Biological and chemical corrosion of cement materials modified with polymer

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Abstract. The article presents the effect of the addition of polymer to mortars with CEMI and its influence on durability under conditions of sulfuric acid or nitric and sulphur bacteria or nitrogen (nitrification and denitrification). Both acids corresponds to the products of metabolism of bacteria *Acidithiobacillus thiooxidans* and *Thiobacillus denitrificans*, *Paracoccus denitrificans* by the literature is about 0.15 mmol/dm^3. The changes in tightness materials studied by determining moisture mass and absorption. Corrosion processes were identified by examination in a scanning microscope equipped with an X-ray microanalyzer and a mercury porosimeter. The research results presented showed that the solution has a significantly weaker effect on the composite cement and cement-polymer compared with the action of bacteria. The action of both environments caused two opposing processes: unsealing the structure and deposition of corrosion products.

Key words: sulphuric acid, nitric acid, sulphur bacteria, nitric bacteria, cement, polymer.

1. Introduction

Biodeterioration of inorganic building materials is a common phenomenon [1, 2]. One of the areas of concern are concrete structures used for sewage transportation and treatment. Corrosion of sewers and sewage treatment plants is a serious problem and its effects cause a billion dollars loss annually [3, 4]. A deeper understanding of damaging mechanism of these facilities, both concrete itself and protective coating, could extend significantly its period of the safe use. Therefore, it is important to identify both microorganisms causing deterioration of concrete structures and products of its metabolism enhancing this process.

The most severe corrosion damage occurs in sewer pipes [5]. Generally, it is thought that corrosion of these facilities caused by microorganisms is connected with sulphuric acid as the main excretory product of its metabolism. Bacteria activity leads to sulphur circulation in a system and in consequence to production of sulphuric acid causing concrete corrosion. It is thought that the following bacteria: *Thiobacillus thiooxidans*, *Thiobacillus neapolitanus* and *Thiobacillus intermedium* are responsible for concrete corrosion [6–8]. The concrete deterioration mechanism related to bacteria activity, for example *Thiobacillus*, consists in oxidizing hydrogen sulphide to sulphuric acid that causes acid sulphate corrosion. These reactions can proceed due to metabolic activity of bacteria that liberate sulphuric acid (VI) or nitric acid (V). Sulphur reduces bacteria (SRB) by production of hydrosulphuric acid. Sulphur oxidizing bacteria (SOB) produce sulphuric acid (VI), that in reaction with calcium hydroxide or calcium carbonate gives gypsum [9], or later ettringite and sometimes, although rarely, thaumasite (CaSiO$_3$·CaCO$_3$·CaSO$_4$·15H$_2$O), when the temperature of a system is <15°C) [10, 11].

$$SO_4^{2-} + 2H^+ + 4\,H_2\ SRB \rightarrow H_2S + 4H_2O$$
$$SRB - Sulphate\ Reducing\ Bacteria, \qquad (1)$$

$$H_2S + 2O_2\ SOB \rightarrow H_2SO_4$$
$$SOB - Sulphur\ Oxidizing\ Bacteria, \qquad (2)$$

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 \cdot 2H_2O\ (gypsum), \qquad (3)$$

$$3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O + 2(CaSO_4 \cdot 2H_2O)$$
$$+\ 16\ H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O. \qquad (4)$$
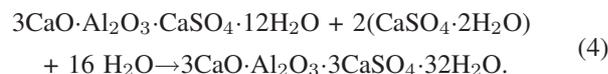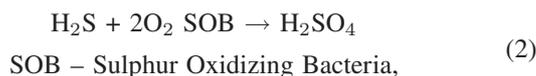
Equally severe damages may occur in nitrification pools in sewage treatment plants. In such aerated tanks ammonia is oxidized to nitrates. In the first step, ammonia is oxidized to nitric acid (III), and to nitric acid (V) in the second step [5]:

