




# Study of Magnesium Hydroxide Protective Coating against Corrosion, Applied on Poly(methyl methacrylate) Plates, By Using the Sulfuric Acid Attack Acceleration Test <sup>†</sup>

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**Abstract:** Microbiologically induced corrosion (MIC) leads to the degradation/deterioration of concrete pipes, due to the formation of gypsum. Magnesium hydroxide powders may protect the concrete surface by maintaining alkaline pH values at the surface, or by neutralizing the biogenic produced sulfuric acid. An accelerated sulfuric acid spraying test in a custom-made spraying chamber used to examine the consumption of magnesium hydroxide coating, which was applied on poly (methyl methacrylate) plates, instead of applying it on concrete substrates. In that way, only the magnesium hydroxide coating can interact with the acid and can be examined separately. Surface pH measurements and the mass changes were daily conducted, during the four-day accelerated spraying test. The mineralogical phases of the surface were determined by using X-ray Diffraction (XRD) measurements.

**Keywords:** concrete corrosion; corrosion control; magnesium hydroxide coating; sewerage pipe systems; acid spraying test



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## 1. Introduction

The degradation and collapse of sewage pipes system can lead to major infrastructure problems in urban communities, by creating unhealthy conditions and costly replacement expenses [1–3]. Different kinds of corrosion mechanisms (electrochemical corrosion, soil corrosion, microbiologically induced corrosion, etc.) are the main reasons of these problems, so multiple studies are focusing on the mitigation and control of sewerage system corrosion [2–4]. Microbiologically Induced Corrosion (MIC) or bio-corrosion concerns the effect of the biologically produced sulfuric acid on the inner surface of concrete pipes, as well as on the metallic surfaces, commonly used in sewer infrastructure [4].

The MIC initiates after a series of chemical and biochemical processes, taking place in the sewer environment. Firstly, the sulfates transferred with the wastewater are converted to hydrogen sulfide gas, which is subsequently emitted in the upper air phase (“crown”, usually empty of transferred wastewater) of sewer pipes. The produced hydrogen sulfide dissolves in the humidity on the concrete pipe walls and reduces the high alkaline surface pH of them down to 9, favoring the development of Neutrophilic Sulfur Oxidizing Bacteria (NSOB), which subsequently can produce the biogenic sulfuric acid. This results to further surface pH lowering down to values close to 4 and then, the Acidophilic Sulfur Oxidizing Bacteria (ASOB) colonize the surface. These bacteria produce additional biogenic sulfuric acid, which in turn reacts with the (still) alkaline cement paste of concrete, forming gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). The consumption of cement paste of concrete and the formation of gypsum lead to the erosion, degradation, and finally, destruction of concrete pipes [5–9].

The applied corrosion mitigation strategies are mainly focusing on the addition of chemicals or air/oxygen into the transferred wastewater, or the development of new corrosion-resistant concrete materials and the use of protective coatings and linings, applied onto pipe surfaces [2]. The application of coatings is considered as quite an economical way for helping the concrete to preserve its structural properties and mainly, the mechanical strength. In general, organic and inorganic coatings have been applied onto the concrete surfaces as protection films, against different kinds of attack (e.g., chemical attack, biological attack, corrosion, etc.) [10–12]. Alkaline magnesium hydroxide has been already examined as an anticorrosive coating, due to its potential reaction (neutralization) with the produced biogenic sulfuric acid; thus, blocking the reaction between the concrete surface and the acid [1,13–15].

However, the relevant research is rather limited regarding the respective consumption of these coatings and their properties, without the influence of concrete substrate, by using inert poly (methyl methacrylate) substrates. This study focuses on the evaluation of consumption of a magnesium hydroxide coating, as applied onto poly (methyl methacrylate) plates, by using an accelerated sulfuric acid test, in order to simulate the bio-corrosion conditions existing in a sewer concrete pipe. The main objective of this paper is to eliminate the side effects of the concrete substrate and isolate/study the coating alone, in order to examine its anti-corrosion properties (neutralization etc.). In particular, the surface pH values, the mass change, and the changes of the mineralogical phases after a four-day accelerated acid spraying test were examined. The presence of gypsum after the acid spraying test was monitored to conclude whether the coating can also lead to its formation, attempting to use/compare this information with the relevant experiments, when using concrete substrates (where the formation of gypsum is observed).

