CONCRETE CORROSION ON A PRIMARY SETTLING TANK

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ABSTRACT:

This research paper explores the issue of concrete corrosion in sewage treatment plants, highlighting the detrimental effects of aggressive chemicals and high humidity on reinforced concrete structures. The study outlines the corrosion mechanisms, emphasizing the role of sulfuric acid formation from decomposing sewage, which significantly lowers the pH and accelerates concrete erosion. Key factors influencing corrosion include the compactness of concrete, its alkalinity, and the thickness of the protective cover over the steel reinforcements. The paper also investigates the impact of various corrosive agents found in wastewater, including biogenic nitric acid and sulfates, which contribute to the breakdown of concrete integrity. A case study conducted at a sewage treatment plant in Nyíregyháza reveals significant deterioration in a primary settling tank, with visual inspections and nondestructive testing indicating carbonation and corrosion of the concrete structure. The findings underscore the importance of using corrosion-resistant concrete mixes and protective coatings to extend the lifespan of such structures. Recommendations for future construction emphasize adopting modern standards, including lower water-cement ratios and sulfate-resistant materials, to mitigate the effects of corrosive environments. Overall, this research highlights the critical need for proactive measures in designing and maintaining concrete structures in wastewater treatment settings.

KEYWORDS:

concrete corrosion, wastewater, structural integrity, testing, protective coatings

1 INTRODUCTION

Concrete corrosion is a particularly common problem on structures within sewage treatment plants, as the plants operate in an environment where these structures regularly come into contact with aggressive chemicals and high humidity. The hardened cement (i.e. cement stone) within the reinforced concrete structures is the first component to break down due to corrosion processes [1, 2]. The aggressive substances within the wastewater attack and damage concrete surfaces and other equipment that comes into direct or indirect contact with it. When sewage decomposes and ferments, sulfur compounds are produced, which are easily converted to sulfuric acid in the watery, oxygen-rich environment. Sulfuric acid and other acids have a low pH, while concrete has a high pH (12.5-13.5). The oxygen-deficient acidic medium dissolves the calcareous binder, which causes the concrete to become porous and begin to erode and decompose guickly [3]. For this reason, it is important to use concrete resistant to aggressive effects in water treatment and wastewater treatment facilities. In order to minimize corrosion, it is important to choose the right concrete structures and coatings that are resistant to these harmful processes. Concrete structure tests are essential in these situations since they can be used to recognize signs of corrosion and the degree of damage during the elapsed time [4].

2 THEORETICAL BACKGROUND

2.1 THE BASIC DRIVING MECHANISM OF CONCRETE CORROSION

Concrete corrosion is a multifaceted process that can result from various mechanical, physical, chemical, and biological factors. Mechanical damage can arise from repeated stress cycles or vibrations that may lead to micro-cracks, providing pathways for corrosion to initiate. Physical effects, such as frost damage, occur when water within the concrete freezes and expands, causing cracking and spalling. The use of deicing salts exacerbates this issue by introducing chlorides that can penetrate the concrete and initiate corrosion of the reinforcing steel [5]. The compactness of the concrete, its resistance to water ingress, and the adequacy of the protective cover thickness are critical in mitigating these physical and mechanical effects. If these conditions are suitable, the corrosion of the steel bars is less likely. The concrete's natural alkalinity helps protect the steel reinforcement within it from corrosion. However, if the pH level drops due to carbonation or chloride ingress, the steel becomes vulnerable to rust [6].

Chemical corrosion involves reactions between concrete and aggressive chemicals. Acidic environments lead to the dissolution of the cement paste, while alkaline environments might trigger alkali-silica reactions that cause swelling and cracking. Carbonation is another chemical process where carbon dioxide penetrates the concrete and reacts with calcium hydroxide to form calcium carbonate, reducing the pH and compromising the protective alkaline environment around the steel reinforcement. A significant drop in pH

makes the steel susceptible to rust, which expands in volume compared to the original steel, exerting pressure on the surrounding concrete and causing cracks [7].

Biological or microbially influenced corrosion involves microorganisms within the biofilm or biological membrane on the concrete surface. These microorganisms can produce acids as metabolic byproducts, further lowering the pH and accelerating the degradation of concrete. This type of corrosion is particularly prevalent in environments such as wastewater treatment facilities, where moisture and organic matter provide an ideal setting for microbial activity.

