

ANALYSIS OF CONCRETE CORROSION OF MANHOLE LOCATED NEAR SOURCE OF ODOROUS EMISSION

Bożena GIL ^a, Barbara SŁOMKA-SŁUPIK ^{b*}, Katarzyna KOWALSKA ^c, Karol JASIŃSKI ^d

^a PhD; Faculty of Environmental Engineering and Energy, Silesian University of Technology, Konarskiego 18, 44-100 Gliwice, Poland

^b PhD; Faculty of Civil Engineering, Silesian University of Technology, Akademicka 5, 44-100 Gliwice, Poland

*E-mail address: *Barbara.Slomka-Slupik@polsl.pl*

^c PhD; Faculty of Environmental Engineering and Energy, Silesian University of Technology, Konarskiego 18, 44-100 Gliwice, Poland

^d MSc; Faculty of Environmental Engineering and Energy, Silesian University of Technology, Konarskiego 18, 44-100 Gliwice, Poland

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Abstract

The problem of corrosion of sanitary sewer concrete concerns the elements located just behind the expansion well. Evolving odorogenic substances and bioaerosols spread in the sewage system, cause in adverse conditions both chemical and biological corrosion of concrete. The paper presents the results of tests of samples taken from the top concrete circle and from a corroded cast iron hatch of 7 years old manhole located below the expansion well. Well elements were subjected to a strong interaction of hydrogen sulphide, which average concentration in the sewage air, during an exemplary 84 hours was 29 ppm. Concrete was gelatinous fine with noticeable outer pellicular layer of 1 mm thick and the inner layer containing aggregates (grain < 1 cm). Sulfur oxidizing, sulfates reducing, Fe²⁺ oxidizing bacteria, aerobic heterotrophs, anaerobic heterotrophs, nitrifiers and denitrifiers were determined. In the concrete sample, no sulfate-reducing bacteria were detected under the film-like layer and in the cast-iron manhole material, while the hatch also did not contain anaerobic heterotrophs, nitrifying and denitrifying bacteria. The sulphate content in the concrete samples tested was very high, about 20% in the mass of concrete and 50% in the weight of the binder soluble in HCl. Microscopic investigations showed that the outer layer of the concrete was very rich in gypsum, and the pH of the aqueous extract was in the range of 7–8.

Keywords: Concrete; Cast iron; Sewage wells; Biodeterioration; Corrosion; Gypsum.

1. INTRODUCTION

At the design stage of the sewerage network, it is assumed that the average period of its use should be about fifty years [1]. In addition to many factors affecting the sureness of its functioning, the impact of wastewater and sewage air components is important [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11]. Currently, the problem of corrosion of concrete concerns small fragments of the sanitary sewerage network, mainly with a diameter ranging

from 200 mm to 350 mm, located below the expansion well, to which sewage from sewage pumping stations is supplied [12]. The sewage retention time in the pumping station, is often so extended that, as a result there are already significant physical, chemical and biochemical transformations with oxygen depletion. In addition, in the expansion well there is a rapid change in hydraulic conditions, associated with vigorous evolution of odors (olfactory system stimulants [13]) to sewerage air. The main cause of the occurrence of odors in the

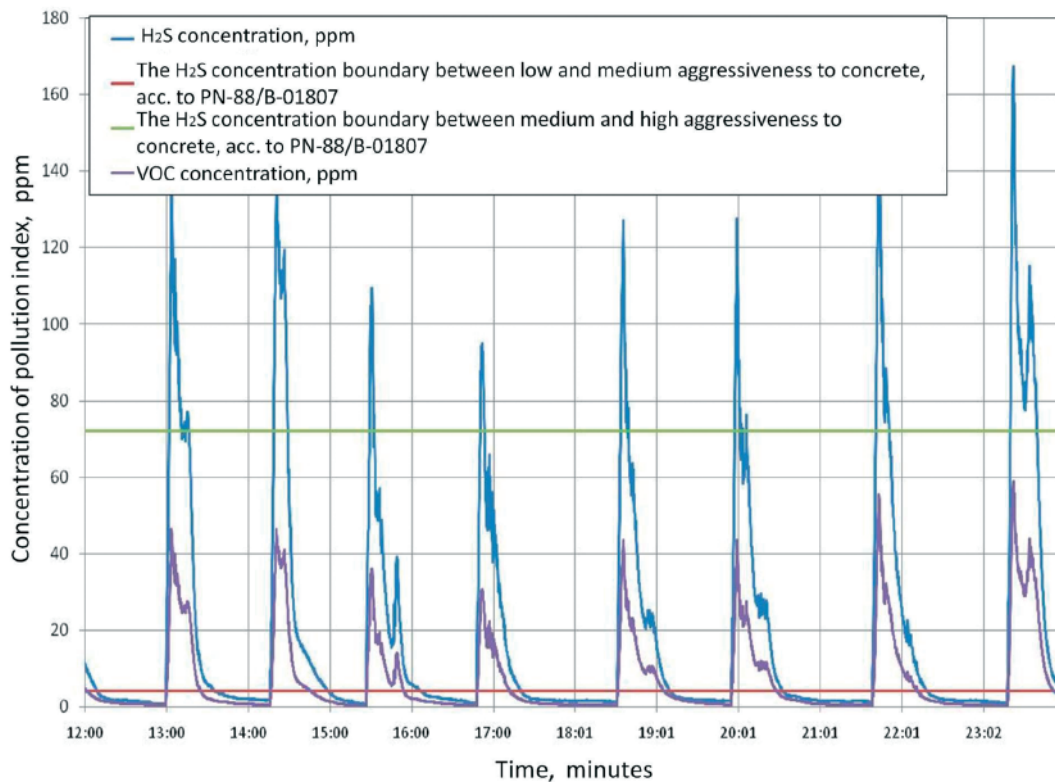


Figure 1.

Example of a change in the concentration of hydrogen sulphide and volatile organic compounds (VOC) in an expansion well, average retention time of sewage about 2 hours, pumping station for household sewage, measurements made with a multi-gas meter MX6 iBrid, measurement accuracy $\pm 0.1\text{ppm}$, enabling data registration [16]

sewer recognizes hydrogen sulphide [14, 15], and an exemplary distribution of its concentration over time in an expansion well is shown in Fig. 1.

