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Portland cement-based penetrating electrically conductive composition for protection against electrocorrosion

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A conductive composition of penetrating action based on Portland cement with a complex chemical additive and graphite filler has been developed. The composition is intended to protect reinforced concrete structures from electrocorrosion due to the formation of an electrically conductive coating on their surfaces with a simultaneous increase in the electrical resistance of the surface layer of the structure itself. Experimental studies have been carried out, incl. electron microscopic, spectroscopic, X-ray phase analysis. The regularities of the formation of the electrophysical and physical-mechanical properties of the composition, their dependence on the composition are established.

Keywords: graphite, Portland cement, chemical additives, hydration, electrical conductivity.

Електропровідна композиція проникної дії на основі портландцементу для захисту від електрокорозії. *А.А.Плугін, О.А.Плугін, В.В.Касьянов, О.і.Дьоміна, Д.О.Бондаренко*

Розроблено електропровідну композицію проникної дії на основі портландцементу з комплексною хімічною добавкою і графітовим наповнювачем. Композиція призначена для захисту залізобетонних конструкцій від електрокорозії за рахунок утворення на їх поверхнях електропровідного покриття з одночасним підвищенням електричного опору поверхневого шару самої конструкції. Проведено експериментальні дослідження, у т.ч. електронно-мікроскопічні, спектроскопічні, рентгенофазовий аналіз. Встановлено закономірності формування електрофізичних та фізико-механічних властивостей композиції, їх залежності від складу.

Разработана электропроводная композиция проникающего действия на основе портландцемента с комплексной химической добавкой и графитовым наполнителем. Композиция предназначена для защиты железобетонных конструкций от электрокоррозии за счет образования на их поверхностях электропроводного покрытия с одновременным повышением электрического сопротивления поверхностного слоя самой конструкции. Проведены экспериментальные исследования, в т.ч. электронно-микроскопические, спектроскопические, рентгенофазовый анализ. Установлены закономерности формирования электрофизических и физико-механических свойств композиции, их зависимости от состава.

1. Introduction

At present, electrically conductive composite materials based on mineral binders are getting increasingly widespread [1]. Electrically conductive concretes are based on Portland cement [2–6] and alkaline binders [7–9]; electrical conductivity is provided by the introduction of electrically conductive fillers such as carbon-graphite [3, 7] and metal-containing fillers [4]. Portland cement and carbon-graphite fillers are affordable and cheap materials. At present, penetrating waterproofing compounds based on Portland cement are being created; these are applied to the concrete surface, and the hydration products of which clog the pore space of concrete and seal its surface layer [10]. These hydration products are formed owing to the interaction of aluminate phases of Portland cement clinker with the addition of carbonates, nitrates, sulfates, calcium chlorides and sodium chlorides with the formation of Friedel's salts and others [11, 12].

The electrical conductivity of concretes and compositions depends on the chemical composition (ratio of components) [5], structure [4, 6, 8], especially microstructure [4, 8, 9], technological effects during manufacture [5, 13, 14], and actual humidity level [15]. The electrical conductivity is usually controlled empirically during the production of composites by experimentally investigating its dependence on formulation and technology factors. In [16], the calculation method of electrical conductivity control for the intended use of the composition has been substantiated.

Electrically conductive concretes are used mainly for heating elements [2, 3, 7], for protection against ionizing radiation [4], for grounding elements [2]. No case of their use for conductive grounded screens as a protection measure against electrocorrosion has come to our notice. Moreover, the authors do not know any work on the analysis of the mechanism of electrical conductivity of Portland cement-based graphite-containing compositions.

The purpose of the research is to establish the effect of graphite fillers on the hydration and electrophysical, hydrophysical, physical and mechanical properties of Portland cement-based compositions with a complex chemical admixture of carbonates, nitrates, sulfates, calcium chlorides and sodium chlorides; to develop an electrically conductive composition capable of forming an electrically conductive coating on the surface of the structure while improving the electrical resistance of the surface layer of the structure itself, which will reduce the electric current intensity in the structure.

2. Experimental

For experimental studies, two types of graphite powder were used. G1: foundry graphite with a particle content of up to 160 μm over 60 %; and G2: lubricating graphite with a particle size of up to 6 μm over 60 %. G1 larger particles are marked by a scaly shape. The composition under investigation consisted of the following mass fractions: Portland cement CEM I-500N: 32 (31.0 to 33.0); quartz sand with a fineness modulus of 1.2 to 1.5: 53 (52.1 to 56.0); complex chemical admixture on average 5 %, including sodium nitrate: 1 (0.15 to 1.0); calcium salt of weak inorganic acid: 1 (0.2 to 1.33); calcium chloride: 0.5 (0.10 to 0.67); sodium sulfate: 0.5 (0.10 to 0.67); sodium carbonate: 0.5 (0.10 to 0.67); calcium hydroxide: 1 (0.25 to 1.68); rust converter: 0.1 (0.025 to 0.17); corrosion inhibitor: 0.1 (0.025 to 0.17); superplastifier, sulfo-naphthalene formaldehyde: 0.3 (0.05 to 0.34). The content of graphite fillers varied about 10 % (from 0 to 20 %) by weight of the composition, while the content of other components varied proportionally.

