IDENTIFICATION OF BIOGENIC SULPHATE CORROSION OF CONCRETE IN SEWAGE TREATMENT PLANT SETTLING TANK WALLS

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A b s t r a c t

One of the basic threats in terms of concrete used for tanks or ducts applied in wastewater management is the phenomenon of biogenic sulphate corrosion (BSC). BSC is a particular case of corrosion caused by the action of sulphuric acid (IV), which is formed as a result of a number of biochemical processes, which can take place, e.g. in an environment encountered within the aforementioned structures. Ions present in sulphuric acid react with cement hydration products, which leads to replacing the primary cement matrix components with compounds easily-soluble or highly-swelling during crystallization. The outcome of advanced corrosion is usually an observed formation of a white, amorphous, sponge-like mass, which is easily separated from the underlying concrete. The article discusses a case study of a BSC process in a newly constructed primary settling tank in a municipal wastewater treatment plant.

Keywords: corrosion of concrete, biogenic sulphate corrosion, wastewater management, environmental protection facility, case study

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1. INTRODUCTION

The infrastructure used for wastewater discharge and treatment has been undergoing systematic development in Poland over the recent decades, e.g. as a consequence of the political changes of the 1990s and EU requirements in this respect [11]. According to the data of the Central Statistical Office (GUS), the total length of the domestic active sewage network increased from 51k km to 160.7k km from 2000 to 2018, the share of population benefiting from wastewater treatment plants increased from 53% to 74%, and simultaneously, the share of the volume of treated wastewater with increased biogene removal increased severalfold [6]. Developed infrastructure will require gradually increasing outlays, necessary to maintain its correct functionality. An OECD report from 2016 indicates that ageing or lack of infrastructure will be one of the greatest challenges in terms of effective water resources management in large cities [16]. For example, the repair costs for all damaged elements of the German wastewater management system were estimated at EUR 100 bn per year at the end of the 20th century [8].

One of the basic threats in terms of concrete applied in tanks or ducts used in wastewater treatment plants is the phenomenon of biogenic sulphate corrosion (BSC). Despite many years of research, it has not yet been properly studied [9, 15], and is not duly taken into account when engineering and operating infrastructure, the negative effects of which are described in this article.

2. BIOGENIC SULPHATE CORROSION

BSC is a particular case of corrosion caused by the acidic (H^+ ions) and sulphate (SO_4^{2-} ions) action, thoroughly discussed in the source literature on concrete [3, 5, 10, 12]. Concrete, due to the natural alkaline reaction, is highly susceptible to acid attack. Ions present in sulphuric acid react throughout the exposed material surface with basic cement hydration products, the C-S-H gel and $Ca(OH)_2$ [5, 9], which leads to the formation of $CaSO_4*2H_2O$. Subsequently, in favourable conditions, gypsum can react with the components of cured slurry, forming ettringite and sometimes thaumasite (at <15 °C) [1, 9, 10]. The outcomes of the aforementioned changes are very unfavourable causing the replacement of basic cement matrix components with compounds easily-soluble or strongly-swelling during crystallization [1, 5], leading to decreased cohesion forces in the slurry and slurry adhesion to aggregate grains. The outcome of advanced corrosion is usually an observed formation of a white, amorphous, sponge-like mass, which is easily separated from the underlying concrete. Aggregate grains (usually silicate) often become visible on its surface, since the attack affects cured cement slurry, which is rich in calcium compounds [9, 15]. Corrosion products

are not an obstacle for the migration of an aggressive medium [9], which is why the changes reach ever deeper, weakening the concrete cross-section and leading to the exposure of re-bars (if present), which are then also subjected to corrosion in an acidic environment.

The aforementioned mechanism is a component of BSC, however, for it to occur earlier, a number of biochemical processes, which determine the uniqueness and complexity of such corrosion must take place. As a result, a medium with low aggressiveness towards concrete, such as usually sewage, indirectly leads to very rapid material degeneration, at a hardly predictable rate, estimated at 19 mm/annum [1] or even 25 mm/annum [9]. Subsequent BSC stages can be described as follows:

- Anaerobic bacteria inhabiting wastewater, especially the sludge (biofilm) layer covering submerged surfaces of conduits or tanks, reduce the sulphates present in the water. Their metabolism products are S^{2-} ions, which in favourable conditions combine with hydrogen ions in the wastewater and as hydrogen sulphide, H_2S, are released in gaseous form to the gaseous space above the waterline [1, 3, 9, 15].
- The atmosphere above the wastewater waterline usually exhibits high relative humidity, and the surfaces present there are covered by a layer of condensate. Hydrogen sulphide dissolves in the thin water layers, and, provided that the concrete surface pH decreases (e.g. as a result of carbonatation), aerobic bacteria, which oxidize hydrogen sulphide to H_2SO_4 begin to colonize them [9, 15]. Acid concentration depends on numerous factors and is likely to vary over time, e.g. due to periodic drops in atmospheric humidity and condensate evaporation. It is estimated that it can reach 10%, which is equivalent to a pH equal to 1 [1]. It cannot be ruled out that the process can also undergo in anoxic conditions, e.g. in digesters, abiotically or with the participation of other bacterial strains [2, 13, 20].
- The presence of sufficiently concentrated sulphuric acid on the concrete surface (or its protective coating) initiates the aforementioned destructive reactions, with the bacteria providing constant supply of sulphuric acid.
- After reaching a certain concrete transformation degree, a weakened and porous layer of corrosion products is formed on its surface, with the products likely to come off spontaneously or, e.g. as a result of humidity and temperature changes or a dynamic increase in the wastewater flow rate within the conduit. Subsequent material layers are exposed and the corrosion cycle is resumed [9].

A multi-stage and complex BSC process, still not fully studied and burdened with certain doubts, is conditioned by a number of various factors, which determine its occurrence or intensity. The phenomenon is facilitated by [3, 4, 9, 15, 21]: high biological and chemical oxygen demand in wastewater (BOD and

COD), high total organic carbon (TOC) content, elevated temperature (approximately 30°C), high relative humidity and hydrogen sulphide atmospheric concentration (poor ventilation), high flow rate turbulence, long residence times for wastewater in the conduit or tank, low content of oxygen dissolved in wastewater, low flow rates (low drops), low fluid or concrete surface pH, high concrete porosity, specific wastewater types (e.g. containing tanning industry waste). Carbonatation [9, 21], biogenic acids other than sulphuric [5, 11, 19] and the existence of certain species of fungi [5, 20] are also mentioned as the coexisting synergistic phenomena relative to BSC.

The specificity and hazards associated with BSC induced a need to develop a number of specific methods for protecting exposed structures, which include coatings or additives and admixtures to concrete mixes – improving acid resistance and bactericidal impact, still largely at the research and development stage [14]. A frequent case in practice is that structures exposed to BSC are protected with universal materials and according to mixture formulations appropriate for the XA3 exposure class, which means the strongest classified chemical attack pursuant to PN-EN 206+A1:2016-12 [18] and characterized in Tab. 1 [18]. It should be emphasized that the document provides for the occurrence of such conditions in the case of "concrete exposed to contact with ground and groundwater", while there is no exposure class representing processes similar to BSC. Furthermore, the XA3 class is not "open", i.e., has upper limits on medium aggressiveness. In practice, it is hard to determine reliable aggressive ion concentrations in the case of a dynamic BSC process, while reported pH values in the order of 1.0 [1] exceed well beyond the limit value of 4.0. The described approach is not adequate in terms of the specificity of the discussed phenomenon, resulting in overshot requirements for concrete constantly submerged in water (which in many cases is not exposed to strong corrosion) and highly insufficient protection of the zones exposed above the wastewater line (cf. Fig. 1 and Fig. 2). This can also lead to neglecting extra-material aspects, such as appropriate ventilation of the gaseous space, monitoring or modifying wastewater contents, etc.
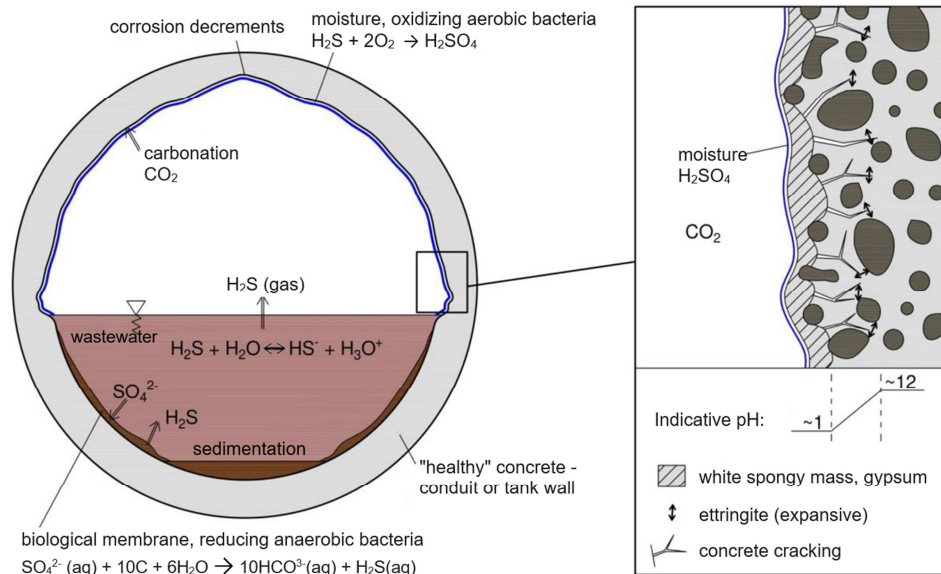
Fig. 1. Schematic representation of a BSC process in a concrete-walled sewage conduit or closed tank of a wastewater treatment plant. Developed based on [1, 3, 9, 20]

