



Article

# Influence of Sulphate Attack on Properties of Modified Cement Composites

Grigoriy Yakovlev <sup>1</sup>, Irina Polyanskikh <sup>1</sup>, Anastasiya Gordina <sup>1</sup>, Igor Pudov <sup>1</sup>, Vít Černý <sup>2</sup>, Alexander Gumenyuk <sup>1</sup> and Olga Smirnova <sup>3,\*</sup>

- Department of Geotechnical Engineering and Building Materials, Kalashnikov Izhevsk State Technical University, 426009 Izhevsk, Russia; gyakov@istu.ru (G.Y.); irina\_maeva@mail.ru (I.P.); afspirit@rambler.ru (A.G.); pudovia@ya.ru (I.P.); aleksandrgumenyuk2017@yandex.ru (A.G.)
- Faculty of Civil Engineering, Brno University of Technology, CZ-6S1200 Brno, Czech Republic; cernyv@fse.vutbr.cz
- Department of Constructing Mining Enterprises and Underground Structures, Saint-Petersburg Mining University, 199106 Saint-Petersburg, Russia
- \* Correspondence: smirnovaolgam@rambler.ru

Abstract: Monitoring the condition of building structures based on composite materials in aggressive environments shows that the deterioration of basic properties occurs under the influence of various factors such as temperature and humidity changes, in addition to changes in the chemical composition of air environment. In addition, the composite materials during the operation must retain not only the mechanical properties laid down at the design stage, but also the electro-physical characteristics, regardless of the type of destructive effects. In the current study, the quantitative assessment of the result of the interaction of an aggressive sulphate-containing medium with composites modified with conductive and dielectric additives was carried out. The effect of sulphate attack on the specific electrical conductivity of cement composites was studied. The nature of the interaction was evaluated by changing the properties of the samples of the developed compositions under the influence of a single-normal solution of sodium sulphate. The analysis was carried out by means of potentiometric titration using the exchange interaction method by fixing the degree of absorption of sulphate ions and determining the concentration of calcium ions in the solution. The measurement of the solution potential allowed determination of the quantitative indicators of the rate of calcium hydroxide leaching from the sample structure, which is necessary to assess the intensity of the destruction process and determine the nature of the change in strength properties. Measurements of the electrical resistivity of samples under the constant influence of sulphate aggression were taken during 28 days of observation. A method for quantifying the effect of a sulphate medium on a cement matrix was proposed that enables the material durability to be predicted. The features of changes in the morphology of structural components after exposure to aggressive solution were determined by physical and chemical methods.

**Keywords:** concretes; mechanical properties; sulphur compounds; sulphate attack resistance; impedance; electrical properties; sulphate attack



Citation: Yakovlev, G.;
Polyanskikh, I.; Gordina, A.; Pudov, I.;
Černý, V.; Gumenyuk, A.;
Smirnova, O. Influence of Sulphate
Attack on Properties of Modified
Cement Composites. *Appl. Sci.* 2021,
11, 8509. https://doi.org/10.3390/
app11188509

Academic Editor: Luigi Biolzi

Received: 20 June 2021 Accepted: 30 August 2021 Published: 13 September 2021

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

## 1. Introduction

The durability of cement composite is determined not only by its physical and mechanical properties, but also by its electrical characteristics, and can ensure the operational reliability of materials. Studies aiming to stabilize the dielectric properties and the resistance to sulphate attack of electrically insulating concrete have been successfully performed in recent decades [1–3]. However, the corrosion resistance to sulphate attack of electrically conducting composites has not been sufficiently studied. At present, the purpose of preserving the electrical properties and durability of cement concretes is primarily to

Appl. Sci. 2021, 11, 8509 2 of 13

protect against aggressive influences. Waterproofing via surface penetration of the compositions or bulk thermocatalytic impregnations can be distinguished as the main methods of waterproofing building capillary-porous materials [4–6].

As the most widespread and hybrid type of destructive process, the degree of material resistance to sulphate corrosion is considered to be the main criterion for the effectiveness of waterproofing [7–9]. Hybridity relates to the fact that sulphates in water increase the solubility of the components of cement matrix, and also initiate the development of exchange reactions between the components of cement matrix and a sulphate-containing solution [2,6,7].

In addition, the action of sulphates can cause the crystallization and accumulation of secondary poorly soluble reaction products with an increase in the volume of the solid phase of the ettringite-taumasite system. This creates internal stress and leads to damage to the concrete structure [6,7,10].

The degree of material resistance to sulphate attack is the main criterion for the effectiveness of waterproofing measures [7,8] because sulphate attack is the most common type of destructive processes in cement matrix. This process is accompanied by the formation of compounds with a high quantity of crystallization water and the formation of the ettringite-taumasite system [9,10].

Studies of sulphate attack and the formation of crystallohydrates of calcium hydrosulphoaluminate (ettringite) and calcium hydrosulphocarbosilicate (taumasite) in the structure of solid phase of concrete are widely presented in the literature of recent years [11–15]. Analysis of the studies has shown [7,16,17] that the formation of ettringite-type crystal hydrates occurs due to the reaction of sulphates with hydro-aluminates, whereas thaumasite is formed due to the presence of sources of calcium silicates, sulphates, and carbonates at relatively low ambient temperatures less than 15  $^{\circ}$ C.

Studies of synthesized pure samples of ettringite and thaumasite, and hydration products formed in the structure of cement matrices [2,7], have shown that it is not possible to draw unambiguous conclusions about the volume of these minerals [2,6,7,10].

Most researchers describe the effect of sulphate attack as a process in which the sulphate ions in water, when penetrating into concrete, significantly increase the solubility of the components of the solid phase of concrete, which accelerates the corrosion of the first type [2,6]. Simultaneously, the development of exchange reactions occurs with the substitution of the cation in the sulphate for the calcium ion from the concrete, which initiates corrosion of the second type [2,6].