The effect of graphite fillers on the hydration of Portland cement and the morphology of hydration products was investigated by X-ray analysis, infrared absorption spectrum analysis, scanning electron microscopy with electron probe microanalysis. Compositions with 10 % of G2 graphite filler and without filler were investigated for verification.

Diffraction patterns were obtained using a DRON-1.5 X-ray diffractometer with an X-ray tube with an iron cathode (1.6БСВ27-Fe). The diffraction patterns were registered in the following mode: angle range of 2θ is from 7 to 80 deg; cathode voltage is 30 kV; current intensity is 20 mA. Infrared absorption spectra in the range of wave numbers of 400 to 4000 cm^{-1} were obtained from tablet samples using a Bruker Alpha IR Fourier spectrometer and OPUS software. To obtain a sample, a weighed portion of the composition was ground in a pounder, mixed with potassium bromide and pressed in a mold under a pressure of 8 to 8.5 MPa.

Electron microscopic studies of morphology and electron probe microanalysis of the local elemental composition of the cured composition chips were performed using a JSM-6390LV scanning electron microscope with an AZtechEnergy X-max^n 50 energy dispersive spectrometer. The mapping was performed at an accelerating voltage of

15 kV. On X-ray maps of the elements, the lighter areas correspond to the larger content of the element, the darker ones show its smaller content (dark areas can also correspond to the shadows of chip roughness that interfere with the output signal).

The electrical resistivity of the composition in a 2 mm thick coating on the long surface of a cement-sand mortar bar 160×40×40 mm was determined using an ohmmeter (digital multimeter Sanwa PC510) with superimposed porous rubber electrodes impregnated with a saturated solution of copper sulfate. The hydrophysical properties, water absorption and water resistance coefficient (softening), as well as physical and mechanical properties of the compositions were determined by methods adopted for testing building materials.

The efficiency of electrically conductive compositions for grounded coatings was studied using original experimental samples, each of which comprised a model of a structure — a prism made of heavy concrete with a compressive strength of 20 MPa, on which a steel reinforcing bar is concreted. The test composition was previously applied to the prism in the form of a screen coating, which was included in the electrical circuit to simulate grounding. The prism was placed in a metal container filled with soil such as very fine sand, which was moistened during the experiment. The reference specimens were prisms without any grounded screening coating. The current flowing to the structure from the electrified rail track was generated (simulated) by a direct current source by applying a potential difference of 40 V between the tank and the reinforcement bar under control of a voltmeter. The current strength in the structure (reinforcement bar) and the protective screen (ground circuit) was determined using ohmmeters connected to the circuit (Sanwa PC510). The indicator of the efficiency of the electrically conductive composition was taken as the percentage of current reduction through the reinforcement and concrete due to the use of a grounded screening coating. The measurements started when the soil was dry, then it was saturated with water and the measurements were continued for 240 h at intervals of 1 h, then 6, 12 and 24 h. The measurement results were presented in the form of graphs of the time dependences of the current strength and the magnitude of the decrease in the current strength through concrete and reinforcement for the model with protection in comparison with the model without protection; then the results were analyzed.

3. Results and discussion

3.1. Theoretical studies of the effect of graphite fillers on the electrical conductivity of the composition

An electrically conductive composition under study can be represented as a composite with a matrix of cement stone and graphite particles as filler. Graphite is one of the polymorphic modifications of carbon, a first species conductor with electronic conductivity. Cement stone is a water-dispersed system where the dispersed phase consists of particles of hydration products, and the dispersion medium is a pore electrolyte, which is a saturated solution of $Ca(OH)_2$. The electrical conductivity of the pore electrolyte is much higher than that of the particles of hydration products; therefore, the pore electrolyte provides the electrical conductivity of cement stone and is a second species conductor with ionic conductivity, which is provided by Ca^{2+} cations and OH^- anions. Thus, electrode processes should take place at the contact of graphite particles with cement stone, in particular, pore electrolyte (Fig. 1). Depending on the direction of the applied electric potential, the surfaces of graphite particles are divided into anode and cathode areas (Fig. 1), where the reactions can occur in an alkaline medium [17]:

— Anodic reaction:

$$C + 3H_2O - 4e^- \rightarrow CO_3^{2-} + 6H^+; \quad (1)$$

— Cathodic reaction:

under aerobic conditions:

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^-; \quad (2)$$

under anaerobic conditions:

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2. \quad (3)$$

Since Portland cement-based compositions are permeable to air, the cathodic reaction will take place under aerobic conditions (Fig. 2b). The products of the anodic reaction in the medium of cement stone are bound by Ca^{2+} and OH^- ions to calcite (or calcium hydrocarboaluminate) and water, respectively:

$$Ca^{2+} + CO_3^{2-} = CaCO_3; \quad (4)$$

$$H^+ + OH^- = H_2O. \quad (5)$$

The products of the cathodic reaction: the OH^- ion binds to the H^+ ion according to reaction 5, the gaseous hydrogen H_2 is released into the air.