## 2. Materials and Methods

### 2.1. Surface Coating

The adhesion ability of magnesium hydroxide coatings onto concrete (considering the potential coating application) was found to be very small (almost zero). Therefore, the addition of 0.4% wt. content of methyl-cellulose, as an adhesion promoter, was found to offer sufficient adhesion ability to the magnesium hydroxide coatings [14] and the same amount of cellulose was selected for this study. In order to prepare slurry with 57.5% wt. content of solids, considering workability, deionized water was added and mixed with the magnesium hydroxide powder. Also, a common dispersant polymer for mineral slurries (Acumer 9300) was added at 0.6% wt. of solids content, to improve the workability and to enhance the time-stability of slurries/dispersions. The coatings were applied onto poly (methyl methacrylate) plates with dimensions of  $50 \times 50 \times 5$  mm.

According to the relevant literature and the preliminary testing, the thickness of applied coatings was selected to be between 1.0–1.5 mm [12,14,16]. This thickness was expressed, according to a specific amount of applied coating, i.e.,  $0.0018\text{--}0.0020$  g/mm<sup>2</sup>. The coatings were then dried for 3 days under normal laboratory conditions (i.e.,  $21 \pm 2$  °C and relative humidity  $60 \pm 10\%$ ) before testing.

### 2.2. Sulfuric Acid Spraying Test

The magnesium hydroxide coatings can offer protection to concrete surfaces against corrosion by maintaining the surface pH to alkaline values (and block the development of sulfur oxidizing bacteria), and/or by reacting with the biogenic-produced sulfuric acid, leading to neutralization of it (in case the microorganisms may be developed on the concrete surface).

In order to study the surface pH and the consumption of magnesium hydroxide coatings in a relatively short time period, an accelerated sulfuric acid spraying test was applied. The acid spraying test was performed in a custom-made spraying laboratory chamber. The conditions in the chamber were also closer to simulate the usual sewer pipe conditions, i.e., maintaining the temperature at  $20 \pm 2$  °C and 99% relative humidity.

In order to study the coating without the side effects of concrete's presence, such as reaction of concrete surface with sulfuric acid, the poly (methyl methacrylate) plates were used as proper substrates. These plates do not react during the experimental time with the used sulfuric acid solution (due to low solution concentration); hence, the observed changes, i.e., either mass changes, or mineralogical phase changes, are due solely to the reaction between the coatings and the sulfuric acid. In this way, the coating can be studied separately from the concrete surface.

A 0.2 M sulfuric acid solution was used in the acid spraying test, while the required sulfuric acid amount to be sprayed was determined by the respective stoichiometry calculations, according to [14]. The magnesium hydroxide and the calcium hydroxide, both existing in the used raw material, can react with the sulfuric acid (1:1 reaction), resulting in magnesium sulfate and calcium sulfate as products.

#### 2.2.1. Surface pH Measurements

In order to evaluate the ability of magnesium hydroxide coatings to preserve the (desired) alkaline surface pH values, regular surface pH measurements performed, by using a flat surface pH electrode (Extech PH100: Waterproof ExStik pH meter, Extech Instruments). The surfaces to be measured were wetted with 1 mL of deionized water prior to the measurement. The starting pH values of coated specimens were recorded before the initiation of sulfuric spraying applications.

#### 2.2.2. Mass Measurements

The consumption of coating can be examined by mass measurements of coated specimens during the acid spraying process. An electronic balance Kern PCB 4000-2 ( $4.000 \pm 0.001$  g) was used for the daily mass recordings throughout the experiments. Firstly, the initial weight of all uncoated poly (methyl methacrylate) specimens was recorded, as well as their weight after the application of the coating, in order to calculate the mass of dry coatings. Then, the final mass of each specimen was recorded after the spraying process, to calculate the coating consumption.

