

Proceedings

Study of Corrosion Protection of Concrete in Sewage Systems with Magnesium Hydroxide Coatings [†]

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Abstract: The purpose of the present work was to study the corrosion protection that relatively low-cost magnesium hydroxide coatings offer to concrete by stabilizing the surface pH. To facilitate the material's adhesive ability, methyl-cellulose and carboxymethyl-cellulose were used as environmentally friendly additives in three different concentrations, 1, 0.4 and 0.1 wt.% of solids, respectively. The coatings were applied on the surface of concrete blocks, in two different coating thicknesses. A sulfuric acid solution was used to simulate the biologically produced acid in sewer pipes. Sulfuric acid was sprayed on the specimens, while the total amount of acid sprayed was calculated, in order to correspond to a specific reaction's stoichiometry daily. The surface pH of coated specimens was monitored daily with a surface pH meter. The gypsum production was studied with X-ray diffraction, to evaluate the coatings' protection. The experimental time period that coatings were consumed was compared with the theoretically consumption time.

Keywords: concrete protection; corrosion control; sewage systems; magnesium hydroxide coatings

1. Introduction

The sewer pipe network functions as a reactor in which many chemical and biochemical reactions take place. The increased microbiological activity in wastewater leads to the formation of hydrogen sulfide, which is released in the pipe's atmosphere. Subsequently, the diluted hydrogen sulfide on pipe's walls is oxidized and sulfuric acid is produced [1]. The surface pH of the concrete walls decreases and favors the development of acidophilic sulfur-oxidizing bacteria [1,2]. These bacteria produce biogenic sulfuric acid, which reacts with the hydrated cement paste of concrete and leads to the concrete pipe's degradation [3,4].

Restoration and replacement of degraded sewer pipes may cost several billions of USD/year around the world. Much research has been made in order to find ways to control concrete corrosion, such as new concrete materials [5,6], protective linings [7,8] and adding chemicals in the wastewater [9,10]. Magnesium hydroxide was studied before as a neutralizing agent in wastewater [11] and as a coating through crown spray process [12].

However, little it is known about the way the coating’s thickness or the adhesion additives can affect the consumption of the coating and the formation of gypsum. This study is evaluating the influence of the amount of adhesion additives (celluloses) and thickness to the adhesion of the coating to the concrete and to the protecting properties of the coating.

2. Materials and Methods

2.1. Concrete Preparation

Concrete type MC 0.45, with a water/cement ratio of 0.45, was chosen according to EN 1766:2000 [13] and BS EN 196-1:1995 [14] standards, in order to simulate the type of concrete used in sewer pipes. Cement type CEM I 42.5 R, natural aggregates (limestone sand 0–4 mm and limestone grit 4–8 mm), tap water and a Sika Viscocrete superplasticizer were used for the synthesis, according to the composition of Table 1. The components were mixed in a cement mixer, and the prepared concrete was poured into wooden molds. Concrete samples of different dimensions were formed, depending on the tests (200 × 200 × 20 mm, 50 × 50 × 20 mm). After 24 h the specimens were ready to de-mold and cured in water for 27 days at 20 ± 2 °C.

Table 1. Concrete mix composition.

Material	Type	Composition
Cement	CEM I 42.5 R	410 kg/m ³
Water	Tap water	184.5 kg/m ³
Limestone sand	0–4 mm	895 kg/m ³
Limestone grit	4–8 mm	895 kg/m ³
Plasticizer	SP Viscocrete	0.5 wt.% of cement

2.2. Preparation and Application of Coatings

Magnesium hydroxide powder (MH) 89%, supplied by Grecian Magnesite S.A. (Gerakini, Greece), used as the main component of the surface coatings. As adhesives for the coatings, methyl-cellulose (MC) and carboxymethyl-cellulose (CMC) were added and deionized water was used in all coatings. In order to reduce the viscosity of the mixture, Acumer 9300 (Dow Acumer 9300 Dispersant Polymer for Mineral Slurries) was used in these syntheses, at 0.6 wt.% of solids. Table 2 presents the magnesium hydroxide powder composition.

Table 2. Magnesium hydroxide powder composition (%).