Today, materials based on cement composites are increasingly used at the intersection of construction materials science and instrument engineering. Accordingly, the need arises for the development and research of new cement composites with a number of functional properties. In addition to the study of physical and mechanical properties, during the past ten years, active attention has been paid to the study of the electrical properties of the solid phase in concrete and, as a result, concrete compositions with specified electrical properties have been developed [18–21]. However, studies of the corrosion resistance of cement composites with electrical properties are insufficient. Analysis and evaluation of changes in the electrical resistivity under the influence of a complex of external factors [22] is a priority in research, and considers promising practical applications of the modified cement-based composites, such as resistive self-heating of road surfaces [23], grounding, elimination of static electricity, and lightning protection [24,25].

Studies have shown [26,27] that the analysis and assessment of the degree of influence of external factors on the solid phase of cement-based composites is possible due to laboratory modeling of the hydrosulphate corrosion process, which consists of holding samples in solution with a sodium sulphate amount of 1 to 10%. The use of the solution of sodium sulphate [28,29] is preferred. This solution, unlike, for example, magnesium sulphate [30], allows the ettringite—thaumasite system to be fully synthesized due to the absorption of  $SO_4^{2-}$  ions by samples from a  $Na_2SO_4$  solution. This process intensifies the

Appl. Sci. 2021, 11, 8509 3 of 13

crystallization of salt in a moist environment, and leads to the salt crystallization in samples and the further formation of cracks [23].

Studies of the mechanism of electrical conductivity of the solid phase of composite based on Portland cement show that the hydrated concrete is a combination of hydration products with non-hydrated clinker minerals [1,23], with thermodynamically unstable compounds having imperfectly ordered crystal structures. It is shown [31] that the total calculated change of the entropy in the reactions of the formation of calcium silicates, aluminates, and aluminoferrites is significantly less than the entropy of the clinker materials themselves. In turn, these data confirm that the solid phase of concrete is not a regular crystal lattice with the presence of vacancies in the nodes and a variety of ions in the internodes. The bonds of these ions are significantly weaker than those in regular crystals, which affects all the physical and chemical properties of cement-based composites, including their electrical conductivity [1]. As a result, the combined action of thermal motion and the electric field can lead to the creation of certain conditions under which a particular ion can become a current carrier. Thus, the electrical conductivity of clinker minerals can be attributed to the ionic type that is characterized by a strong dependence of the electrical conductivity of concrete on the order of ions in its structure [23].

The quantitative values of the electrical conductivity of hydrated clinker minerals are discussed in detail in paper [32]. The crystalline hydration products permeating the cement gel contain water molecules in a chemically bound form. During the independent synthesis of crystal hydration products and their subsequent study [23], it was found that the nature of the electrical conductivity of these new formations is similar to the nature of the electrical conductivity of clinker minerals. In the works of many authors, it has been stated that the specific electrical resistances of the crystal hydration products of the concrete are in the range from  $10^6$  to  $9 \times 10^9$   $\Omega/cm$ .

It can be stated that the mineral components of Portland cement, crystal hydrates, and cement matrix, overall, have an ionic character of electrical conductivity that depends on the value of the positive entropy of crystals (crystals in the structure in which there are violations in the arrangement and movement of particles), the degree of crystallization, and the amount of adsorption-bound water.

The use of electrolytic additives effects the structure formation, and changes the dispersion, quantity, and shape of hydrates [33–35]. In a number of studies [36,37], it was found that the use of an electrolyte such as calcium nitrate reduces the degree of structure crystallization of concrete in the long term due to the interaction of nitric acid salt with aluminum-containing phases of Portland cement forming calcium hydronitroaluminates and calcium hydroxynitrates. Due to their shielding ability, these compounds slow the recrystallization of cement matrix. Despite the compacting effect and the increase in water resistance with the addition of calcium nitrate, its use in concretes exposed to aggressive media is limited because it enhances the corrosion processes of the solid phase of cement matrix [7,38,39].

Analysis of the durability of cement-based composites is difficult because no unambiguous criterion currently exists for evaluating this parameter, in contrast to the mechanical and electrical properties. Despite certain successes in laboratory studies of destructive processes [12,13,40], the degree of reliability of quantitative analysis remains low due to the high coefficient of variation of experimental data. To save resources, and to improve the accuracy and sensitivity of the obtained data, a stochastic dynamic model for assessing the effect of internal fluctuations on the destructive process of hydrosulfate corrosion was proposed [11].

The proposed model focuses on the analysis of three aspects: the process of sulphate ion transfer [7]; chemical reactions caused by the process of sulphate corrosion [6]; and the combination of the hydraulic pressure of the solution and the chemical reaction between the sodium sulphate solution and the components of solid phase of concrete [2].

At present, several basic methods exist for studying hydrosulphate corrosion: the use of stochastic dynamic reactions of nonlinear systems [11], the potentiometric method [41],

Appl. Sci. 2021, 11, 8509 4 of 13

the Moskvin and Kind methods [7], etc. The potentiometric method of analysis is widely used because it allows the capabilities of the analysis of organic and inorganic substances to be expanded with the provision of the most sensitive and accurate data.

The aim of the study was to evaluate the effect of hydrosulphate corrosion on the electro-conducting properties of cement composite by means of the potentiometric method and titrimetric analysis of a mono-normal solution of sodium sulphate, with subsequent assessment of the morphological changes in the material structure.

#### 2. Materials and Methods

## 2.1. Materials

The following components were used for the preparation of samples: Portland cement CEM I 32.5 N of the Novorossiysk Cement Plant with the chemical composition: CaO—66.73%; SiO<sub>2</sub>—23.22%; Al<sub>2</sub>O<sub>3</sub>—5.16%; Fe<sub>2</sub>O<sub>3</sub>—4.42%; SO<sub>3</sub>—0.47%; mineral composition: C<sub>3</sub>S—65%; C<sub>2</sub>S—13%; C<sub>3</sub>A—4%; C<sub>4</sub>AF—18% according to the test certificate from manufacturer; the fine aggregate is fractionated quartz sand with the fineness modulus (Abram's fineness modulus) of  $M_f$  = 1.25; the mixing liquid with pH of 6.8  $\pm$  0.01; modified technical sulfur as the electro-insulating ultrafine additive; suspension of technical soot UPC-MIX-1 produced by Novy Dom LLC as the electrically conductive component. Types and quantities of modifiers were determined previously [42,43].