#### 2.2.3. XRD Analysis

The mineralogical phases of coating were determined in order to evaluate the respective changes in the mineral structure. Moreover, the origin of gypsum, in experiments using concrete substrates [14,15,17], should be properly defined, i.e., whether it is the product of the reaction between the concrete surface and the sulfuric acid, or the product of the reaction between the calcium hydroxide (of the coating) and sulfuric acid.

After the ending of acid spraying tests, the specimens were dried at 40 °C for 24 h and then, the remaining amount of coating was scratched from the top of specimens, ground, and measured. The structural phases (mineralogical composition) of the obtained samples were analyzed by XRD measurements, using a PW 1840 Phillips diffractometer with CuK $\alpha$  radiation, step size of 0.02°, and step time of 0.4 s, operating at 30 kV and 10 mA. The obtained diffractograms were quantified by following the Rietveld methodology, using the FullProf Suite Software.

### 3. Results

#### 3.1. Characteristics of Magnesium Hydroxide Powder

The Particle Size Distribution (PSD) and the Specific Surface Area (SSA) of the raw material are presented in Table 1.

The composition of magnesium hydroxide powder is presented in Table 2. The total mass loss at 1000 °C (Loss on Ignition, LOI) corresponds to all water and CO<sub>2</sub> content of the respective powder.

**Table 1.** The Specific Surface Area (SSA) and the Particle Size Distribution (PSD) of used magnesium hydroxide powder (MHP).

Material	SSA (m <sup>2</sup> /g)	PSD	
		d <sub>50</sub> (μm)	d <sub>90</sub> (μm)
MHP	7.0	3.8	13.1

**Table 2.** Composition of used magnesium hydroxide powder (%).

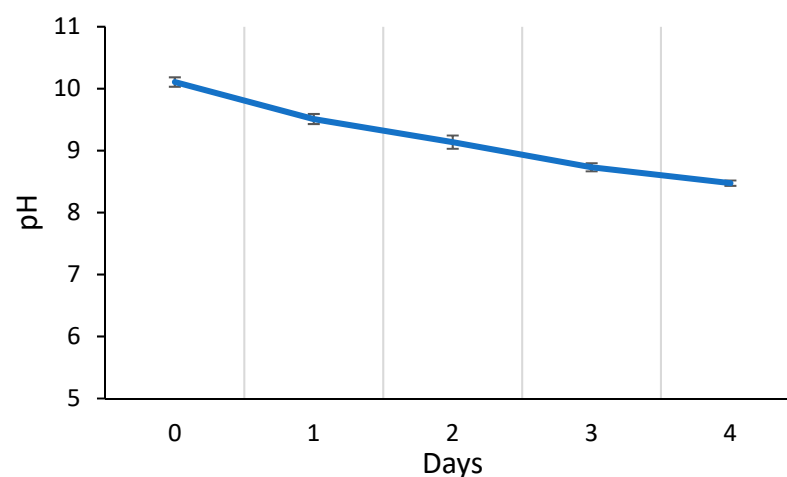
Material	MgO	SiO <sub>2</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>	LOI
MHP	62.81	4.25	2.46	0.25	0.10	0.02	30.11

### 3.2. Accelerated Acid Spraying Test

All specimens were sprayed daily with 25% of the respective reaction's stoichiometry, using a sulfuric acid solution (0.2 M) for four days. Each day, four specimens were removed from the spraying process and were examined, regarding pH surface values, mass changes, and determination of the main crystalline phases (by XRD). The applied coating was expected to be fully consumed at the fourth day, according to the stoichiometry calculations. However, a quantity of coating continues to remain on the specimen/plate surface, even after four days of acid spraying. A possible explanation is that the sprayed sulfuric acid, corresponding to the total amount of coating, could reach (and react) only with the (gradually) exposed coating surface, instead of the whole quantity/mass of coating.

#### 3.2.1. Surface pH Results

Figure 1 presents the results of daily recordings of surface pH values of the coating. The results are given as the mean values of four specimens in each case, along with the respective standard deviation. Day zero, indicated in the Figure, corresponds to the initial surface pH values of the specimens.