As you can see, graphite dissolves in the anode areas of the surface of the particles;

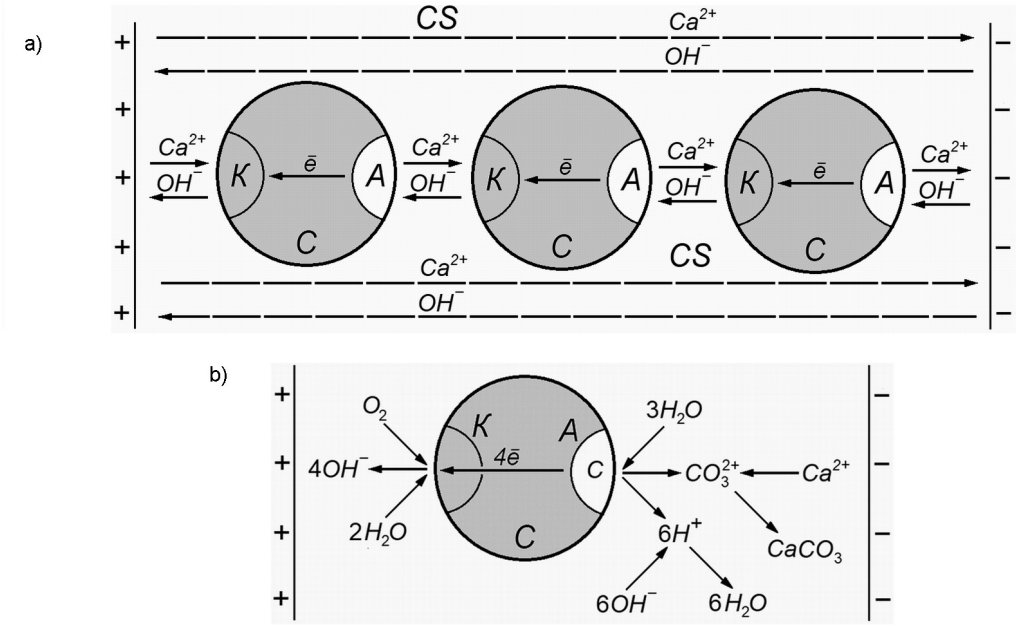

Fig. 1. Electrical conductivity of the Portland cement-based composition with graphite filler: a) circuit of electric current flow: C) graphite filler (carbon), CS) cement stone (pore electrolyte), A) anode and K) cathode areas of the graphite surface; b) electrochemical reactions at the interface between graphite and pore electrolyte of cement stone under aerobic conditions.

therefore, the durability of the composition in terms of electrical conductivity will be due to the amount of electricity passed by the graphite particles.

3.2. Physical-chemical studying the effect of graphite fillers on the hydration of Portland cement

The bar graphs and infrared absorption spectra of the Portland cement-based composition with a complex chemical admixture without filler and with graphite filler are shown in Fig. 2.

The diffraction patterns of the compositions without filler and with graphite filler are generally similar and contain diffraction maxima (lines) of the main hydration products of Portland cement. The line corresponding to $d = 3.34$ Å, which appears on the diffraction pattern of the composition with a graphite filler (Fig. 2a), although it coincides with one of the lines of quartz, belongs to graphite. The decrease in the intensity of portlandite lines as a result of the introduction of graphite filler, especially $d = 4.92$ Å from 93 to 51 %, clearly shows a certain decrease in the degree of hydration of the cement. The decrease in the intensity of the line $d = 2.65$ Å from 7.2 to 6.1 %, the disappearance of the line $d = 2.65$ Å of $C_2SH(A)$, and the appearance of the line $d = 2.73$ Å CSH(B) indicates a decrease in the basicity of calcium hydrosilicates.

The IR spectra (Fig. 2b) have absorption lines of compounds with wave numbers (cm^{-1}): 3441, 3425, 2920, 2852 are stretch vibrations of the OH^- bound groups of all hydrates; 2516, 713 (weak) are deformation vibrations of Ca–O carbonate groups; 1630 relates to stretch vibrations of H_2O molecules; 1440 (intense, imposed on 1477–1479) and 876 (narrow intense) are stretch vibrations of Ca–O bonds of carbonates; 1083, 1084 (intense) and 462 are stretch and deformation vibrations of the Si–O bond of silicates, regardless of the type of crystal lattice, and quartz. As can be seen, there are absorption lines on the IR spectra of the bonds and groups specific to Portland cement hydration products. The spectra differ little from each other, so it can be concluded that graphite does not affect the composition of hydration products of Portland cement.

