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Corrosion prediction using the weight loss model in the sewer pipes made from sulfur and cement concretes and Response Surface Methodology (RSM)



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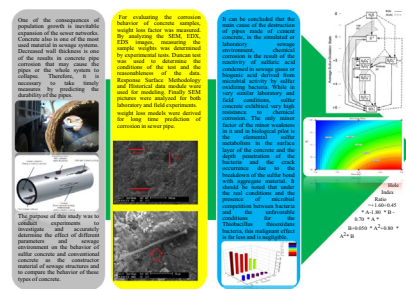
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HIGHLIGHTS

- Corrosion of cement and sulfur concrete surface was investigated in a sewage system.
- Corrosion prediction based on weight loss model were derived by RSM.
- Field experiments were done for evaluating the laboratory data.
- Sulfur concrete had more resistance to bio-chemical corrosion than cement concrete.

GRAPHICAL ABSTRACT



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ABSTRACT

Corrosion of concrete sewer pipes is one of the most serious problems in sewerage works today. This paper describes a new procedure for testing two types of concrete, namely Cement Concrete (CC) and Sulfur Concrete (SC), under the severe chemical and biological conditions. To this aim, two kinds of experiments were performed: 1) in situ experiments on sewer concrete pipes; and 2) in vitro experiments on cubic specimens. *Thiobacillus thiooxidans* bacterium was selected for performing in vitro biological experiments. Weight loss measurement of samples was used as an indicator for corrosion behavior. The results showed that SC was considerably resistant to severe acid attacks (chemical corrosion) in comparison with CC but less resistant to microbial corrosion attacks.

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1. Introduction

Concrete sewer pipe corrosion is a serious problem in sewage works today. The construction and replacement of such pipes are

very expensive and their failure can extensively cause underground water pollution. Today, great projects of sewer collection systems are in progress in the different provinces of Iran. More than 10,000 km of sewer pipes have been already established and further 50,000 km of them have been estimated to be added to this network up to the end of the development program. BSA attacks to CS pipes besides the activities of treatment plants and wastewater collection systems can result in severe damages as described to have occurred in Germany [12,13], Japan (Mori et al., 1991, [10]),

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and the United States by Islander [15] and Padival [16], as well as some other places in the world. Corrosive attacks to CS pipes can develop up to several millimeters per year. It seems that 20% of the total damage to CS structures is caused by sulfate and sulfuric acid attacks [17]. Many efforts have been made to understand the rapid corrosive effects of *Thiobacillus* population on concrete surfaces since its discovery by Parker in 1945 [11,2]. In the biological tests conducted in the present study, the corrosive impact was demonstrated to be largely induced by the metabolic effects of the studied microorganism. In some studies, the corrosion triggered by biogenic sulfuric acid has been mainly investigated by the direct use of sulfuric acid as the corrosive agent. They have shown that concrete does not always provide a good resistance to BSA even though it indicates a certain resistance to sulfuric acid [13]. Some research groups have attempted to examine both the chemical (pure sulfuric acid attack) and bacterial processes of corrosion via simulation.

Chemical and bacterial activities inside sewer pipes can lead to bacterial sulfuric acid formation via the generation of a sulfur cycle. A slow sewage flow or long retention time would result in the reduction of sulfur compounds to H_2S under the activities of sulfate-reducing bacteria like *Desulfovibrio* under anaerobic conditions. H_2S may escape into the sewer atmosphere under the effects of pH decline and turbulence. It can be then transformed into sulfuric acid after its sorption into the concrete or onto the pipeline surface bio-film above the water line under aerobic conditions. In addition, it may turn into elemental sulfur by reacting with oxygen and subsequently precipitate on the sewer wall. Sulfur can provide a substrate for many *thiobacilli*, including *Thiobacillus thiooxidans*, *Thiobacillus neapolitanus*, and *Thiobacillus intermedius*. Concrete deterioration may be caused by sulfur metabolism into sulfuric acid when induced by these bacteria.

Sulfide generation in new collection systems can be suppressed by the proper designing of pipes. Sewer pipes can be ventilated and force mains may be aerated to reduce anaerobic sulfide production, while deposit scouring can be exerted to maintain the aerobic conditions of sewage by keeping high flow velocities. Alternatively, resistant materials can be employed to produce plastic lined pipes, pipes containing alkaline aggregates, and sulfur concrete pipes, which are resistant to acid attacks and consequent corrosions.

This paper aimed at examining the potential resistance of SC and CC to corrosion under severe chemical and biological conditions and based on a new procedure for a simulated sewer system. So far, some numeric models have been suggested for investigating and controlling the relevant corrosion process. Based on the information required for the prediction models, multiple control efforts must be made to overcome the difficulties of remediation and high costs of replacement in some systems.

2. Materials and methods

Two kinds of experiments were performed in this investigation: 1) in situ experiments on SC pipes; and 2) in vitro experiments on cubic specimens. This decision was made for studying the chemical and microbial corrosion processes of CC and SC in their worst cases, as well as under controlled conditions in the laboratory scale, while observing natural microbial corrosion in a real situation within a sewer treatment plant.

2.1. Concrete samples

For the exposure tests, CC samples were prepared by mixing Portland cement (I), standard sand, and water at a weight ratio of 2:6:1.

SC specimens were produced through a mix design method incorporating standard sand (70%), elemental sulfur (25%), and SMZ additive (5%) according to ACI 548.2R-93 (ACI, 1993).

Solid aggregates were preheated at 120–160 °C and then mixed with melted sulfur and sulfur cement as an additive in a mixer at 120–140 °C until a substantially homogeneous mixture was achieved.

The produced mixture was subsequently cast and shaped into a pipe mold with a length, diameter, and thickness of 100, 15, and 3 cm and cubic mold of 5 × 5 × 5 cm, respectively. Fig. 1 shows the specimens, as well as the casting procedure.

After producing the two kinds of concrete samples, the pipe specimens were installed in the sewer entrance canal of Shahid Mahallati Wastewater Treatment Plant, which had been provided with online monitoring systems for measuring sewer quality parameters, such as pH, temperature, BOD, COD, and TDS. The average amount of these parameters were recorded for further corrosion behavior of samples. Canal dimension was 1.5 × 2 m² with hydraulic slope of 1% and flow rate of 40 m³/hr. Each pipe was removed every 3 months so as to measure the corrosion reactions of the materials. The experiments were continued up to 12 months, during which the related data were obtained.