$$NH_3 + 1.5\ O_2 \rightarrow NO_2^- + H_2O + H^+, \qquad (5)$$

$$NO_2^- + 0{,}5\ O_2 \rightarrow NO_3^-, \qquad (6)$$

$$NH_3 + 2O_2 \rightarrow NO_3^- + H_2O + H. \qquad (7)$$
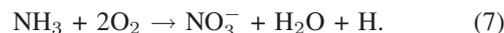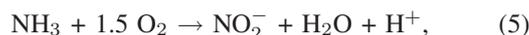
Autotrophic nitrifying bacteria include *Nitrosomonas*, *Nitrobacter*, *Nitrospira* and *Nitrosococcus* species [12, 13]. Hydronium ions released from oxidation of ammonia and nitric anhydride (V) are buffered by hydrogen carbonate present in sewage: in turn hydrogen carbonate reacts with free ammonia from the nitrification process [5]:

$$H^+ + HCO_3^- = CO_2 + H_2O, \qquad (8)$$

$$NH_3 + 2O_2 + HCO_3^- \rightarrow NO_3^- + 2H_2O + CO_2. \qquad (9)$$
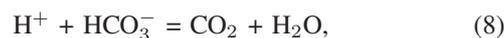
Nitric acids (HNO$_2$ and HNO$_3$) react with hydrates of the cement matrix and with calcium carbonate from the carbonization process in surface concrete layers producing calcium nitrates (V) of better water solubility. This leads to decomposition of cement hydration products and causes the cement matrix deterioration proceeding inwards.

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An effect of biochemical mechanisms in microbiological corrosion of building materials depends on chemical properties of phases present inside them. These mechanisms include the following processes:

- acidolysis leading to the release of sulphuric and nitric acids to the environment,
- complex formation with biogenic organic acids from metabolism of microorganisms,
- oxidation-reduction reactions,
- organic matter accumulation and oxygen production [2].

Thus, concrete corrosion induced by bacteria activity can result from interaction of various acids produced in its metabolism process. Therefore, the materials of increased resistance to biocorossion and material and technological solutions facilitating repairs of damaged structures are being sought. Such repair materials may be composites with a cement-polymer matrix [14]. It is important to answer to the question: whether and to which extent these materials are susceptible to microorganism growth and what is the destruction mechanism of the latter?

The aim of this study is to assess an effect of sulphur and nitrogen bacteria on the cement mortar with 3% polymer addition, compared to the effect of the solutions of sulphuric and nitric acids at concentrations corresponding to acidic products of bacteria metabolism [0.15 mmol/dm^3] [15].

2. Materials

When selecting polymers its differentiation by chemical reactivity and function performed in cement materials was taken into account. From pre-mix material group [16] acrylic resin, polysiloxane latex and polycarboxylic resin were chose as modifiers. These resins are modifiers of cement-polymer materials used in building engineering. Preliminary tests [17] indicated that 3% content of pre-mix polymers to cement within a relatively short period of time (6 months) has an effect on susceptibility to microorganism growth.

For a testing purpose the rods of $20 \times 20 \times 160$ mm in size made of cement-polymer mortars were prepared. The water content in resin dispersions, used as modifiers, was 1.5% of a polymer mass. Thus, the w/c ratio in each of tested mortar was 0.5. The composition of composites under investigation are presented in Table 1.

Table 1
The composition of the tested composites

Composite tested	Designation	Content [g]			
		CEM I 42.5	Quartz sand	Water	Polymer modifier
Cement mortar	CNP	100	300	50	–
Mortar modified with acrylic resin	CMPA	100	300	48.5	3
Mortar modified with polysiloxane latex	CMPSi	100	300	48.5	3
Mortar modified with polycarboxilic resin	CMPK	100	300	48.5	3

The prepared samples were demoulded after 48 hours. After removing from the moulds the samples were matured under a plastic sheet for 3 month at $+20°C \pm 2°C$ and relative humidity of $60\% \pm 5\%$. Afterwards, the samples were subject to bacteria and acid actions under the following conditions:

- in a biological chamber under activity condition of the following bacteria: sulphur bacteria *Acidithiobacillus thiooxidans* and (bS) and *Thiobacillus denitrificans* – sulphur bacteria having the properties of denitrification and denitrifying bacteria *Paracoccus denitrificans* (bN). *Acidithiobacillus thiooxidans* obtained from the culture on a medium Waksman. *Thiobacillus denitrificans* and *Paracoccus denitrificans* obtained from the culture on a mineral medium Winogradskiego for a first nitrification phase (containing ammonium cations + soil). The same medium was inoculated in a medium Winogradskiego for the second phase (containing nitrites). The incubation, at room temperature, lasted 14 days, the products were tested for nitrification phase I (nitrites) and phase II (nitrates). The samples were inoculated with bacteria suspensions containing on an average 10^6 cells/ml. The condition inside the chamber: temperature $+30°C \pm 2°C$, relative humidity $95\% \pm 5\%$.
- in water solutions of sulphuric and nitric acids. The concentration of both acids correspond to the product of metabolism of bacteria *Acidithiobacillus thiooxidans*, *Thiobacillus denitrificans* and *Paracoccus denitrificans*, which according to the literature is about 0.15 mmol/dm^3 [15]. Continuous solution flow through the samples was maintained, while keeping practically the constant acid concentration. The process was carried out at 25°C.