To mitigate these diverse corrosion mechanisms, strategies such as using materials and design approaches that enhance the compactness and impermeability of concrete are essential. Applying protective coatings can help resist chemical and microbial attacks, while regular maintenance and inspections allow for early detection and remediation of corrosion. Although these factors are widely recognized, some researchers advocate for advanced materials like self-healing concrete, which can autonomously repair microcracks and extend the lifespan of structures.

2.2 CONCRETE RESISTANT TO AGGRESSIVE ENVIRONMENTS

Both inorganic and organic acids can damage concrete. In this process, portlandite—a component of the cement stone, also known as calcium hydroxide—serves as the primary reactant with acids. The acid resistance of concrete can be improved by breaking up the (continuous) structure of free calcium hydroxide and limiting or binding the amount of portlandite. Therefore, cement that contains little portlandite should be used. Furthermore, it is advisable to use an additional material that binds the calcium hydroxide in the concrete, for example, silica dust, metakaolin, slag, or coal ash. The concrete must be composed of a low water-cement ratio, so an additive must be used to ensure good workability. The latter is used to reduce the number of capillary pores and increase compactness [8].

2.3 THE IMPACT OF WASTEWATER ON CONCRETE

The primary settling tank plays a crucial role in the wastewater treatment process by facilitating the removal of suspended solids and organic matter from the incoming wastewater. As the first significant treatment stage, it allows heavier particles to settle at the bottom, creating a sludge that can be further processed. However, the environment within these tanks presents several challenges due to the aggressive nature of wastewater.

Wastewater is an aggressive medium that, in addition to degrading concrete structures, causes corrosion of equipment that partially or completely comes into contact with it [9]. In the oxygen-rich, wet environment of a primary settling tank, sulfur compounds formed during sewage decomposition can transform into sulfuric acid. This acid significantly lowers the pH compared to the inherently alkaline concrete, which typically ranges between 12.5 and 13.5. When chemicals with a pH below 9 are introduced, the risk of initiating corrosion of steel reinforcements in concrete structures increases. This is particularly concerning in primary settling tanks, where such conditions are prevalent. Furthermore, the presence of microorganisms on the concrete walls in the form of biofilms contributes to the corrosive environment. In the aerobic, acidic conditions typical of these tanks, these microorganisms can dissolve the lime-containing binder from the concrete over time. This dissolution renders the concrete porous, accelerating the onset of corrosion processes [5].

Thus, both chemical and biological corrosion mechanisms are actively at play in primary settling tanks, necessitating vigilant maintenance and protective measures.

One of the corrosive substances is the aggressive carbon dioxide. The free calcium hydroxide (portlandite) found in the cement stone turns into calcium carbonate ($CaCO_3$) as a result of the present carbon dioxide. This process is called carbonation. The positive effect of carbonation is that the rapidly soluble calcium hydroxide is converted by carbon dioxide into a difficult-to-dissolve calcium carbonate, in contrast to carbonic acid corrosion [4]. The resulting calcium carbonate temporarily reduces the porosity of the concrete by clogging its pores, but the dissolution of the calcium carbonate leads to an increase in the concrete's pH value. This can be represented by equations (1) and (2).

Equation (1) gives the reaction that results in the formation of calcium carbonate, which can temporarily reduce the porosity of concrete by filling its pores. This is beneficial for structural integrity. The presence of calcium hydroxide, a strong base, means the initial environment is highly alkaline. As calcium carbonate forms, the pH can slightly decrease but remains on the alkaline side due to the residual calcium hydroxide.

Equation (2) gives the reaction that shows the dissolution of calcium carbonate back into an aqueous form, which can lead to increased porosity of the concrete if it occurs extensively. When calcium carbonate dissolves into calcium bicarbonate, the pH tends to drop since bicarbonate is less alkaline than carbonate, leading to a more neutral pH over time.

