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The effect of various polymer-based coating types on the biological corrosion resistance of mortar

Tahir Gonen[1,2] and Tayfun Uygunoglu[3]

[1]Usak University, Engineering Faculty, Department of Civil Engineering. Atatürk Blv, 64000, Usak, Turkey.

[2]Kyrgyz Turkish Manas University, Vocational School. Dcall, 56 Mir Ave, Bishkek, 720044, Bishkek, Kyrgyzstan.

[3]Afyon Kocatepe University, Engineering Faculty, Department of Civil Engineering. Erenler, Afyonkarahisar Merkez/ Afyonkarahisar, 03200, Afyon, Turkey.

e-mail: tahirgonen@gmail.com, uygunoglu@aku.edu.tr

ABSTRACT

As the urban population increases and the level of social life advances, the amount of wastewater originating from houses, institutions and industries increases as well. It is necessary for the infrastructure systems in settlements to be sustained under healthy conditions. Since the subsequent repair of infrastructure systems is difficult, appropriate selection of the materials used in these systems is of importance. Concrete pipes are widely used in sewerage systems. In the present study, it was aimed to improve the biological corrosion resistance of concrete pipes via coating with various materials. For this purpose, firstly mortar samples were coated with epoxy, crystalline insulation mortar, and polyester. Finally this specimens subjected to 0.1, 0.5, 1, and 1.5 mol sulfuric acid solutions for 7, 14, 21, 28, 35, and 42 days. It was observed that the coating materials significantly improved the biological corrosion performances of the mortar samples.

Keywords: Mortar, microbiological corrosion, coating materials, sewerage systems.

1. INTRODUCTION

Over time, deterioration is observed in the structural elements that constitute sewerage systems and these require repair. One of the most commonly encountered problems in sewerage systems is biological organisms that cause acid attack within the system. The economic loss resulting from microbiologically-induced corrosion and the resulting repair and maintenance costs cause billions of dollars of loss in European countries [1–3]. Microbiologically-induced corrosion leads to a decrease of approximately 50–70% in the service life of concrete structures [4]. Domestic wastewater is typically alkaline and does not damage concrete. However, this type of waste contains sulfur components. Sulfate and certain proteins in sewage wastes form hydrogen sulfide (H_2S), which is not extremely detrimental to concrete, in anaerobic (oxygen-free) environments [5, 6]. H_2S is a colorless gas that is heavier than air, possesses a characteristic rotten egg odor, and is commonly found in oil fields, sewage, and chemical industry areas. Anaerobic bacteria are organisms that do not require air and survive by receiving oxygen from sulfates [7]. These bacteria break down sulfates in the soil, subsurface or wastewater and release H2S, which rapidly corrodes iron alloys. High temperatures accelerate the speed of the reaction. H_2S is separated from sewage due to factors such as the chemical balance, movement and turbulence of the environment, and melts within the moisture in the sewage walls. The H_2S released merges with the O_2 in the air and produces the H_2SO_4, which is known as sulfuric acid (Figure 1) [8, 9].

Sulfuric acid reacts with a variety of substances, particularly calcium hydroxide, found on the roof surface of concrete pipes [5, 6, 10]. Bacteria begin to develop on the surface when the pH of the concrete starts to drop (9–9.5). The formation of bacteria is aided by a reduction in concrete pH. The pH drops further as the formation of carbon dioxide and hydrogen sulfide in wastewater increases. The calcium hydroxide in the concrete reacts with sulfuric acid and neutralizes it andconcrete materials get damaged. The main components of concrete, calcium silicate, calcium carbonate, and calcium hydroxide, react with sulfuric acid [5, 10]. Gypsum (CaSO4.2H2O), the primary corrosion product, is 24% higher in volume than the main component of concrete [11]. It reacts with calcium sulfate (CaSO4 2H2O) on the concrete pipe roof surface in the sewage and tricalcium aluminate in the concrete [10]. Calcium sulfate aluminum hydrate is formed. The volume expands 2–7 times further, causing substantial damage to the concrete pipe. Because these volume expansions cause the concrete surface to fracture, moisture, acid, and bacteria are more easily transferred to the enlarged inner surface area, causing further damage.

