JUSTYNA ZAPAŁA

Kielce University of Technology
al. Tysiąclecia Państwa Polskiego 7
25-314 Kielce, Poland
e-mail: j.zapala@tu.kielce.pl

NEGATIVE ASPECTS OF THE IMPACT OF BACTERIA ON CONCRETE

Abstract

This paper presents the most frequently occurring cases of cement paste corrosion caused by living organisms. Concrete is exposed to the effects of corrosive factors. One of the factors which cause corrosion are living organisms. The key role is played by bacteria, algae, fungi, lichen. The role of microorganisms is essential in the destructive processes. The enzymes and metabolites secreted by microorganisms contribute to the destruction of the material by dissolution, hydrolysis, crystallization of the products of corrosion. Also, the settlement of microorganisms on the surface of a material, the biofilm effect, may lead to the processes of destruction.

Keywords: alga, bacteria, biodegradation, biofilm, cement paste,enzymes, fungi, lichen, microorganisms, metabolites, hydrolisis, crystallization

1. Introduction

Destruction of the cement matrix is caused by the corrosive action of an environment. Deterioration of concrete due to corrosion causes the disturbance of material continuity. As a consequence, it leads to the worsening of its utility properties. The physical and chemical processes leading to the destruction of concrete are synergic one. So, the corrosive factors affecting the material are not separated. On the contrary, they mutually enhance their effect.

The maintenance of proper strength, esthetic parameters and economic reasons are the one, which should be considered. As the stronger concrete implies the smaller number of defects, less frequent repairs, and longer lifetime of a building. Therefore the investigations of the corrosive processes are important one.

2. Biological corrosion

The factors causing corrosion of concrete paste should include biological factors. Numerous physical and chemical transformations occurring in concrete and cement paste are the effect of metabolic activities of microorganisms.

The processes of material destruction stimulated by the activity of living organisms are defined as biological corrosion or biodegradation [1]. Mechanisms of effects are complex and the destructive processes occur on many stages.

According to standard PN-EN 201-1 biological corrosion is classified as a special case of chemical corrosion [2]. This standard in the exposition class – threat of chemical corrosion XA – distinguishes three levels of aggressiveness of environmental influence.

With regard to biological corrosion, the material deterioration is usually caused by the enzymes and metabolites. They are secreted by microorganisms, which dissolve substrate compounds and react with them. In consequence, they are creating the expanding products, hydrolyzing salts, soluble complex salts and water-absorbing gels. Thus, corrosive processes includes external factors (i.e. microorganisms, water, surface pollutants, dusts, compounds from sewage) and internal materials (i.e. substrate components).

Among chemical compounds which are the products of bacterial metabolism, the most aggressive include, mineral acids: sulphur acid (VI) and nitric acids [3]. The disproportionate role which the biofilm plays in initiation and development of biological corrosion is mentioned by some investigators [4, 5].

2.1. Biofilm as the initiator of biological corrosion

Biofilm is a complex hydrogel structure. It is created as a result of adsorption on the material surface of some species of bacteria and primeval organisms. They bind with the surface by means of mucus secreted by microorganisms. Mucus constitutes a matrix in which cells of microorganisms settle. It retains humidity and absorbs the products of transformations of substances present in the environment. Also those, which result from the metabolic processes of microorganisms [6].

Figure 1 shows a microscope image of biofilm on the surface of more than 60-year old concrete found in fort underground housing in Lower Silesia.