**Figure 1.** Surface pH values of the coating applied on poly (methyl methacrylate) specimens during the acid spraying test application. The data points and the error bars denote the mean and the standard deviation, respectively [18].

The starting surface pH of coating was around 10, but it was slightly decreased after the initiation of the acid spraying process (days 1, 2, 3, 4). However, these values were still located in the alkaline region of pH scale. The surface pH values ranged between 8 and 10 throughout the acid spraying test. According to these results, the coating seems to present high capacity in maintaining sufficiently alkaline pH values.

### 3.2.2. Mass Change Results

The mass of the coated specimens was also recorded, in order to examine the consumption of coating during the acid spraying test. The consumption of the coating, without the side effects of concrete substrate (not existing in this case), gives specific information, regarding the performance of the coating for the intended application on the inner surface of concrete pipes. This information can be further used to evaluate the duration for the total consumption of coating and therefore, the time period that the coating can effectively protect the concrete.

Table 3 presents the daily mass change of the coating during the acid spraying test. It can be concluded that the mass change was linear and presented an almost 25% decrease compared with the initial coating mass. It is obvious from these results that only an amount of the coating was consumed after four days of acid spraying. The total sprayed sulfuric acid corresponded (according to the neutralization chemical equation) to the total mass of the coating, in terms of an ideal reaction between the two substances, i.e., magnesium hydroxide and sulfuric acid. However, in this experimental process the magnesium hydroxide was in the form of a coating; hence, blocking the reaction of its total mass, because the sulfuric acid can only affect (neutralize) the surface of coating. This fact, in combination with the surface pH results, indicates that the coatings can last longer than the expected and calculated duration time (i.e., showing excess of coating).

**Table 3.** Mass changes (%) of examined coatings, during the acid spraying test application.

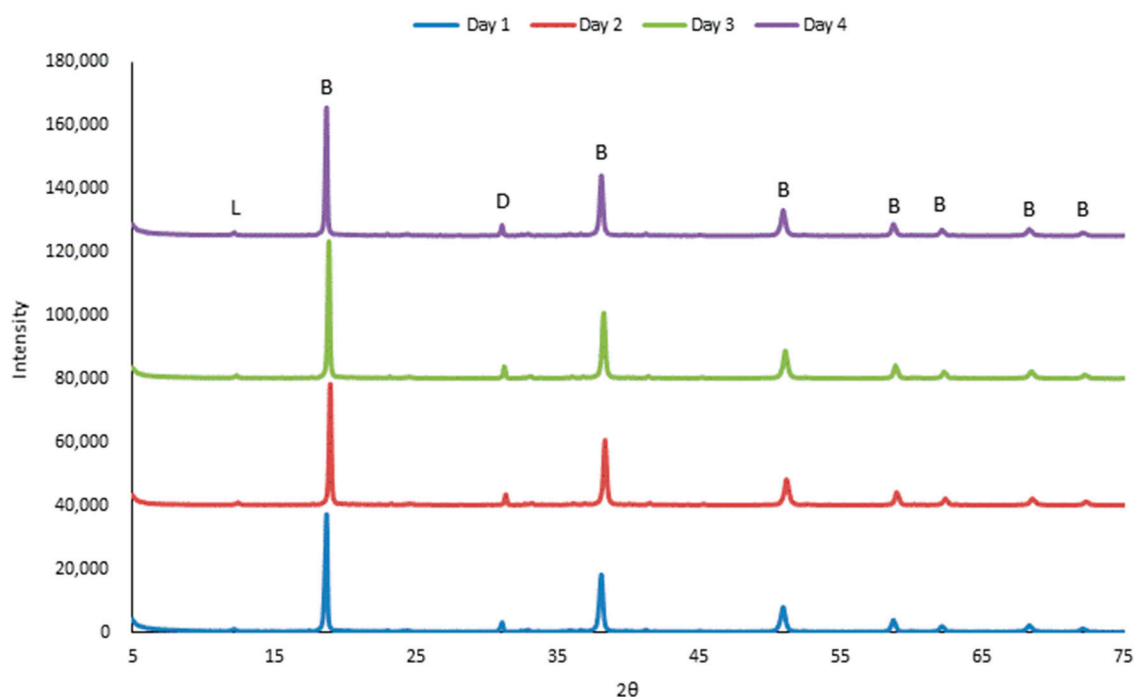
	Day 1	Day 2	Day 3	Day 4
Mass change (%)	−3.9	−6.6	−15.7	−24.6