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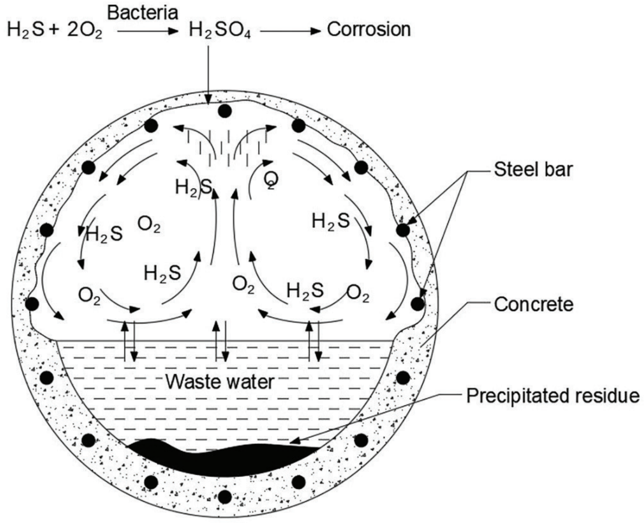


Figure 1: Formation of the H_2SO_4 in sewage systems.

As a result, a weaker surface layer emerges [12–14]. The wear on the concrete surface of the sewer pipe is roughly 6–20 mm per year in areas where hydrogen sulfide content is high. The mechanical strength of the deteriorated concrete material decreases. The sewer system develops holes over time. From degraded places, wastewater spills underground. In regions where the sewage system is destroyed, both underground and surface waters are at risk.

H_2SO_4, a strong acid, settles on the concrete surface and causes the pH level in the area to fall, while also dissolving cement hydration products and easily reaching the steel reinforcement carrying tensile stress. This corrosion event particularly takes place in upper regions. As hydrogen sulfur concentration decreases, corrosion is minimized in the upper region of the sewage system. In environments where the hydrogen sulfur concentration within the sewage system is 6 mg/L on average, concrete is exposed to corrosion at a rate of approximately 5.8–12 mm/year. The mechanical endurance of the concrete material exposed to corrosion decreases. Calcium sulfate ($CaSO_4$ $2H_2O$) and calcium sulfate aluminum hydrate ($3CaO$ Al_2O $3CaSO_4$ $31H_2O$) are formed on the sewage surface. The resulting calcium sulfate is separated from the surface. Due to the impact of high hydrogen sulfur, the concrete surface within the sewage is exposed to corrosion at a rate of approximately 6–20 mm. When the thickness of the concrete cover layer is taken into consideration, the concrete cover will have fallen in approximately 2–2.5 years. Sulfuric acid has a very negative impact on not only concrete, but also steel. As a result of this effect, also known as biological corrosion, weight and section loss occurs in concrete and, by extension, bearing capacity decreases [15]. Although many studies [16–19] have been carried out on steel reinforcement rather than concrete corrosion, most of these have covered chloride corrosion, considering that the structures in Turkey are located on coastlines. However, with the developments in concrete technology, the use of concrete elements in underground structures has been becoming increasingly common and the corrosion of these elements has gained importance. One of the leading causes of corrosion in concrete elements used in underground structures is sulfuric acid-induced biological corrosion [16–19].

There is no standard test method towards determining concrete biological corrosion resistance. For this reason, concrete performance is aimed to be determined by researchers using different methods. In studies conducted to determine the biological corrosion resistance of concrete, sulfuric acid is widely used [20–25, 14]. There are previous studies in the literature aiming to improve the biological corrosion resistance of concrete through the adjustment of water/cement rate [20, 22], use of geopolymer cement [21], substitution of Class C fly ash [23] or changing cement type [25]. Apart from these, other studies have aimed to prevent biological corrosion by adding different polymers [24, 14]. There are not enough studies conducted to prevent biological corrosion using coating materials. With the present study, chemical coating materials produced for various purposes in the sector and generally used for waterproofing were used to coat concrete and it was aimed to measure their effects on biological corrosion resistance.