Table 1. Characteristics of the XA3 exposure class and the its corresponding requirements for a concrete mix [18]

Limit values for the XA3 exposure class - apply to groundwater					Requirements for concrete as for exposure class XA3		
SO_4^{2-} [mg/l]*	pH [-]*	CO_2 aggressive [mg/l]*	NH^{4+} [mg/l]*	Mg^{2+} [mg/l]*	Min. cement content** [kg/m3]	Max. w/c [-]	Min. comp. strength class
> 3000 ≤ 6000	< 4.5 ≥ 4.0	> 100 (until saturation)	> 60 ≤ 100	> 3000 (until saturation)	360	0.45	C35/45

* methods for testing the chemical properties are referred to in PN-EN 206+A1:2016-12 [18]

** for the XA2 and XA3 exposure classes, it is required to use SR or HSR cements resistant to sulphates, as well as concrete surface protection

The further section of the article presents a case study of BSC in a primary settling tank of a municipal wastewater treatment plant.

3. CASE STUDY

3.1. Characteristics of the structure

The structure in question is a reinforced concrete cylindrical primary settling tank in a municipal wastewater treatment plant, covered with a light-weight dome with an air extraction system. The internal diameter of the tank is 16.0 m, the depth by the side wall is ca. 5.5 m, and the thickness of the walls and bottom is 40.0 cm. Cylindrical, monolithic walls, anchored to the bottom slab. The bottom slab inclined downwards toward the central part of the settling tank, where a sludge hopper, for collecting and discharging sludge, is located. Waterbars were used in the construction joints between working sections. There are no expansion joints within the structure. The structure was designed in accordance with [17, 18] – exposure classes XC2, XD2, XA3. C35/45 (CEM I HSR) concrete, with a composition pursuant to standard recommendations was used for the construction. A flexible mineral coating resistant to aggressive environments (XA3 class) was used as wall protection. The radial sludge scraper structure was made of 1.4301 (0H18N9) stainless steel. Until the site inspection, the structure had been operating for ca. 2 years.

Over the operation period, the primary settling tank has been subjected to contact with wastewater and an aggressive gaseous environment, the friction of a rubber scraper against the floor and wastewater sloshing.

The state of the structure is described in two parts. The first one relates to the technical condition of the wall surfaces above the wastewater level, whereas the second one concerns the surfaces below the wastewater level.

3.2. Surfaces above wastewater level

The protective coating above the wastewater level was detached and partially destroyed, with yellow tarnish found on its remains, and a cream-white structure appeared on the exposed concrete surface. Local, very significant corrosion pits in the steel structures of auxiliary devices (sometimes through the plates) were also observed precisely at the wastewater table level – in the drainage flume and the radial scraper, most probably caused by the action of sulphuric acid (VI) near the surface of the wastewater. Examples of corrosive environment actions are shown in Fig. 2-7.

Fig. 2. Destroyed protective coating from the wastewater line upwards

Fig. 3. Corroded concrete surface after detachment of the protective coating

Fig. 4. Corrosion of the concrete wall (left) and the drainage flume overflow ridge steel

Fig. 5. Close-up onto a steel element of the drainage flume overflow ridge

Fig. 6. Radial scraper lattice; visible strong concentration of steel element corrosion on the wastewater table level

Fig. 7. Broken suspension line for radial scraper blades; aggregate in the bottom slab exposed as a result of excessive friction

3.2. Surfaces below wastewater level

Below the wastewater table, the wall protective coatings, apart from local damage – osmotic bubbles, exhibited good adhesion to the substrate (Fig. 2). The bottom slab surface showed clear traces of mechanical abrasion, most probably resulting from the defective operation of the scraper, caused by breaking of the lines suspending the blade assembly. The coating was completely abraded in many places, with exposed aggregate (Fig. 7).