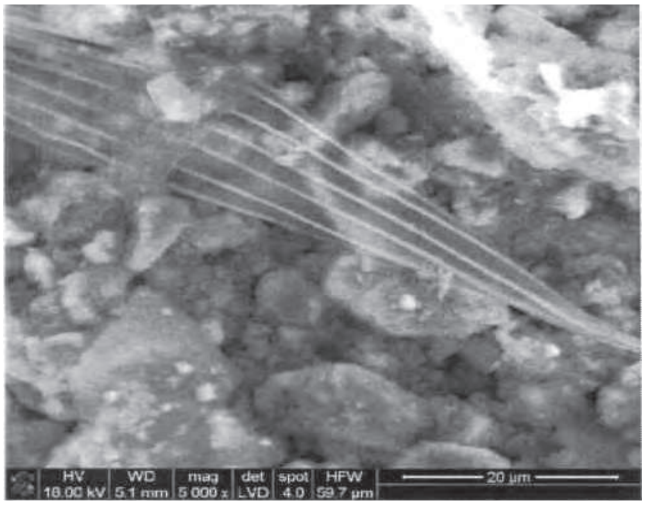

Fig. l. Concrete surface with a visible element of biofilm (SEM)

The colonization of a material and formation of a biologically active layer are initiated by so-called pioneer-phototrophic species. They facilitate colonization by forming good conditions for chemolitoautotrophic organisms (i.e. those which are the right force that causes corrosion). The settlement of pioneer species on the substrate built of cement paste is possible after a pH partial neutralization from about 12 to about 8.5. That results from carbonatization. The surface material which is porous and abundant in pore openings filled with capillary water also facilitates colonization by bacteria. Creation of a biological film makes it possible to expand the range of microorganisms by other species of bacteria, fungi, alga, unicellular organisms. They can react with the hardened cement paste, which originally could not have survived in such a strong alkaline environment (such conditions do not correspond to their range of tolerance). A biological film, rich in organic and mineral compounds, constitutes a ecosystem.

Figure 2 shows the present bacteria cells in the earlier sample of concrete.

Mucus which penetrates the capillary pores of the material causes mechanical stresses in the structure. This results in an increase of the size of pores, facilitates water transport and penetration of heat. The hardened cement paste also deteriorates. It is due to diffusion from the inside of chemical substances necessary in the metabolic processes of organisms. Microorganisms that develop on the material surface begin to absorb some elements e.g. calcium, silicon, magnesium. This phenomenon causes additional pores and cracks in the material [7].

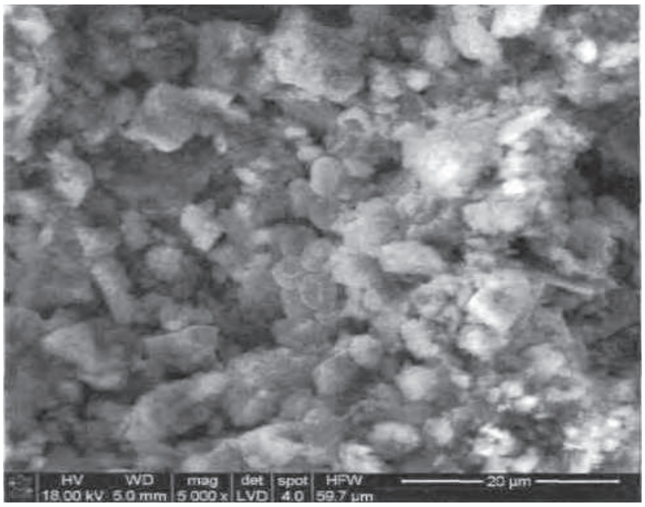

Fig. 2. Surface of concrete with visible bacteria cells (SEM)

The increase in chemical corrosion of the material caused by the colonization of microorganisms often leads to formation expansive or hydrolyzing salt complex, soluble salt, the water absorbent gel. That may manifest itself by the loss of cohesion and exfoliation of the material.

2.2. Biogeochemical deterioration of concrete caused by bacteria

The matrix of cement binder is destroyed due to biological corrosion. It's caused by organic acids and acid metabolites secreted by microorganisms, such as, inter alia, nitric and sulphuric acids.

