was also prepared. A series of samples modified with silicon dioxide fluorine-containing was synthesized. SDFC concentration was calculated so that the fluorine content in the samples of both series was equivalent.

The high-silica materials were synthesized by non-fired technology. Mineral placeholder underwent mechanical activation by simultaneous grinding in a planetary mill. The liquid glass and modifying additives that affect the rate of curing of composites (Na_2SiF_6 and SDFC) were added to the obtained homogeneous mixture. The samples were compacted from prepared raw mass and then subjected to heat treatment. Measurement of the physical and mechanical properties was performed in accordance with existing methods. Testing of materials on fungicidal properties was conducted in accordance with the national standard 9.049-91 by two ways [3]. Biological resistance of the materials was evaluated by the degree of their fungus fouling, using optical microscopy (Olympus BX51 microscope).

RESULTS AND DISCUSSION

The obtained high-silica composite materials possess satisfactory technological properties. It was found that the modification of raw mixes fluorine-containing additives (Na_2SiF_6, SDFC) increases the water-resistance of synthesized materials (Fig. 1a); decreases porosity and water uptake of the composites (Fig. 1b) as well as a positive effect on their strength (Fig. 2). The value of bending strength is 30 MPa and the value of compressive strength is 60 MPa. These values are more than two times higher than the corresponding values for the original unmodified compositions.

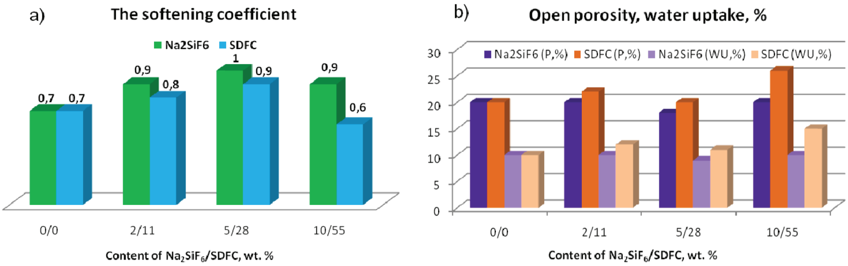

Fig. 1. The influence of modifiers for water resistance (Fig. 1a) and water uptake (Fig. 1b) of the high-silica composites.

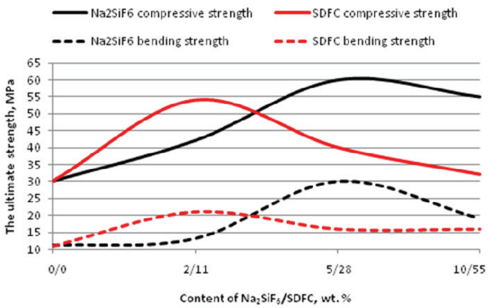

Fig. 2. The influence of fluorine-containing additives on the mechanical properties of the synthesized composites.

A nature of the selected raw materials greatly influences on the physical and mechanical properties of the composites, namely high microhardness and chemical resistance of quartz sand, high reaction activity of glass-furnace slag towards the alkaline binder and good adhesion properties of the liquid glass.

Structure formation in the synthesized compositions is due to astringent properties of liquid glass, i.e. the ability to self-curing, to form an artificial silicate stone, which allows obtaining a strong material without high-temperature treatment.

Structure and properties of materials based on liquid glass binder depends on the completeness of the colloid chemical processes accompanying the interaction of a water solution of sodium silicate with particulate placeholder. The main stages of the curing process include allocation of silicic acid, a further polycondensation, gelation and the transition to the xerogel. Acting as a binder, liquid glass enters into chemical interaction in primarily with the active amorphous phases of placeholder, due to which silicates with low modulus become the silicates with higher content of SiO_2, i.e. insoluble form. This is the reason for increased strength and water resistance of the compositions. The main reactions taking place during curing of the system are the reaction of the polymerization of silica gel and the reaction of formation of carbonates and hydrosilicates in amorphous or microcrystalline form. At the last stage the maturation of the gel, i.e. allocation of water of the during of polycondensation, and the gradual aggregation of particles, leading to the dense structure takes place. Under normal conditions, the reaction rate between the components of raw mix is low, and the growth of new crystal phases occurs during months. As a result of heat treatment, as well as the interaction of fluorine-containing additives with liquid glass curing rate samples increases. It is known when the fluorosilicate decomposes occur allocation of additional silicic acid, which compacting of system [2]. Increase of the density of the material occurs also due to the intensive formation of a new crystalline phase which fills the pores and reinforces the structure.