### 3.2.3. XRD Analysis

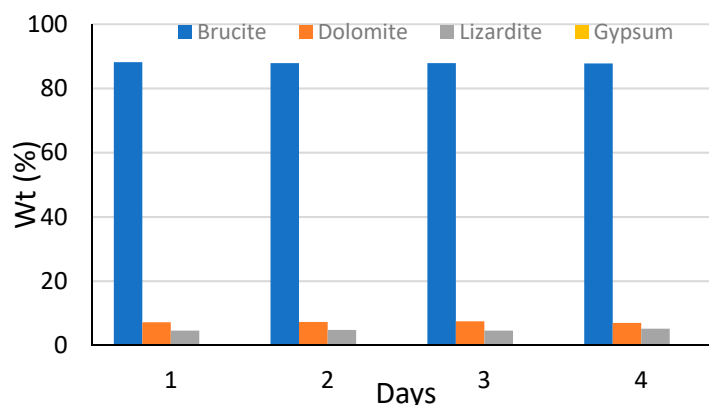
An overlay of the XRD diffractograms, regarding the examined coatings, during the acid spraying process, is presented in Figure 2. In particular, the diffractograms represent the respective samples from day one until day four (after the end of the procedure) of sulfuric acid spraying (0.2 M).

The main peaks of brucite ( $\text{Mg}(\text{OH})_2$ ), dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ), and lizardite ( $\text{Mg}_3(\text{Si}_2\text{O}_5)(\text{OH})_4$ ) are indicated in Figure 2. It is obvious from the comparison of the diffractograms that the same mineralogical phases continue to exist after four days of sulfuric acid spraying. It is interesting to note that neither gypsum nor magnesium sulfate is present in the crystalline phases of the coating. However, the formed magnesium sulfate is rather water-soluble and thus, it can be easily rinsed and removed; therefore, it cannot always be traced on the samples after the acid attack. The absence of gypsum indicates that any potential formation of gypsum, when concrete substrates are studied, is due to the reaction between concrete and sulfuric acid.

The respective XRD diffractograms were further quantified by using the Rietveld methodology and are presented in Figure 3. The results show that the mineral composition of the coating was stable during the four days of acid spraying. Thus, there is not observed any product formation or transformations regarding the coating's crystalline phases. The formed magnesium sulfate may be rinsed, due to the applied several spraying applications, because of the relatively small concentration of used sulfuric acid (0.2 M). However, it is a fact that the coating reacts with the sulfuric acid and is therefore consumed (as noticed by the mass change). The excess of brucite indicates that the coating could keep offering protection to the coated substrate.



**Figure 2.** XRD overlay diffractograms of the coating samples during the acid spraying test application; L: Lizardite, B: Brucite, D: Dolomite.



**Figure 3.** The quantitative results of XRD analysis, regarding the presence of crystalline phases in the coating samples during the acid spraying test application.

#### 4. Conclusions

The results of this research showed that the mass of the magnesium hydroxide coating was decreased with time, due to the reaction with sulfuric acid and reached almost –25% of the initial coating mass. Additionally, it was demonstrated that the surface pH of coatings was preserved (i.e., remain in the alkaline region) and therefore, can block the development of undesired microorganisms. The study of crystalline phases indicated that no other products (such as gypsum) were formed, and the mineral composition of the coating was the same after the four days of the accelerated acid spraying test.

To sum up, during the aforementioned experiments, there was no gypsum formation observed, and when coatings are applied onto concrete substrates, its formation is due to the reaction of concrete surface with the sulfuric acid.

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A.Z.; Supervision, E.A. and A.Z.; Project administration, E.A. and A.Z. All authors have read and agreed to the published version of the manuscript.

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