Furthermore, a series of laboratory experiments were conducted with cubic samples, which were placed in a biological growth chamber consisting of a glass box (40 × 20 × 10 cm) accommodating 6 CC and 6 SC cubic samples (5 × 5 × 5 cm). Then, they were placed into an incubator. Each month, two specimens were removed for the test analyses.

Sewage has a large variety of bacteria, some of which can be considered as corrosion operators since inducing material or biogenic acid degradations. Sulfur is a substrate for many *thiobacilli*, such as *Thiobacillus thiooxidans*, *Thiobacillus neapolitanus*, and *Thiobacillus intermedius* [8], which metabolize it into sulfuric acid.



Fig. 1. Specimens and the casting procedure.

Although sulfuric acid does not have the same severe corrosion impacts on SC as on CC, its metabolism procedure must be studied in the former case as well.

Since the population and presence probability of *Thiobacillus thiooxidans* microorganism in the domestic sewers were more than any other species, this bacterium was selected for laboratory experiments. The bacterium seed was obtained from the microorganism bank of Iranian Biological Resource Center (IBRC). The culture medium was made for bacterial propagation based on IBRC instructions. The bacteria were cultured in 200-mL flasks containing a solution of mineral salts (100 mL) supplemented with sulfur as the energy source [4]. Microscope observations were made to ensure adaptation of the bacteria to the culture medium and propagation process. The flasks were incubated on a rotary shaker at 28 ± 2 °C for 2 weeks. The preferred pH growth range for this bacterium was about 0.5–3. Fig. 2 depicts the preparation steps.

2.2. Chemical and biological experiments

Short-term chemical experiments were carried out over a period of 30 days so as to compare the degradation processes after using biogenically and chemically produced sulfuric acid. Therefore, the concrete samples were exposed to sulfuric acid solutions with the constant pH values of 1.0 and 2.0 using an autotitrator. For each set-up (pH 1.0 and 2.0), two concrete samples were analyzed. The pH of the acid solution was determined for each sample position and re-adjusted every day by titrating 0.5 M H_2SO_4 and 0.1 M H_2SO_4 so as to maintain the pH values of 1.0 and 2.0, respectively. Acid consumptions were recorded continuously. Due to the limited capacity of the beaker, 30 mL of the corrosion solution was removed at certain intervals for further analysis [6].

During the biological experiments and after exposing both concretes to the concentrated bacterial culture, pH values were measured for recognizing the bacteria activity and exploring their concentration via the plate-counting technique. Also, a nutrient solution (designed to support the bio-reactor and culture medium) would be added if necessary. The reactor was designed with an adequate open surface to be aerated properly by maintaining sufficient oxygen during the incubation. A fresh sterile growth medium was added every 2 weeks to provide severe microbial corrosion conditions [3]. Fig. 3 exhibits the experiment conditions.

2.3. Online monitoring system

The sewage quality monitoring systems of Shahid Mahallati Wastewater Treatment Plant were integrated with multichannel analyzers capable of directly measuring pH, TSS, and flow parameters with the help of optical sensors and ultrasonic flow meters connected to 999 V Submersible Data Loggers (SDLs). The obtained data were used for further analysis during the experiment period.



Fig. 3. Biological experiments.

2.4. Response surface method (RSM)

In this study, the regression tool employed in the Design-Expert⁷® software was intended to provide the Response Surface Method (RSM), which was then applied to the historical data. Therefore, the measured data obtained from the following different tests were imported into the software to perform the statistical analyses.

2.5. Sample tests

The most important factors describing concrete corrosion can be ordered as chemical changes to a concrete surface, mass loss, conversion of mechanical properties, and porosity. All these factors were measured and the results were used for the statistical analyses.

2.5.1. Determination of element compounds in concrete samples

To further discuss the bacterial effects on the concrete corrosion, it was necessary to know the distributions of elements on the concrete surface. For this purpose, X-Ray Fluorescence (XRF) and X-Ray Diffraction (XRD) methods were utilized. XRF analysis determines the chemistry of a sample by measuring the fluorescence (or secondary) X-ray emitted from that sample after being excited by a primary X-ray source. XRD is a versatile and non-destructive analytical technique that reveals detailed structural and chemical information about the crystallography of materials. The elemental composition of a sample is determined via XRF analysis, but it does not provide any information concerning how the different elements are combined together. After analyzing the concrete samples through XRF and XRD methods, more than 90% of sulfur in the SC was not observed in a specific compound, but rather as elemental sulfur.



Fig. 2. Culture medium and microscope inspection of bacteria.

2.5.2. Mass loss determination

One of the main analyses for quantitatively describing concrete corrosion is the determination of a sample mass loss. For this purpose, the weights of the untreated samples were measured at the beginning of the experiments using a digital scale with an accuracy of 0.1 mg (Huber et al., 2017). After conducting the experiments, the samples were removed from the reactors and then rinsed to remove the residual solutions. Next, they were dried at 40 °C until weight constancy. Afterwards, they were weighed out again and their weight differences were documented.

2.5.3. Determination of the mechanical properties of the concrete samples

Compressive strength determination was performed in accordance with ASTM C109/C109M (ASTM 2016). The cubes of $5 \times 5 \times 5$ cm were treated in the reactor at different settling times and then removed from the pilot. A compression machine (Forney, Zelienople, Pennsylvania) was utilized to perform the test. The cubes were loaded at $P = 60\text{--}180$ KN until the maximum load was reached. Out of this test, the peak stress (f_c) was calculated by dividing the ultimate load at peak (P) by the average initial cross-sectional area (A) using the following equation:

$$f_c = \frac{P}{A}$$

2.5.4. Inductively coupled Plasma-Optical emission spectrometry (ICP-OES)

After determining the extent of concrete corrosion, the reactor solutions containing the corroded elements were analyzed through ICP-OES. This method can help to: 1) characterize changes in a concrete composition; and 2) identify the corrosion products and elements leaching out of the samples. Element precipitation in the solution reactor is an indicator for the concrete corrosion procedure. In this research, an ICP-OES instrument, model VISTA-PRO, a CCD detector, and a concentric nebulizer were selected at the plasma flow of 15 L/min and feed rate of 1.4 mL/min.