3. Methods of research

To evaluate changes in mortar properties due to acid and bacterial corrosion, the following parameters were selected:

- moisture content (μ_M) – wet mass according to PN-EN ISO 12570:2002 [18] and absorbability or water absorption (n_o) – determined according to PN-85/B-04500 [19];
- microstructure was examined under a scanning electron microscope (SEM) equipped with a FEG (Field Emission Gun) electron gun or the Schottky type, manufactured by FEI Nova NanoSEM 200 and with the Quantachrome Poremaster Nova1000e mercury porosimeter.

3.1. Moisture content by mass (μ_M) and water absorption (n_o). The moisture sorption of the mortars (on $20 \times 20 \times 160$ mm samples) tested was determined through moisture content by mass and water absorption measurements.

Moisture content by mass was determined using the contaminated and uncontaminated samples. The test materials were weighed and then they were dried at 105°C to a constant mass.

Moisture content by mass is calculated according to the following formula: $\mu_m = (m_w - m_s)100\%/m_s$ where m_w – mass of damp sample [g], m_s – mass of dry sample [g].

The water absorption test was conducted according to PN-85/B-04500. The specimens were dried at 105°C in oven until mass difference between two measurements at intervals of

24 h was less than 0.5%. After cooling down, the specimens were immersed in water at around 21°C for 48 h.

Water absorption is calculated according to the following formula: $n_m = (m_n - m_s)100\%/m_s$, where: m_n – mass of sample saturated with water [g]; m_s – mass of dry sample [g].

3.2. Porosity determined using a mercury intrusion porosimetry.
Porosity was determined using the Quantachrome Poremaster Nova1000e mercury porosimeter.

This method permits us to determine porosity and pore size distribution within the radius range from 4 to 30000 nm. The test involves filling material pores with mercury at increasing pressure and simultaneous recording changes in mercury levels. The procedure of this test is described in detail [20, 21]. Two small samples with a diameter of 10 mm and 10–15 mm in length (each sample weighed ca. 2 g), were taken from the concrete beams and used for MIP tests. The small specimens were dried in an oven at 105–110°C for 24 h and stored in a desiccators until testing. Test results are shown as graphs demonstrating the relationship between pore volume and diameter obtained using the Poromaster programs.

3.3. Structure analysis.
One small sample with a diameter of 15 mm and 10–15 mm in length, was taken from the concrete beams.

The morphology and chemical constituents of the concrete samples were analysed with SEM and EDX, respectively. Samples were completely dried at room temperature, and then examined at accelerating voltages ranging from 15 to 25 kV by a SEM (FEI Nova NanoSEM 200). In the present investigation, the SEM was used in its most common mode, the emissive mode. Samples were carbon coated with a sputter coating Emitech K575 prior to examination. Mineral constituents of the materials were further characterized by EDS analysis.

4. Analysis of the results

The obtained results regarding mortar humidity and absorbability are presented in Fig. 1. The means of 6 measurements made after keeping the samples in solutions of sulphuric and nitric acids and sulphur and nitrogen bacteria for six months. The scatter of the results did not exceed 0.1%.

The action of sulphur bacteria causes more than threefold increase of moisture content in mortars under investigation. The composite with polycarboxylic resin had the lowest moisture content, however, 2.5 times greater than that of the reference (control) sample. For sulphuric acid the moisture content increased twice, and the mortar with polycarboxylic resin admixture showed also the lowest moisture content.

The moisture content resulting from the action of sulphuric acid is significantly lower (from about 15 to 42%) compared to sulphur bacteria. The mortar with polycarboxylic resin admixture shows the smallest difference.