Structures especially susceptible to the activity of biological factors include elements of settling tanks, collectors, pipelines, supports, and sewage facilities. Corrosive processes are intensified just above the surface of a liquid. Although aggressiveness of sewage-polluted waters is small (exposition class XA1), they may lead to material structure changes, in case they contain large amounts of organic substances. Tiobacteria, nitrifying bacteria and ureolytic bacteria play an important role here.

2.2.1. Deterioration of cement binder caused by the activity of biogenic sulphuric acid

An important role in the process of deterioration of materials on the cement binder is played by chemolithotrophic aerobic bacteria of Thiobacillus type and chemoorganotrophic anaerobic bacteria of Desulfovibrio type.

Anaerobic heterotrophic bacteria of Desulfovibrio type reduce sulphates to hydrogen sulphide. Hydrogen sulphide comes also from reactions of anaerobie decomposition of organic compounds containing sulphur i.e. proteins. Anaerobics decompose proteins into the thiosulphate ion. It is subsequently oxidated into sulphates and sulphuric acid, mercaptans and other volatile sulphur compounds. PH of the material decreases due to diffusion of hydrogen sulphide deep into the material. Neutrofilic bacteria settle on the surface of the hardened cement paste. Access to oxygen and humidity makes microorganisms oxidate sulphur compounds into elemental sulphur, polythionic acids, which causes further decrease of pH to neutral and acidic conditions. Then acidofilic bacteria Thiobacilli, inter alia: T.intermedium, T.neapolitanus, oxidating sulphur, settle on the surface and oxidate hydrogen sulphide into sulphuric acid, maintaining oxidation until pH below 5 is achieved. With pH below 5 T.thiooxidans increase and produce large amounts of sulphuric acid. If these bacteria have a sufficient number of components from which, due to transformations, energy is derived, they can lower pH of the material even to 0. Therefore, T.thiooxidans are regarded as key organisms, markers for biological corrosion caused by sulphuric acid [8].

Diffusing sulphate ions attack calcium hydroxide. Calcium hydroxide is the component of the cement paste, forming gypsum, an important product for the progressing sulphate corrosion.

$$Ca(OH)_2 + SO_4^{2-} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + 2OH \quad (1)$$

Gypsum crystals formed as a result of the reaction are expansive products. They disintegrate the structure due to their immense capacity (130% of the initial capacity of the solid substrate). Even greater stresses, cracks in the hardened cement paste, scratches, are formed in the second phase of the corrosive process. Gypsum reacts with nonhydrated tricalcium aluminate forming Candlota salt (ettringite). It crystallizes with an increase in capacity up to 227% of initial capacity of solid substrate [9].

$$3CaO \cdot Al_2O_3 + 3(CaSO_4 \cdot 2H_2O) + 26H_2O \rightarrow \rightarrow 3\,CaOAl_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \quad (2)$$

In the second phase of the reaction, gypsum can react with monosulphate also forming an expansive product

$$Ca4Al_{2(}OH)_{12} \cdot SO_4 \cdot 6H_2O + 3(CaSO_4 \cdot 2H_2O) + + 26H_2O \rightarrow 3CaOAl_2O_3 \cdot 3CaSO_4 - 32H_2O \quad (3)$$

The formed ettringite causes deterioration only of the hardened cement paste which does not show a large ability of the accumulation of strains. The formed microcracks lead to the weakening of a concrete structure.

2.2.2. Deterioration of the cement paste caused by the activity of biogenic nitric acid

Corrosion of concrete materials is also caused by the action of nitric acid. Nitrifying bacteria can be an agent producing nitric acids.