2.5.5. Scanning electron microscopy (SEM), SEM-MAP, and energy dispersive X-ray (EDX) spectroscopy

SEM, SEM-MAP, and EDX analyses provide alternative approaches to the corrosion detection of concrete surfaces and microbial effects on the Hole Index Ratio (HIR) by obtaining further information on their microstructures and element distributions. To this aim, the surfaces of the specimens were coated with a thin layer of gold to avoid charging. A scanning electron microscope (VEGA3-TESCAN, Czech Republic) was employed at an accelerating voltage of 20 kV. Element distributions over the displayed areas were detected by using a MAP detector (RMRC RONTEC, Germany).

3. Results and discussion

3.1. Microbial activity and biogenic acid effect

Aerobic microbial oxidation of hydrogen sulfide into biogenic sulfuric acid and sulfur degradation process are complex and may occur in several steps. A simplified sketch of the trend towards several oxidized forms of sulfur is illustrated in Fig. 4.

Elemental sulfur can be produced and used in the reactions of treated SC surfaces at low pH values. This kind of reaction rapidly occurs through thiosulfate oxidation below a pH value of 4 [5]. The crowns of corroded pipes often display yellow deposits. Elemental sulfur is apparently utilized by some microorganism species as the preferred or even the only sulfur substrate. It was found by Hutchinson et al. [7] to provide *Thiobacillus thiooxidans* growth at lower pH values compared to any other substrates. This type of

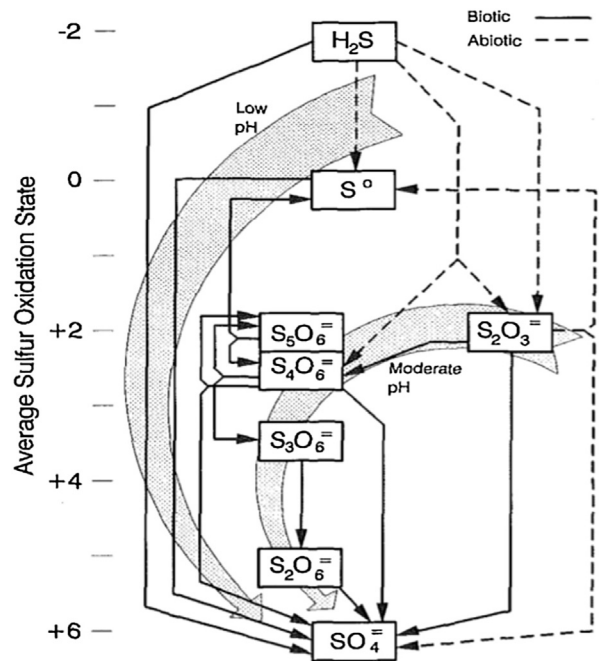


Fig. 4. Sulfide oxidation pathways.

microbial activity was observed to reach its maximum level by providing the worst case while keeping pH at low ranges under laboratory conditions. Sulfide oxidation results in 8 electrons (23.8 kcal/mole per sulfide equivalent). Carbohydrate oxidation yields 4 electrons (29.9 kcal/mole per carbon equivalent) [14]. Thus, sulfide input energy is equal to 2.6×10^4 mol of carbohydrate/m²/hr. Consequently, the organics excreted by acid-producing bacteria can be degraded as a mutualistic relationship is established between them and acidophilic heterotrophs required for their continued rapid growth. In this research, *Thiobacillus thiooxidans* produced BSA, which could affect CC but not SC corrosion though sulfur metabolism in the latter case was in need of further studies.

It is more likely that acid production by this type of organism becomes self-inhibitory as a result of pH limitation. This probability was supported by the laboratory observations on the solution pH values in the reactor, while *Thiobacillus thiooxidans* growth could be significantly slowed down in the natural sewer canals due to the presence of a higher pH range of 5–8. It could be concluded that elemental sulfur oxidation was the most significant cause of SC microbial corrosion in case of available preferred conditions.

3.2. Visual inspection of samples

A comparison between the treated and untreated specimens in a laboratory reactor and a sewer canal can elaborate the differences in the observed degradations. In this study, almost no degradations were observed in the field samples, while a thin layer of salt crystals was detected on the concrete surfaces in the laboratory samples. The concentrations of this layer demonstrated a seemingly higher HIR factor for the treated compared to the untreated samples.

3.3. Analysis of the test results

3.3.1. PH variation analysis

The secondary pH values of both the chemical and bacterial treatments changed during the experiment procedure. This

variation in the chemical reactors was caused by the dissolution of surface elements in the acid solvent with the media renewal after titrating 0.5 M H₂SO₄ and 0.1 M H₂SO₄ to continuously maintain pH 1.0 and pH 2.0. Fig. 5 shows this variation for the two concrete types and experiment times.

The concrete body of a CC shows a moderately porous mixture of mineral aggregates and inorganic precipitates. Being highly alkaline, it can slowly dissolve in water to provide a pH range of 10–11 in the solution. The structural integrity of the material composition can be destroyed by the initial reaction of a strong acid with lime and then with calcium oxides.

In this investigation, acid solution did not have a significant effect on the SC corrosion; yet, the slight increase in the secondary pH was the result of less significant occurrence of surface element separation in the SC compared to the CC samples.