Hydrogen sulfide escaping into the sewage air in the expansion well spreads through sewerage pipes, usually with the direction of sewage flow [17]. Therefore, the risk of corrosion of the concrete applies not only to the expansion well, but also to several subsequent wells [4]. In this work, the analysis of the technical condition of the sewage well located 67 m just behind the expansion well was carried out, where problems with odors were observed. Focused mainly on sulphate corrosion. The aim of the article is to present the results of tests of samples taken from the corroded upper elements of “S50” sewage well – the concrete taken from the internal layers of the last circle called narrowing circle and samples from cast iron hatch. The drawing of concrete well elements is shown in Figure 2.

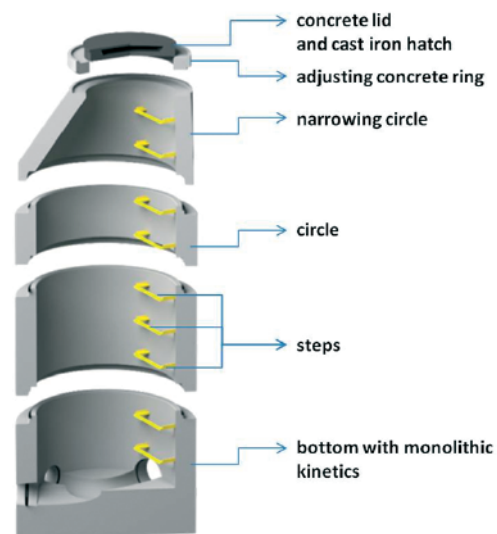


Figure 2.
Elements of concrete well (manhole)

The work concerns sewage systems in the area of medium density of buildings, typical urban areas without participation of industrial sector. This paper is a part of works on biodeterioration of sewage wells caused by the influence of the internal environment in gravity sewerage.

The occurrence of sulphate corrosion significantly reduces the durability and load-bearing capacity of concrete elements. As a consequence, there are breakdowns that threaten the collapse of the terrain [2, 3]. Research conducted by Boehm et al. [17] showed that in the case of hydrogen sulphide concentration in the sewerage system of about 5 ppm, the corrosion rate of concrete can range from 0.12 to 10.8 mm/year, which leads to damage to the top layer of concrete circle in sewer manholes from 0.8 mm to 76 mm in 7 years, while the average thickness of a concrete circle is about 150 mm.

The sulfate corrosion of concrete, from the macroscopic point of view, can have many forms. The effect of sulphate corrosion in concrete is visible as [18]:

- gradual loss of binding properties, uncovering of aggregate grains, formation of gypsum
- swelling and cracking, the formation of colloidal ettringite
- flaking and chipping of surface layers, which is accompanied by swelling or loss of strength of concretes exposed to mixed environments.

Most often, this type of concrete corrosion is tested by using aggressive solutions which are made from pure chemical reagents. Biological solutions are rarely used.

In the sewage system, in reality, there is corrosion caused mainly by the action of biogenic forms of the sulphate residue. The most commonly mentioned is biogenic sulfuric acid. However, the presence of other cations in the sewage environment is also important, and their aggressiveness towards concrete falls in a series $\text{NH}_4^+ > \text{Mg}^{2+} > \text{Na}^+ > \text{Ca}^{2+}$ [6, 19]. In addition, it should be emphasized that the rate of sulphate corrosion depends on the temperature, so that it occurs at 5°C the fastest and decreases gradually with its increase [6].

Microorganisms play an inseparable role in the destruction of concrete in sewage infrastructure [8, 9, 10, 11]. Corrosion caused by the action of bacteria was noticed in various forms in prefabricated sewage wells. It is estimated that about 20% of the destruction of concrete sewage constructions is caused by the activity of microorganisms [2].

2. THE FACTORS INCREASING THE LIKELIHOOD OF CONCRETE CORROSION OF SEWAGE WELLS

The corrosion of sewage wells is synergistically influenced by chemical, biochemical and biological processes that occur simultaneously with mechanical and physical influences [9]. The degree of aggressiveness of the sewage system in relation to concrete elements is considered according to the non-valid PN-88/B-01807 standard [20], both because of the quality of wastewater and sewage air. The indicated norm, in contrast to newer ones, is more accessible and gives corrosionists a broader view of the environment.

In the case of sewage discharged into the sanitary sewage system, the sulphate concentration is analyzed to determine the degree of aggressiveness towards the concrete. According to the literature, the average concentration of sulphates in domestic wastewater is from 15 to 30 mg/dm³ [19]. Thus according to the concrete standard PN-88/B-01807 [20], domestic sewage is a poorly aggressive environment, and considering the flow, this aggressiveness is at most medium. However, in the sewage air, hydrogen sulfide H₂S is present whose concentration can be very diverse [4]. It depends, among others, on the emission of odorous compounds in the expansion well, ventilation conditions of the gravity canalization and hydraulic conditions prevailing in the network. Exemplary studies [4] show that the concentration of hydrogen sulfide, for a total period of about seven hours (the analysis covered 12 hours) did not exceed 5 ppm, which poses the risk of a poorly aggressive environment to concrete [20]. On the other hand, for a total of about 4 hours, the hydrogen sulfide concentration ranged from 4 ppm to 72 ppm, which in turn corresponds to an environment that is moderately aggressive towards concrete [20]. The H₂S concentration above 72 ppm for about 1 hour corresponds to strongly aggressive environment to concrete [20]. Figure 3 presents frequencies and sums of the frequency of occurrence of hydrogen sulphide concentrations in the expansion well, determined based on the data presented in Fig. 1.

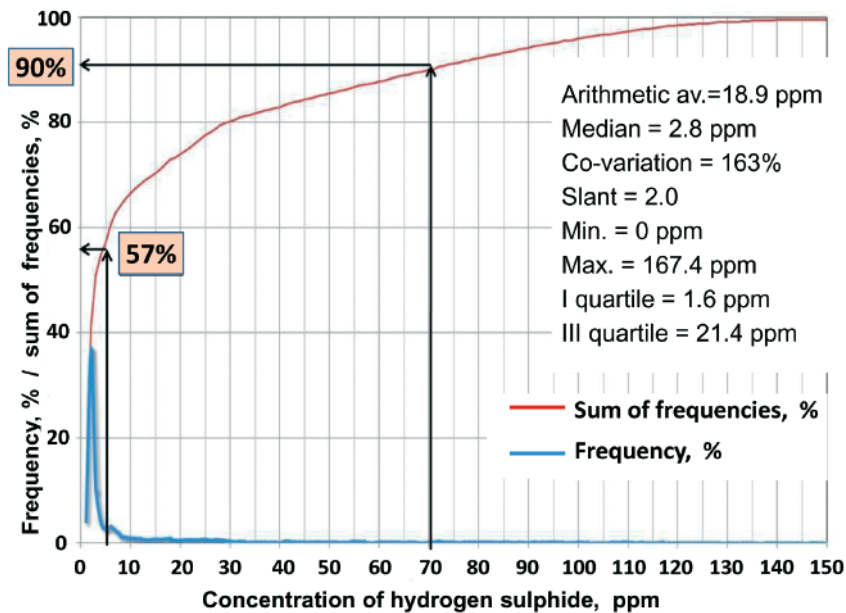


Figure 3.