3.3. Primary settling tank concrete tests

A pit was drilled in the concrete above the wastewater level, underneath a detached section of protective coating. Some of the concrete cover, approx. 3 cm thick, was completely corroded (total cover thickness was 6 cm). No corrosion of re-bars was identified. The phenolphthalein test did not indicate a decrease in the pH of concrete under the layer of white spongy corrosion products. Concrete samples taken from the drilled pit were subjected to XRD and SEM-EDS.

3.3.1. X-ray diffraction analysis (XRD)

Testing with the use of X-ray diffraction analysis (XRD) were conducted at the Department of Inorganic Chemistry at the Faculty of Chemistry of the Warsaw University of Technology. The phase composition of the material was determined in two samples: P1 – concrete sampled from the outer layer (Fig. 8), with an appearance of a white spongy mass, and P2 – visually "healthy" concrete, constituting the direct cover of steel bars (Fig. 9).
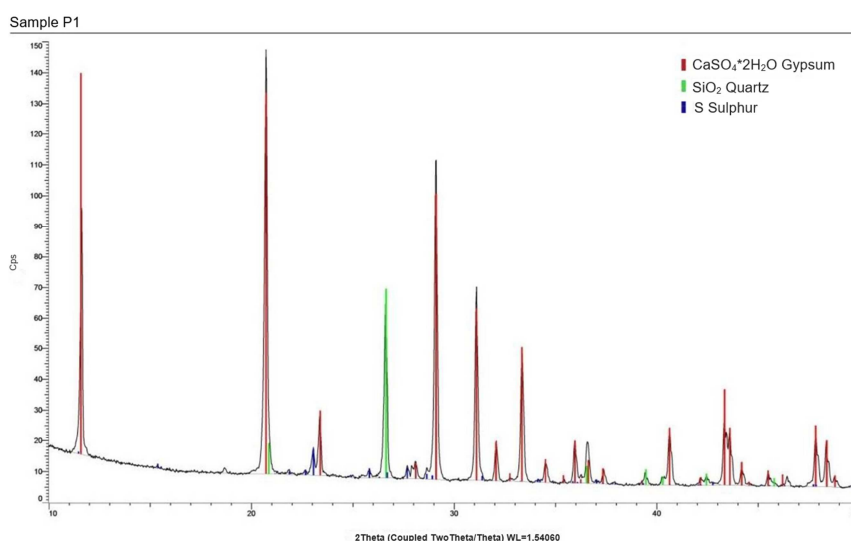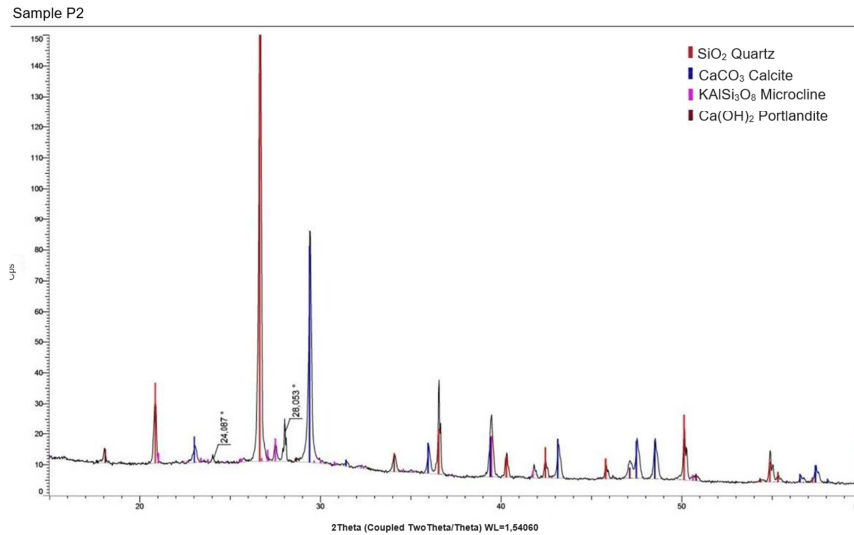

Fig. 8. P1 sample diffraction pattern

Fig. 9. P2 sample diffraction pattern

The image shown on the diffraction pattern, which contains the phases identified in sample P1 (Fig. 8), confirms the total destruction of the outer concrete cover. The resulting gypsum is the end product of sulphate corrosion. The P2 sample diffraction pattern image (Fig. 9) indicates phases occurring in the concrete, which has not yet been subjected to corrosion.