The modified sulphur was obtained from sulphur of technical grade 9998 corresponding to the Russian standard of 127.1–93. The main physical properties of technical sulphur are: particle shape-hemispherical; bulk density—1.3 g/cm³. Chemical and material composition: mass fraction of sulphur—99.99%; mass fraction of ash—0.005%; mass fraction of organic substances—0.005; mass fraction of water—0.01%. Surface modification of sulphur was carried out to ensure its uniform distribution in the structure of the material, as considered in detail in paper [42].

The study of the effect of hydrosulphate corrosion on the electrical, physical, and mechanical properties of cement matrices was carried out on three compositions. The compositions are shown in Table 1.

Sample	CEM I 42.5 g	Quartz Sand	Industrial Soot, %	Industrial Sulfur, %	Calcium Nitrate %	Water-to- Cement Ratio	Polymer- Cement Ratio
Control			-	-	-		-
Non-conductive concrete	800	1600	-	7	-	0.5	0.05
Electrically conductive concrete			7	-	3		-

**Table 1.** Composition of the samples under study.

## 2.2. Sample Preparation

Studies of the corrosion resistance of concrete show the need to plan experiments by choosing the optimal geometric dimensions of samples that allow the most reliable results to be obtained. Cubes with a size of  $20 \times 20 \times 20$  mm were used to assess the degree of aggressive influence. These dimensions were chosen on the basis of previous studies by Kind [7,42], and on the basis of the need for parallel tracking of several characteristics. The small size of the samples allows the test time to be reduced because the small samples contribute to the rapid interaction of the aggressive solution with the entire volume of cement matrix. Cubes with a size of  $70 \times 70 \times 70$  mm were used to evaluate the strength and electrical properties of materials [44,45].

Additives of modified industrial sulphur and suspensions of industrial soot were used to obtain the conductive and non-conductive materials and to evaluate their behavior in aggressive environments [42,43]. Additives were added in the amount of 7% of binder mass, for which the optimal quantity was determined on the basis of previous studies [43].

Appl. Sci. 2021, 11, 8509 5 of 13

Demolding the samples was carried out after 2 days. Samples with modified technical sulphur were subjected to additional volumetric thermocatalytic treatment at 180 °C for 60 min, and then gradually cooled to room temperature for 2 h [4,5,42]. All samples were stored in wet conditions for 28 days and then, after 28 days, the samples were loaded into the aggressive hydrosulphate medium. Studies of physical, chemical, and technical characteristics were carried out after storage in the aggressive environment.

#### 2.3. Solution Preparation

The potentiometric method was used to analyze the effect of the aggressive sulphate medium on the properties of cement matrix [41]. This method includes the reconstruction of hydrosulphate corrosion conditions using the 1% Na<sub>2</sub>SO<sub>4</sub> solution, in addition to the titrimetric analysis of the solution within the control time to assess the rate of absorption of  $SO_4^{2-}$  ions and the release of calcium hydroxide. The method of solution preparation was as follows: the distillate with a temperature of 20  $\pm$  1 °C was poured into a measuring cylinder; the powder of Na<sub>2</sub>SO<sub>4</sub>  $\times$  10H<sub>2</sub>O was poured into water and mixed in a laboratory vessel for 3–5 min until the salt was completely dissolved in the water. Further, the cubes of 20  $\times$  20  $\times$  20 mm and 70  $\times$  70  $\times$  70 mm were placed in the resulting solution in the desiccator, and the percentage of Na<sub>2</sub>SO<sub>4</sub> was defined due to the short-term exposure of the samples to sulphate attack [46,47]. The samples were kept in solution for 28 days with control measurements on the 7th, 14th, and 28th day of exposure. The samples were removed from the solution at each target date and subjected to strength tests and electrical resistance measurements. The physical and chemical properties of the samples were determined after 28 days of exposure in solution.

## 2.4. Testing Methods

The compressive strength of the samples was determined using aPGM-100MG4-A hydraulic press.

The determination of the change in the resistance of samples was carried out using a MNIPI E7-20 device. The resistivity index was calculated in units of  $\Omega \times \text{cm}$  (Ohms,  $\Omega$ ). The resistivity was calculated based on the data obtained from the device and the geometric parameters of the samples according to the formula [25]:

$$\rho = R \cdot A / L, \Omega \times cm, \tag{1}$$

where  $\rho$  is the specific electrical resistance of the sample; R is the resistance of sample; Lis the distance between the probes; A is the cross-sectional area of sample.

Titrimetric analysis [48] was used to determine the process of sulphate corrosion. As ST5000-F pH meter with an ST350 electrode was used to determine the hydrogen index. Each two days, until 28 days, the hydrogen index and titration tests were performed. In the titration test, the 1% H<sub>2</sub>SO<sub>4</sub>solution and phenolphthalein were used to define the volume of solution required for neutralization. This method (titrimetric analysis) quantifies the expended volume of the titrant (a solution of a reagent with a precisely known concentration) required for the reaction with the titrated substance. Lime released from cement matrix reacts with sulphate ions, releasing sodium hydroxide into the solution when the samples are in the sodium sulphate solution. Crimson staining occurs when phenolphthalein is added to this solution. The reaction proceeds according to the following scheme:  $Ca(OH)_2 + Na_2SO_4 + 2H_2O \rightarrow CaSO_4 \times 2H_2O + 2NaOH$ . At the control time, the titration of the resulting solution is performed with the 1% H<sub>2</sub>SO<sub>4</sub> solution without removing the samples from the aggressive medium. Neutralization occurs by the reaction:  $NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$ . The amount of the consumed  $H_2SO_4$  solution used to neutralize the indicator shows the volume of sulphate ions absorbed by samples. The higher the volume of the spent reagent, the lower the corrosion resistance of samples.