2. MATERIALS AND METHODS

2.1. Materials used

CEM I-42.5/R-type Portland cement was used as the hydraulic binder in the preparation of mortar admixtures. Table 1 shows the physical and chemical properties of the cement used. The specific gravity of the cement used is 3.07 and its fineness is 3212 cm^2/g. Polyester resin, epoxy and crystalline waterproofing mortar were used as

Table 1: Characteristic properties of the cement (%).

CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	K_2O	Na_2O	LOSS ON IGNITION
63.56	19.30	5.57	3.46	0.86	2.96	0.80	0.13	1.15

coating materials. The mortars were produced using natural stream sand with a sieve opening of 0–4 mm. The aggregate surface was saturated water before being added to the mixture. The aggregate surface has a specific gravity of 2.59 and a water absorption rate of 3.73%.

2.2. Sample preparation

The water/cement rate of the mortars was fixed at 0.50 and the amount of cement was fixed at 350 kg/m^3. Three epoxies, polyester, crystallized, and reference samples were prepared for each molarity. The reference samples are those that have not been coated with any coating material and have been exposed to the solution directly. A total of 48 samples were subjected to a sulfuric acid solution of four distinct molarities: 0.1 M, 0.5 M, 1.0 M, and 1.5 M.

A mortar mixer with a capacity of approximately 5 liters was used to produce the mortars. Following the dry mixing of the aggregate and cement for 1 minute, roughly two-thirds of the mixing water was added to the mortar mixture. The mixing process was continued for 3 minutes after the remaining water was added. The mixtures produced were poured into 25 × 25 × 180 mm prismatic molds. After 24 hours, the samples were removed from the molds and standard-cured for 28 days in 20 ± 2 ºC lime-saturated water. On a stone cutting machine, 24 samples were divided in half, yielding 48 prismatic samples with dimensions of 25 × 25 × 90 mm. The coating components were prepared according to the manufacturer's specifications and applied to the concrete surface in one layer with a brush while wet and allowed to dry. The coating thickness of the coating ingredients that were applied in a single layer was not measured. As illustrated in Figure 2, 12 Epoxy (E), 12 Polyester (P), and 12 Crystallized (K) samples were applied to the samples as thin-film layers. After that, it was kept until it was completely dry, as illustrated in Figure 3.

Figure 2: Coating the mortar samples with polyester, epoxy and crystallized waterproofing mortar.

Figure 3: Drying the samples coated with polyester, epoxy and crystallized waterproofing mortar.

2.3. Biological corrosion experiments

The solutions were prepared into 4 different glass jars with a capacity of 5 liters. H_2SO_4 (sulfuric acid) was used as the acid material. Equation 1 shows the formula to calculate the volume of acid to be added into the solution after the necessary values are input on Solution Molarity M1, jar volume V1, acid molarity M2 and acid volume V2.

$$M1 \times V1 = M2 \times V2 \tag{1}$$

The samples were exposed to the H_2SO_4 solution at mol concentrations of 0.1, 0.5, 1, and 1.5 for 7, 14, 21, 28, 35, and 42 days to determine the resistance of polyester, epoxy, and crystalline waterproofing mortar applied to the sample surfaces against biological corrosion. On the 7th, 14th, 21st, 28th, 35th, and 42nd days, the weights of the samples exposed to these solutions were weighed, and the weight loss resulting from biological corrosion was calculated.

2.4. Determination of physical properties

The unit volume weight, specific gravity and void volumes of the samples prepared were determined using the Archimedean Principle. After the weight of oven-dried sample (W0), the dry saturated weight (W1) and in-water weight (W2) of the surface were calculated, the apparent porosity in gr/cm^3 was determined for days 7, 14, 21, 28, 35, 42 according to Equation 2 while the total volume cm^3, void volume cm^3, solid volume cm^3 and weight losses were determined as physical properties.

$$Apparent\ porosity = \frac{w_0}{w_1 + w_2} \tag{2}$$

3. RESULTS AND DISCUSSION

Sulfuric acid reacts with a variety of substances, particularly calcium hydroxide. Bacteria begin to develop on the surface when the pH of the concrete starts to drop (9–9.5). As carbon dioxide and hydrogen sulfide formation in wastewater increases, the pH drops further, accelerating the formation of bacteria. When it penetrates the concrete, it causes significant corrosion damage [19].