An example of the frequency and sum of the frequency of occurrence of hydrogen sulphide (H₂S) concentration in the expansion well, determined based on the data presented in Fig. 1

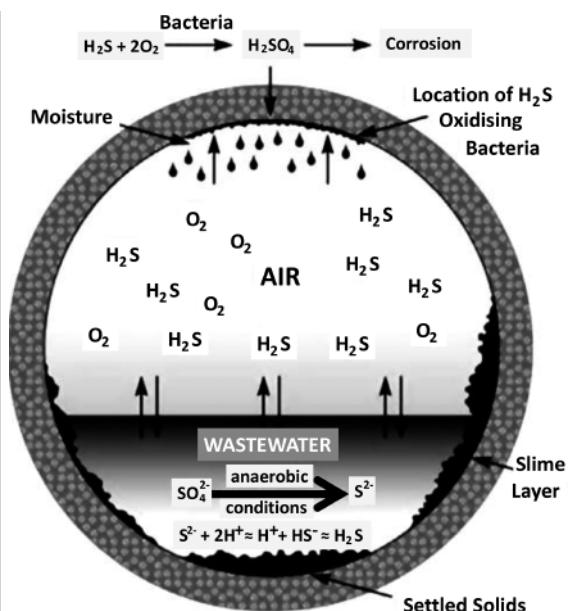


Figure 4.

Diagram of corrosive interactions and transformations of sulfur compounds, source: [21]

Released hydrogen sulphide in sewage may occur in the sewage system, both in gaseous form and in dissolved form – Fig. 4. The state of equilibrium which is established between these forms depends on the

reaction of the environment, the ionic strength of the aqueous solution, the type of metals present in the sewage (having the ability to form sparingly soluble salts), but also on physical conditions, i.e. on pressure and temperature. For example, the amount of hydrogen sulphide separated in a gaseous form depends on the pH of the environment [15]. The higher pH of sewage, the dissolved form of hydrogen sulphide in the sewage dominates. At the pH below 6, the hydrogen sulfide in a gas form dominates, in the pH range from 6.0 to 8.5 H₂S and HS⁻ appears. The state of equilibrium between the dissolved and gaseous form occurs at a pH of approximately 7.3 [15].

Hydrogen sulfide released into the sewerage air can be oxidized in contact with moist sewage air to sulfuric acid – Fig. 4 [17, 21]. The intensity of this process decreases with the increase of temperature (because both the adsorption of gases on the concrete surface as well as the dissolution of hydrogen sulfide in water decreases with the increase of temperature [22]). H₂S may come from sulphates found in flowing sewage but it may also come from dissimilatory sulfate reduction under anaerobic conditions as a result of the activity of *Desulfovibrio* and from other bacteria and sulfur-reducing fungi. Hydrogen sulphide, next to ammonia and carbon dioxide, also comes from the decomposition of organic com-

pounds in anaerobic biochemical transformations [8, 9, 10, 11, 15].

Corrosion of concrete is a complex process [23], it has a dynamic character and a specific development cycle and, in the initial period of its impact, mainly favors pH lowering of the concrete. In the first stage of corrosion of concrete, hydrogen sulphide can react directly with calcium components of concrete, in particular with $\text{Ca}(\text{OH})_2$ creating calcium bisulfite [2, 3]. In the next stage of corrosion resulting from the interaction of sulfuric acid, ettringite $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$ is formed, and then gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, because of lowering pH [24, 25]. In several cases, a fine plastic, mushy mass was also observed, which was associated with a drop in adhesion and strength of the concrete [3, 18]. It can therefore be assumed that one more dangerous sulphate is produced in the corroded concrete of sewage systems, which is formed either by itself or from a solid solution with ettringite, when the pH drops and then the gypsum begins to form. Thaumasite $\text{CaSiO}_3 \cdot \text{CaCO}_3 \cdot \text{CaSO}_4 \cdot 15\text{H}_2\text{O}$ having no-binding properties, totally disintegrates hardened cement matrix, and its presence in the discussed conditions of strong declacification is possible [10, 25, 26, 27].

Chemical corrosion of concrete in the sewage system is associated with the corrosion products with increased volume and the formation of low strength compounds. Gradual loss of binding properties of concrete, uncovering of aggregate grains, formation of gypsum, swelling and cracking of concrete, flaking and chipping of surface layers reduce the durability of sewage wells [9, 28]. The factors that support the

corrosion process are the presence of other cations in the sewage environment, the most dangerous are NH_4^+ and Mg^{2+} [23, 25, 26]. Ammonia is released as a result of anaerobic biochemical changes, which intensifies the process of concrete corrosion. The most exposed to sulfuric acid is the part of concrete occurring at the cope of a sewage well (Fig. 5a) or above the wastewater table in concrete canals (Fig. 5b). In the concrete which has undergone sulphate corrosion, zonal changes are macroscopically observable (Fig. 5a).

In the sewage system, thanks to the high humidity and content of nutrients in the sewerage air, there are favorable conditions necessary for the development of microorganisms with the ability to form biofilms on the inner walls of the sewer wells [29]. Biofilm formation protects microorganisms from adverse conditions of the external environment, it also allows sorption and providing microorganisms with nutrients [8, 29].