Fig. 3 shows electron microscopic images of the chip of the cement composition with a complex chemical admixture and G2 graphite filler. From Fig. 3 it can be seen that graphite is distributed on the surface of the chip in the form of individual dark gray particles. Only the largest particles of 5 and 30 μm (Fig. 3f, g) and 250 μm (Fig. 3a, b) got into the chip, apparently due to their splitting along the planes of the cleavage (Fig. 3b),

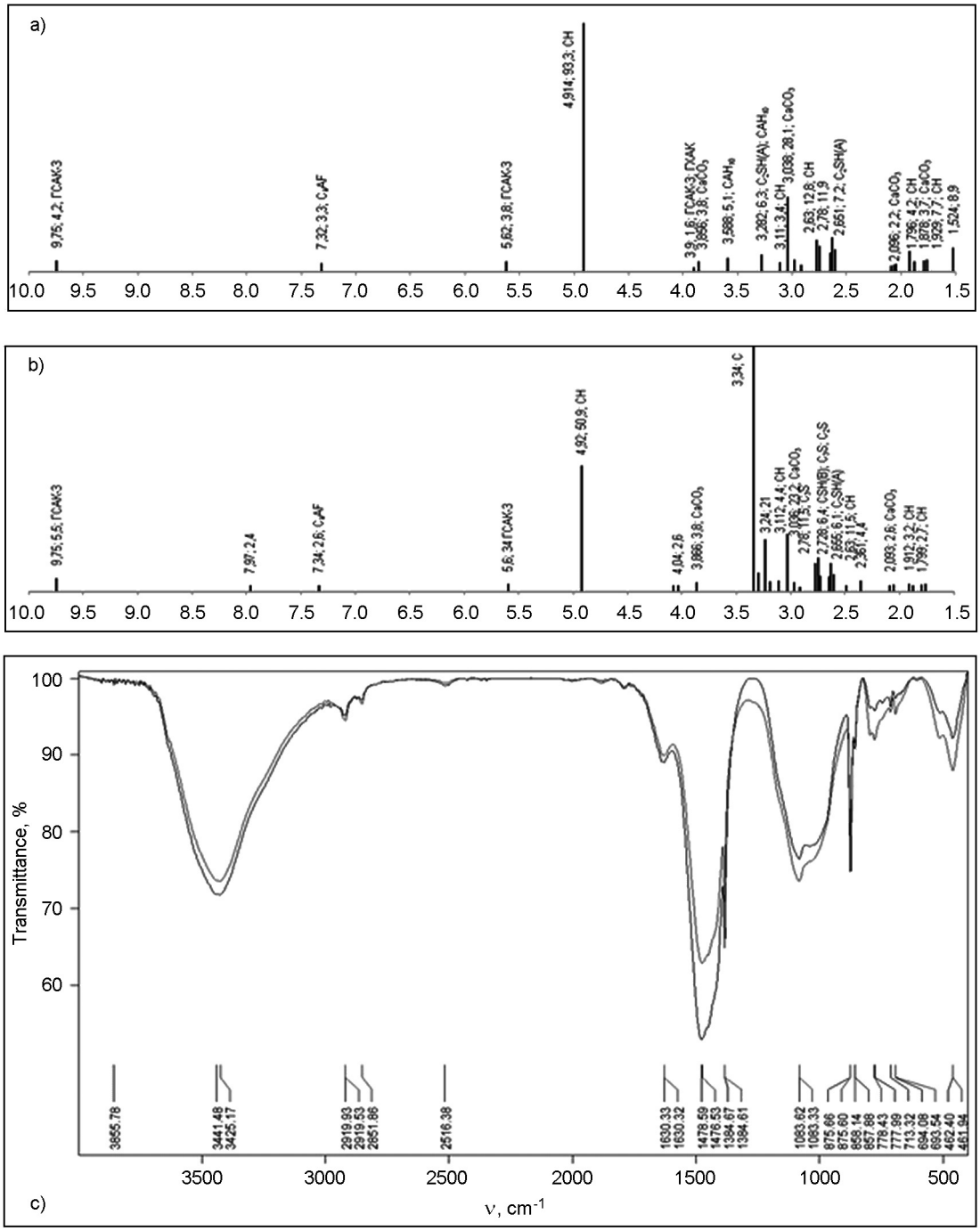

Fig. 2. Results of physical-chemical research of the Portland cement-based composition with a complex chemical admixture: a), b) bar graphs (quartz diffraction maxima are not shown) of specimens of the composition without filler (a) and with graphite filler (b); c) infrared absorption spectra of the specimens of the composition without filler (top) and with graphite filler (bottom).