It should be noted that in all the subsequent chemical reactions the square parathensis indicates the compound state, i.e., [s] for solid, [l] for liquid, [g] for gas, and [aq] for aqueous – dissolved in water.

$$Ca(HCO_3)_2[aq] + Ca(OH)_2[s] = 2 \cdot CaCO_3[s] + 2 \cdot H_2O[l]$$
 (1)

$$CaCO_3[s] + CO_2[g] + H_2O[l] = Ca(HCO_3)_2[aq]$$
 (2)

Carbonic acid also plays a role in the corrosion of the steel bars in reinforced concrete when moisture and oxygen are present. Due to the carbonic acid, ferro-carbonate is formed from the steel. As a result of oxidation, ferrohydrocarbonate forms basic iron(III)-oxide, i.e. iron rust [10].

Equation (3) represents the reaction that results in the formation of iron carbonate, which can coat the surface of iron structures. While initially protective, this coating can become brittle and lead to further corrosion if the protective layer is compromised. Additionally, the release of hydrogen gas indicates a reduction process. The reaction itself doesn't directly change the pH of the surrounding environment significantly, but the presence of CO_2 can lead to the formation of carbonic acid when dissolved in water, potentially lowering the pH.

Equation (4) demonstrates the reaction that shows the conversion of solid iron carbonate into soluble iron bicarbonate, increasing the corrosion risk as the protective layer is dissolved. During this transformation, the pH may decrease slightly since bicarbonate formation involves carbonic acid's influence, leading to a more acidic environment over time.

$$Fe[s] + CO_2[g] + H_2O[l] = FeCO_3[s] + H_2[g]$$
 (3)

$$FeCO_3[s] + CO_2[g] + H_2O[l] = Fe(HCO_3)_2[aq]$$
 (4)

Biogenic nitric acid causes corrosion, primarily in aeration tanks. The pH value of the biofilm layer that forms on the surface of the concrete can drop to 5-7, causing corrosion. The damage is most extensive in locations where nitrification takes place within the aeration tanks.

Ammonium salts, present when exchange decomposition occurs in the wastewater environment, decompose into ammonium nitrate, chloride, sulfide, sulfate, and hydrogen carbonate, causing damage to the concrete's structure. During the reaction of ammonium chloride and lime hydrate in the cement stone, ammonia and easily soluble calcium chloride are formed at the same time [8].

The sulfates found in wastewater can cause swelling corrosion of the concrete because they interact with the aluminate-hydrates and free calcium-hydroxide found in the cement stone, thereby creating large-volume secondary ettringite crystals. These crystals swell and can completely crack the concrete. The lower the amount of tricalcium-aluminate-hydrate in the cement, the lower the chance that secondary ettringite will form and swelling corrosion will occur [11].

The pH value of municipal wastewater also affects the corrosion process. According to Biczók [4], if the pH value decreases and the medium becomes acidic, the sulfate corrosion increases proportionally since the solvent effect of acidic waters is more intense. Through chemical effects, acidic water also breaks down the components of concrete that pure water cannot.

On the other hand, the hardness of the water is also an important factor because lime salts are more difficult to dissolve in hard, calcium-rich water, so significant corrosion is rarely experienced in waters above 24 nk°. As the hardness of wastewater increases, the chemical corrosion of concrete generally decreases [4].

3 CASE STUDY

The research detailed in this paper was conducted at Nyíregyháza's primary sewage treatment facility, focusing on the number three Dorr-type primary settling tank, as depicted on Figure 1. This plant, a cornerstone of the town's wastewater management since its establishment, has played a crucial role in treating and purifying wastewater, thereby safeguarding the local water bodies and environment.

The sewage treatment plant operates as a multi-stage system, beginning with the primary treatment phase where settling tanks, like the one studied, play a critical role in removing suspended solids from incoming sewage. The Dorr-type tanks are designed to enhance sedimentation efficiency, ensuring the effective separation of solid waste from liquid. This is followed by secondary treatment processes aimed at biodegrading organic matter, and sometimes tertiary treatments for further purification, depending on the plant's design and capacity.

Since its inception, the plant has undergone several upgrades to incorporate modern technologies and increase its capacity, reflecting the town's growth and the increasing

demand for effective wastewater management. Originally built with basic infrastructure, the plant now features advanced systems to meet environmental standards and handle the complexities of urban sewage treatment.

