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Influence of reactive fillers on concrete corrosion resistance

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Abstract. Contact surfaces represent the weakest link in a conglomerate structure of materials. They ensure the diffusion of aggressive agents inside the material. To reduce the conductivity of contact surfaces it is advisable to use reactive fillers, which interact with cement matrix via certain mechanisms, which in turn, reduces the permeability of the contact layer and fosters durability of products. The interaction of reactive fillers with calcium hydroxide of a concrete liquid phase in a contact area leads to the formation of hydrated calcium silicates of a tobermorite group. Such compounds, being settled in pores and capillaries of a product, colmatage and clog them to some extent thus leading to diffusion delay (inhibition) with regard to aggressive components of external media inside porous material, which in turn inhibits the corrosion rate. The authors studied and compared the corrosion of cement concrete with a standard filler (quartz sand) and a reactive filler (perlite and urtit). The experiments confirmed the positive influence of active fillers on concrete corrosion resistance.

1. Introduction
The main approach to increase the strength of cementous construction materials is to decrease the content of aluminates in cement clinker, to introduce mineral additives of binding calcium hydroxide and to decrease the porosity of concrete. The latter condition provides for diffusion delay of aggressive components of external media into the concrete due to filling of transport pores with corrosion products [1-4]. It is possible to enhance the diffusion resistance to propagation of aggressive ions and gases through the decrease in permeability of a contact area by introducing active fillers [5-6]. Fillers from slag, volcanic rocks, etc. have chemical activity in relation to Ca(OH)2 in normal conditions. However, the slag filler increases water demand of a concrete mixture, which reduces the overall effect of an active filler [7-8]. Therefore, the study of a possibility to increase the corrosion resistance of fine-grained concrete using perlite- and urtit-based fillers is of primary concern.

Quartz sand has very small activity to interact with calcium hydroxide at room temperature, which fits with practical experience of using quartz sand and quartzitic sandstone as fillers [9].

High-temperature variations of silica – α-tridimit, kristobalit and amorphous silica – differ in higher activity. Consequently, when choosing among active fillers it is advisable to select rocks containing specified variations of silica. They include perlite, which is available and serves a large-tonnage raw material for consumption. It mainly consists of silica and acid silicates being in either glassy or cryptocrystalline state. It is known that at room temperature, they posess reaction capacity in relation to calcium hydroxide, present in the liquid phase of concrete mixtures and the reinforced concrete.

Nepheline rocks (urtits) are byproducts of apatite-nepheline field development [10-11]. The

performed termodynamic calculations [12] indicate some relative activity of various compositions as concrete filler components: nepheline > vitreous wollastonite > quartz > microcline > albite > anortite > crystalline wollastonite. Hence, nepheline has enhanced chemical activity in relation to calcium hydroxide contained in concrete pore liquid, which justified the choice of nepheline-containing rock (urtit) as an active filler of the I type.

The purpose of this work is to conduct a comparative study of corrosion of cement concrete with standard and reactive fillers.

2. Materials and methods

Natural perlite of the Mukhor-Talinsky field and urtit of the Hibinsky Massif of apatite-nepheline ore fields, obtained via crushing on laboratory twin jaw crusher, were used to study the corrosion resistance of concrete with active fine-grained fillers ($\mu m=2.5$). The chemical composition of perlite, %: $SiO_2=70.4$; $Al_2O_3=14.7$; $Fe_2O_3=0.7$; $FeO=0.4$; $CaO=0.8$; $MgO=0.3$; $TiO_2=0.1$; $K_2O=3.9$; $Na_2O=3.4$; $H_2O=5.3$. Nepheline serves a source mineral for urtit with the content of approximately 71.3%, aegirine – 16.4%, fieldspar – 6.2%, sphene – 2.8%. The SO3 content does not exceed 0.18%; the soluble silica content on average makes 20 mmol/L. Fine-grained concrete on quartz sand of the Nizhneolshansky field ($\mu m=1.2$) with the following chemical composition, %: $SiO_2=96.4$; $Al_2O_3=0.3$; $Fe_2O_3=0.7$; $CaO=1.8$ %; $MgO=0.2$; $SO_3=0.05$; $R_2O=0.3$; percentage of other impurities=1.9 was used as a test sample.

Medium aluminate portland cement CEM I 42.5 N (CJSC Belgorodsky Tsement) with the following mineral structure, %: $C_3S=63.2$; $C_2S=14.8$; $C_3A=6.9$; $C_4AF=13.1$; n=2.25; p=1.24; KH=0.92 was used as a binding agent.