In the present study, sulfuric acid experiments were conducted using prismatic mortar samples of 25 × 25 × 90 mm. For 7, 14, 21, 28, 35, and 42 days, the samples were maintained in 0.1, 0.5, 1, 1.5 molar sulfuric acid solutions. Weight losses were calculated as a result of examining the corrosion of coated mortar samples in the H_2SO_4 solution over time, and the findings are shown in Figures 4–7, respectively.

When the molarity of the solution is maintained constant, hydrated products gradually move away from the environment, resulting in weight loss. The weight losses of the mortars increased over time in all batches, depending on the sulfuric acid molarity. Uncoated and polyester-coated samples exhibited higher losses than epoxy and crystallized waterproofing mortar. Particularly in the 1.5 M solution, losses neared 100%. In all molarities, uncoated control samples lost the most mass. In all molarities, 7 days of sulfuric acid exposure had a minor effect on epoxy-coated samples. At 0.1% molarity, weight loss stayed below 5% for the next few days.

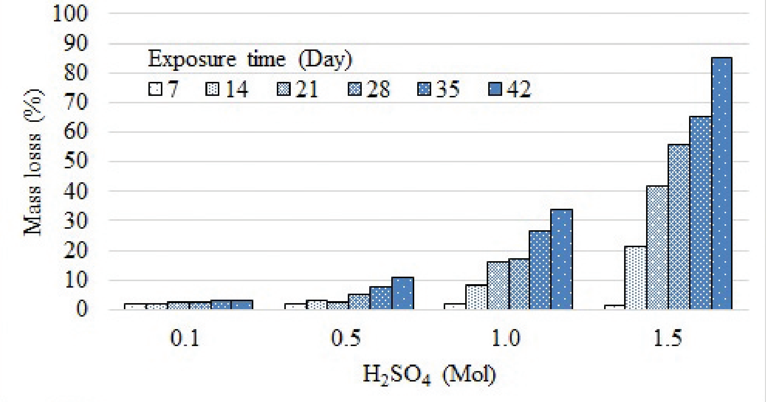


Figure 4: Weight losses of the samples coated with epoxy.

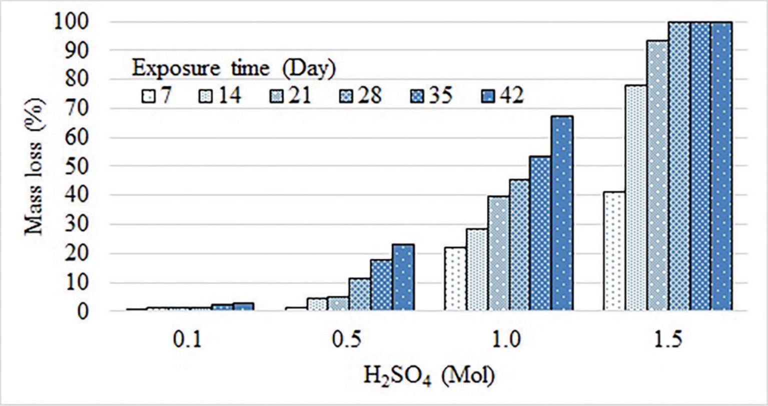


Figure 5: Weight losses of the samples coated with polyester.