Biodeterioration. The mechanism of concrete damage respecting the activity of microorganisms is related to biophysical as well as biochemical deterioration of concrete. *Biophysical* deterioration of concrete includes the absorption of compounds contained in the air, the diffusion of vapor within the biological membrane and intensification of the migration of metabolites of biochemical transformations penetrating into the concrete through cracks. *Biochemical* deterioration of concrete, on the other hand, is described by processes that trigger metabolic products, e.g. sulfuric and carbonic acid, and organic acids, which cause a further stage of environmental modification. These new conditions favor the devel-

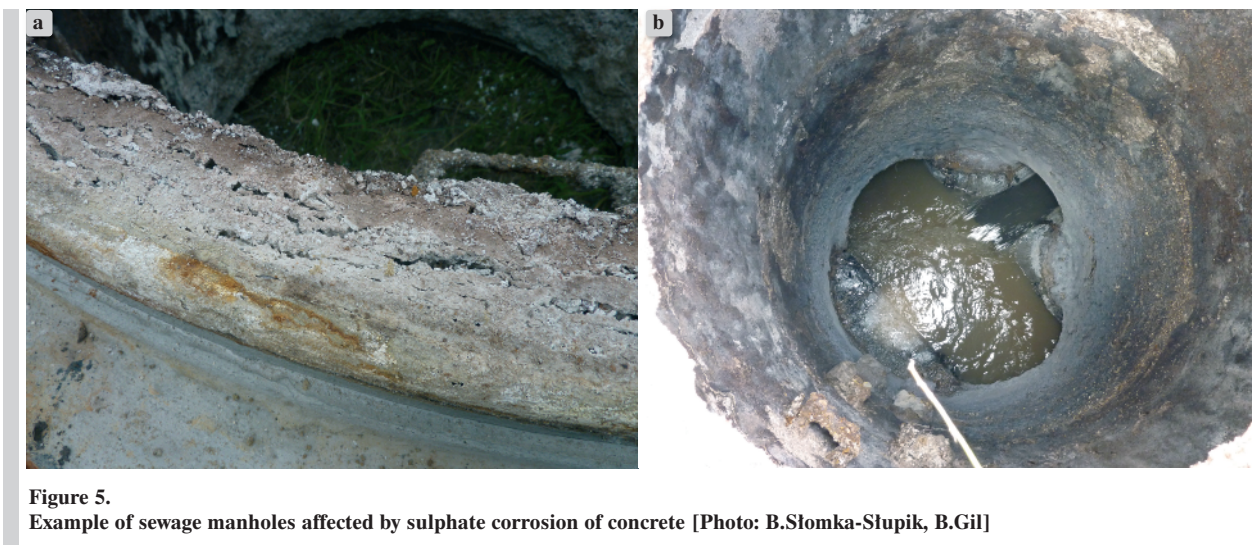


Figure 5.
Example of sewage manholes affected by sulphate corrosion of concrete [Photo: B.Słomka-Słupik, B.Gil]

opment of further groups of microorganisms and further stages of corrosion of concrete elements [30, 31]. The effects of metabolic activity of various microorganisms can lead to biophysical as well as biochemical damages of concrete. Colonization of the material and the formation of a biological membrane start the so-called pioneer species that create favorable conditions for the development of other groups of microorganisms. The metabolic activity of microorganisms initiates and can even accelerate, both mechanical and chemical, rate of concrete corrosion [2, 3, 9, 10, 11, 19, 28, 29, 30, 31, 32].

Damage to the upper layers of concrete sewage wells due to chemical corrosion, increasing porosity of the material, lowering pH below 9 creates a favorable conditions for the growth of bacteria [8]. Among them are *Delsulfovibrio* – sulphate reducing bacteria (anaerobic corrosion), which transform sulphates from sewage to H_2S . The separated hydrogen sulphide can react over the waste water table with oxygen, and the product of this reaction is sulfur – a substrate for many bacteria from the chemolithotrophic *Thiobacillus*, which metabolize it to sulfuric acid [2, 3, 9]. Furthermore H_2S can react with water vapor, forming sulfuric acid residues condensing on concrete walls above the water table. Such an acidified surface of concrete usually favors the development of acidophilic bacteria *Thiobacillus* functioning at pH: 2–3, mainly *Acidothiobacillus thiooxidans* also known as *Thiobacillus concretivorus* (concrete devourers). H_2S it can therefore be oxidized in multi-stage reactions in the aerobic environment to sulfuric acid by green and purple sulfur bacteria (close anaerobes) [2, 3, 8].

3. MATERIALS AND METHODS

The analysis of the technical condition of the S50 sewage well located at a distance of 67 m behind the expansion well was performed in the work. The S50 well was located in the odor zone emerging from the sewage network located in one of the agglomerations of Upper Silesia. To analyze the issue, a part of the sewerage network to which it is pumped was selected:

- a) municipal sewage from the catchment area of 3.5 ha by a single pipe Ø 315 mm length 1914 m, with an average wastewater retention time of approx. 6 hours;
- b) domestic sewage from the drainage area of 2.5 ha, characterized both by low buildings as well as multi-family housing, by a single pipe Ø 160 mm length of approx. 500 m, the average retention time of these wastewater was about 2.5 hour.

Analysis of the quality of sewage gas in S50 well was based on the measurement of hydrogen sulphide with a OdaLog meter with measurement accuracy ± 1 ppm. The measurement was carried out in the period of dry weather, which preceded the period of about 7 rainy days before measurements, and when the average daily ambient temperature was above 16°C.

After visual assessment of the technical condition of the S50 well, a detailed chemical and microbiological analysis of the samples taken from it was carried out. Concrete samples were taken from the inner part of the highest concrete circle, from a height of about 2.20 m above the sewage level. Visually, it was possible to separate a part of the non-cohesive surface in the form of a “film” having a thickness of 1–2 mm from material under it having thickness of about 2 cm. Both concrete zones were incoherent and crumbled. The film layer was above mushy and greasy. In this study “concrete” was a material composed of aggregate with corrosion products and biological membrane – from the inner side of the well.

Chemical tests included checking the pH of an aqueous concrete extract and the content of sulphate ions in concrete. The aqueous extract was made from 20 g of material and 100 ml of distilled water with a conductivity of 0.66 μS . After 1 day, mixing twice per each twelve hours, for 1 min.; the pH of the filtrate was tested. The humidity of the samples was also determined by drying them in 100°C until constant weight.

The content of sulphate ions was tested in the state of natural humidity using the method given in the cement standard [33]. This method consists in the precipitation of barium sulphate using a barium chloride solution from previously separated SO_4^{2-} ions from concrete dissolved in hydrochloric acid. The results are given in weight % of SO_4^{2-} ions in relation to the weight of the concrete and in relation to the acid soluble parts of the concrete considered as the binder. Calculations of sulphate content in “binder” were made – after deducting the mass of insoluble in HCl parts of the collected material (remaining on the filter), aggregate. The calculations were made with the assumption that sulphates do not react corrosively with aggregate. “Binder” should be interpreted as the sum of cement paste with the content of other HCl-soluble corrosion products and microorganisms in the biological membrane. The content of sulphate ions was calculated as the average out of two preparations whose maximum error was 4%.