which is quite perfect in graphite crystals. Smaller particles, most of which are not visible in the graphite filler, are obviously covered with cement hydration products; this shows that the contact strength between them is greater than between the components of the hydration products and between the layers of graphite itself. This is evidenced by the accumulation of cement hydration products on the surface of graphite (Fig. 3a, b), mainly calcium hydrosilicates C_2SH and CSH, and close contact be-

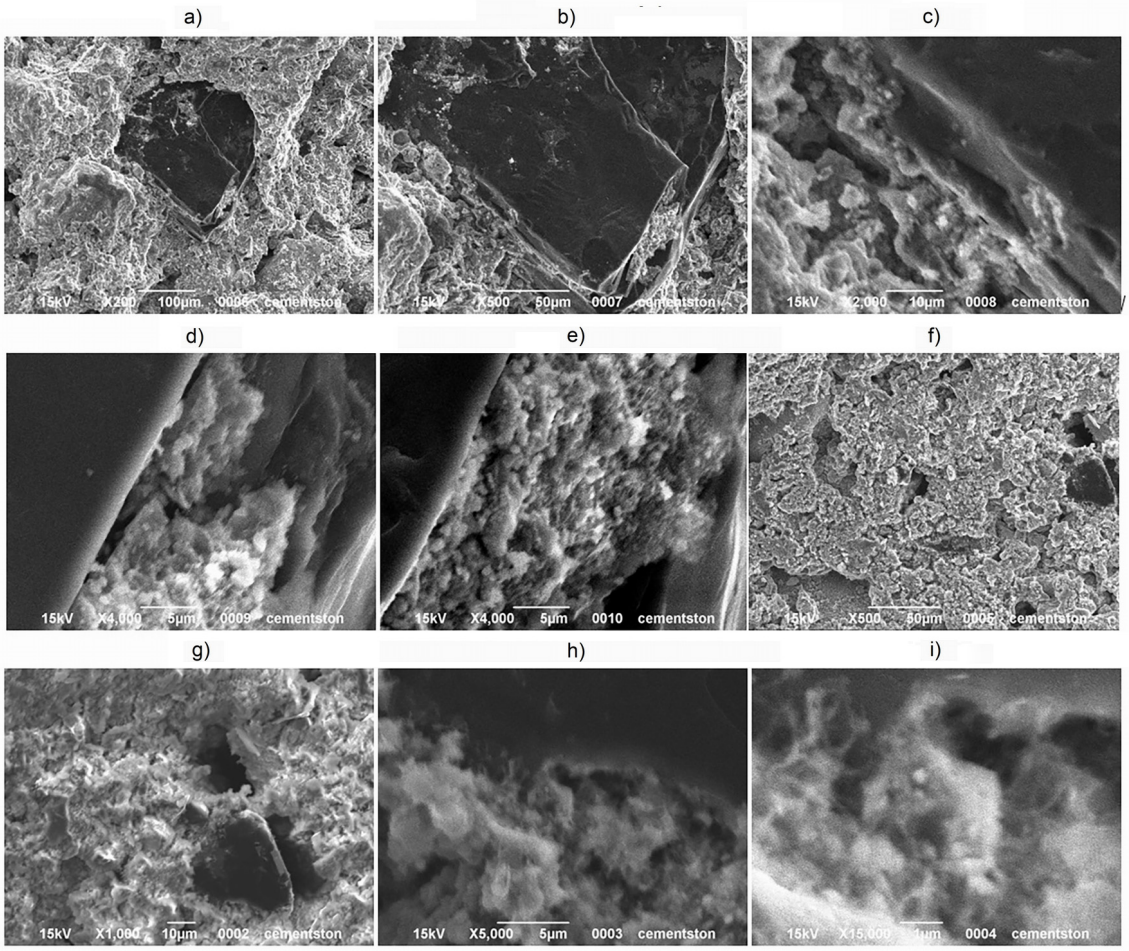

Fig. 3. Electron microscopic images of chips of the electrically conductive Portland cement-based composition with a complex chemical admixture and graphite filler: a) to e): a fragment of chip 1, with 100× to 4000× magnification; f) to i): a fragment of chip 2, with 500× to 15000× magnification.

tween them (Fig. 3d, e, h). The predominance of calcium hydrosilicates on the surface of graphite allows us to conclude about its positive surface charge in the electrolyte of cement stone. The structure of hydration products is dense (Fig. 3a, f) and contains capillary pores with a size of 5–50 μm. Among the hydration products, gel-like structures of C_2SH and CSH calcium hydrosilicates in the form of scales, plates, and needle-like growths less than 1 μm in size prevail (Fig. 3c, d, e, h, i). Hexagonal layered crystals of portlandite (in the lower left corner of Fig. 3b) are detected a smaller than usual amount in the hydration products of Portland cement. Fig. 3g and h, shows hexagonal crystals of obviously, portlandite, hydroaluminates, hydrochloroluminates, calcium hydrocarboaluminates; Fig. 3i shows individual needle-like crystals no more than 1 μm in size, probably of trisulfate form of calcium hydrosulfoaluminates.