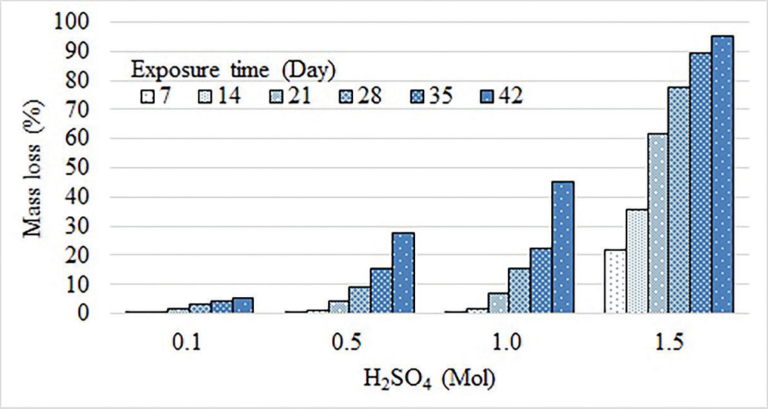


Figure 6: Weight losses of the samples coated with crystallized waterproofing mortar.

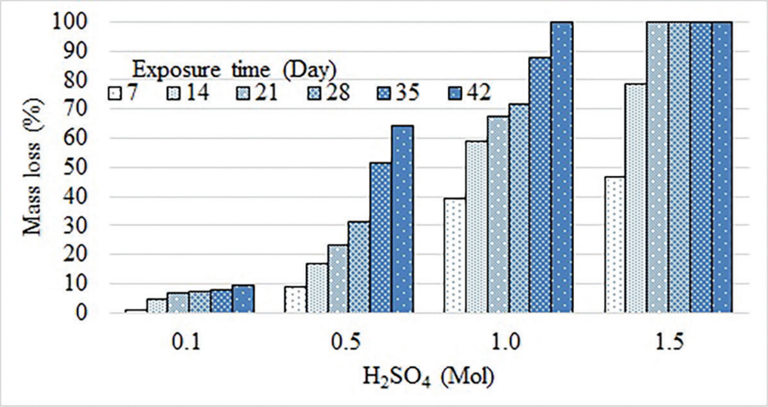
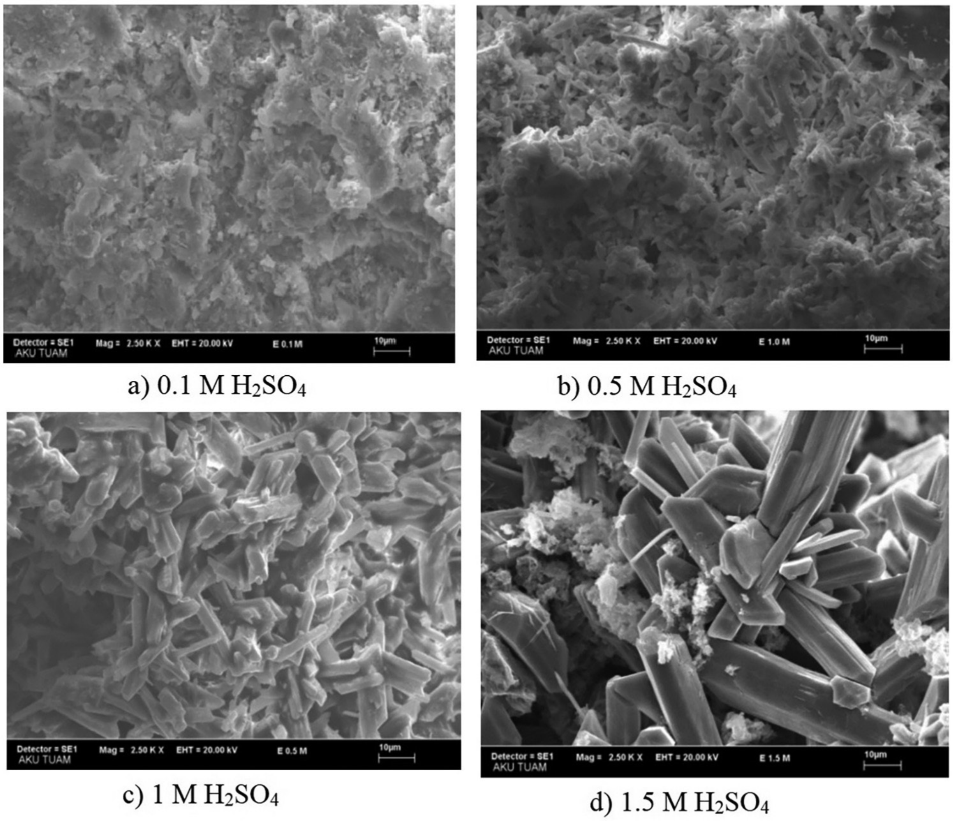


Figure 7: Weight losses of the uncoated control samples.