Chemical analysis of sulphate content was confirmed by observations made in the high-resolution scanning

Table 1.**Composition of microbiological media used for screening of selected groups of microorganisms**

Waksman medium		9K Silverman and Lundgren medium		Winogradski medium	
Component	Concentration g/l	Component	Concentration g/l	Component	Concentration g/l
(NH ₄) ₂ SO ₄	0.2	K ₂ HPO ₄	0.5	(NH ₄) ₂ SO ₄	2.0
KH ₂ PO ₄	3	(NH ₄) ₂ SO ₄	3	K ₂ HPO ₄	1.0
MgSO ₄ · 7 H ₂ O	0.5	MgSO ₄ · 7 H ₂ O	0.5	MgSO ₄ · 7H ₂ O	0.5
CaCl ₂ · 6 H ₂ O	0.025	Ca(NO ₃) ₂	0.01	NaCl	2.0
FeSO ₄ · 7 H ₂ O	traces	KCl	0.1	FeSO ₄ · 7H ₂ O	0.4
S ⁰	10	FeSO ₄ · 7 H ₂ O	44.2	CaCO ₃	10.0

Table 2.**Media used to determine the presence of selected groups of microorganisms in the samples**

Medium	A group of microorganisms	Method for determining the presence of microorganisms
Waksman	Sulfur-oxidizing bacteria	Determination of changes in SO ₄ ²⁻ ions concentration using reagent tests cat. No. 114791 (Merck, Germany) before and after incubation
9K	Iron (II) ions oxidizing bacteria	Determination of changes in Fe ²⁺ and Fe ³⁺ ions concentration using a titration method with a EDTA solution against the sulfosalicylic acid index
Winogradski	Nitrifying bacteria	Determination of changes in NH ₄ ⁺ and NO ₃ ⁻ ions using reagent tests cat. No. 100683 and cat. No. 109713 (Merck, Germany) before and after incubation

electron microscope (SEM) Mira3 by Tescan.

In the microbiological tests, beside the concrete, an additional material was taken from the cast iron plate. Prior to the microbiological tests, all samples (fragment of a corroded cast-iron plate, concrete film and corroded concrete) were shaken in physiological saline by 30 min by 150 RPM in room temperature. The suspension, containing biological material, were used to carry out the appropriate tests. Exhibiting corrosion potential with respect to concrete and metallic materials, biochemical tests API 20E and API 20 NE and selection substrates were used (Waksman medium, 9K Silverman and Lundgren medium, Winogradski medium in order to determine the presence of selected groups of microorganisms) – Table 1.

Selective substrates (Table 1) were inoculated with 1 ml of the previously prepared suspensions (fragment of a corroded cast-iron hatch, concrete film and corroded concrete). For further analysis, samples of the inoculated substrates were taken before incubation and after 5 days of incubation at temperature of 37°C. A list of selected media with the groups of microorganisms designated therein are collected in Table 2.

The presence of denitrification bacteria, sulphate reducing bacteria and heterotrophic bacteria, both aerobic and anaerobic, was determined based on selected biochemical tests included in the strip of

API 20E and API 20NE (BioMerieux, Poland) accordingly the test of NO₂ / N₂, test of H₂S, tests of GLU, MAN, INO, SOR, RHA, SAC, MEL, AMY, ARA and test of GLU (anaerobic conditions).

4. TEST RESULTS WITH DISCUSSION

In the first stage, a visual analysis of the technical condition of the well was carried out. In the bottom of the kinetas and around the periphery of inner walls of the concrete well rusty formations were observed. The cavities caused by the crushed concrete reached 6 cm thick concrete circle. Also iron steps corroded (Fig. 6).



Figure 6.
The interior of the S50 well

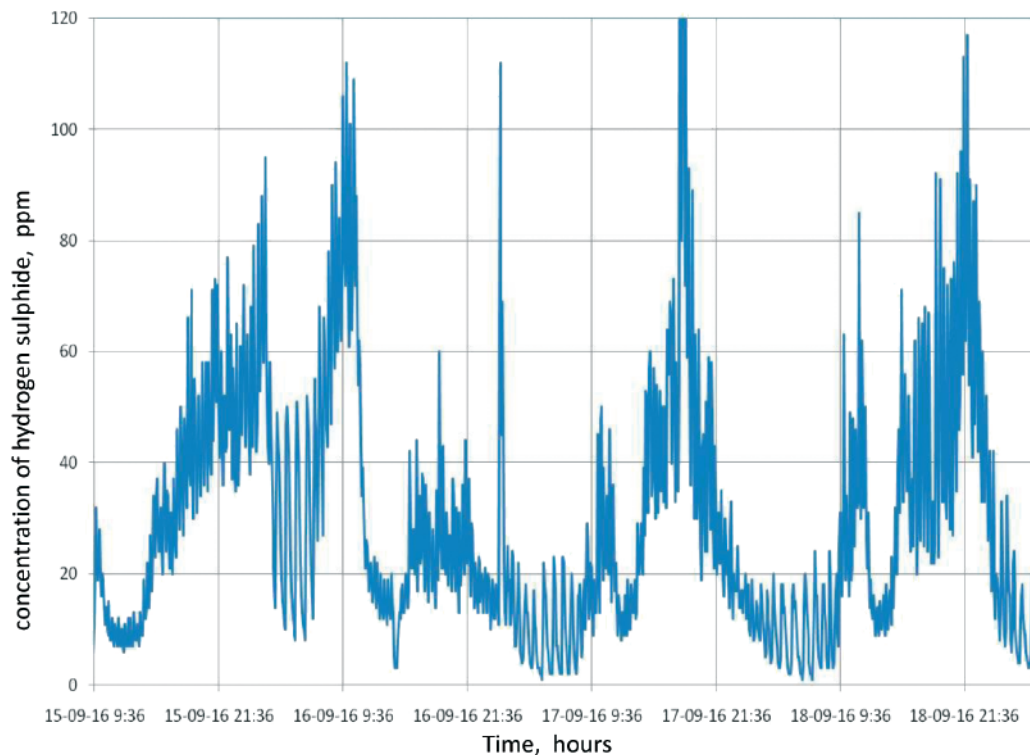


Figure 7.