Fig. 4 and Table show the results of X-ray microanalysis of the chip of the electrically conductive Portland cement-based composition with a complex chemical admixture and graphite filler: diffraction pattern (a), electron microscopic image of the selected chip section (b) and X-ray maps of the distribution of elements C, O, Si (c to e). Fig. 4b, 4c confirm that the dark gray particles larger than 5 μm in size detected by electron microscopy refers to one of the crystalline forms of carbon C, graphite, the surface of which has not been dissolved in the electrolyte of cement stone. All other parts of the surface (Fig. 4d, e) contain evenly distributed oxygen O and silicon Si specific to calcium hydrosilicates and quartz aggregates. In general, the elemental composition of the chip surface (Table) is characteristic of the hydration products of cement (Ca, Si, O, Al, Fe), including those with a complex chemical additive (K, Na).

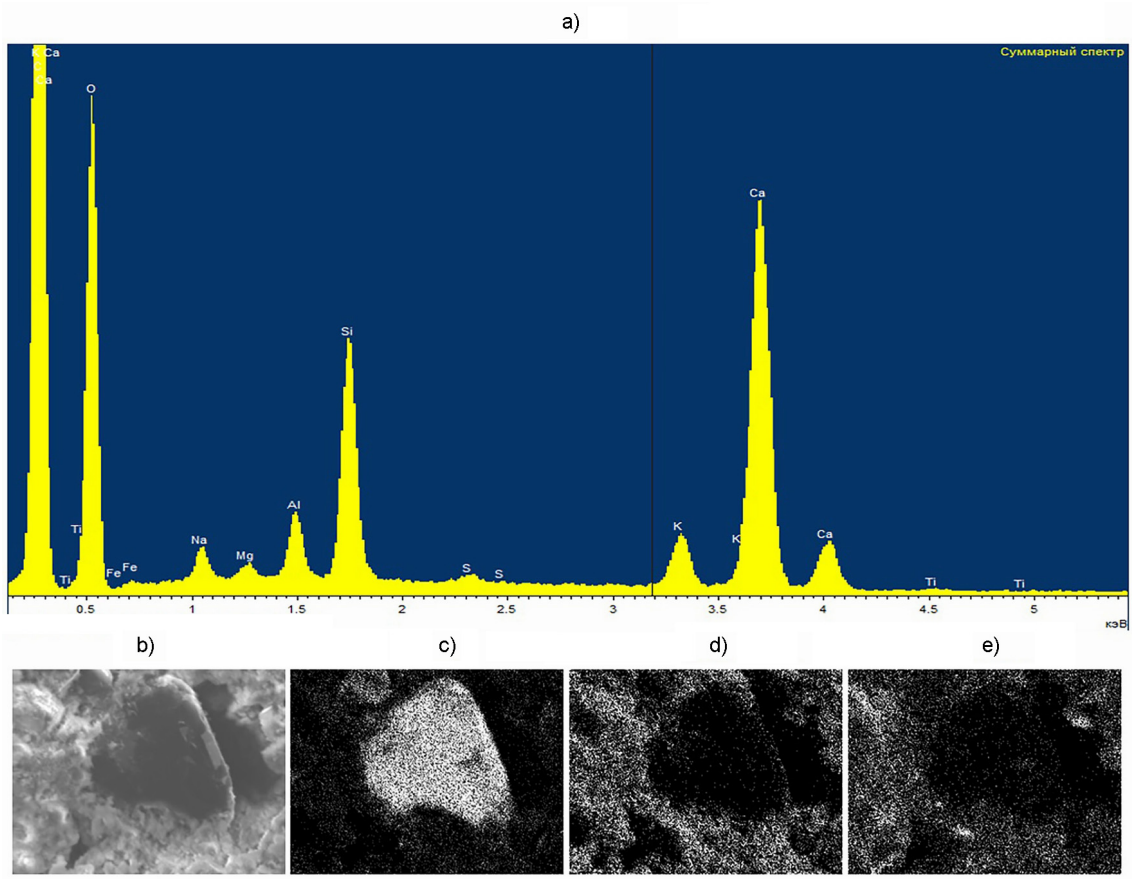

Fig. 4. The results of X-ray microanalysis of a chip of the electrically conductive Portland cement-based composition with a complex chemical admixture and graphite filler: a) diffraction pattern; b) electron microscopic image; c), d), e) X-ray maps of the distribution of elements C (c), O (d), Si (e); 15 kV, 2000×, X-Max.