In the biological treatment, the secondary pH was directly affected by the microorganism activity and leaching elements. In the early stages, the CC surface environment was highly alkaline and displayed a strong and rapidly expressed buffer capacity. Upon providing the suitable condition for adding the bacteria solution at pH 2, acid production occurred so that pH began to decline after several days. By decreasing the pH amount and increasing the bacterial activity, the concrete surface elements leached to the solution, which resulted in the pH increase to 1.8 and accrued

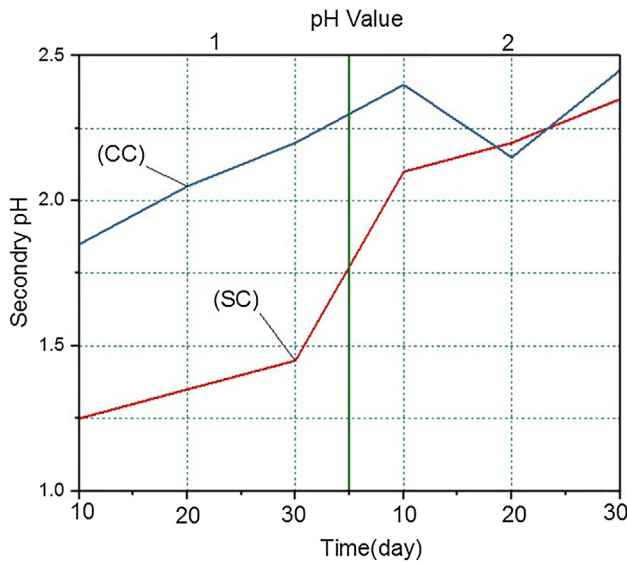


Fig. 5. Secondary pH variation in the chemical reactor.

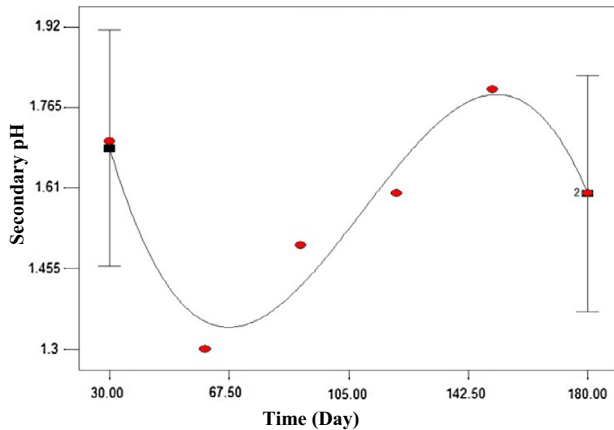


Fig. 6. Secondary pH variation in the biological reactor.

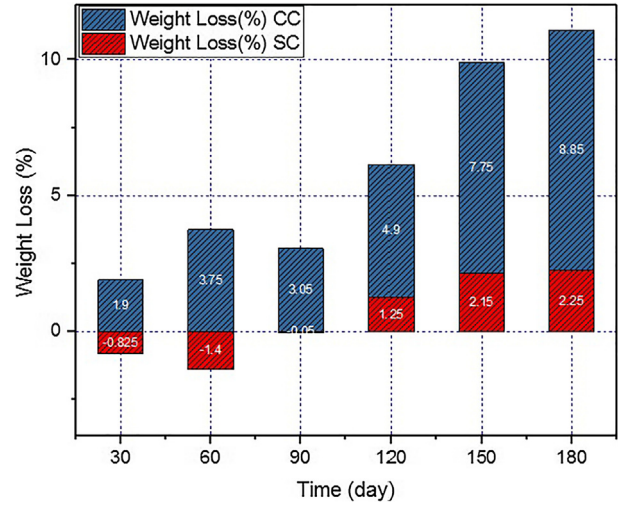
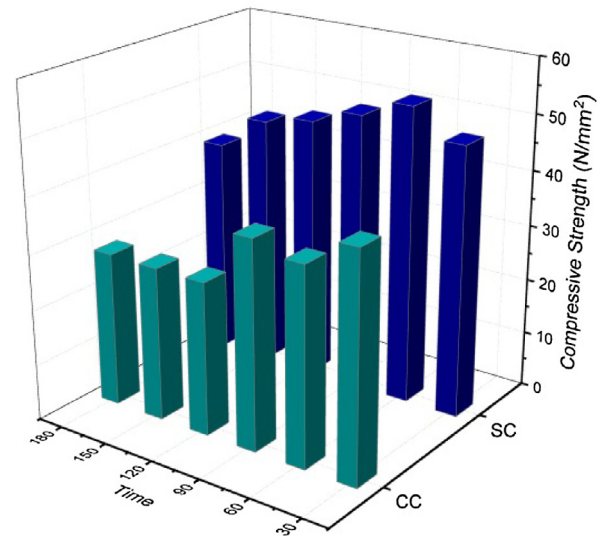
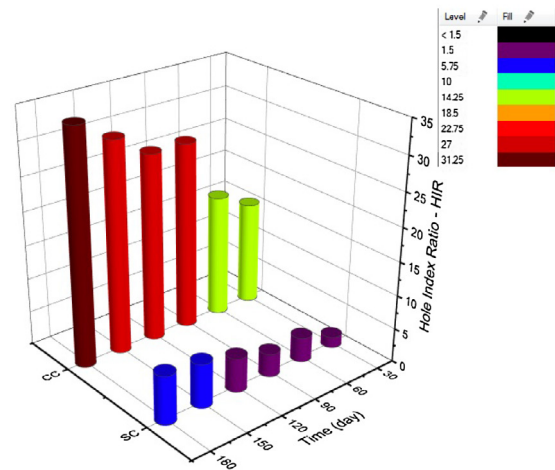


Fig. 7. Weight loss of the samples in the biologic reactor.



a-Compressive strengths of the samples



b-HIR factor during the exposure time

Fig. 8. Changes in the compressive strength and HIR factor.

corrosion in the CC samples. This cycle was continued by the biogenic acid production of *Thiobacillus thiooxidans*. Fig. 6 represents the secondary pH variation in the biologic reactor.

3.3.2 Weight loss

Fig. 7 depicts the mass of a treated sample relative to its mass amount as a function of the exposure time before the test. The samples showing the most extreme behaviors in terms of mass loss provided better conditions for the microbial activity at a longer time compared to the others. The comparable corrosion conditions within the parallel set-up provided more confidence. The slight increase in weight at the beginning of the experiment was due to the salt crystal sedimentation and the concrete matrix densification.