The example of a change in the concentration of hydrogen sulphide in the S50 well. Measurements made with the OdaLog gas detector. September 2016

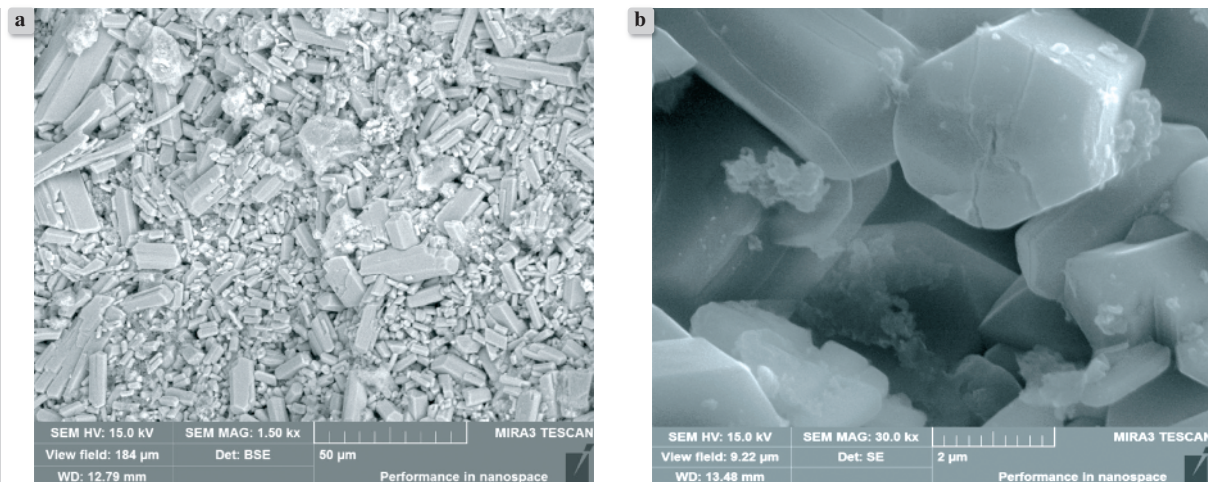


Figure 8.

Gypsum. SEM-BSE images of concrete film sample of 1 mm thick from the inside of the upper circle of the S50 drain well, scale: a) 50 µm, b) 2 µm

The degree of sewage air aggressiveness for concrete in the S50 well was high. The altering of the concentration of hydrogen sulfide within more than 84 hours is shown in Fig. 7. During the period of the tests, the

concentration of hydrogen sulphide over 22 ppm was most common (lower quartile 13 ppm, upper quartile 41 ppm; coefficient of variation: 78%; slant: 1.6).

Table 3.

Average values of sulphate concentration in concrete and pH value, concrete specimens taken from the height of 2.20 m above the level of sewage table, well S50

Specimen	Type of the test	pH	SO ₄ ²⁻ Concentration, %mas	SO ₄ ²⁻ concentration relative to the dissolved phase, %mas	Humidity, %
Concrete film, thickness: 1–2 mm		7.1	22.4	54.8	23
Concrete under the “film”, thickness: 2 cm		7.7	18.5	43.6	25

Table 4.

Types of microorganisms marked in preparations from S50 well

o.n.	Location of sampling in a sewage well			A group of microorganisms
	Cast iron plate of the well	Outer coating of concrete (concrete film, thickness approx. 1–2 mm)	Layer of concrete under the film; thickness about 2 cm	
1	+/-	+	+	sulfur-oxidizing
2	-	-	+	sulfate-reducing
3	+	+	+	Fe ²⁺ -oxidizing
4	+	+	+	aerobic heterotrophs
5	-	+	+	anaerobic heterotrophs
6	-	+	+	nitrifiers and denitrifiers

Legend: detected (+); not detected (-) group of microorganisms

The content of sulphate ions in the concrete samples was 22.4%_{mas} in the case of a surface film of concrete and 18.5%_{mas} in a 2 cm layer of concrete – Table 3.

Table 3 shows also the results of sulphate content in the binder, after subtracting the weight of the dried aggregate. These values are more than twice higher than in the original material. Corroded concrete from a 2 cm thick layer was characterized by a larger amount of thicker aggregate fraction (max 1 cm) and its humidity was about 25%.

The moisture content of the top film layer was about 23%, and the graining of the aggregate did not exceed 1 mm. The pH of both concrete samples was very low, ranging from 7 to 8, so it can be confirmed that the samples consisted mainly of aggregate, biological film and products of sulphate concrete corrosion [23].

The high content of sulphates in the investigated samples was confirmed by SEM-images depicting mainly hexagonal pillar-shaped gypsum crystals – Fig. 8.

Near the gypsum and the highly decalcified C-S-H phase, next phase present in the tested material in small amounts was probably calcium carbonate, which accompanied gypsum in the strong concrete decalcification conditions [24, 25, 26, 27].

The research on identification of microorganisms groups present in fragments of corroded cast iron manhole plate is presented in Table 4.

Biochemical analysis showed the presence of bacteria that oxidized iron ions Fe²⁺ in all samples (Table 4). These bacteria affect the biocorrosion of concrete and metal-containing materials [12, 34]. As a result of the conducted analyzes, the presence of bacteria oxidizing sulfur in concrete samples (film and deeper layer) was also observed, which indicates the sulphate corrosion occurring in these materials. The result of metabolic processes carried out by this group of microorganisms is the production of biogenic sulfuric acid, which has a corrosive potential and reacts with the components of concrete, mainly with Ca(OH)₂ leading to the formation of gypsum, and as a result of further reactions to ettringite [9, 35, 36]. Sulphide-oxidising bacteria can also cause corrosion of metals and materials containing them [37]. In spite of this, in the examined preparation from cast-iron plate, the activity of sulfur-oxidising bacteria was determined to be relatively low. Detected groups of aerobic and anaerobic heterotrophs on the surface of the upper circles of the sewer well most probably indicate the creation of a concentration gradient of oxygen in the biofilm. Oxygen bacteria – heterotrophic and autotrophic (nitrifying) bacteria appeared in the outer layer of the biofilm. As a result of microbial activity, biogenic acids: nitrite (III) and nitric (V) lowered the pH of the substrate. The nitric acid (V) formed in aerobic conditions, reacted with the components of the concrete, mainly with the binder. As a result, most likely soluble calcium nitrates were