1% solutions of magnesium sulfate and sulfuric acid were used as aggressive environments.

Method. The experiments were conducted using samples of 2.5x2.5x10 cm in size and the composition of portland cement and a filler = 1:3. Concrete samples were made according to GOST 310.4–81; after solidification on the 28th day in normal conditions, they were tested for strength and placed in 1% solutions of sodium and magnesium sulfates. The solutions were periodically changed. After being kept for 1, 3, 6 and 12 months, the samples were exposed to visual analysis, tested for flexural and compression strength, the phase composition of corrosion products (XRF) and the microstructure of the eroded area (SEM) were defined.

The study of the phase composition was carried out using analytical X-ray diffractometer ARL9900 IntellipowerWorkstation and ARLX'TRA via a powder diffraction technique in the range of double angles θ 4÷56° and 8÷80°. Data handling, calculation of phase concentration and sequential analysis of elements was made using the following software: UniQuant 5.56, Siroquantversion 3.0, ICDDDDVIEW 2010, ICDDPDF-2 Release 2010, Difwin, CrystallographicaSearchMatch.

The microstructure was studied via scanning electron microscope TESCANMIRA 3 LM. All measurements were fully automatic and made with appopriate software.

3. Influence of active fillers on concrete corrosion resistance
Sulfate corrosion

The test results of fine-grained concrete samples showed that the filler from perlite and urtit increases strength and resistance of concrete in 1% solutions of magnesium sulfate. The flexural strength of concrete with perlite filler was 72.3% higher and the compression strength was 38.7% higher in 1 year of solidification in sulfate-magnesium media than that of concrete with test composition (Fig. 1). The reduction of flexural and compression strength in 12 months of testing was only noted for samples with test composition; a noticeable drop of strength was recorded after 6 months of testing. This confirms the fact that the corrosion resistance of concrete is mainly defined by permeability of contact surfaces.

Higher strength of samples with perlite and urtit fillers is caused by the fact that already at room temperature they interact with alkaline components of cement concrete with further formation of gelly-like fibrous hydrated calcium silicates of a tobermorite group (CSH) having good binding properties.

This leads to colmatation of coarse-capillary pores around particles of coarse- and fine-grained fillers, which serve as channels of aggressive solutions penetration into concrete and reinforced concrete structures.

Tests of fine-grained concrete with urtit filler carried out within 6 months showed that the flexural and compression strength increased by 46% (R_{com}) and by 43% (R_{bend}). Magnesium sulfate showed high aggression in relation to samples with a quartz filler, the decrease in flexural strength within 3-6 months, and the compression resistance within this interval did not change (Fig. 1).

By the end of one year of tests, the samples of all compositions had no cracks or other visible defects. A typical feature of corrosion in magnesium solutions is the presence of a white film of magnesium hydroxide on the surface of concrete, which is formed during the interaction of $MgSO_4cCa(OH)_2$ diffusing from concrete.

Strength and resistance do not always provide for the development of chemical corrosion, which is caused by the development of simultaneous destructive and constructive processes. In this regard, corroded surface layers of test samples were studied via X-ray phase analysis, fluorescence and microanalysis.
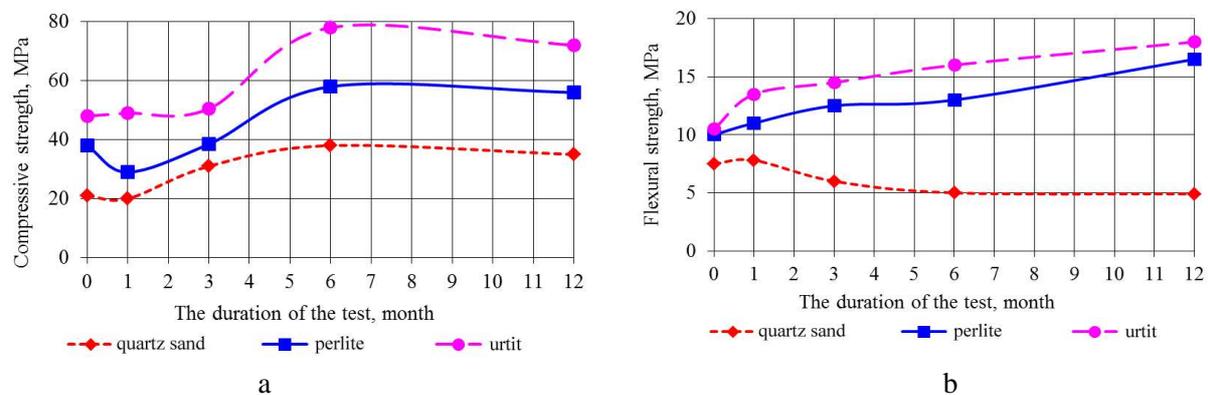
Figure 1. Influence of fillers on strength of cement samples (C:P=1:3) solidified in 1% $MgSO_4$ solution: a – compression strength; b – flexural strength.