3.3.3. Compressive test with HIR factor

The time-dependent changes in the compressive strength are exhibited in Fig. 8. The decreases in the compressive strength were believed to be largely attributable to cracking within the specimens [1]. Another contributor to the reduction of compressive strength was HIR factor enhancement. In fact, both of these 2 factors resulted in the tension concentration and crack expansion. On this basis, the specimens were allowed for the continued penetration of the bacteria colony and enhancement of the damaging cycle. Compressive strength changes in these experiments were remarkably related to HIR factor. The 3D microbial environment around the concrete surface was the result of its being frequently coated with a porous layer of the corrosion products. The compounds and organisms were distributed throughout the whole volume extending beneath the exposed surface. Sulfide dissolution in water and diffusion into the concrete occurred at the surface both in the air and water phases. The deep penetration of sulfide was provided by the sink of microbial oxidation. The inward and subsequent outward diffusion of sulfuric acid through the underlying concrete led to the neutralization of alkalinity. Even a small fraction of the pores of a new concrete of low permeability could provide an adequately large space for the microorganism penetration as the small interconnected gel voids would allow the dissolved compounds to be transferred via diffusion. The concrete porosity

was enhanced by its quick chemical gradients. Calcium hydroxide dissolution caused by acid resulted in the gradual enlargement of the pores and slowly increased penetration of the microorganisms into the concrete during the corrosion process.

A partial concrete destruction of up to the depth of 6 cm in the Hamburg sewer system was observed by Sand and Bock [2].

3.3.4. ICP test of the reactor solution

As mentioned in the SC corrosion process, sulfur polymer deterioration can lead to the precipitation of some aggregate elements in the solution reactor, which is a good indicator for the process analysis and element distribution on the concrete surface. As shown in Fig. 9, the concentrations of sulfur, calcium, and siliceous elements in the solution are enhancing by increasing the exposure time. The concrete acid corrosion results in the accumulation of a white precipitate layer on the surface. Precipitations of the dissolved cement ions as the products of corrosion include a combination of sand and unreacted cement particles, as well as a variety of sulfates.

3.3.5. SEM results

The SEM results in Fig. 10a–c and 11a–c indicate the corrosion effects in different experiments periods on samples surface. It can be observed that the majority of concrete matrixes are composed of sulfur or cement coated materials (aggregates and fillers). Considering the result of XRD about element distribution on concrete surface before and after the experiments, more details are provided. SC was resistant to mineral and biogenic acids and high-salt environments [9], while it had low resistance to severe microbial attacks.

Moreover, the SEM analysis revealed the presence of the bacteria in the concrete holes (Fig. 12). MAP analysis of the concentrations of the elements in these locations (Fig. 13) clearly depicted sulfur degradation and aggregate outcast. By adjusting these results to those of the ICP analysis, we were able to clearly justify the microbial corrosion in the SC and chemical corrosion in the CC samples.

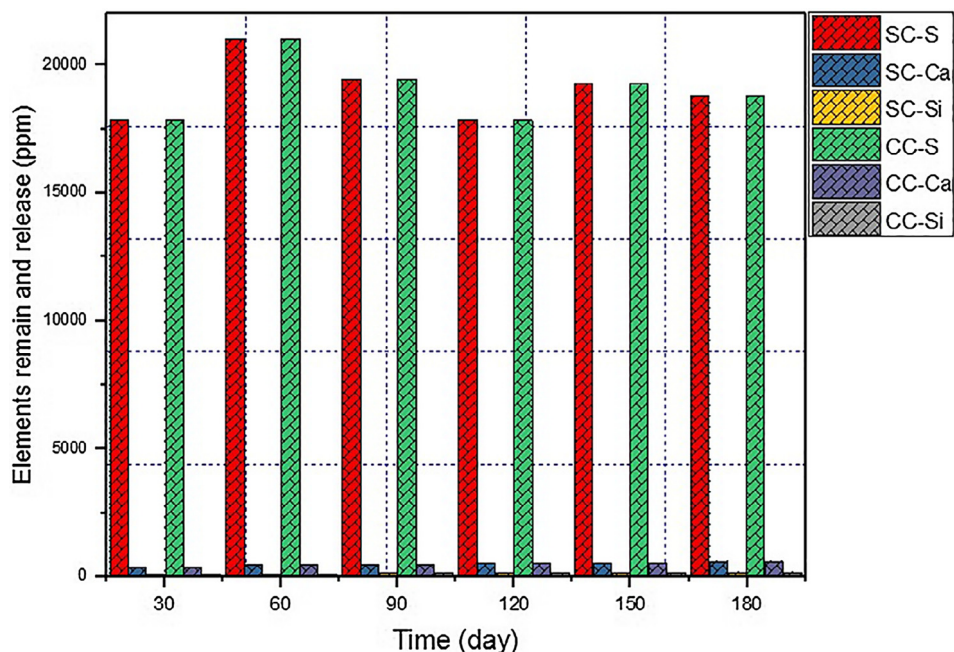


Fig. 9. ICP detection of the leached elements.

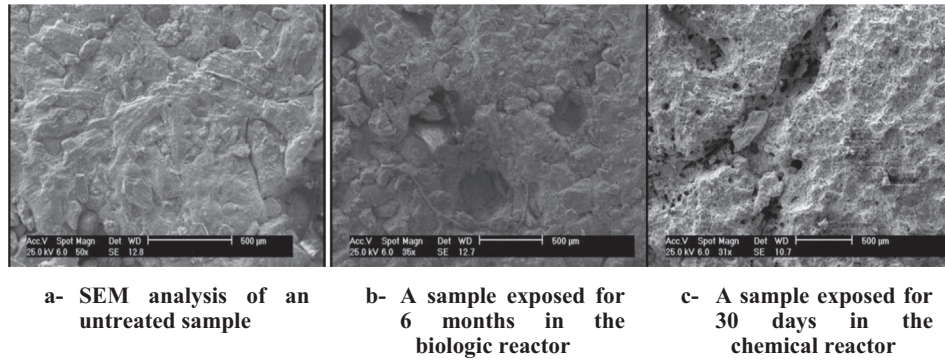


Fig. 10. SEM results for CC samples.