The nature of structural changes was assessed using Thermo Fisher Scientific Quattro S and Tescan Mira3 XMU, Waltham, MA, USA scanning electron microscopes. The Thermo Fisher Scientific Quattro S survey was performed in the low-vacuum mode at 20 kV without

Appl. Sci. 2021, 11, 8509 6 of 13

sputtering at the pressure of 50 Pa. The survey on the Tescan Mira 3 XMU was carried out at 20 kV with gold deposition on the samples.

Studies of the physical and chemical characteristics of compositions were carried out using the differential thermal analysis with a combined thermogravimetric analysis device and differential scanning calorimetry TGA/DSC 1 manufactured by CJSC Mettler-Toledo Vostok.

Infrared spectroscopy of samples was performed on the "IRAffinity-1" Shimadzu, Japan, which registers the adsorption spectra of various substances and measures the transmittance in the range from 4000 to 450 cm<sup>-1</sup>. The error of the spectrophotometer on the wave number scale is  $\pm 0.5$  cm<sup>-1</sup>.

#### 3. Results and Discussion

It is known the nature of the microstructure and composition of the solid phase play an important role in determining the physical and mechanical properties of cement matrix. The process of capillary diffusion is initiated when the samples are immersed in an aggressive solution. The sulphates penetrate into cement matrix and enter the exchange reaction with the reactively active components to form the products of the expansive phase.

The titrimetric analysis shown in Figure 1 indicates that the solid phase of the control and electrically conductive concretes intensively absorb sulphate ions during the first 14 days in the volumes of 26.2 mL (the control composition) and 26.7 mL (the electrically conductive composition). According to previous research data, this volume of absorbed sulphate ions can be considered to be directly proportional to the volume of leaching portlandite [7,41]. The correlation of the data on the absorption of sulphates with the loss of mechanical strength suggests that a significant leaching of portlandite from the solid phase leads to a decrease in the compressive strength of both compositions due to formation of pores and voids. By analyzing the rate of leaching of components of these compositions, it is possible to predict a significant loss of strength in the long term associated with sample decomposition.

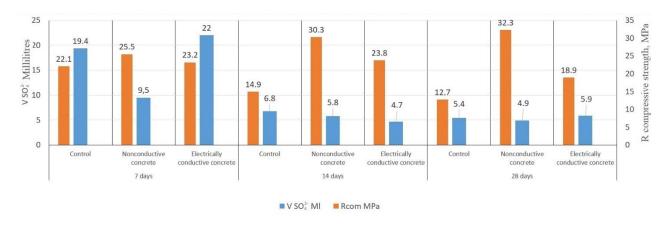


Figure 1. The rate of absorption of  $SO_4^{2-}$  ions by concrete samples from a 1N aqueous solution of  $Na_2SO_4$ . (The coefficient of variation in determining the strength was V=4.3% (control composition); V=5.2% (electrical insulation composition); V=4.8% (electrically conductive composition). Rcom—compressive strength, MPa).

According to the data presented in Figure 1, and confirmed by the coefficient of variation, the electrical insulation composition demonstrates consistently high mechanical compressive strength for 28 days, in contrast to the control and the electrically conductive compositions. The volume of sulfates absorbed by the electro-insulating cement composite after 28 days was 20.2 mL. During the absorption of the solution, the appearance of micro-and macro-cracks in the sample was not detected. Analysis of the volume of the absorbed solution enables an assumption to be made about the optimality of the pore space in samples. The control composition and the conductive composition have a more developed

Appl. Sci. 2021, 11, 8509 7 of 13

pore structure that leads to a significant absorption of the aggressive solution. The electrical insulation composite is characterized by a low leaching rate of portlandite.

The study of the electrical resistivity under the influence of hydrosulphate corrosion shows that a significant quantity of mobile ions appears as a result of the diffusion of an aggressive solution in the solid phase of cement matrix that, accordingly, reduces the electrical resistivity of samples. In the future, the expansive phase (minerals formed with significant volume, such as ettringite) in the concrete structure reduces the volume of the pore space due to the formation of a low-conducting crystal-hydrate structure, which increases the specific electrical resistance of the compositions. It is necessary to note the preservation of the effect of the electrical insulation layer because the resistivity of the non-conducting composition is four-fold higher than the resistivity of the conducting composition on the 28th day of the test (Figure 2).

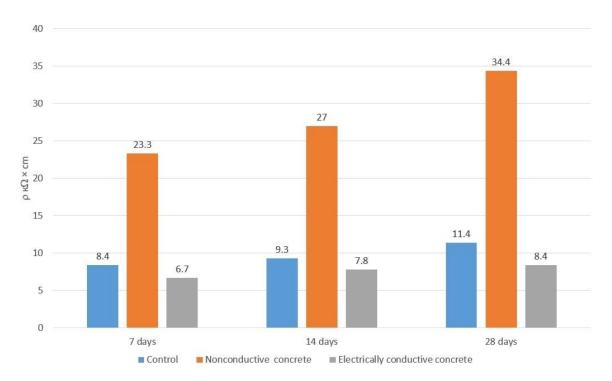
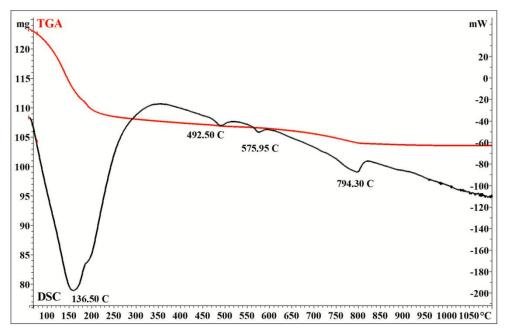


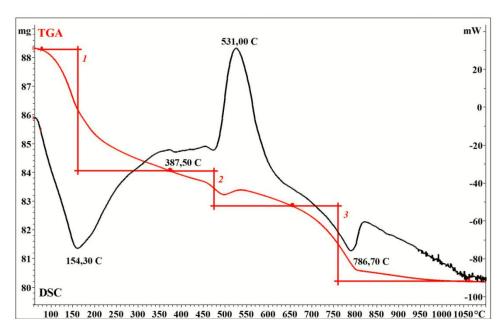
Figure 2. Effect of sulphate attack on the electrical resistivity of samples.