Material	MgO	SiO ₂	CaO	Fe ₂ O ₃	Al ₂ O ₃	SO ₃	LOI
Mg(OH) ₂	63.12	4.25	2.46	0.25	0.1	0.02	30.11

Two series of slurries were synthesized with different concentrations of celluloses. The first series was magnesium hydroxide slurries with 1, 0.4 and 0.1 wt.% of solids of methyl-cellulose (M1m, M2m, M3m); the second series was magnesium hydroxide slurries with 1, 0.4 and 0.1 wt.% of solids of a mix of methyl-cellulose and carboxymethyl-cellulose (M1mc, M2mc, M3mc). The mix of celluloses in the second series of slurries was in a ratio of MC/MCM = 4/1. The percentage of solids was 57.5 wt.% in all slurries.

For the preparation of the coating Acumer 9300 and celluloses were added to deionized water at 90 °C, under stirring. The solution was stirred until room temperature and magnesium hydroxide was added under mechanical stirring for 1h.

The concrete surface was moistened with deionized water to enhance the slow dry of the coatings and block the formulation of cracks on their surfaces. The application of the coatings on the concrete specimens was made manually with a spatula. The coatings were applied on concrete blocks, in two different amounts (thickness). The applied coating amount was 0.0008–0.001 gr/mm² for the thin layer and to 0.0018–0.002 g/mm² for the thick layer. The coated specimens were stored at normal

laboratory conditions 21 ± 2 °C and relative humidity $60 \pm 10\%$, for 3 days, so that the coatings were dried.

2.3. Pull-Off

The pull-off bond testing method, according to the standards EN 1542:1999 [15] and EN 13578:2003 [16], was used to measure the tensile bond strength between the coatings and the concrete substrate. Concrete specimens of dimensions $200 \times 200 \times 20$ mm were drilled with a diamond coring barrel to a depth of 5 mm into the concrete substrate. After the coating application on the specimens, an adhesive was applied on the coatings' surface and the dollies were placed on the adhesive. When the adhesive had hardened, the pull-off equipment (Digital pull-off strength tester, Matest), was used to measure the load at failure, while the type of failure was also recorded.

2.4. Acid Spraying

The protecting ability of the coatings was evaluated using a method of spraying sulfuric acid on the specimens, in order to simulate the created drops of sulfuric acid onto the pipes' walls. However, this was an accelerated experiment, in contrast with the slow processes that take place in a sewer. Sulfuric acid subsequently reacted with the coatings and/or the concrete. Under this test, the pH variation of coatings were examined, since the decrease of pH values can create the proper conditions for microorganisms' development.

The coatings were applied on the one side of concrete tiles of dimensions $50 \times 50 \times 20$ mm (50×50 mm), as described in previous section. A sulfuric acid solution of 95–97 wt.% was used to prepare a 4M working solution. The number of daily acid sprayings was adjusted, so that 7%, 17% and 35% of the reaction's stoichiometry, between the acid and the coating, can be achieved each day. According to the chosen daily stoichiometries, the theoretically expected time of the coatings' consumption is 15, 6 and 3 days, respectively. As for the stoichiometry, the coatings' composition was calculated according to the magnesium and calcium content, expressed as MgO and CaO, respectively.

The spraying process was held until the coating was consumed, or until there was observed optically the extended formation of gypsum, due to the chemical reaction between the concrete and sulfuric acid.

A flat surface pH electrode (Extech PH100: Waterproof ExStik pH meter, Extech Instruments) was used to measure the specimens' surface pH. One milliliter of deionized water was applied on the studied surfaces in order to conduct the measurement. All samples' pH values were recorded before spraying as starting values. The specimens were placed in a climatic test chamber at 20 ± 2 °C and 99% relative humidity, simulating the pipe's conditions.

2.5. XRD Analysis

For the determination of mineralogical composition X-Ray Diffraction analysis was performed by PW 1840 Phillips diffractometer and diffractograms were evaluated using FullProf Suite Software. The samples were scratched from the surface of the specimens and they were dried at 60 °C for 24 h. Afterwards, the samples were ground and measured.

3. Results

3.1. Pull-Off

Pull off measurements were conducted in order to evaluate the adhesion of the coatings onto the concrete substrate. Two thicknesses (thin-thick) were applied and examined in all coatings. The tensile bond strength was calculated to the nearest 0.1 MPa, using the formula:

$$f_h = 4F_h/\pi D^2 \quad (1)$$

where f_b is the bond of the specimens, in megapascals; F_b is the failure load, in Newtons; D is the mean diameter of the test specimen, in millimeters [15]. Table 3 presents the pull off results, i.e., the tensile bond strength and the type of failure.