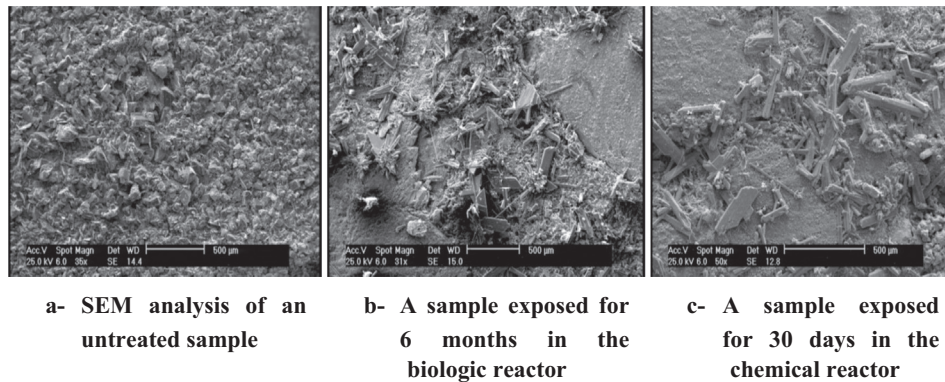


Fig. 11. SEM results for SC samples.

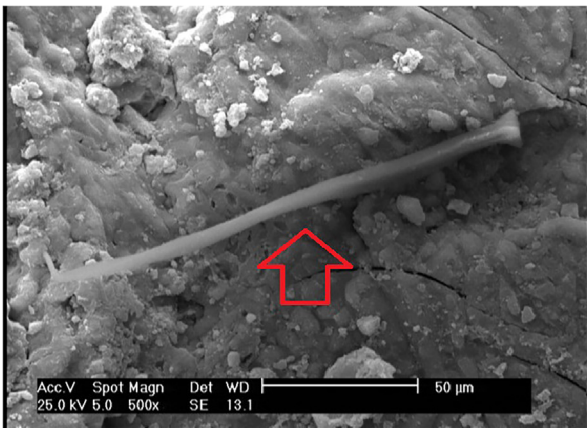


Fig. 12. Bacterial detection via SEM analysis.

3.3.6. Statistical analysis

The statistical analyses were performed according to the results obtained from the chemical and bacterial experiments so as to explain the differences between the two concrete types. The comparison results for the chemical and bacterial experiments are shown in Tables 1 and 2, respectively. In this research, Duncan test was used to determine the conditions of the test and the reasonableness of the data.

A method widely used to compare all pairs of averages is the Duncan multi-domain test (1955). To run this test, the average of the treatments is incrementally ordered and the standard error of each mean is determined as $S_{\bar{Y}_i} = \sqrt{MSE/n}$. For samples with different volumes, n is replaced by the mean consonant {ni} i.e. $n_h = \frac{a}{\sum_{i=1}^a (y/n_i)}$, then, with the definition $R_p = r_a(p, f) S_{\bar{Y}_i}$, $p = 2, 3, \dots, a$, the comparison is made between the averages. The values $r_a(p, f)$ at the significance level α and f degrees of freedom

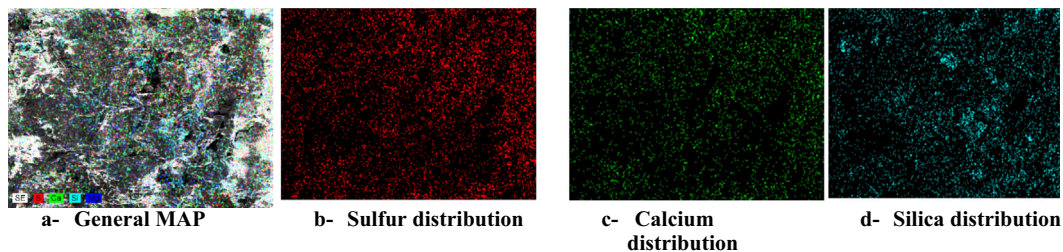


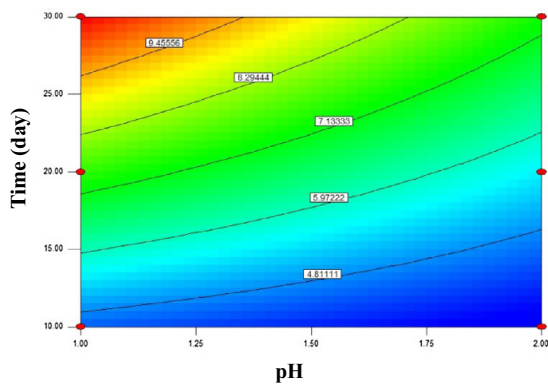
Fig. 13. MAP Analyses of S, Ca, and Si.

Table 1
Statistical comparisons for the chemical experiments.

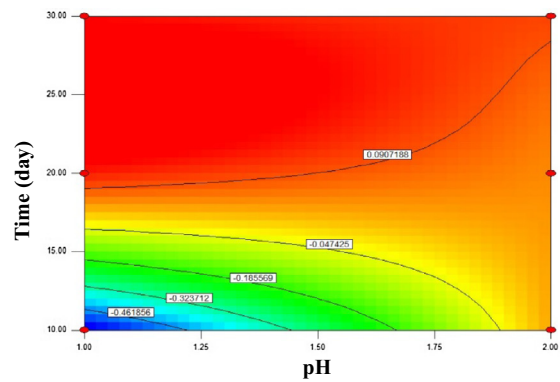
Source	DF	MS							
		Weight Loss (%)	Compressive Strength (N/mm ²)	Water Absorption (%)	S Remain (ppm)	Ca Release (ppm)	Si Release (ppm)	Secondary pH	Hole Index Ratio (HIR)
Conc	1	244.2 **	2357.9**	103.6 **	618,084,251 **	470792.0 **	74262.7**	0.96 **	1628.5 **
pH	1	5.5 **	311.5 **	0.03 ns	440,917 **	4914.0 **	43.4*	2.0417 **	21.0 **
day	2	14.8 **	31.3 **	0.9 **	1,594,623 **	1475.2 **	943.0 **	0.1029 **	41.5 **
Conc*pH	1	7.0 **	25.0 **	0.5 **	4,833,935 **	3496.9 **	72.7 **	0.4817 **	1.6 ns
Conc*day	2	10.0 **	9.4 **	0.7 **	4,583,230 **	1193.0 **	428.9 **	0.0088 ns	19.9**
pH*day	2	1.1 **	25.3 **	0.1 ns	178,857 **	1.6 ns	189.4 **	0.0254 ns	2.4 *
Concph*pH*day	2	0.4 **	2.5 ns	0.07 ns	582,677 **	10.6 ns	18.7 ns	0.0279 *	1.3 ns
Error	12	0.0	1.0	0.04	1345	9.1	5.0	0.0067	0.5
CV (%)	7.2	3.09	6.1	0.40	0.9	1.6	4.12	6.8	

Table 2
Statistical comparisons for the biological experiments.