Both in anaerobic and aerobic conditions, nitrogen compounds contained in sewage can undergo ammonification i.e. change of organic nitrogen (inter alia from proteins) into ammonium. Then ammonium may be nitrified i.e. biologically oxidated into nitrates. This process occurs at two stages and only in the presence of oxygen. At the first stage bacteria of Nitrosomonas type: Nitrosococcus oceanus, Nitrosolbus multiformis, Nitrosomonas europaea oxidate the ammonium ion into nitrites and at the second stage bacteria of Nitrobacter type oxidate nitites into nitrates [10].

$$\begin{array}{l} NH_4^+ + 3/2O_2 \rightarrow NO_2^- + H_2O + 2H^+ \\ \underline{NO_2^- + 1/2O_2 \rightarrow NO_3^- + H_2O + 2H^+} \\ NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+ \end{array} \quad (4)$$

Nitrifying bacteria, sensitive to light, are carried into the deeper parts of the material by capillary water. They derive energy from the decomposition of inorganic substances. Their development is based on derivatives of industrial and anthropogenic ammonium settled on the particles of dusts. The gathering of pollutants and microorganisms is prevented by the application of plaster with cement that contains nanometric titanium dioxide. The solution consists in self-cleaning concrete formed by introducing nanometric titanium dioxide into cement. This reduces the level of harmful oxides that lead to corrosive processes at the further stage.

Nitrifying bacteria are also a component of soil flora, where they take part in initiating the cycle of nitrogen compounds. The formed nitric acids react with the calcium carbonate and other minerals. This leads to creation of nitrate which is better water-soluble than native chemical compounds contained in the cement paste minerals.

2.2.3. Deterioration of cement binder caused by actions of bacteria of other types

Anaerobic bacteria that bind nitrogen has an ability to form the oleic acid from fat compounds e.g. in municipal collectors. This acid causes destruction of the hardened cement paste as a result of the formation of calcium oleate, and subsequently as a result of decomposition of calcium hydroxide. In the reaction of the oleic acid with the calcium hydroxide, calcium soap, well-soluble in liquids, is formed. Then the calcium hydroxide is washed out of the cement paste. Leaching corrosion is dangerous especially in case of fresh cement paste. The reason for this is that the calcium hydroxide first released from a supersaturated solution in more reactive colloidal form [11].

$$C_{17}H_{33}COOH + Ca(OH)_2 \rightarrow \rightarrow (C_{17}H_{33}COO)_2Ca + 2H_2O \quad (5)$$

Intensive washing out of the binder occurs mainly in the zones of fluctuating levels of wastewater in biological settling tanks.

Among bacteria causing biological corrosion, ureolytic bacteria should be mentioned. They act on urea contained in wastewater and hydrolize it. At the same time they release ammonium and carbonic acid.

$$CO(NH_2)_2 + H_2O + BACTERIA \rightarrow \rightarrow NH_4OH + CO_2 \rightarrow NH_3 + H_2CO_3 \quad (6)$$

$$NH_4OH + Ca(OH)_2 + CaSO_4 + H_2O \rightarrow \rightarrow CaSO_4(NH_4)_2SO_4\text{-}32H_2O \quad (7)$$

In the presence of calcium hydroxide, ammonium, by interacting with sulphates forms well-soluble salt.

3. Conclusions

- Life processes of microorganisms may contribute to quickened biological corrosion of cement paste and concrete.
- Numerous physical and chemical transformations occurring in the material are a result of the metabolic activity of microorganisms such as for example bacteria. Due to acid and leaching corrosion the material is destroyed.
- The effect is the formation of expansive products of the reaction such as gypsum, ettringite or the processes of washing out of calcium hydroxide, the formation of products better soluble than native compounds of the cement paste.
- The application of coatings based on titanium dioxide prevents an increase in microorganisms on the surface of the material