3.3.2. Scanning electron microscopy (SEM-EDS)

Tests using an electron microscope (SEM) with EDS analysis were conducted at the Micro-Area Analysis Laboratory of the Polish Geological Institute. This technique was used to determine the phase composition of the material in two samples: P1 (Fig. 10) and P2 (Fig. 11) (similarly to XRD).
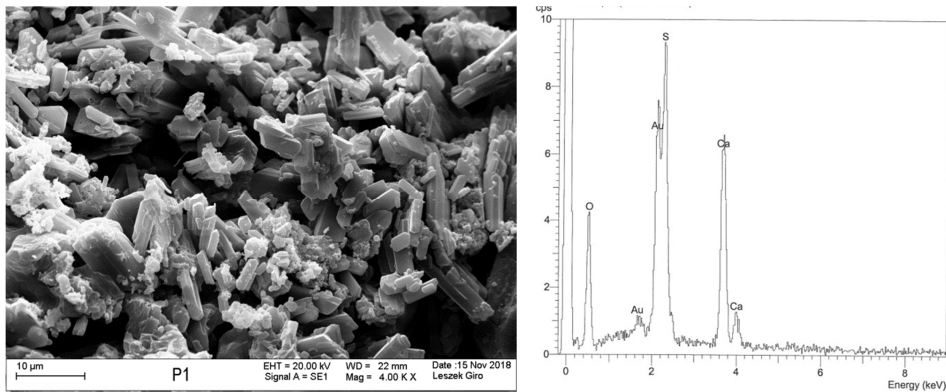

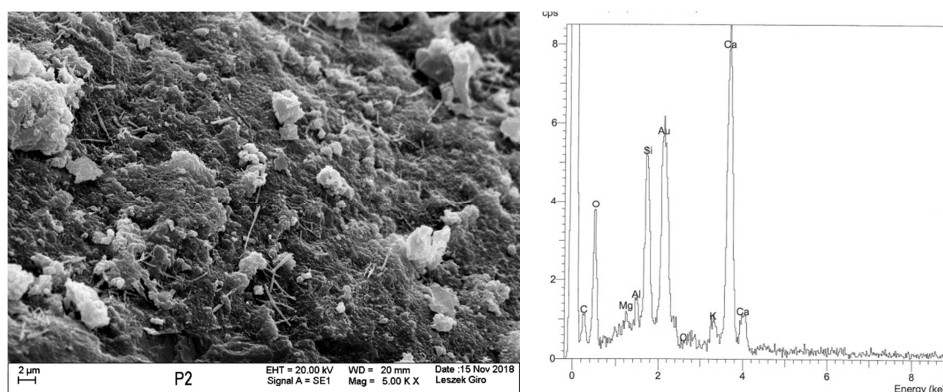Fig. 10. Corroded concrete sample microstructure – sample P1

Fig. 11. "Healthy" concrete sample microstructure – sample P2

The results again showed that the outer concrete layer (approx. 3 cm thick from the wall face) was fully destroyed due to corrosion – resulting in the formation of crystallized gypsum (Fig. 11); part of the cover in direct vicinity of the re-bars did not exhibit any traces of sulphate corrosion (Fig. 11).

4. SUMMARY AND CONCLUSIONS

The main cause behind the observed damage to reinforced concrete walls above wastewater level was a highly aggressive environment, which initiated acid corrosion above the wastewater table. The materials used for construction and protection (pursuant to standard requirements), as well as the air extraction system, failed to provide sufficient structural protection over an operating period of approximately 2 years. The concrete degradation rate was ca. 15 mm/annum, which corresponds to the source literature data [1, 9]. In the case in question, strong acid corrosion also lead to the failure of auxiliary equipment (radial scraper).

BSC is a complex phenomenon, as a result of which a medium with low aggressiveness towards concrete, such as wastewater, indirectly leads to very rapid material degeneration, with the rate of the process that is hard to predict. This process particularly endangers new wastewater management facilities due to their tightness-related requirements, which create excellent conditions for BSC development. Furthermore, the scope of the applicable concrete standards, i.a. [18], does not include a biochemical exposure class, which does not help the designers consider this phenomenon at the technical documentation development stage.

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