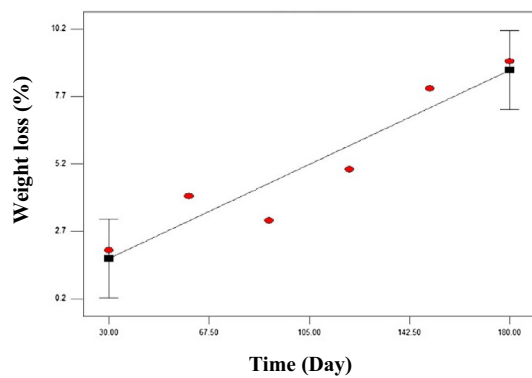
Source	DF	MS							
		Weight Loss (%)	Compressive Strength (N/mm ²)	Water Absorption (%)	S Remain (ppm)	Ca Release (ppm)	Si Release (ppm)	Secondary pH	Hole Index Ratio (HIR)
Conc	1	119.9 **	1254.9 **	120.6 **	0 ns	0 **	0 ns	0 ns	2707.2 **
day	5	17.3 **	93.7**	1.1 **	5733489.7 **	24111.9 **	7072.5 **	0.1 **	87.8 **
Conc*day	5	2.3**	20.6 **	1.1 **	0 ns	0 **	0 ns	0 ns	32.4 **
Error	12	0.0	0.6	0.2	5390.4	44.8	46.4	0.0	0.5
CV (%)	7.7	2.0	11.7	0.4	1.3	4.4	0.0	4.9	



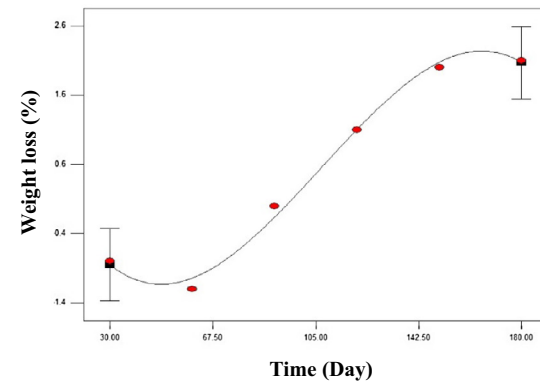
a- CC in the chemical reactor



b- SC in the chemical reactor



c- CC in the biological reactor



d- SC in the biological reactor

Fig. 14. Weight loss comparison of the samples.

Table 3
The coded weight loss model.

	Weight loss models for CC	Weight loss models for SC
Chemical reactor	Weight loss = +6.53–1.03* A + 2.45* B–0.60 * A * B	Weight loss = +0.050 + 0.040* A–0.080* B–0.34* A * B + 0.010* A ² + 0.37* A ² * B
Biological reactor	Weight Loss = +5.18 + 3.49 * A	Weight loss = +0.47 + 3.24 * A + 0.15* A ² –1.78 * A ³

(equal to the degree of freedom of error) are obtained from the Duncan significant range table.

The test of difference observed between the mean values starts with the difference between the largest and the smallest mean which is compared with the minimum significant range of R_a . Then the test of difference observed between the largest and the second smallest mean is calculated and compared with R_{a-Y} , this procedure continues until all the $\frac{a(a-Y)}{7}$ average pairs are examined. If a observed difference is larger than the minimum relevant domain, the result is that the pair of problem averages have a significant difference.

According to the comparisons, it could be understood that the corrosion behaviors of the concretes based on the considered factors were significantly different. In the chemical experiments, concrete type, pH, and days of exposure resulted in significant differences in the weight loss factor, respectively. The greatest difference was related to the concrete type.

Also, in the biological experiments, the difference between the concrete types affecting the weight loss factor representing the main corrosion effect was highly significant in comparison with the experiment duration.

Still, further research is needed to justify the degrees of differences at least affecting one factor, such as weight loss. Fig. 14 shows changes in the weight loss in the chemical and biological experiments on the two concrete types by the use of Response Surface Method (RSM). The RSM technique and statistical analyses have been developed in combination and applied to model weight loss parameter. A central composite design (CCD) as the standard design of the RSM technique was used to evaluate the effects and interactions of related factors. As shown in Fig. 14a and b, weight loss factor, pH, and time have been less influenced by the SC compared to the CC reaction, while the amount of the first parameter has been much less affected by the former concrete. This comparison can demonstrate the fact that acid attack has no considerable effect on SC unlike CC.

In the biological experiments, CC displayed a fixed increasing rate in the weight loss (Fig. 14c), which was affected by the biogenic acid production and secondary pH alongside the bacterial activity, whereas the SC underwent a much less change of weight loss as depicted in Fig. 14d. Thus, SC was significantly different from CC. As depicted in the related graph, the weight loss process was stopped after about 5 months. This was the result of sulfur consumption by the relevant concrete surface coated with the bacteria. After the reduction of the available surface sulfur (as exhibited in Fig. 13b), the microbial corrosion process slowed down and the microorganism penetration became weak.

3.3.7. Corrosion model validation

Regarding the importance of weight loss in concrete corrosion, the weight loss models coded for the concretes are given in Table 3 based on the statistical analyses. “A” and “B” describe the time and pH parameters, respectively. These models can be good indicators of the corrosion procedure in the concretes treated by the sewage environment. As portrayed by the models, the SC weight loss is less affected by pH in comparison with the parameter of bacterial activity, while an increase in the CC weight loss can be obviously observed in the two experiments.

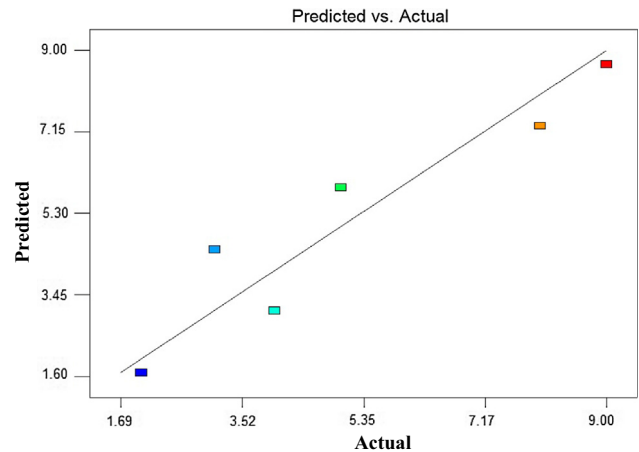


Fig. 15. The predicted vs. actual graph.