Changes in the physical, mechanical, and electrical properties of composites are caused by physical–chemical transitions with the formation and growth of expansive phases. Differential thermal analysis was used to determine the causes of changes in the physical and mechanical properties of the conductive composition, as shown in Figures 3 and 4. The differential thermal spectrum of the control sample (Figure 3)after exposure to aggressive media for 28 days is characterized by an endothermic peak at 136.5 °C (this peak is characteristic of decomposition of free water, calcium hydrosilicates, and ettringite) and the peak of 492.5 °C (this peak is characteristic of the decomposition of portlandite). The uncharacteristically low intensity of the portlandite decomposition peak and the significantly lower mass loss of the sample at this stage should be noted. This effect is associated with a significant amount of portlandite dissolved as a result of aging in the aggressive environment. The endothermic effect at the temperature of 575.95 °C is associated with the partial dissociation of chemically bound water from calcium hydrosilicates. The endothermic peak of 794.30 °C is caused by the process of decomposition of calcium carbonate and dehydration of the CSH phase.

Appl. Sci. 2021, 11, 8509 8 of 13



**Figure 3.** Spectrum of differential scanning calorimetry of the control sample after exposure for 28 days in the aggressive environment.



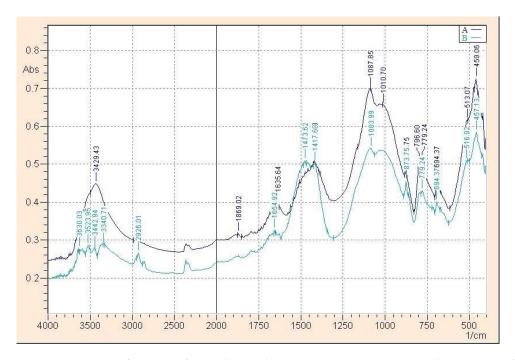
**Figure 4.** The spectrum of differential scanning calorimetry of the sample with the addition of an electrically conductive component of 7% and calcium nitrate of 3% after 28 days in the aggressive environment. 1 stage–mass of sample 83 mg, masse loss 4.49 mg; 2 stage–mass of sample–82.13 mg, mass loss 0.86 mg; 3 stage–mass of sample 80.1 mg, mass loss 2.03 mg.

When comparing the spectra of the control and electrically conducting compositions, it was found that the endothermic peak of  $146.5\,^{\circ}\text{C}$  corresponding to the dehydration of calcium hydrosilicates, free water, and ettringite appears in the electrically conducting composition in the temperature range from 90 to  $400\,^{\circ}\text{C}$  on the DTA curve. In addition, the mass loss of the sample in this stage is higher, which may indicate a larger volume of formed ettringite. The endothermic peak of  $451.3\,^{\circ}\text{C}$  corresponds to the beginning of the thermal decomposition of calcium hydroxide and calcium hydrosilicates. Free calcium oxide is formed during the endothermic reaction. In the air environment, free calcium oxide reacts actively with carbon dioxide, leading to the process of secondary carbonation. The

Appl. Sci. 2021, 11, 8509 9 of 13

burning of organic products in the material composition, which leads to the intensification of the process described above, should also be noted. An intense exothermic effect with the temperature peak of  $528.0~^{\circ}\text{C}$  corresponds to the oxidation reaction of carbon black, whereas the formation of gaseous products leads to the appearance of a local curvature on the thermogravimetric curve. The endothermic effect in the temperature range of  $600-1000~^{\circ}\text{C}$  (including the peak of  $778.6~^{\circ}\text{C}$ ) with the loss of 2.7% of the sample mass corresponds to the decomposition of calcium carbonate, and the removal of chemically bound water from calcium hydrosilicates and ettringite. The increase in mass loss can also be due to the secondary carbonation of cement matrix. Repeated thermal analysis in an inert gas environment is necessary to clarify the features of the process.

The temperature peaks corresponding to the decomposition of ettringite and thaumasite due to their crystal-chemical similarity coincide on the thermograms [49]. Based on this, the IR analysis method was used to obtain additional information, as shown in Figure 5. The results of scanning electron microscopy are shown in Figure 6.

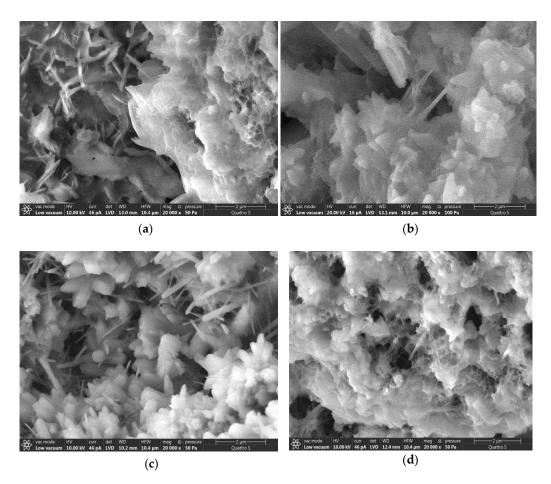


**Figure 5.** IR spectra of samples after 28 days in the aggressive environment: (A) the spectrum of the sample with 7% of the conductive component and 3% of the calcium nitrate; (B) the spectrum of the control sample.

Analysis of the IR spectra of the control and electro-conducting composites showed the presence of -Si-O- groups in the composition of calcium hydrosilicates, and characteristic peaks of the absorption of duplets in the range from 1083.99 to 1010 cm<sup>-1</sup> were observed in the structure of materials after exposure to aggressive environment. In addition, a duplicate peak in the region of 694 cm<sup>-1</sup> indicates the presence of sulphate groups because the main reflection is superimposed on the silicate groups. The peaks in the region of 3340.71–3630.03 cm<sup>-1</sup> correspond to the valence vibrations of OH<sup>-</sup> groups that are in free and chemically bound form, and are included in portlandite, hydrosilicates, and ettringite. An increase in the peak intensity in this region in the electrically conducting composition in comparison with the main component—the silicate phase—indicates the formation of a larger amount of hydrosilicate gel in the material volume. The deformation and valence vibrations of the C-O bond characteristic of calcite are indicated by peaks of 1417 and 873 cm<sup>-1</sup>. The peak intensity of 1417 cm<sup>-1</sup> is responsible for the degree and depth of carbonation [50,51]. The shift of the peak from 1473 to 1417 cm<sup>-1</sup> indicates a decrease in

Appl. Sci. 2021, 11, 8509 10 of 13

the carbonation degree of modified composition, which may be due to a large volume of dissolved portlandite.