Table 3. Tensile bond strength and type of failure.

Coating	Thick Layer			Thin Layer		
	f_b (MPa)	Type of Failure		f_b (MPa)	Type of Failure	
		A/B (%) ¹	B (%) ²		A/B (%) ¹	B (%) ²
M1m	0.6	20	80	0.5	30	70
M2m	0.3	30	70	0.3	70	30
M3m	0.1	100	0	0.1	90	10
M1mc	0.3	100	0	0.3	100	0
M2mc	0.1	100	0	0.1	95	5
M3mc	0.1	100	0	0.1	95	5

¹ Adhesion failure between the substrate and the first layer of coating, ² Cohesion failure in the first layer of coating.

The coatings with MC additive presented higher tensile bond strength than those with the mix of celluloses (MC and CMC). In particular, M1m coating (1% MC) showed the best adhesion ability on concrete substrate, both in thin and thick layer.

Furthermore, MC coatings exhibited cohesion failure in the coating’s layer, apart from adhesion failure between the coating and the concrete. This indicates better adhesion ability for these coatings. On the other hand, the coatings with MC and CMC presented mainly adhesion failure. It can be concluded that the addition of CMC reduces the adhesion ability of the coatings. Additionally, the reduction of the amount of celluloses leads to tensile bond strength reduction in both type of coatings (MC/MC and CMC). The thickness does not seem to affect the adhesion of the coatings.

3.2. Accelerated Acid Spraying Test

The samples were sprayed until the coating was consumed or until gypsum was formed. Table 4 shows the duration of the coatings in respect to the theoretical consumption time, as a percentage.

Table 4. Experimental duration in respect to the theoretical duration time (%).

	7%		17%		35%	
	Thin Layer	Thick Layer	Thin Layer	Thick Layer	Thin Layer	Thick Layer
M1m	+21	+40	+67	+133	+67	+167
M2m	+7	+20	+67	+133	+67	+133
M3m	+18	+33	+67	+100	+33	+100
M1mc	+14	+40	+67	+133	+67	+133
M2mc	+14	+33	+67	+150	+67	+133
M3mc	+7	+47	+67	+100	+67	+100

According to Table 4, thickness can affect the consumption of the coatings. It can be concluded that the double thickness offers a double duration time, while spraying with the corresponding amount of sulfuric acid. All coatings withstood more than the expected consumption time. It can be assumed that while the daily stoichiometry of the reaction reduced, the experimental duration time of coatings seems to approach the theoretical duration time. M1m coating showed slower consumption than the other two coatings of the series (M2m, M3m) in the three different reaction’s stoichiometries. M3mc coating presented the fastest consumption of all coatings.

The daily surface pH values for specimens sprayed with 7% of the reaction’s stoichiometry are presented in Figure 1 for thin layer and thick layer, while in Figures 2 and 3, the surface pH values for specimens sprayed with 17% and 35% of the reaction’s stoichiometry are showed, respectively. It was showed that all coatings can preserve the surface pH values in alkaline region. The surface pH maintained above eight in all cases. All coatings had starting pH values around 10. The coatings

created a buffer-like behavior on the concrete surface; the surface pH values were decreased and increased continuously, and the values were ranged around 1 unit during the acid spraying experiment.

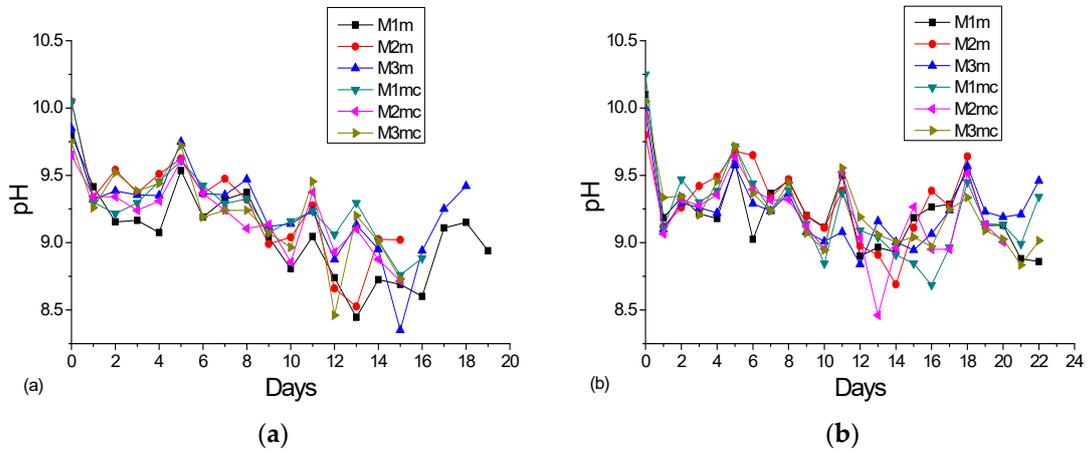


Figure 1. Surface pH values for specimens sprayed with 7% of the reaction's stoichiometry: (a) Thin layer of coating; (b) Thick layer of coating.