When analysing the absorbability results one can note that sulphur bacteria reduces this parameter by 13% for CMPA and by more than 40% for CMPK. However, the solution of

H_2SO_4 increases absorbability up to 2% for CMPK and up to 45% for CMPA compared to the control samples. When comparing the sorption parameters under examination it is possible to conclude that the moisture content of a material exposed to biological environment (bacteria action) is almost two times higher than absorbability. However, the absorbability of materials after acid action is about 1.5 times higher. Such anomaly may be explained partly as a more intensive bacteria action and the so called biofilm formation. This is a biological membrane adhering to the solid surfaces or cell surfaces of other organisms [22–24]. It may contain bacteria, fungi, algae and protozoans [25]. A biofilm is formed by complex multi-cell structures, where numerous cells of microorganisms are enclosed with a mucus layer [26].
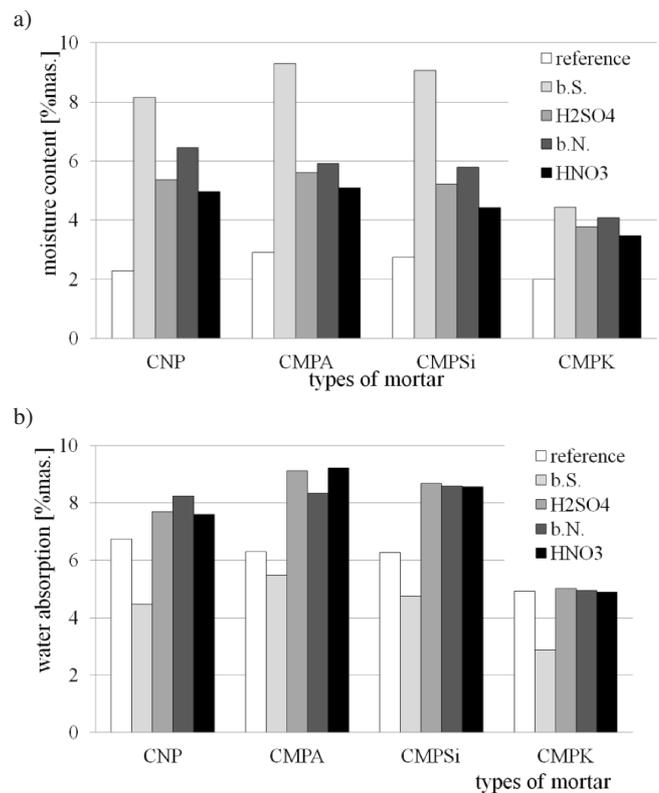
Fig. 1. Changes of a) moisture content and b) water absorption with respect to different types of mortars

The exposure of tested materials to nitrogen bacteria for 6 months has a strong effect on the moisture content. The moisture content in samples exceeds more than two times the moisture level in materials not exposed to corrosive environment. The mortar without polymer admixture show the greatest difference (almost 3-fold). However, the mortar modified with polycarboxylic demonstrates the lowest absorbability (0.46%mas) compared to that of the control samples. The remaining values increase by 22% for CNP and by 37% for CMPSi.

The moisture content in samples exposed to nitric acid increases by 61% for CMPSi and by 118% for CNP regarding the moisture content of the control samples. The absorbability of the mortar modified with polycarboxylic shows practically

no changes after exposure in the solution of HNO_3. For other materials it increases by 12% for CNP and by 46% for CMPA.

When comparing the corrosive action of nitrifying bacteria and the solution of nitric acid, the biological environment causes a higher moisture content. It increases by 16% for CMPA and by 31% for CMPSi compared to the materials in the nitric acid environment. The mortar without modifier (CNP) shows the greatest changes of this feature in both environments. The absorbability of the CMPSi and CMPK samples contaminated by nitrogen bacteria is comparable with that of the sample exposed to the solution of nitric acid. The unmodified mortar shows an increase in absorbability by about 8%. In the case of polyacrylic resin the action of nitric acid increases absorbability by 10% compared to the action of bacteria.