The first task was the analysis of the design plans and technical specifications of the studied primary settling tank. The examined reinforced concrete structure was made according to the (now outdated) MSZ 4720:1961 and MSZ 15022-1:1961 standards. This implies that the concrete load-bearing classification should be converted in accordance with the currently valid standard. Hence, the structure's technical specifications are:

- Wall thickness: 25 cm
- Thickness of protective layer: 22 mm
- Classification of concrete: Bt 200/300 C500P és C500S \rightarrow C16/20 CEM I 42,5 and CEM III 42,5



Figure 1: The number three primary settling tank

The converted concrete grades clearly show that this composition would no longer meet the current requirements, as structural concrete must be at least of C35/45 quality.

The on-site inspections were conducted by visual examination. Since the settling tank has been drained for 2 years, the inside of the tank was clearly visible, showing how discoloured the concrete surface was. The concrete cover had come off in several places, the reinforcing bars were exposed, cracks were visible, and the scraper bridge and mechanical equipment were corroded. The presence of lime was visible on the outside walls of the settling tank, the concrete bottom was crusted where the scraper wheels run, and the concrete cover had come off from the underside of the cantilevered service walkway.



Figure 2: The missing concrete cover from the inner part of the tank edge

The on-site examinations commenced with a visual inspection of the structure. Given that the pool had been drained for two years, the interior was clearly visible, revealing significant discoloration on the concrete surface. Observations indicated several areas where the concrete cover had detached, exposing the reinforcing steel bars. Cracks were visible, and corrosion was noted on the scraper bridge and mechanical equipment. Externally, limestone efflorescence was observed, and the pool bottom exhibited crusting in areas where the scraper wheels run, along with detachment of the concrete cover from the underside of the cantilevered service walkway. To assess the concrete's condition accurately, six specific measurement locations were selected for the Schmidt hammer test. These sites were strategically chosen to reflect different states of the concrete surface, providing a comprehensive understanding of the structural integrity. The selected areas displayed varying degrees of degradation: some showed significant wear and detachment, while others exhibited surface-level cracking and discoloration.



Figure 3: Wear of the tank's bottom plate along the wheels

For the assessment, a Schmidt hammer, commonly known as a rebound hammer, was employed. The Schmidt hammer, also known as a rebound hammer, is a non-destructive tool used to evaluate the surface hardness of concrete and estimate its compressive strength. During measurements, the hammer is held perpendicular to the concrete surface, and a spring-loaded mass is released to impact the concrete [12]. The hammer then measures the rebound distance of the mass, which is read on a graduated scale. This rebound value is indicative of the surface hardness of the concrete: the higher the rebound value, the harder and potentially stronger the concrete. Multiple readings are typically taken at various points on the concrete surface to ensure accuracy and account for any surface irregularities. The average of these readings is used to estimate the concrete's compressive strength, providing valuable data for assessing structural integrity.

Based on the non-destructive testing, the current compressive strength class of the settling tank's concrete corresponds to C25/30, whereas the compressive strength class at the time of construction, converted to the current standard, was C16/20.

The samples for carbonation depth measurements were taken from the edge or surface of the concrete specimen, specifically from locations where a fresh fracture could be observed and was accessible for testing with phenolphthalein solution [13]. This approach ensures that the measurement reflects the distance from the exposed external face toward the interior of the concrete, allowing for accurate determination of the carbonation front.

A carbonation depth check was also conducted in two places on the tank's edge. A phenolphthalein indicator solution was needed for the examination. For the measurement, the concrete cover had to be chiselled at designated locations to obtain a surface that had not yet been exposed to air, as the surface of the concrete began to carbonate from the carbon dioxide in the atmosphere.



Figure 4: Concrete strength measurement on the tank edge



Figure 5: Due to the porosity of the concrete and the looseness of the concrete cover, carbonation is significant, and the concrete is rusty in several places

Figure 5 shows that carbonation has reached the steel reinforcements on the fractured surface, and gaps and larger pores have also formed in the concrete. As a result, there was a hairline crack between the examined piece and the fractured surface, allowing the carbon dioxide content of the air to cause carbonation over a significant area. Where the porosity of the concrete was low and hermetically continuous with the concrete edge, the solution turned purple, indicating that the pH value was greater than 9.

There are well-established limiting values and standards for the chemical concentration of chloride ions in concrete, and chloride ions are monitored closely because they are a primary cause of corrosion of steel reinforcement—unlike sulfate ions, which have different mechanisms and risk profiles.