XRF showed that the main product of corrosion is the gypsum (peaks: 7.56; 4.27; 3.059 Å). The concentration of applied sulfate solutions exerts a strong influence on the formation of ettringite and gypsum. The gypsum is formed if the concentration of sulfates makes more than 1500 mg/l, and hence is not commonly used in practice and only in small amounts.

The lack of ettringite can be caused by sample drying at a temperature of more than 60°C and as a result of partial dehydration it transfers into roentgen-amorphous state. The X-ray fluorescence analysis made it possible to state that in surface layers of fine-grained concrete (1–2 mm) with quartz sand the SO_3 content makes 2.19%, which exceeds a similar indicator for fine-grained concrete with perlite filler – 1.84%.

Micrographs of surface chips of fine-grained concrete samples solidified within 12 months in sulfate solution confirm the formation of contact layers on active fillers in aggressive environments. The contact area between quartz sand and a cement stone grows by gypsum crystals; dense twinning of a filler with a cement stone is observed in concrete with a perlite filler (Fig. 2).
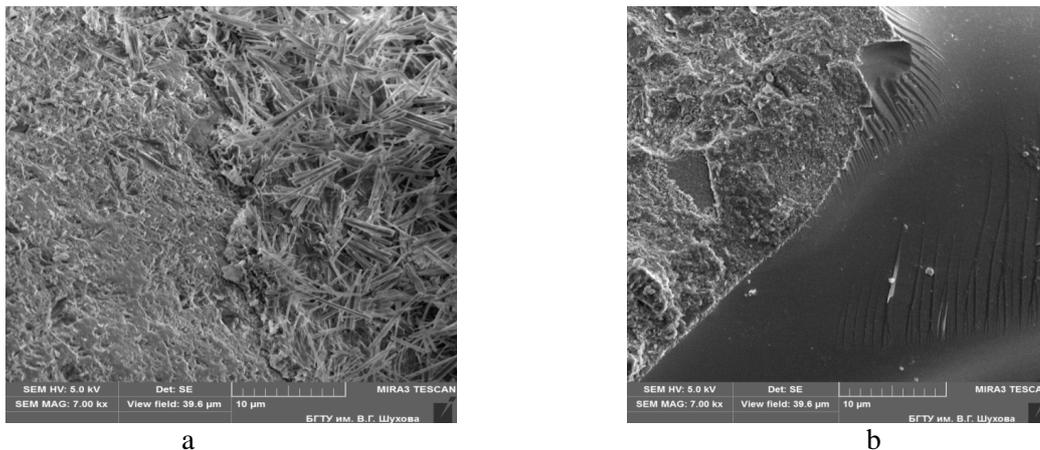
Figure 2. Contact layer kept for 12 in 1% magnesium sulfate solution on a surface: a – quartz sand; b – perlite filler.

Fig. 3 shows the contact layer of urtit filler and a cement stone. The left image shows a side, cut of this layer, filled with a layer of hydrated calcium silicates, formed as a result of interaction of a filler surface with $Ca(OH)_2$ of pore liquid.

The right image (Fig. 3, b) shows the section of a layer at larger resolution making a fine-crystalline structure of gel hydrate compositions visible. It is seen that this layer has a cell structure of triangular shape, which is typical for autoclaved samples in the SiO_2–CaO–H_2O system.
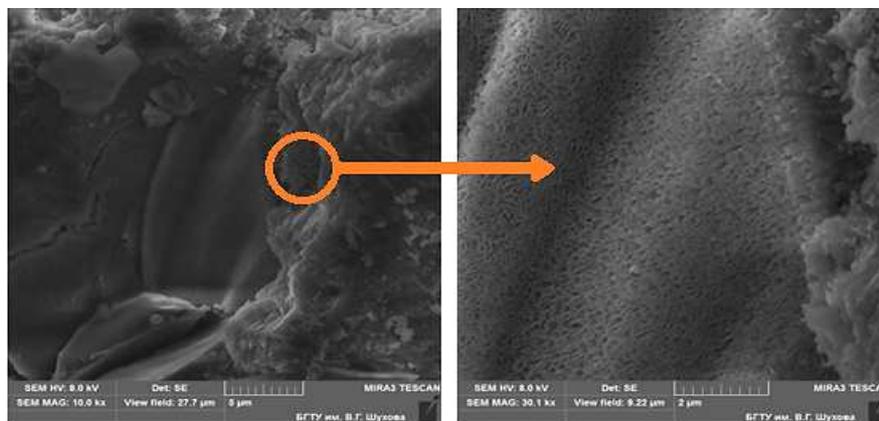
Figure 3. Layer of hydrated calcium silicates upon contact of urtit filler with cement stone.