Thus, following the results of physico-chemical studies it has been found that graphite does not participate in the hydration of Portland cement and scarcely affects the composition of its hydration products, except for a certain decrease in the degree of hydration of cement and the basicity of calcium hydrosilicates.

3.3. Experimental studies of the effect of graphite fillers on the physical-mechanical, hydrophysical and electrophysical properties of the composition

The results of experimental studies of the dependences of physical-mechanical, hydrophysical and electrophysical properties of the compositions on the content of graphite fillers are shown in Fig. 5.

The analysis of Fig. 5 showed the following. The obtained dependences prove the correctness of the model developed in the paper [17] for predicting the electrical resistivity of the composite according to the data on the electrical resistivity of its components and the generalized characteristics

Table. The content of elements on the surface of the chip of the electrically conductive Portland cement-based composition with a complex chemical admixture and graphite filler

Element	Percentage, %	
	Weight	Atomic
C	35.55	48.16
O	40.37	41.06
Ca	16.01	6.50
Si	3.22	1.86
K	1.79	0.75
Al	1.11	0.67
Na	0.71	0.50
Fe	0.71	0.21
Mg	0.26	0.18
S	0.15	0.07
Ti	0.11	0.04

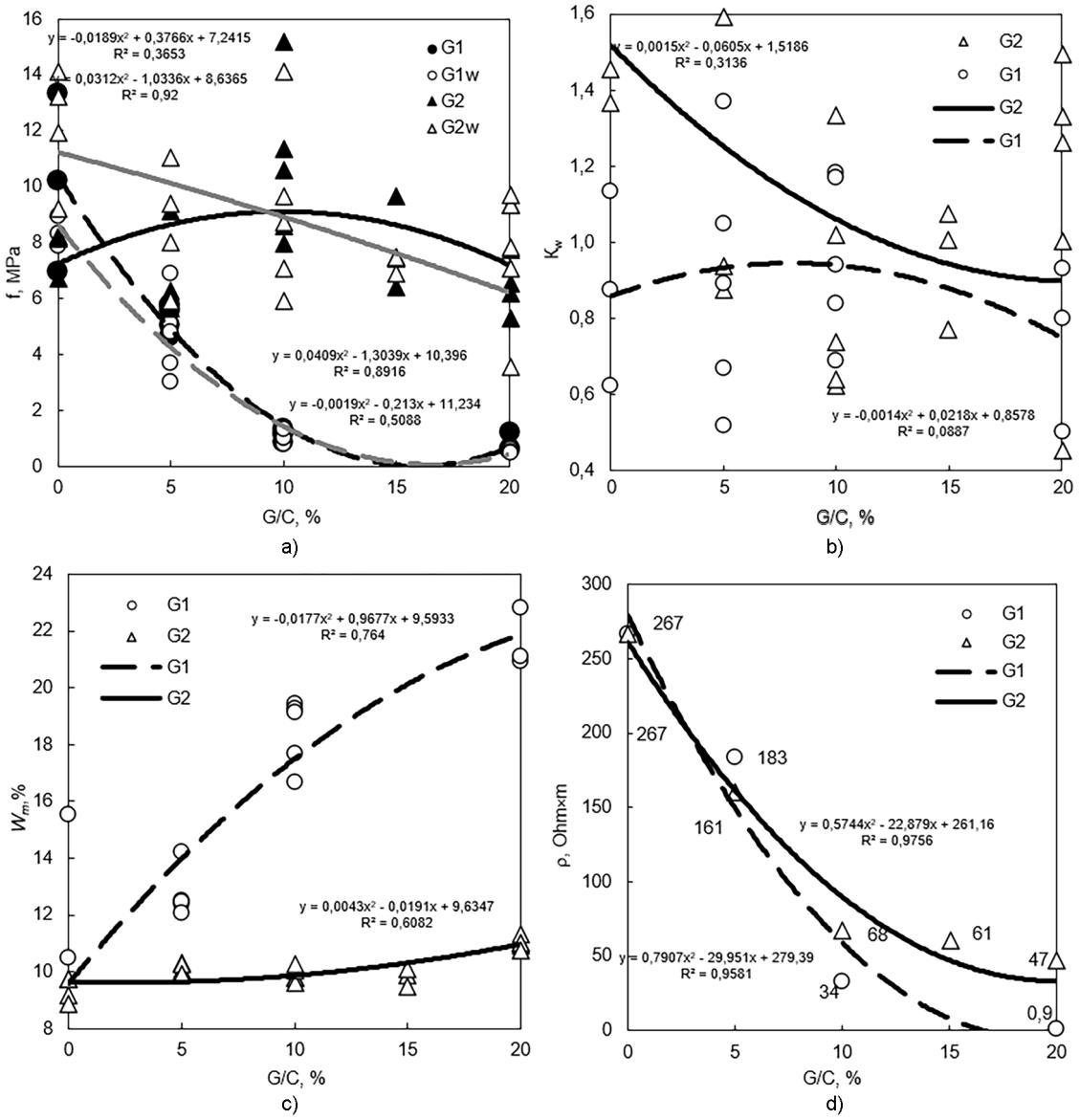

Fig. 5. Dependences on the content of graphite filler G1 and G2, % by weight, in the Portland cement-based composition with a complex chemical admixture: a) joint strength f in the dry and water-saturated conditions; b) water resistance coefficient (softening) K_w; c) water absorption by weight, W_m; d) electrical resistivity ρ.

of the composition. The compositions have a water resistance coefficient K_w not less than 0.8, i.e. they are waterproof in the case of the graphite filler G1 content up to 15% and in the case of the graphite filler G2 content up to 20 %. The K_w values exceeding 1.0 are due to the additional hydration of the compositions of the specimens exposed to water saturation, in comparison with the reference specimens which are simultaneously kept in dry conditions.

As far as the content of graphite filler G/C increases from 0 to 10–15 %, the value of electrical resistivity decreases. A further increase in the G/C content does not significantly reduce the electrical resistivity. Graphite G1 provides the maximum reduction in electrical resistivity, more than 10 times. However, an increase in the content of graphite filler (especially G1 due to the scaly structure of its larger particles) causes a decrease in strength, water resistance and water absorption by weight of the composition. Therefore, finely dispersed graphite G2 and its reasonable content within 10 % are chosen for the electrically conductive composition.

Water saturation of the composition provides a twentyfold reduction of its electrical resistivity to 2.8 Ohm·m, which makes it advisable to use this composition for protective screens that provide drainage of leakage currents which increase many times to dangerous values in wet weather.

Experimental studies carried out using a unique technique have shown that the current through the reinforcement and concrete of the sample with a grounded screening coating made of the composition is 73–88 % less than the current through the reinforcement and concrete of the sample without coating.

3.4. Recommendations for the application of research results