**Figure 6.** Microstructure of samples after corrosion resistance tests at 20,000 times magnification: (**a**,**b**)-control sample on 7th and 28th days, (**c**,**d**)-electrical composition on 7th and 28th days.

Analysis of the microstructure of the control sample showed the presence of an amorphous hydrosilicate phase with characteristic crystalline inclusions. The microstructure of the electrically conductive concrete in Figure 6 is characterized by a smaller amount of the crystalline phase, probably due to the significant amount of the added electrically conductive modifier, which can affect the formation of hydration products. Both compositions are characterized by the presence of pores and voids caused by the influence of the aggressive environment. Moreover, portlandite and calcium hydro-aluminates are almost absent in the microstructure after the sample was aged under aggressive conditions. The microstructure of the samples is also characterized by the presence of hexagonal prismatic needle-like structures, which are typical for thaumasite. These features lead to a decrease in the strength characteristics of the samples.

Structural optimization of the electrically conductive composition with the directed formation of low-soluble calcium hydrosilicates is necessary in further research.

## 4. Conclusions

The influence of hydrosulphate corrosion on the electrical and mechanical properties of the solid phase of cement matrices modified with electrically conductive and non-conductive components was studied.

Titrimetric analysis can be used for the indirect assessment of the nature of the pore space of fine-grained concrete, in addition to the determination of the degree of corrosion processes under the influence of a sulphate aggressive environment.

Appl. Sci. 2021, 11, 8509 11 of 13

Analysis of the rate of absorption of sulphate ions by cement matrices with different modifiers showed that the control and conductive composition are significantly more susceptible to sulphate corrosion (the volumes of the absorbed solution on the 28th day were 31.6 and 32.6 mL, respectively). From the perspective of the durability of the electrically conductive composite, it is necessary to optimize the pore space of the modified matrix, in combination with the use of construction methods.

Analysis of changes in the strength characteristics confirmed the need to use protective non-conductive layers to increase the durability of electrically conductive materials. The compressive strength of the control and conducting compositions after 28 days of exposure to the aggressive environment were almost the same (22.1 and 23.2 MPa, respectively). The compressive strength of the non-conducting composition was 30% higher, at 34.4 MPa.

Physical and chemical studies of control and electrically conductive cement composites have shown that increasing the durability of these materials is possible with the use of additional protective layers when operating in an aggressive sulphate environment. The process of ettringite formation begins when interacting with the aggressive environment, which is accompanied by the leaching of portlandite from the material structure. This leads to a decrease in compressive strength during long-term operation. To better understand the effects of long-term exposure of modified composites to sulphate attack, further investigation must be carried out.

**Author Contributions:** Conceptualization, A.G. (Alexander Gumenyuk) and I.P. (Irina Polyanskikh); methodology, G.Y. and A.G. (Alexander Gumenyuk); software, O.S.; validation, V.Č. and I.P. (Igor Pudov); formal analysis, A.G. (Anastasiya Gordina); investigation, A.G. (Alexander Gumenyuk) and V.Č. and A.G. (Anastasiya Gordina); resources, G.Y.; data curation, O.S.; writing—original draft preparation, A.G. (Alexander Gumenyuk) and I.P. (Irina Polyanskikh); writing—review and editing, O.S.; visualization, A.G. (Alexander Gumenyuk) and A.G. (Anastasiya Gordina); supervision, G.Y.; project administration, G.Y.; funding acquisition, G.Y. and V.Č. All authors have read and agreed to the published version of the manuscript.

**Funding:** The reported study was funded by RFBR and Czech Science Foundation according to the research project No. 19-53-26011 and with the financial support from the Czech Science Foundation under the project with registration No. 20-09072J.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Acknowledgments:** REM study was performed using a Thermo Fisher Scientific Quattro S microscope in the Center of Shared Facilities "Surface and new materials" of UdmFRC UB RAS, supported by Russian Ministry of Science and Higher Education (project NO RFMEFI62119x0035).

Conflicts of Interest: The authors declare no conflict of interest.

## References

- Cleven, S.; Raupach, M.; Matschei, T. Electrical Resistivity of Steel Fibre-Reinforced Concrete—Influencing Parameters. *Materials* 2021, 14, 3408. [CrossRef]
- 2. Zhou, R.; Li, Q.; Wang, J.; Zhou, K.; He, R.; Fu, C. Assessment of Electrical Resistivity and Oxygen Diffusion Coefficient of Cementitious Materials from Microstructure Features. *Materials* **2021**, *14*, 3141. [CrossRef]
- 3. Dong, W.; Huang, Y.; Lehane, B.; Aslani, F.; Ma, G. Mechanical and electrical properties of concrete incorporating an iron-particle contained nano-graphite by-product. *Constr. Build. Mater.* **2021**, 270, 121377. [CrossRef]
- 4. Trushko, O.V.; Trushko, V.L.; Demenkov, P.A. Arrangement of multistory underground parking garages in complex engineering and geological environment. *Int. J. Math. Eng. Manag. Sci.* **2020**, *5*, 897–912.
- 5. Goldobina, L.A.; Demenkov, P.A.; Trushko, O.V. Ensuring the safety of construction works during the erection of buildings and structures. *J. Min. Inst.* **2019**, 239, 583–595. [CrossRef]
- 6. Shagiakhmetov, A.M.; Raupov, I.R.; Terleev, A.V. Investigation of selective properties of the gel-forming composition for the limitation of water inflow to carbonate reservoirs conditions. *Int. J. Civ. Eng. Technol.* **2019**, *10*, 485–492.
- 7. Liu, S.; Zhu, M.; Ding, X.; Ren, Z.; Zhao, S.; Zhao, M.; Dang, J. High-Durability Concrete with Supplementary Cementitious Admixtures Used in Corrosive Environments. *Crystals* **2021**, *11*, 196. [CrossRef]
- 8. Zhao, G.; Shi, M.; Guo, M.; Fan, H. Degradation Mechanism of Concrete Subjected to External Sulfate Attack: Comparison of Different Curing Conditions. *Materials* **2020**, *13*, 3179. [CrossRef]