Thus, perlite and urtit fillers with increased activity in comparison with quartz sand in relation to calcium hydroxide act as active fillers ensuring colmatation of coarse-capillary pores on the interface of fillers with a cement matrix of concrete, which fosters the increase in corrosion resistance of cement concrete.

Acid corrosion

At present, the issue of the increase of acid resistance of concrete in relation to small concentration environments [13-16] remains urgent since acid resisting concrete functions at high acid strength and is not efficient at 0.1-10% of acid concentrations. To operate at average and low acid strength, it is advisable to use inorganic concrete since organic materials are very expensive, less technological and insufficiently resistant in acids with oxidizing properties, for instance, in nitric and nitrous acids, their mixture with hydrochloric acid, etc.

The study of corrosion resistance of fine-grained concrete with perlite and urtit fillers was carried out via the developed method that implies the use of materials with the above listed composition. Test

results showed that the strength of fine-grained concrete samples with perlite fillers exceeded samples with quartz sand both in case of hydraulic setting and in 1% solution of sulfuric acid. The concrete samples with quartz sand kept in sulfuric acid are characterized by almost complete loss of both flexural and compression strength.

Microanalysis of a corroded zone of fine-grained concrete (Fig. 4-5) showed a clear difference between active and inactive fillers. Grains of quartz sand "fall out" of a cement matrix of concrete and are replaced by rather large gypsum crystals visible in the void formed (Fig. 4, a). A perlite filler (Fig. 4, b) makes a firm union with a cement matrix of concrete.
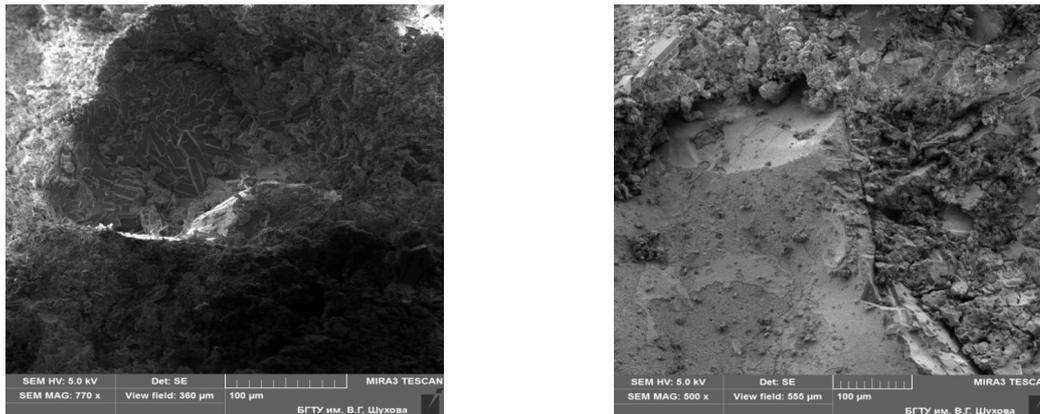
Figure 4. Corroded concrete layer: a – quartz sand; b – perlite filler.