The results of porosity examination of cement and cement-polymer mortars not exposed to the action of corrosive environment by using the mercury porosimetry method are presented in Fig. 2. The results for the samples contaminated with sulphur and nitrogen bacteria are shown in Fig. 3, while for the samples exposed to the solutions of H_2SO_4 and HNO_3 are illustrated in Fig. 4.
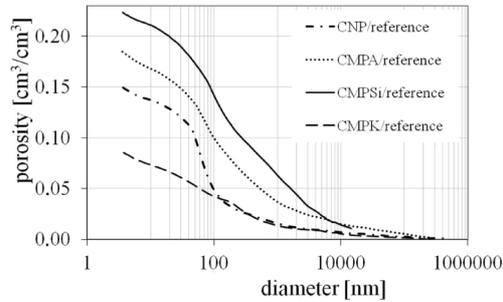
Fig. 2. Change of porosity of cement materials not exposed to corrosive media

a)

b)
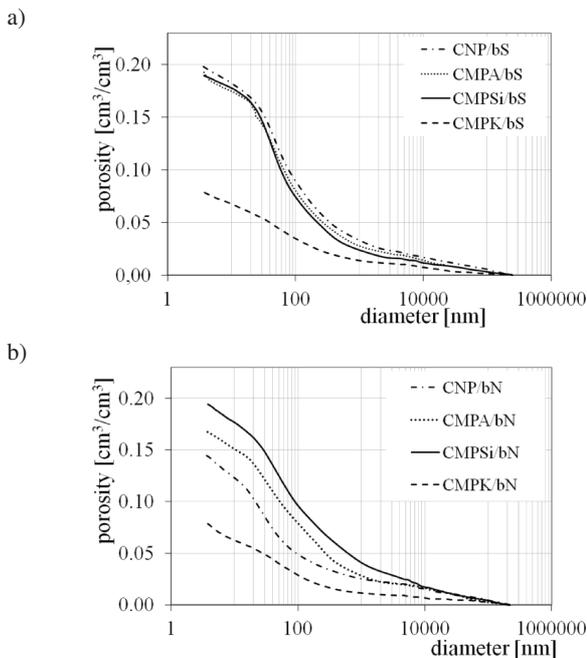
Fig. 3. The change in porosity of cement materials by the action of: a) sulfur bacteria, b) nitric bacteria

a)

b)
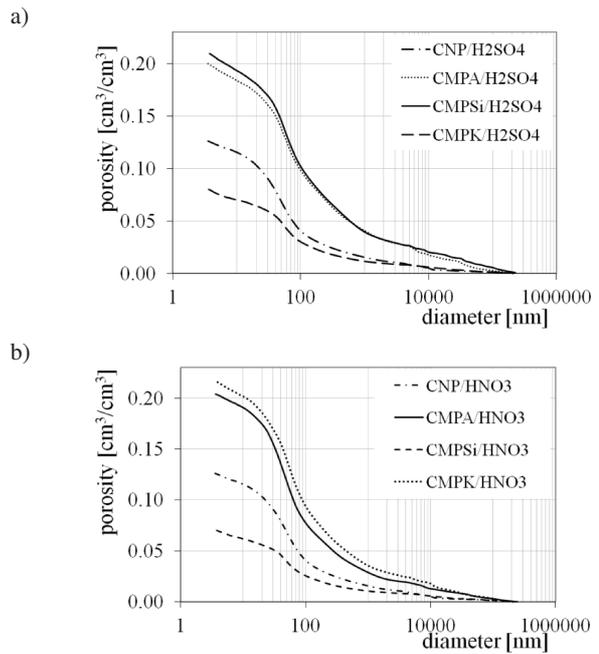
Fig. 4. The change in porosity of cement materials by the action of: a) sulfuric acid, b) nitric acid

The examined cement mortars without polymers show the highest contribution of pores of diameters within the range of 10–100 nm in a porosity structure and its total content is 0.15 cm^3/cm^3. The modification of materials with polysiloxane and polyacrilic resin increases the pore content up to 0.25 cm^3/cm^3 and 0.18 cm^3/cm^3, respectively with the highest contribution of pores with diameter in the range of 80–800 nm. Polycarboxylic resin fills up the mortar pores, decreasing its content two times.

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Effects of sulphur bacteria:

• increase the total pore content in the unmodified mortar (CNP) in which both porosity and pore distribution are comparable with those of material modified with acrylic resin (CMPA) and polysiloxane (CMPSi). The porosity of CMPA and CMPSi decreases compared to materials not exposed to corrosive agents, and pores of diameters between 10 and 80 nm predominate,

• do not affect the pore content and distribution in the mortar with polycarboxilic resin.