Chloride ions are aggressively involved in the breakdown of the passive protective film on steel. Once the chloride concentration at the steel surface exceeds a threshold, it can initiate pitting and rapid corrosion—even if the concrete remains alkaline. On the other hand, sulfate ions can cause concrete deterioration mainly through chemical attack on the cement paste (sulfate attack), leading to expansion and cracking, not direct steel corrosion. While sulfate testing is important in some scenarios (e.g., in sulfate-rich soils), it is not the main indicator for reinforcing steel corrosion risk and thus not universally monitored like chloride.

A chloride ion content test of the concrete was conducted in a laboratory, for which drill dust samples were taken from the upper edge of the structure. The measurement was performed based on the Mohr method [14], guided by the principle that chlorides react with silver ions, and in the presence of chromate ions, an insoluble precipitate will form. The tested concrete surface has a pH value of 10.5, which, although above the critical limit of 9.0 for corrosion, does not provide protection for the reinforcing bars.



Figure 6: The measured drill dust sample homogenized with distilled water

Based on the result, it can be determined that 5 g of concrete dust contains 0,0032 g of chloride ions, which is 0,064% by weight. This complies with the regulations that the chloride ion in the cement content by mass percentage must not exceed the 0,10 m/m% allowed for reinforced concrete structures according to the standard (MSZ 4798:2016/1M 2017), although the chloride content generally rarely exceeds the required limit. The results of the measurements are presented in Table 1.

Table 1: Measurement results

Parameter	Result	Details
Testing Method	Mohr Method	Chlorides react with silver ions, forming an insoluble precipitate with chromate ions.
Concrete surface pH	10,5	Above the critical corrosion limit of 9.
Chloride Ion Content	0,0032 g/5g	Equating to 0,064% by weight.

Understanding the evolution of concrete standards is essential for combating the pervasive issue of chloride-induced corrosion, which threatens the structural integrity and longevity of concrete constructions. Over the years, advancements in materials science and engineering have led to significant changes in concrete specifications and construction practices. These changes are motivated by the need to enhance durability and improve resistance to chloride penetration, ensuring that structures can withstand harsh environmental conditions while meeting growing demands for sustainability and safety.

Therefore, the standards used during the construction of the structure were compared with the ones currently valid (Table 2) to see what changes have occurred over the years. This was necessary because in the 1960s, old concrete and cement labeling was used, and by researching these, it could be determined what the current concrete mix composition could be interpreted as. On the one hand, at that time, only concrete of exposure class XA3 (with regard to corrosive environments) could be produced, and on the other hand, the concrete cover was 22 mm instead of the current minimum of 45 mm. In terms of compressive strength, at least C35/45 class concrete should be used as structural, the concrete mix

should be made with a higher cement content but a lower water-cement ratio, achieving greater compressive strength. During construction, pozzolan and blast furnace slag additive-containing Portland cement were used in the concrete mix, whereas nowadays, sulfate-resistant blast furnace slag cement is the best for aggressive environments, as it is more corrosion-resistant.

Table 2: Comparison of concrete standards

MSZ 4720:1961	MSZ 4798:2016/3M.2021
XA3 environmental class	XA5(H) environmental class
Min. compressive strength C16/20	Min. compressive strength: C35/45
Cement content: 300 kg/m ³	Cement content: 330 kg/m ³
Water/cement ratio: 0.45	Water/cement ratio: 0,42
Concrete cover: 22 mm	Concrete cover: 45 mm
Homogeneous Portland cement CEM I 42.5	Cement to be used according to
and special Portland cement CEM II 42.5 (C	environmental class: CEM III/B 32.5 N-SR
500P and C 500S)	

4 RESULT ANALYSIS

Relying on the measured hardness from the nondestructive tests, the estimated compressive strength of the tested concrete was 25 N/mm², corresponding to C25/30 concrete quality. However, this estimation should be approached with caution due to the limited number of testing locations, which may not provide a comprehensive assessment of the concrete's overall condition. Consequently, it cannot definitively be stated that the compressive strength has increased compared to the original, as there is no certainty about the current compressive strength or the actual strength of the concrete when it was originally placed. Despite these limitations, the condition of the structure is considered satisfactory based on several key findings.