Appl. Sci. **2021**, 11, 8509

9. Du, J.; Li, G.; Wu, J. Concrete sulfate corrosion coupled with hydraulic pressure. *Mar. Georesour. Geotechnol.* **2020**, *38*, 40–47. [CrossRef]

- 10. Zhao, G.; Li, J.; Shi, M.; Fan, H.; Cui, J.; Xie, F. Degradation mechanisms of cast-in-situ concrete subjected to internal-external combined sulfate attack. *Constr. Build. Mater.* **2020**, 248, 118683. [CrossRef]
- 11. Li, T.; Zhang, B. Stochastic Dynamic Model of Sulfate Corrosion Reactions in Concrete Materials considering the Effects of Colored Gaussian Noises. *Complexity* **2019**, 2019. [CrossRef]
- 12. Ikumi, T.; Cavalaro, S.H.P.; Segura, I.; Aguado, A. Alternative methodology to consider damage and expansions in external sulfate attack modeling. *Cem. Concr. Res.* **2014**, *63*, 105–116. [CrossRef]
- Gu, Y.; Martin, R.P.; Metalssi, O.O.; Fen-Chong, T.; Dangla, P. Pore size analyses of cement paste exposed to external sulfate attack and delayed ettringite formation. Cem. Concr. Res. 2019, 123, 105766. [CrossRef]
- 14. Ochkurov, V.I.; Vilenskii, M.Y. Comparative evaluation of the saving of binder with fine ground slag. *IOP Conf. Ser. Mater. Sci. Eng.* **2019**, *666*, 012026. [CrossRef]
- Kazanskaya, L.F.; Isakovsky, V.I.; Fadeeva, S.A. Technological properties of self-compacting concrete mixtures with ground quartz sand. Int. J. Innov. Technol. Explor. Eng. 2019, 8, 799–803.
- 16. Barnett, S.J.; Adam, C.D.; Jackson, A.R.W. Solid solutions between ettringite, Ca6Al2(SO4)3(OH)12·26H2O, and thaumasite, Ca<sub>3</sub>SiSO<sub>4</sub>CO<sub>3</sub>(OH)<sub>6</sub>·12H<sub>2</sub>O. *J. Mater. Sci.* **2000**, 35, 4109–4114. [CrossRef]
- 17. Barnett, S.J.; Macphee, D.E.; Lachowski, E.E.; Crammond, N.J. XRD, EDX and IR analysis of solid solutions between thaumasite and ettringite. *Cem. Concr. Res.* **2002**, *32*, 719–730. [CrossRef]
- 18. Urkhanova, L.A.; Buyantuev, S.L.; Urkhanova, A.A.; Lkhasaranov, S.A.; Ardashova, G.R.; Fediuk, R.S.; Svintsov, A.P.; Ivanov, I.A. Mechanical and electrical properties of concrete modified by carbon nanoparticles. *Mag. Civ. Eng.* **2019**, *92*, 163–172. [CrossRef]
- 19. Sassani, A.; Ceylan, H.; Kim, S.; Arabzadeh, A.; Taylor, P.C.; Gopalakrishnan, K. Development of carbon fiber-modified electrically conductive concrete for implementation in Des Moines International Airport. *Case Stud. Constr. Mater.* **2018**, *8*, 277–291. [CrossRef]
- 20. Baeza, F.J.; Galao, O.; Vegas, I.J.; Cano, M.; Garcés, P. Influence of recycled slag aggregates on the conductivity and strain sensing capacity of carbon fiber reinforced cement mortars. *Constr. Build. Mater.* **2018**, *184*, 311–319. [CrossRef]
- 21. El-Dieb, A.S.; El-Ghareeb, M.A.; Abdel-Rahman, M.A.H.; El Sayed, A.S. Multifunctional electrically conductive concrete using different fillers. *J. Build. Eng.* **2018**, *15*, 61–69. [CrossRef]
- 22. Dehghanpour, H.; Yilmaz, K.; Ipek, M. Evaluation of recycled nano carbon black and waste erosion wires in electrically conductive concretes. *Constr. Build. Mater.* **2019**, 221, 109–121. [CrossRef]
- 23. Cordon, H.C.F.; Tadini, F.B.; Akiyama, G.A.; de Andrade, V.O.; da Silva, R.C. Development of electrically conductive concrete. *Cerâmica* **2019**, *66*, 88–92. [CrossRef]
- 24. Bernatskii, A.F.; Tselebrovskii, I.U.N.; Chunchin, V.A. Electrical Properties of Concrete; Energiya: Moscow, Russia, 1980.
- 25. Wang, H.; Yang, J.; Liao, H.; Chen, X. Electrical and mechanical properties of asphalt concrete containing conductive fibers and fillers. *Constr. Build. Mater.* **2016**, *12*, 2184–2190. [CrossRef]
- 26. Santhanam, M.; Cohen, M.D.; Olek, J. Modeling the effects of solution temperature and concentration during sulfate attack on cement mortars. *Cem. Concr. Res.* **2002**, 32, 585–592. [CrossRef]
- 27. Diab, A.M.; Abd Elmoaty, A.E.M.; Aly, A.A. Long term study of mechanical properties, durability and environmental impact of limestone cement concrete. *Alex. Eng. J.* **2016**, *55*, 1465–1482. [CrossRef]
- 28. Li, J.; Xie, F.; Zhao, G.; Li, L. Experimental and numerical investigation of cast-in-situ concrete under external sulfate attack and drying-wetting cycles. *Constr. Build. Mater.* **2020**, 249, 118789. [CrossRef]
- 29. Gopalakrishnan, R.; Chinnaraju, K. Durability of ambient cured alumina silicate concrete based on slag/fly ash blends against sulfate environment. *Constr. Build. Mater.* **2019**, 204, 70–83. [CrossRef]
- 30. Xu, P.; Jiang, L.; Guo, M.Z.; Zha, J.; Chen, L.; Chen, C.; Xu, N. Influence of sulfate salt type on passive film of steel in simulated concrete pore solution. *Constr. Build. Mater.* **2019**, 223, 352–359. [CrossRef]
- 31. Averbakh, E.E.; Luginina, I.G.; Smogorzhevsky, V.I. Study of electrical conductivity of clinker minerals and cements. *Cement* **1963**, 6, 6–7.
- 32. Ghazizadeh, S.; Hanein, T.; Provis, J.L.; Matschei, T. Estimation of standard molar entropy of cement hydrates and clinker minerals. *Cem. Concr. Res.* **2020**, *136*, 106188. [CrossRef]
- 33. Dehghanpour, H.; Yilmaz, K. Heat behavior of electrically conductive concretes with and without rebar reinforcement. *Mater. Sci.* **2020**, *26*, 4. [CrossRef]
- 34. Mobili, A.; Giosuè, C.; Bellezze, T.; Revel, G.M.; Tittarelli, F. Gasification char and used foundry sand as alternative fillers to graphene nanoplatelets for electrically conductive mortars with and without virgin. *Recycl. Carbon Fibres Appl. Sci.* **2021**, *11*, 50. [CrossRef]
- 35. Hong, S.; Yuan, T.; Choi, J.; Yoon, Y. Effects of steelmaking slag and moisture on electrical properties of concrete. *Materials* **2020**, 13, 2675. [CrossRef] [PubMed]
- 36. Justnes, H. Properties of gypsum-free Portland cement. Cem. Based Mater. 2014, 3, 128–139. [CrossRef]
- 37. Justnes, H. Calcium nitrate as a multi-functional concrete admixture. Concrete 2010, 44, 34–36.
- 38. Karagöl, F.; Demirboğa, R.; Kaygusuz, M.A.; Yadollahi, M.M.; Polat, R. The influence of calcium nitrate as antifreeze admixture on the compressive strength of concrete exposed to low temperatures. *Cold Reg. Sci. Technol.* **2013**, *89*, 30–35. [CrossRef]