In a corroded zone of concrete (Fig. 5, a), the contact area of quartz sand and its surface accrues corrosion products, at the same time corrosion products are not observed on the surface of the perlite filler and in the contact area (Fig. 5, b).
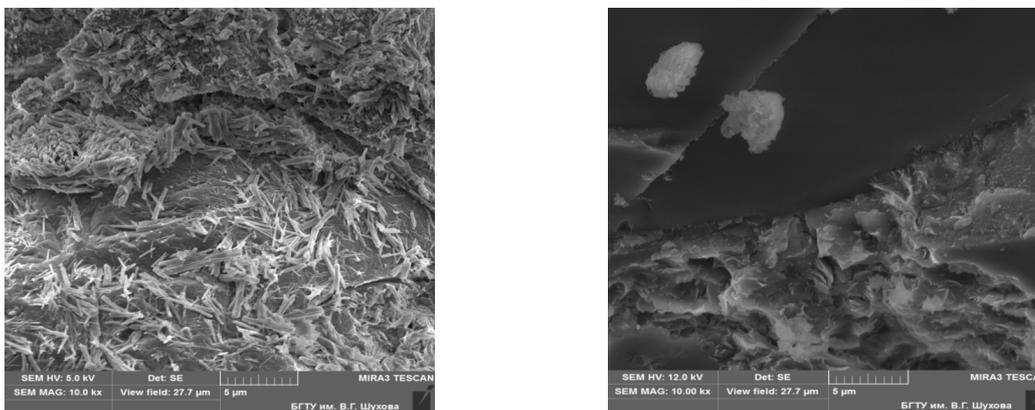
Figure 5. Contact area between a filler and a cement matrix in a corroded zone: a – quartz sand; b – perlite filler.

In the solution of sulfuric acid, throughout the entire test, flexural and compression strength increased by 36% for concrete samples with the urtit filler, while for concrete samples with quartz sand the strength decreased after 3 months.

The diagrams in Fig. 6 show that the compression strength of samples with urtit fillers increases in both environments within 6 months of tests. At the same time, in the solution of sulfuric acid, the strength increases in 1 month, and in the solution of magnesium sulfate - in 3 months, which, apparently, is caused by positive influence of a bridging agent (gypsum).
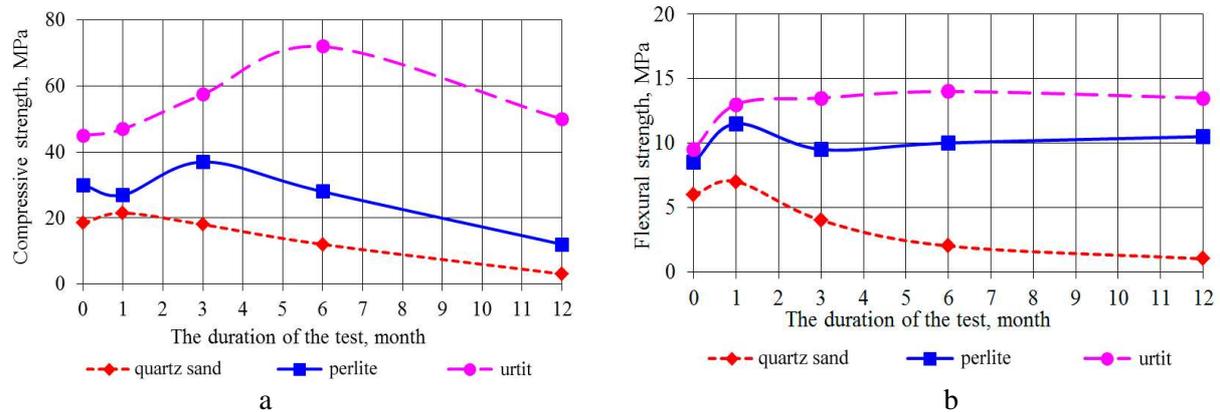
Figure 6. Influence of fillers on strength of cement samples (C:P=1:3) solidified in 1% H_2SO_4 solution: a – compression strength; b – flexural strength.

It should be noted that there is a substantial difference in strength of concrete with urtit before and after tests in aggressive solutions, as well as of a test concrete. After curing in magnesium sulfate and sulfuric acid solutions, the compression strength was 2-3 times higher, while the flexural strength was 1.7-2 times higher. The resistance coefficient in H_2SO_4 solution made $KC_{360}=1.2$, in $MgSO_4$ solution – $KC_{360}=1.02$, which is 1.3–3.2 times higher than the resistance coefficient of concrete with quartz sand (Fig. 7).