References

[1] Warscheid Th., Brahms J.: *Biodeterioration of stone: a review*, International Biodeterioration and Biodegradation 46(2000), p. 351.
[2] Czarnecki L.: *Beton według normy PN-EN 206-1 -komentarz*, Polski Cement 2004, s. 242
[3] Sand W.: *Microbial mechanisms of deterioration of inorganic substrates – a general mechanistic overview*, International Biodeterioration and Biodegradation 40 (1997), pp. 183-184.
[4] Javaherdashti R., Nieraz H., Borowitzka M., Moheimani N., Oliwia M.,: *On the impact of alga on accelerating the biodeterioration/biocorrosion of reinforced concrete: a mechanistic review*, Europan Journal of Scientific Research 36 (2009), p. 398.
[5] Brown E., Moore S.: *Microbiological characterization of biofilms on concrete structures*, Alaska Cooperative and Public Facilities Research Program 1992, pp. 1-3.
[6] Sałek A.: *Biofilm, mechanizm powstawania, struktura i zagrożenia*, International Bioconsulting, Germany 2008.
[7] Javaherdashti R., Nieraz H., Borowitzka M., Moheimani N., Oliwia M.: *On the impact of alga on accelerating the biodeterioration/biocorrosion of reinforced concrete: a mechanistic review*, Europan Journal of Scientific Research 36 (2009), p. 398.
[8] Diercks M., Sand W., Bock E.: *Microbial corrosion of concrete*, Experientia 47 (1991), pp. 514-516.
[9] Madryas C., Wysocki L.: *Doświadczenia ze stosowania betonu w obiektach gospodarki wodno – ściekowej*, Sympozjum naukowo-techniczne „Cement – właściwości i zastosowanie" 2005, s. 86.
[10] Kim S., Miyahara M.: *Nitrous oxide – emission from nitrifying activated sludge dependent on denitrification by ammonia oxidizing bacteria*, Bioresource Technology 2010, pp. 3958-3963.
[11] Karyś J.: *Biologiczne i chemiczne skutki powodzi w obiektach budowlanych*, Ochrona przed korozją 1 (2006), s. 33.

Justyna Zapała

Negatywne aspekty oddziaływania bakterii na beton

1. Wprowadzenie

Beton, podobnie jak większość materiałów budowlanych narażony jest na działanie czynników korozyjnych. Kluczową rolę odgrywa świat organizmów żywych tj. bakterie, glony, grzyby, porosty. Rola mikroorganizmów, często zaniedbywana przez projektantów betonu jest istotna w zachodzących procesach destrukcyjnych. Wydzielane przez mikroorganizmy enzymy i produkty metabolizmu przyczyniają się do destrukcji materiału. Również samo osadzanie się mikroorganizmów na powierzchni materiału, efekt biofilmu może prowadzić do procesów niszczenia. W pracy przedstawione zostały najczęściej występujące przypadki korozji zaczynu cementowego wywołane działaniem organizmów żywych.

2. Korozja biologiczna

Liczne przemiany fizykochemiczne zachodzące w betonie i zaczynie cementowym są skutkiem aktywności metabolicznej mikroorganizmów. Procesy niszczenia materiałów stymulowane aktywnością organizmów żywych określane są mianem korozji biologicznej, biodeterioracji. Rozpatrując korozję biologiczną, zazwyczaj deterioracja materiału wywołana jest wydzielaniem przez mikroorganizmy enzymów i produktów metabolizmu, które rozpuszczają związki podłoża i reagując z nimi tworzą ekspandujące produkty, hydrolizujące sole, rozpuszczalne sole kompleksowe, żele chłonące wodę. W procesach korozyjnych biorą więc udział czynniki zewnętrzne tj. mikroorganizmy, woda, zanieczyszczenia powierzchni, pyły, związki pochodzące ze ścieków i materiały wewnętrzne czyli składniki podłoża. Utworzenie błony biologicznej umożliwia poszerzenie gamy mikroorganizmów o inne gatunki bakterii, grzyby, glony, jednokomórkowce, które mogą oddziaływać ze stwardniałym zaczynem cementowym, a które pierwotnie nie mogłyby przeżyć w tak silnie zasadowym środowisku.

Matryca spoiwa cementowego ulega zniszczeniu w wyniku korozji biologicznej na skutek wydzielanych przez mikroorganizmy kwaśnych metabolitów, między innymi kwasów azotowego i siarkowego, a także za przyczyną kwasów organicznych. Znaczącą rolę odgrywają tutaj tiobakterie, bakterie nitryfikujące oraz urolityczne.