When examined in terms of weight loss, it was determined that the most durable samples were those coated with epoxy. On the other hand, the samples coated with the crystallized waterproofing mortar produced similar results with the epoxy-coated samples. The highest loss in the epoxy-coated samples took place at the end of 42 days in the 1.5 M sulfuric acid solution at a rate of 85% while this rate was 95% in the samples coated with crystallized waterproofing mortar under the same conditions. The polyester-coated samples, on the other hand, reached 100% in 1.5 M sulfuric acid at the end of 28 days.



a) 0.1 M H_2SO_4 b) 0.5 M H_2SO_4

c) 1 M H_2SO_4 d) 1.5 M H_2SO_4

Figure 8: Microstructures of epoxy-coated samples stored in H_2SO_4 solutions of various molarities.

Since Portland cement is highly alkaline, it is prone to attacks by acids or acid-forming substances. The chemical attack is observed in the form of decomposition of cement hydration products, separation of the ensuing soluble compounds from the concrete, and disintegration of the concrete by the resulting insoluble products.

The component most vulnerable to acid attack is $Ca(OH)_2$. Acid reactions vary in rate and intensity depending on acid type, exposure time, and acid density. The solubility of the calcium salt generated is, however, the most critical element. The damage caused by the compounds carried by water increases as the solubility increases. Softening and porosity appear in hardened concrete starting at the surface, depending on how the reactions progress. Furthermore, weak acids can become strong acids as a result of biological growth, as in sewer pipes. Figure 8 shows SEM images of epoxy coated samples stored in H_2SO_4 solutions of various molarities. When the microstructures of the epoxy coated samples are investigated, it can be seen that the hydrated products disintegrate in parallel with the increase in acid intensity.

4. CONCLUSION AND EVALUATION

Particularly reinforced concrete structural elements used in infrastructure systems are widely exposed to the effects of the bacteria created by wastewater and, as a result of this, hydrogen sulfide acid. In the present study, experiments were carried out to determine the physical properties of mortar samples coated with different materials, and the results are summarized as follows.

- As H_2SO_4 molarity increases, the corrosion of the samples subjected to its effects increased. The weight loss in the control samples was below 10% in 0.1 M acid while this rate reached 100% in 1.5 M acid. Samples coated with epoxy and crystallized waterproofing mortar generally exhibited less weight loss.
- Epoxy-covered samples suffered less damage within the H_2SO_4 solution of different molarities compared to the other types of coating.
- Polyester-coated samples demonstrated high rates of weight loss within acid levels of 0.1 M, 0.5 M, 1.0 M up to the final weeks while breakups were observed in most of the samples in 1.5 M acid at the end of week 3 and weight losses neared 100%.

- It was revealed through the experiments that the samples coated with crystallized structure materials produced similar values with epoxy in the H_2SO_4 solution.
- At the end of 42 days, a weight loss of approximately 64% was observed in the uncoated reference samples even in 0.5 M acid while this rate increased to 100% beyond 0.5 M.
- The hydrated products in the samples were withdrawn from the environment as the acidity level grew, depending on the coating type and acid level, and dispersions and fragmentation were identified on the samples, according to the microstructure examination.

In conclusion, based on the experiment results and microstructure examinations, it was determined that weight losses increased and sample structures deteriorated over time to be dissolved. In this case, the structural element loses its bearing capacity and will not be able to operate properly. In mortar samples, the desired level of endurance is achieved using epoxy, a resin-based structure material, as well as the crystallized waterproofing mortar. However, in terms of cost, it is more suitable to use crystallized waterproofing mortar rather than epoxy in the inner regions of infrastructure systems as the former is more economical. This will reduce maintenance and repair costs in the establishment of longer-lasting service periods.

5. ACKNOWLEDGMENTS

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