Table 4
Error analysis and Error bar.

	Concrete	Chemical Test	Bacterial Test
Mean	CC	6.326	5.033
	SC	–0.054	0.563
Std.Error	CC	0.704	0.754
	SC	0.083	0.428
Error bar	CC	1.380	1.455
	SC	0.163	0.826

In most cases, the values predicted by the mentioned models had a good correlation with the actual values as can be seen in Fig. 15.

The error analysis for each test according to concrete type is shown in Table 4. It can be concluded that bacterial test had more error in test performance according to its complex set up and CC had less error in both tests in comparison with SC. This can show that SC is more affected by biological process while CC is more impressed by chemical effects.

4. Conclusion

Corrosion test for construction and building materials especially for concrete has always been a concern. In most studies, cement concrete corrosion in acidic and alkaline environments has been focused. But in this study, in addition to evaluating the effects of chemical corrosion, biological corrosive effects on cement and sulfur concrete in wastewater condition were considered for the first time. SC corrosion factors can be better studied in the corrosive field and laboratory environments in a microstructure scale. In this investigation, SC was concluded to be significantly resistant to severe acid attacks as compared to CC, but less resistant to microbial corrosion attacks, especially by sulfur oxidizing bacteria. This condition in the sewer environment could be differently affected by some factors, including pH variations and limited microbial attacks by the competitions from other bacteria. Moreover, SC material was found to have properties superior to CC material in some

applications due to its long-term durability against deterioration and successful usability in severely aggressive environments like arid and semi-arid areas. Some of its other numerous advantages over CC include high strength, impermeability, resistance against acid and salt attacks, lack of being influenced by sulfuric acid or hydrogen sulfide generations, and being economical in its large-scale applications. Furthermore, utilization of the large amount of sulfur waste produced by the oil-refining plants in SCs can alleviate the significant environmental problems associated with its storage.

Conflict of interest

None.

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References

- [1] S. Asamoto, A. Ohtsuka, Y. Kuwahara, C. Miura, Study on effects of solar radiation and rain on shrinkage, shrinkage cracking and creep of concrete, *Cem. Concr. Res.* 41 (6) (2011) 590–601.
- [2] E. Bock, W. Sand, M. Meincke, B. Wolters, B. Ahlers, C. Meyer, F. Sameluck, Biologically induced corrosion of natural stones—strong contamination of monuments with nitrifying organisms. *Biodeterioration* 7 (pp. 436–440) (1988), Springer, Dordrecht.
- [3] L. Ding, W.J. Weiss, E.R. Blatchley III, Effects of Concrete Composition on Resistance to Microbially Induced Corrosion, *J. Environ. Eng.* 143 (6) (2017) 04017014.
- [4] J.D. Gu, T.E. Ford, N.S. Berke, R. Mitchell, Biodeterioration of concrete by the fungus *Fusarium*, *Int. Biodeterior. Biodegrad.* 41 (2) (1998) 101–109.
- [5] A.P. Harrison Jr, The acidophilic thiobacilli and other acidophilic bacteria that share their habitat, *Annual Rev. Microbiol.* 38 (1) (1984) 265–292.
- [6] B. Huber, H. Hilbig, J.E. Drewes, E. Müller, Evaluation of concrete corrosion after short-and long-term exposure to chemically and microbially generated sulfuric acid, *Cem. Concr. Res.* 94 (2017) 36–48.
- [7] M. Hutchinson, K.I. Johnstone, D. White, Taxonomy of the genus *Thiobacillus*: the outcome of numerical taxonomy applied to the group as a whole, *Microbiology* 57 (3) (1969) 397–410.
- [8] D.P. Kelly, J.K. Shergill, W.P. Lu, A.P. Wood, Oxidative metabolism of inorganic sulfur compounds by bacteria, *Antonie Van Leeuwenhoek* 71 (1–2) (1997) 95–107.
- [9] W.C. McBee, H.H. Weber, Sulfur polymer cement concrete. In Proceedings of the Twelfth Annual Department of Energy Low-level Waste Management Conference CONF-9008119 National Low-Level Waste Management Program, Idaho Natl. Engineering Lab., Idaho Falls, Idaho, 1990, August.
- [10] T. Mori, T. Nonaka, K. Tazaki, M. Koga, Y. Hikosaka, S. Noda, Interactions of nutrients, moisture and pH on microbial corrosion of concrete sewer pipes, *Water Res.* 26 (1) (1992) 29–37.
- [11] R.D. Pomeroy, J.D. Parkhurst, The forecasting of sulfide buildup rates in sewers, *Prog. Water Tech.* 9 (3) (1977) 621–628.
- [12] W. Sand, Microbial mechanisms of deterioration of inorganic substrates—a general mechanistic overview, *Int. Biodeterior. Biodegrad.* 40 (2–4) (1997) 183–190.
- [13] H. Schmidt, S. Langenfeld, R. Nass, A new corrosion protection coating system for pressure-cast aluminium automotive parts, *Mater. Des.* 18 (4–6) (1997) 309–313.
- [14] W. Stumm, B. Sulzberger, The cycling of iron in natural environments: considerations based on laboratory studies of heterogeneous redox processes, *Geochim. Cosmochim. Acta* 56 (8) (1992) 3233–3257.
- [15] Robert L. Islander et al., Microbial ecology of crown corrosion in sewers, *J. Environ. Eng.* 117 (6) (1991) 751–770.
- [16] Navnit A. Padival, William A. Kimbell, John A. Redner, Use of iron salts to control dissolved sulfide in trunk sewers, *J. Environ. Eng.* 121 (11) (1995) 824–829.
- [17] W. Kaempfer, M. Berndt, Estimation of service life of concrete pipes in sewer networks, *Durability build mat. Componen* 8 (1999) 36–45.