3. Degradacja spoiwa cementowego wywołana działaniem biogennego kwasu siarkowego

Ważną rolę w procesie degradacji materiałów na spoiwie cementowym odgrywają chemolitotroficzne bakterie aerobowe(tlenowe) rodzaju Thiobacillus oraz anaerobowe(beztlenowe) chemoorganotroficzne bakterie rodzaju Desulfovibrio.

Beztlenowe bakterie heterotroficzne rodzaju Desulfovibrio redukują siarczany do siarkowodoru czego skutkiem jest spadek pH. Na powierzchni stwardniałego zaczynu cementowego osadzają się bakterie neutrofilowe. Dostęp tlenu i wilgoć powoduje, że mikroorganizmy utleniają związki siarki do siarki elementarnej, kwasów politionowych co powoduje dalszy spadek pH do warunków obojętnych i kwasowych. Następnie bakterie acydofilowie osadzają się na powierzchni i przeprowadzają proces utleniania siarkowodoru do kwasu siarkowego. PH materiału spada do wartości 5 przy czym T.thiooxidans mogą obniżyć pH materiału nawet do wartości 0. Dlatego też T.thiooxidans są uważane za kluczowe organizmy, markery dla korozji biologicznej wywołanej kwasem siarkowym.

W wyniku reakcji jonów siarczanowych z wodorotlenkiem wapnia powstaje gips, produkt ekspansywny dezintegrujący strukturę. W drugiej fazie procesu korozyjnego, w wyniku reakcji gipsu z niehydratyzowanym glinianem trójwapniowym utworzony zostaje ettringit, który krystalizuje ze zwiększeniem objętości sięgającym 227% objętości początkowej substratu stałego.

4. Degradacja spoiwa cementowego wywołana działaniem biogennego kwasu azotowego

Korozję materiałów betonowych wywołuje również działanie na nie kwasu azotowego. Czynnikiem produkującym kwasy azotowe mogą być bakterie nitryfikujące. Proces przebiega dwuetapowo i tylko w obecności tlenu. W pierwszym etapie bakterie z rodzaju Nitrosomonas: Nitrosococcus oceanus, Nitrosolbus multiformis, Nitrosomonas europaea utleniają jon amoniowy do azotynów by w kolejnym etapie bakterie z rodzaju Nitrobacter utleniły azotyny do azotanów. Bakterie nitryfikujące rozwijają się w oparciu o pochodne amoniaku pochodzenia przemysłowego i o charakterze antropogenicznym, osadzone na cząstkach pyłów.

Gromadzeniu się zanieczyszczeń i mikroorganizmów zapobiega zastosowanie tynku z cementem zawierającym nanometryczny dwutlenek tytanu.

Powstałe kwasy azotowe reagują z węglanem wapnia i innymi minerałami co prowadzi do powstania azotanów lepiej rozpuszczalnych w wodzie od rodzimych związków chemicznych zawartych w minerałach zaczynu.

5. Podsumowanie

Procesy życiowe mikroorganizmów mogą przyczyniać się do przyspieszania korozji biologicznej zaczynu cementowego i betonu. Liczne przemiany fizykochemiczne zachodzące w materiale są skutkiem aktywności metabolicznej mikroorganizmów takich jak np. bakterie. W wyniku korozji kwasowej i ługującej następuje niszczenie materiału. Skutkiem jest powstawanie ekspansywnych produktów reakcji takich jak gips, ettringit czy też procesy wymywania wodorotlenku wapnia, powstawanie produktów lepiej rozpuszczalnych od związków rodzimych zaczynu cementowego. Należy więc ograniczać osadzanie się mikroorganizmów na powierzchniach betonowych. Zastosowanie powłok na bazie dwutlenku tytanu zapobiega wzrostowi mikroorganizmów na powierzchni materiału.