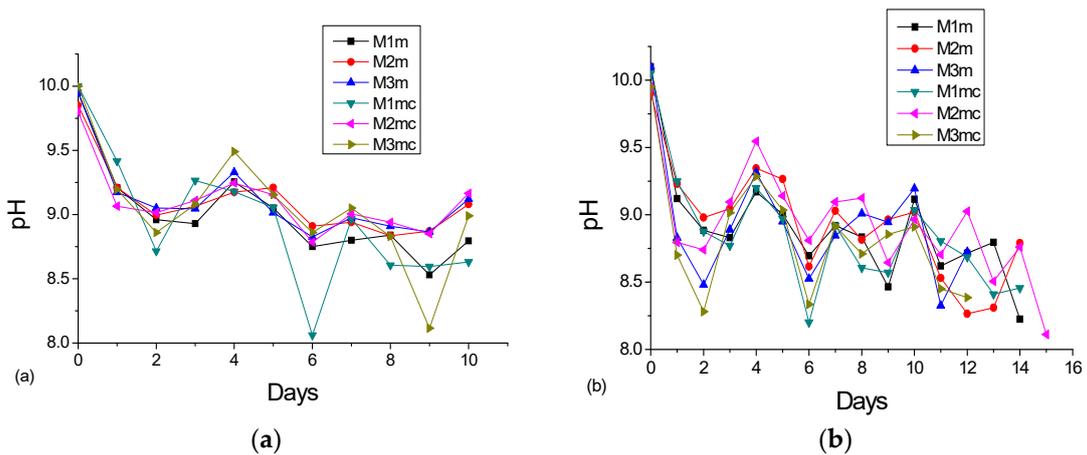


Figure 2. Surface pH values for specimens sprayed with 17% of the reaction's stoichiometry: (a) Thin layer of coating; (b) Thick layer of coating.

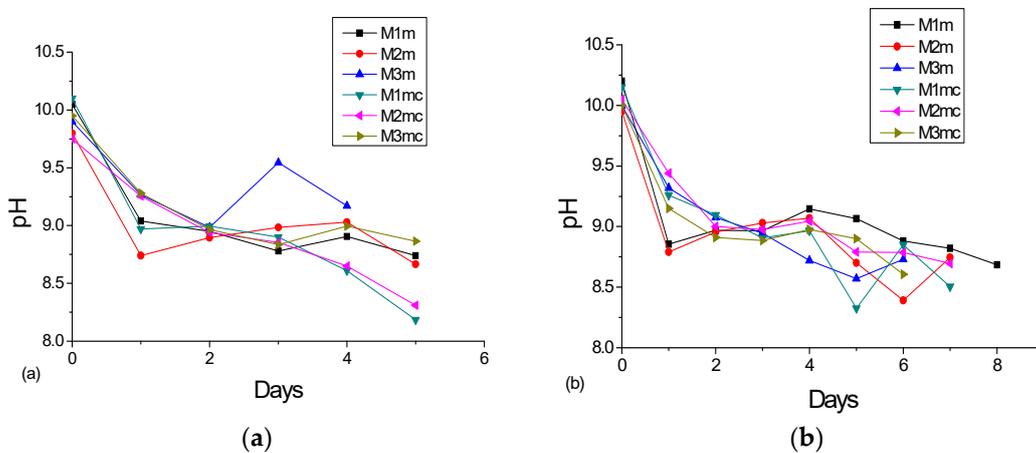


Figure 3. Surface pH values for specimens sprayed with 35% of the reaction's stoichiometry: (a) Thin layer of coating; (b) Thick layer of coating.