The chloride content was found to be below the acceptable limit, suggesting that the concrete has not been significantly compromised by chloride-induced corrosion, which is a common cause of structural degradation in reinforced concrete. Furthermore, although carbonation had penetrated to a depth of 3-4 cm at the surface, reaching the reinforcing bars, the overall structural integrity remains intact. This conclusion is supported by visual inspections, which confirmed that, while some areas of concrete cover had deteriorated, the majority of the structure remains robust.

In specific areas where the concrete cover had either completely fallen off or decreased, the concrete became porous and exhibited a lower pH value, leading to localized steel corrosion. These observations indicate that while there are some concerns, they are not widespread enough to undermine the overall structural health. Such issues can be effectively managed with appropriate maintenance measures, including the application of protective coatings and regular monitoring to prevent further deterioration.

Overall, the combination of these findings supports the conclusion that the structure is in a satisfactory state. With continued monitoring and targeted interventions, the structure

can maintain its functionality and service life. These interventions can include routine inspections and timely repairs to address the identified areas of concern.

During the course of this research, no measurements of wastewater quality were conducted, resulting in a lack of information on how the chemical composition of the wastewater might have influenced the corrosion process. Understanding the interaction between wastewater constituents and concrete is critical, as factors such as pH, chloride concentration, and sulfate levels can significantly accelerate corrosion. This gap in data highlights the importance of comprehensive monitoring, as it could significantly impact maintenance strategies and the design of future protective measures. By incorporating wastewater quality assessments into future research and maintenance protocols, a more holistic understanding of the factors affecting structural longevity can be achieved, allowing for more effective interventions and enhanced durability of the structure.

To summarize, in the primary settling tank, several types of corrosion have been detected, each contributing to the overall degradation of the structure. The most prominent form is chloride-induced corrosion, where the ingress of chloride ions, albeit below critical limits, poses a risk to the steel reinforcements. Carbonation-induced corrosion is also present, evidenced by the penetration of carbonation to a depth of 3-4 cm, which has reached the reinforcing steel in some areas. This type of corrosion is exacerbated by a drop in pH, leading to the breakdown of the protective alkaline layer around the steel bars. Additionally, localized corrosion is observed in areas where the concrete has become porous or where the cover has deteriorated, further exposing the steel to corrosive elements.

To comprehensively assess the level of damage to the concrete tank, additional tests should be considered. Core sampling and petrographic analysis can provide detailed insights into the internal condition of the concrete, including the extent of microcracking and aggregate quality. Electrochemical tests, such as half-cell potential measurements, can help evaluate the likelihood of corrosion activity in the reinforcement. Additionally, advanced imaging techniques like GPR or X-ray tomography could be employed to detect voids and assess the uniformity of the concrete structure. Implementing these tests would allow for a more thorough understanding of the tank's condition, enabling targeted maintenance strategies to be developed and enhancing the overall durability of the structure.

5 CONCLUSION

The presented research aimed to use tests to infer the condition of the primary settling tank's concrete structure, to understand what deterioration processes have occurred over the past 60 years, and to determine whether the concrete mix was appropriately chosen at the time of construction. Naturally, in the 1960s, construction standards were different, and much stricter regulations have been established since then, so it was expected that the guality of the concrete mix would fall short of what is currently considered adequate.

To understand the processes, the corrosive effects of wastewater and what causes these processes were examined. This highlighted the importance of selecting corrosion-resistant concrete and coatings. If a structure is to be built in a wastewater environment in the future, efforts should be made to choose a concrete mix with a low water/cement ratio and replace Portland cement with more sulfate-resistant blast furnace slag cement.

In conclusion, while the research provided valuable insights into the condition and maintenance needs of the concrete structure, the absence of wastewater quality measurements leaves a critical gap in understanding the full scope of environmental impacts on corrosion. Future studies should prioritize the integration of comprehensive wastewater analysis to capture data on pH levels, chloride, and sulfate concentrations, among other factors. This approach would allow for a more detailed assessment of how these variables contribute to corrosion processes, leading to more targeted and effective mitigation strategies. By addressing these gaps, future research can refine maintenance practices and inform the development of robust design standards for structures exposed to aggressive wastewater environments.

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