formed, which were dissolved and washed away from the surface zones of concrete, which led to deterioration [8, 38]. The presence of heterotrophic aerobic bacteria was also determined in all samples. These bacteria can also affect the corrosion of various materials because organic acids are formed as a result of their metabolic activity. These substances have a corrosive potential, and reacting with the components of concrete caused its destruction. For example, gluconic acid formed as a result of oxidation of glucose may react with calcium ions [39]. In the inner layer of the biofilm, anoxic and anaerobic conditions could also occur, as evidenced by the presence of denitrifying, sulphate-reducing and anaerobic heterotrophic bacteria. Although there are no results of studies showing the influence of denitrification bacteria on the biocorrosion of concrete, their impact in the destruction of sewage channels can not be unambiguously eliminated. It has been shown that the oxidation of metallic iron can be related to the reduction of nitrites (III) and nitrates (V) [40]. The occurrence of anaerobic heterotrophic bacteria in concrete samples may indicate fermentation processes. As a result of fermentation, biogenic organic acids (e.g. butyric acid, acetic acid, lactic acid) are produced which are corrosive. These compounds react with the contained in concrete $\text{Ca}(\text{OH})_2$ and CaCO_3 cause dissolution of the hardened cement paste matrix. The soluble organic calcium salts can then be rinsed off the surface of the concrete, affecting its destruction [41]. In addition, biogenic organic acids can cause biocorrosion of metallic materials [42, 43].

5. SUMMARY AND CONCLUSIONS

Currently, the problem of sulphate corrosion in sanitary sewage usually concerns parts of the network (diameter 200–350 mm) below the expansion well, where there are problems with odors. The risk of odors in the sewage system is correlated with the extended sewage flow time in the sewage system, which is accompanied by the formation of anaerobic biochemical changes in sewage sludge. As a result of these changes arise as by-products, among others CO_2 , NH_3 , or H_2S [4, 15, 17].

The analyzed case confirmed that concrete corrosion is a complex process. Most likely, after lowering the pH of the concrete and associated leaching and cracking of the external concrete surface, favorable conditions for the development of the biofilm were created ($\text{pH} < 9$). The development of microorganisms that caused, inter alia, the oxidation of hydrogen

sulphide to sulphates is already the stage of biological corrosion. In the analyzed case, intense corrosion of concrete resulted most probably from the development of chemical and biological corrosion. However, this is a supposition, because even in world-class work there are still disputes regarding the priority and importance of biological processes and biological combined with chemical ones, because the development of the biological membrane has already been noticed even by pH: 11–13 [9].

Tested concrete samples, taken from the well, were characterized by a pH value between 7 and 8 and a very high amount of sulphate ions. This material had no longer binding properties, it was fragile and mushy, it consisted primarily of fine aggregate and gypsum. Under these conditions, the biological membrane functioned as a binder. And it is worth mentioning that the S50 well has worked just for 7 years.

In the 2 cm layer of the concrete that underwent corrosion, predominated oxygen microorganisms that have the ability to oxidize hydrogen sulphide to sulphates. However, the development of *Thiobacillus* under aerobic conditions is possible in the case of a low pH environment, so it was probably preceded by chemical corrosion. Stimulators of chemical reactions may also be nitrifying bacteria that produce nitric acid and nitrous acid to the environment, contribute to the delamination of concrete, or other heterotrophs, both aerobic and anaerobic, which use organic compounds as a carbon source to produce organic acids. Various groups of microorganisms isolated from the film part of the concrete samples may suggest the creation of a biological membrane (biofilm) on the walls of the sewage well. Biofilm production, due to the separation of extracellular polymeric substances (EPS), which affects the change of porosity with the formation of microcracks associated with changes in the vapor diffusion inside the material, results in reducing the surface tension [31]. Biological membrane acts as a pollutants absorber and as a precursor to the formation of shells or encrustation, which leads to increased salt migration as well as to the change of the environment from aerobic to anaerobic [31], and the amount of odors released into the environment is periodic – according to Fig. 1. During the microbiological tests, both organisms from the group of aerobic and anaerobic heterotrophs were isolated. In the deeper layers of corroded concrete, there were also bacteria from the *sulphate-reducing bacteria* group that cause the reduction of sulphates to hydrogen sulphide. The research confirmed that biological corrosion did not concern

only concrete elements of wells, but also steel ones. Confirmation of the last one might be corrosion of cast iron plate of the well caused by various groups of microorganisms. Moreover, the research shows that in the mass of the biofilm that wraps inner parts of the well, corrosion products and thus microorganisms, migrated as evidenced by the presence of bacteria in the outer coating of concrete and in the corroded concrete under the film.

It is generally known that microbial induced corrosion of concrete sewers is a significant problem with global repair costs in the range of billions of dollars per year [9, 44]. Otherwise, it may have an adverse effect not only on the functioning of the sewerage network, or on the continuity of the land surface, but in extreme cases can have a negative impact on the environment.