Building structures and structures operated in the area of action of leakage currents and stray currents, for example, near electrified tracks of railways, trams, subways, are susceptible to electrocorrosion. Electrocorrosion is usually caused by direct current and affects mainly steel structures and steel reinforcement of reinforced concrete structures. Under the effect of current flowing from the railway track in a pulse unidirectional mode during the passage of trains, concrete is also subjected to electrocorrosion, which consists in the electromigration dealkalization of $Ca(OH)_2$ and the formation of cracks. Anodic or cathodic electrochemical protection and electrodrainage [1] are used to prevent electrocorrosion of underground structures. The authors previously proposed the protection of the structures with grounded conductive screens, which can be considered as a type of electrodrainage. Making these screens in the form of metal injection clips or jackets allows rehabilitating or improving the load-bearing capacity of structures. However, metal injection clips are an expensive and time-consuming design and technological solution. Therefore, the developed composition based on mineral binder for electrically conductive coating is recommended for use instead of metal clips.

4. Conclusions

Graphite does not participate in the hydration of cement and scarcely affects the composition of its hydration products, except for a certain decrease in the degree of hydration of cement and the basicity of calcium hydrosilicates.

The electrical conductivity of a composition based on Portland cement with graphite filler is provided in the filler by electronic conductivity, in cement stone — by the ionic conductivity of its pore electrolyte. Electrode processes occur at the contact between the graphite particles and the pore electrolyte. Graphite dissolves and calcite is formed at the anode sections of the surface of the particles; therefore, the durability of the composition in terms of electrical conductivity is due to the amount of electricity transmitted by the graphite particles.

An increase in the content of graphite filler from 0 to 10–15 % in the composition causes a tenfold decrease in its electrical resistivity. A further increase in the filler content does not provide a significant reduction in electrical resistivity. The compositions are waterproof with a water resistance coefficient of not less than 0.8 in the case when the content of graphite filler is not more than 10 %. The increase in the content of graphite filler causes a decrease in strength, water resistance, an increase in water absorption by weight of the composition. Therefore, the reasonable filler content is 10 %.

The water saturation of the composition reduces its electrical resistivity by a factor of 20 (to 2.8 Ohm·m), which makes this compound suitable for use in protective screens that provide drainage of leakage currents which increase many times to dangerous values particularly in wet weather.

A Portland cement-based penetrating electrically conductive composition has been developed, which is able to form an electrically conductive coating on the surface of the structure while improving the electrical resistance of the surface layer of the structure itself. Protection with a grounded screen made from this composition provided a reduction in current through the concrete and reinforcement of the model sample by 73–88 % due to the current flow mainly through the screen.

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