The comparison of resistance coefficients of fine-grained concrete in 1% $MgSO_4$ and H_2SO_4 solutions is of the utmost theoretical and practical interest. It clearly shows advantages of a more active filler (urtit) compared to other low-active and inactive fillers in the H_2SO_4 solution than in the $MgSO_4$ solution.
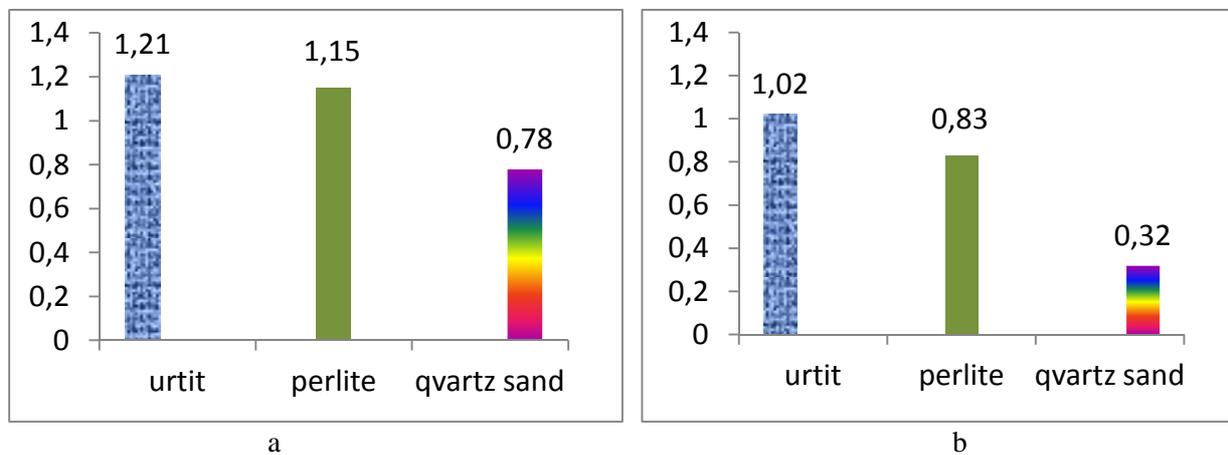
Figure7. Influence of fillers on resistance coefficients of concrete solidified in various aggressive environments in: a – 1% $MgSO_4$ solution; b – 1% H_2SO_4 solution.

The obtained data show that in case of acid corrosion, the major factor ensuring self-retention of heterogeneous physical and chemical processes of acid interaction with cement stone components is not only colmatation of pores of the latter one, but also the formation of a thin viscous gel layer of silica on a surface of product contacting with acid. Silica, being anhydride of H_nSiO_m silicic acid, represents an acid-resisting substance soluble only in fluoric acid. Another factor ensuring self-retention of acid corrosion of cement concrete in strong acid solutions is the following.

Let us consider the surface of a cement concrete sample contacting with acid solution (Fig. 8).
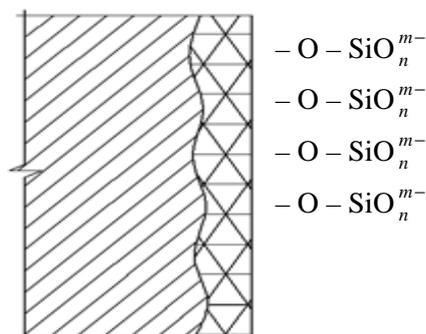
Figure 8. Scheme of silica layer formation.

Within a short time, the gel layer, consisting of silicon acid and its ions, is formed on a product surface. It is clear that when hydrogen ions, more specifically H3O+ ions, interact with a gelly surface of corrosion products, H+ ions are captured by silica anions: H3O + + the H3SiO4th → H4SiO4 + H2O.

This reaction provides exceptional thermodynamic probability due to an extremely low dissociation coefficient of orthosilicic acid, which is close to Kdiss=10-10. This process leads to the fact that inner layers of partially corroded material contact not with free hydroxonium ions, but with weak orthosilicic acid, which is not aggressive in relation to concrete and has a similar chemical composition.

Thus, it is found that urtit-based fillers increase the corrosion resistance of fine-grained concrete in sulfate-magnesium and sulfuric solutions (almost twice) in comparison with the concrete based on quartz sand, which is caused by the decrease in conductivity of a contact area between a filler and a cement matrix due to specific chemical relation of the main rock-forming nepheline mineral to calcium hydroxide. It is advisable to use nepheline-containing fillers for concrete applied in highly intense conditions of acid, salt and biological action.

4. Conclusions

The conducted study of the influence of active filler on concrete corrosion resistance allows considering the obtained results as a physical and chemical model able to solve key issues of active fillers. It is practically viable, however not for an extensive use and only in cases when it is necessary, to ensure safety of concrete operational properties in corrosive media where livestock wastes are accumulated and when there is contact with industrial or sewage waters, etc. The use of concrete in the field of corrosion is a relatively small area where the use of expensive materials is justified.

5. Acknowledgments

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