In the second step of our study we investigated the influence of fluorine-containing additives on the biological stability of the composite materials. Biological stability of the materials was determined by infecting fungi spores in sterile conditions (absence of any pollution) and in conditions simulating mineral and organic impurities (Czapek Dox medium). Found high-silica composites have high biological resistance. No germination of spores and conidia on the samples under the microscope was detected. Duration of the test to assess the biological stability of the materials according to the degree of development of fungi was 28 days with an intermediate examination after 14 days.

It was found that the material does not contain substances that could serve as a breeding ground for mold. We established that the presence external contamination, both organic and inorganic ones, had no significant effect on the biological stability investigated composites.

The samples were placed in a Petri dish with the sowing of fungi in a nutrient medium and incubated under conditions optimal for their development within 56 days in order to determine the fungicidal properties. Two types of mold were used as the test organisms: Aspergillus niger van Tieghem and Trichoderma viride Pens, which are the most typical biodestructors. The results of comparative tests of biological stability of the developed materials are presented in Table. 1.

The presented data reflect the fact that the lowest biostability show initial samples without additives. The presented data reflect the fact that initial samples without additives have the lowest biostability. During observations on the development of fungi it was found that the control samples start to become covered with mycelium of fungi in contact with the nutrient medium in 14 days. On the samples of high-silica composites modified by SDFC, the fungal spores germinate after 28 days. The composites modified with sodium silicofluoride keep showing their fungicidal properties for 56 days. It should be noted that the tests were performed for the samples containing 10 wt. % Na_2SiF_6, and the samples containing 11 wt. % SDFC in which the fluorine content is equivalent to 2 wt. % sodium silicofluoride. Therefore increase in SDFC can result in increased fungicidal properties composites.

Table. 1. The dynamics of the growth of fungi in samples high-silica composites in a nutrient medium.

Additive – Na_2SiF_6 (10 масс.%)		Additive – ДОКФ (11 масс.%)	
Thichoderma	*Aspergillus*	*Thichoderma*	*Aspergillus*
14 days			
			
28 days			
			
56 days			
			

There are many factors, both internal and external, affecting the ability of a material to resist the biological effects of the environment. Among them, the chemical composition of the material, its micro- and macrostructure, the presence of fungicide additive, nature of the environment in which the material is maintained, etc. The possible reasons for stronger or weaker resistance of the material to the development of mold, is an acid-base indicator of a thin film of moisture adsorbed on the surface in which spores develop. Observations show that the most favorable environment for the development of fungi is a weak acidic medium with a pH of 4.5-5.5. Presence of sodium silicate in the studied composites obviously raises the pH (alkalinity) of the absorbed moisture as a result of hydrolytic processes on their surfaces and the environment becomes less favorable for the development of the mycelium. Another reason for the increase of biological resistance of developed composites is their modification with fluoride supplements (Na_2SiF_6 and SDFC). Their fungicidal nature obviously plays an important role.

CONCLUSION

It the present study, it was found that improved service properties of high-silica composite materials based on silica sand and granulated blast furnace slag activated with an aqueous solution of sodium silicate (liquid glass) was realized through compressing in combination with heat treatment and modification of raw mixes sodium silicofluoride.

The experiments show that the developed composite materials are biologically resistant. The compositions which were modified with fluorine-containing additives (Na_2SiF_6 and SDFC) show increased biological resistance and fungistatic effect, which persists for a long time.

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About the authors:

Prof. N. Y. Mikhailenko, Department of Chemical Technology of Glass and Sitall – MUCTR, Moscow, Russia; tel. +7(495)496-92-93, e-mail: glas@rctu.ru;

N. N. Klimenko, Department of Chemical Technology of Glass and Sitall – MUCTR, Moscow, Russia; tel. +7(495)496-92-93, e-mail: klimenko_nata@mail.ru.

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