Appl. Sci. 2021, 11, 8509 13 of 13

39. Milla, J.; Hassan, M.M.; Rupnow, T.; Al-Ansari, M.; Arce, G. Effect of self-healing calcium nitrate microcapsules on concrete properties. *Transp. Res. Record.* **2016**, 2577, 69–77. [CrossRef]

- 40. Kovalchuk, V.S.; Nikolaev, N.I. Carbon additives for high-quality well cementing. *IOP Conf. Ser. Earth Environ. Sci.* **2021**, 677, 052035. [CrossRef]
- 41. Isildak, Ö.; Özbek, O. Application of potentiometric sensors in real samples. Crit. Rev. Anal. Chem. 2020, 1–14. [CrossRef]
- 42. Gumeniuk, A.N.; Polyanskikh, I.S.; Pervushin, G.N.; Gordina, A.F.; Yakovlev, G.I.; Khazeev, D.R. Structuring additive based on production waste for mineral binders. *Constr. Mater.* **2019**, *7*, 41–46. [CrossRef]
- 43. Yakovlev, G.I.; Černý, V.; Polyanskikh, I.; Gordina, A.F.; Pudov, I.A.; Gumenyuk, A.; Smirnova, O. The effect of complex modification on the impedance of cement matrices. *Materials* **2021**, *14*, 557. [CrossRef]
- 44. Qasim, O.A. A Review Paper on Specimens Size and Shape Effects on the Concrete Properties. *Int. J. Recent Adv. Sci. Technol.* **2018**, *5*, 13–25. [CrossRef]
- 45. Su, J.; Ye, J.; Fang, Z.; Zhao, M. Size effect on cubic and prismatic compressive strength of cement paste. *J. Cent. South Univ.* **2015**, 22, 4090–4096. [CrossRef]
- 46. Tian, Y.; Yan, X.; Zhang, M.; Lu, D.; Yang, T.; Wang, Z.; Li, W. Internal transport and corrosion behaviors of sulfate corrosion media carried by recycled aggregate in concrete. *Constr. Build. Mater.* **2020**, *260*, 120480. [CrossRef]
- 47. Al-Dulaijan, S.U.; Maslehuddin, M.; Al-Zahrani, M.M.; Sharif, A.M.; Shameem, M.; Ibrahim, M. Sulfate resistance of plain and blended cements exposed to varying concentrations of sodium sulfate. *Cem. Concr. Compos.* **2003**, *25*, 429–437. [CrossRef]
- 48. Hulanicki, A.; Głąb, S. TITRIMETRY | Potentiometric. Encycl. Anal. Sci. 2005, 114–121. [CrossRef]
- 49. Pipilikaki, P.; Papageorgiou, D.; Dimitroula, M.; Chaniotakis, E.; Katsioti, M. Microstructure changes in mortars attacked by sulphates at 5 °C. Constr. Build. Mater. 2009, 23, 2259–2264. [CrossRef]
- 50. Plugin, A.A.; Pluhin, O.A.; Kasyanov, V.V.; Dyomina, O.I.; Bondarenko, D.O. Portland cement-based penetrating electrically conductive composition for protection against electrocorrosion. *Funct. Mater.* **2021**, *28*, 121–130.
- 51. Jo, B.W.; Sikandar, M.A.; Chakraborty, S.; Baloch, Z. Investigation of the acid and sulfate resistance performances of hydrogen-rich water based mortars. *Constr. Build. Mater.* **2017**, *137*, 1–11. [CrossRef]