Effects of the solution of H_2SO_4 at concentration of 0.15 mmol/dm^3:

- causes no significant changes in porosity structure of CNP and CMPK,
- slightly increases the porosity in CMPSi and CMPA with predominating fraction of pores of diameters of 80–500 nm.

When comparing the effects of nitrogen bacteria and the solution of nitric acid on the materials under examination it is possible to state as follows:

- solution of HNO_3 causes the largest porosity changes in mortars with polyacrylic resin (CMPA).The pore content increases up to 0.8 cm^3/cm^3 (mortars not exposed to corrosive environment) and up to 0.25 cm^3/cm^3, while the pores of diameters in the range 50–100 nm. Other tested materials show no significant changes in porosity structure,
- action of nitrogen bacteria, like sulphur ones, decreases the total porosity in mortars under investigation, while the mortars modified with polysiloxanes underwent the largest changes.

In Fig. 5 the photographs of examined mortars not subjected to corrosive agents are present as a reference for analysing photographs of materials exposed to the corrosion process. The microstructure sealing of materials under investigation and exposed to bacterial activity is shown in Fig. 6. This results from accumulation of $CaCO_3$ in pores. Calcium carbonate comes from the reaction [27] of calcium and carbon dioxide accumulated in a biofilm [4]. The corrosion products are presented in Fig. 7 and 8.

Fig. 5. Mortar a) CNP, b) CMPK – reference samples
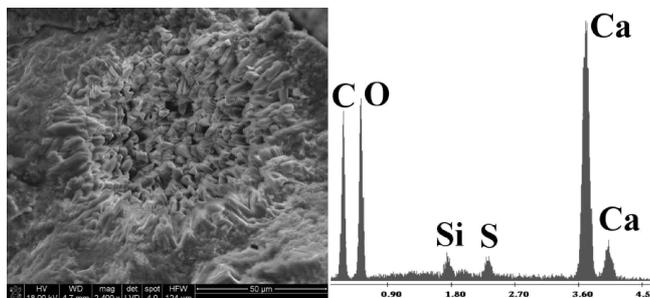
Fig. 6. Unsealing CMPSi microstructure by the action of nitrifying bacteria. EDS analysis shows the presence of $CaCO_3$

Fig. 7. Corrosion products formed in the mortar CMPA by the action of sulfur bacteria. EDS analysis in pt.1 shows the presence of ettringite

Fig. 8. The product of corrosion in mortar CMPA formed by the action of sulfuric acid. EDS analysis in pt.1 shows the presence of ettringite

5. Concluding remarks

It follows from the test carried out that:

1. Bacteria increase the moisture content in tested materials, exceeding the initial absorbability. This is connected with the formation of a highly hydrophilic biofilm on its surface. Bacteria *Acidithiobacillus thiooxidans* to much more extent increase the moisture content compared to bacteria *Thiobacillus denitrificans, Paracoccus denitrificans*.
2. Bacteria *Acidithiobacillus thiooxidans* decrease, while *Thiobacillus denitrificans, Paracoccus denitrificans* increase the mortar absorbability. The absorbability lowering is connected with ettringite accumulation in pores. Sulphur bacteria cause increasing porosity in cement materials.
3. Exposure of mortars to sulphuric and nitric acids causes an increase of both moisture content and absorbability in tested materials.
4. Solutions at concentrations typical for metabolism of sulphur or nitrogen bacteria show a significantly fainter impact on cement and cement-polymer composites compared to bacteria. This is confirmed by the presented microstructure examination.
5. Microorganisms cause two opposing processes. On the one hand, this is related to increased porosity due to washing up soluble corrosion products, on the other hand, the crystallization of sulphide corrosion products (ettringite) and calcium carbonate from the reaction of calcium and carbon dioxide accumulated in a biofilm.

6. An effect of polymer type on the mortar leak tightness evaluated on the basis on moisture content, absorbability and porosity is differentiated. Significant changes that appear after 6 month of exposure apply to unmodified materials and those containing acrylic and siloxane resins. The cement mortars modified with polycarboxylic resin do show practically no leak tightness changes both in biological and chemical environments.

7. Further research should include the cause of increased absorbability with simultaneous porosity decrease. The existence of a biofilm seems to be insufficient to explain it.

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