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REFERENCES

- [1] Błaszczyk, W. (1983). Sewers. Networks and pumping stations. (in Polish) Warszawa: Arkady.
- [2] Haile, T., Nakhla, G., Allouche E. (2008). Evaluation of the resistance of mortars coated with silver bearing zeolite to bacterial-induced corrosion. *Corrosion Science* 50, 713–720.
- [3] Haile, T., Nakhla, G., Allouche, E., Vaidya, S. (2010). Evaluation of the bactericidal characteristics of nano-copper oxide or functionalized zeolite coating for bio-corrosion control in concrete sewer pipes. *Corrosion Science* 52, 45–53.
- [4] Jasiński, K., Gil, B. (2014). Corrosion of concrete in sanitary sewage – a forgotten problem. The Silesian University of Technology. New technologies in water supply and sewage networks and installations (in Polish), 169–188.
- [5] Płaskowski, Z. Roman M. (1975). Building constructions in a sewage treatment plant. Warszawa: Arkady.
- [6] PN-88/B-01807: Anticorrosive protection in construction. Concrete and reinforced concrete constructions. Principles of construction diagnostics.
- [7] PN-EN 206-1. Concrete. Part 1: Requirements, properties, production and compliance.
- [8] Cwalina, B. (2008). Biodeterioration of concrete. *Architecture Civil Engineering Environment*, 4, 133–140.
- [9] O'Connell, M., McNally, C., Richardson, M.G. (2010). Biochemical attack on concrete in wastewater applications: A state of the art review. *Cement and Concrete Composites*, 32, 479–485.
- [10] Saricimen, H. Shameem, M. Barry, M.S. Ibrahim, M. Abbasi, T.A. (2003). Durability of proprietary cementitious materials for use in wastewater transport systems. *Cement and Concrete Composites*, 25(4–5), 421–427.
- [11] Grengg, C. Mittermayr, F. Baldermann, A. Böttcher, M.E. Leis, A. Koraimanne, G. Grunert, P. Dietzel, M. (2015). Microbiologically induced concrete corrosion: A case study from a combined sewer Network. *Cement and Concrete Research*, 77, 16–25.
- [12] Rao, T. S., Sairam, T. N., Viswanathan, B., Nair, K.V.K. (2000). Carbon steel corrosion by iron oxidising and sulphate reducing bacteria in a freshwater cooling system. *Corrosion Science*, 42(8), 1417–1431.
- [13] Kośmider, J., Mazur-Chrzanowska, B., Wyszynski, B. (2002). Odors. (in Polish) Warszawa: Wydawnictwa Naukowe PWN.
- [14] Dieter, W. (2001). Municipal sewage pumping stations. (in Polish.) Warszawa: Wydawnictwo Seidel-Przywecki Sp. z o.o.
- [15] Dąbrowski, W. (2004). The impact of sewerage systems on the environment. (in pol.) Kraków: Wydawnictwo Politechnika Krakowska im. Tadeusza Kościuszki.
- [16] Gil, B., Kawczyński, A. (2017). The analysis of sewer network damage. (in pol.) BK: Optimization of devices and methods in water supply and sewage disposal of urban agglomerations. Silesian University of Technology.
- [17] Witherspoon, J. (2008). Minimization of Odors and Corrosion in Collection Systems. WERF Research Report Series. IWA Publishing.
- [18] Łowińska-Kluge, A. (2008). Copper slag as an ingredient of cement composites with increased durability. (in pol.) Rozprawy, nr 419, Poznań: Publisher of Poznan University of Technology.
- [19] Cywiński, B., Gdula, St., Kempa E., Kurbiel J., Płoszański H. (1983). Wastewater treatment. Part 1. Mechanical and chemical treatment. (in Polish) Warszawa: Arkady.
- [20] PN-80/B-01800. Anticorrosive protection in construction (in Polish).
- [21] Tayfun Uygunoğlu, Ibrahim Gunes. (2015). Biogenic corrosion on ribbed reinforcing steel bars with different bending angles in sewage systems. *Construction and Building Materials*, 96(15), 530–540.
- [22] Basiński, A., Bielański, A., Gumiński K. (1966). Physical chemistry. (in pol.) Warszawa: Państwowe Wydawnictwo Naukowe PWN.

- [23] Kurdowski, W. (2010). The chemistry of cement and concrete. Warszawa: PWN. Kraków: Polski Cement.
- [24] Słomka-Słupik, B., Zybura, A. (2017). Thaumassite non-sulphate attack at ambient temperature and pressure. *Architecture Civil Engineering Environment*, 10(3), 73–80.
- [25] Słomka-Słupik, B. (2009). The changes of phases composition of the paste from cement CEM III/A under the influence of NH_4Cl water solution. *Cement Wapno Beton*, 2, 61–66.
- [26] Słomka-Słupik, B., Zybura, A. (2009). Mechanism of concrete damage in industrial wastewater treatment plant facilities. *Materiały Budowlane*, 448(12), 14–15.
- [27] Słomka-Słupik, B., Zybura, A. (2010). The changes in the microstructure of the hydrated cement paste subjected to decalcification. *Cement Wapno Beton*, 6, 333–339.
- [28] Piasta, W. G. (2000). Sulphate corrosion of concrete under long-term load. (in Polish) Kielce: Kielce University of Technology.
- [29] Kołwzan, B. (2011). The analysis of the phenomenon of biofilm – the conditions of its formation and functioning. (in pol.) *Ochrona Środowiska*, 4, 3–14.
- [30] Cwalina, B., Dzierżewicz, Z. (2007). Factors favoring the biological corrosion of reinforced concrete structures. (in Polish) *Przegląd budowlany*, 7–8, 52–59.
- [31] Cwalina, B. (2003). The role of microorganisms in the deterioration of natural building stones. *Journal of Polish Mineral Engineering Society*, 1, 39–48.
- [32] Melchers, R. E., Wells, P.A. (2007). Modelling the long term corrosion of reinforced concrete sewers. ResearchGate.net.
- [33] EN196-2:2005 – Cement testing methods. Part 2: Chemical analysis of cement.
- [34] Jin, X., Cheng, S. & Maocheng, Y., Fuhui, W. (2012). Effects of sulfate reducing bacteria on corrosion of carbon steel Q235 in soil-extract solution. *International Journal of Electrochemical Science*, 7, 11281–11296.
- [35] Davis, J.L., Nica, D., Shields, K., Roberts, D.J. (1998). Analysis of concrete from corroded sewer pipe. *International Biodeterioration & Biodegradation*, 42, 75–84.
- [36] Węglowski, W. (2008). Modeling of concrete damage caused by sulphate corrosion (dissertation (in pol.), Instytut Podstawowych Problemów Techniki Polskiej Akademii Nauk). Poland, Warszawa.
- [37] Rawat, A., Sharma, N., Khandelwal, A. (2014). Microbiological causes of corrosion, *Digital Refining*, 1–7.
- [38] Zapła, J. (2010). Negative aspects of the impact of bacteria on concrete. *Structure*, 2, 14–17.
- [39] Wołejko, E., Matejczyk, M. (2011). The problem of biological corrosion in construction. *Civil and Environmental Engineering*, 2, 2081–3279.
- [40] Kielemoes, J., Boever, P., Verstraete, W. (2000). Influence of denitrification on the corrosion of iron and stainless steel powder. *Environmental Science & Technology*, 34, 663–671.
- [41] White, C., Tancos, M., Lytle, D. A. (2011). Microbial Community Profile of a Lead Service Line Removed from a Drinking Water Distribution System. *Applied and Environmental Microbiology*, 77, 5557–5561.
- [42] Baszkiewicz, J., Kamiński M. (2006). Corrosion of materials. (in Polish) Warszawa: OWPN.
- [43] Pak, K.-R., Lee, H.-J., Lee, H.-K., Kim, Y.-K., Oh, Y.-S., Choi, S.-C. (2003). Involvement of Organic Acid During Corrosion of Iron Coupon by *Desulfovibrio desulfuricans*. *Journal of Microbiology and Biotechnology*, 13(6), 937–941.
- [44] Valix M., Zamri D. Mineyama H., Cheung W.H., Shi J., Bustamante H. (2012). Microbiologically Induced Corrosion of Concrete and Protective Coatings in Gravity Sewers. *Chinese Journal of Chemical Engineering*, 20(3), 433–438.