3.3. XRD Analysis

The XRD quantitative results were processed with the Rietveld refinement method, using FullProf software. The main phases that were studied, were brucite ($Mg(OH)_2$) (PDF #74-2220), which was consumed by the sulfuric acid, and gypsum ($Ca(OH)_2$) (PDF #70-0982), which was the product of the reaction.

Figure 4 shows the six coatings' diffractograms after acid spraying of 17% of the reaction's stoichiometry. The weight percentage of brucite and gypsum for all coatings is presented in Figure 5. It can be observed that M1m coating had more brucite than gypsum on its surface, in contrast with the M3m coating that gypsum was formed, while brucite was consumed. This series of coatings with MC presented a gradual reduction of brucite and increase of gypsum formation on the surface. The series of coatings with MC and CMC presented an increased formation of gypsum, no matter the brucite consumption.

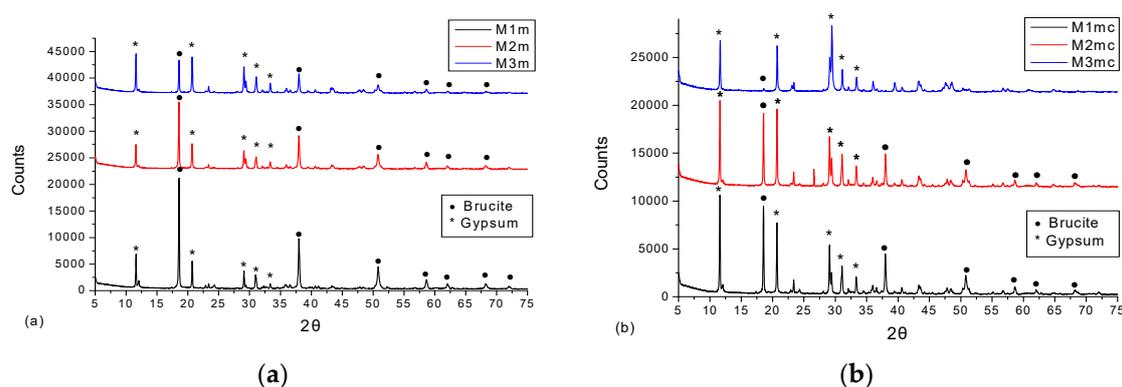


Figure 4. XRD overlay diffractograms of coatings, after acid spraying of 17% of the reaction's stoichiometry: (a) coatings with MC; (b) coatings with MC and CMC.

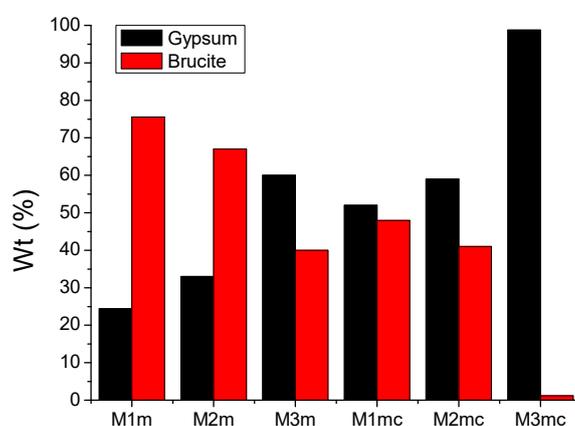


Figure 5. Weight percentage of gypsum and brucite mineral phases of all coatings, after acid spraying of 17% of the reaction's stoichiometry.

4. Discussion

Six different coatings with magnesium hydroxide were applied on concrete surface to evaluate their corrosion protection. The first triplet of coatings had methyl-cellulose as adhesion additive and the second triplet had methyl-cellulose and carboxymethyl-cellulose as adhesion additive. The coatings' adhesion ability was tested with pull-off method. As Table 3 indicates both in thin and thick layers, the coatings with MC exhibited better adhesion with the substrate. The M1m coating had the largest bond strength than all coatings. The bond strength decreases while the amount of cellulose decreases. Moreover, the MC coatings presented cohesion failure, apart from adhesion failure

between the substrate and the coating. This indicates a better adhesion with the concrete for MC coatings.

As far as the acid spraying is concerned, the consumption time of all coatings was increased with respect to the theoretical consumption duration (Table 4). Thick layers provided more durable protection, than thin ones. Additionally, the increased cellulose concentration led to increased consumption time. The surface pH of all coatings remained in alkaline region during the acid spraying. As Figures 1–3 show, the surface pH was above the value of 8 in all cases and that showed that the coatings can block the growth of acidophilic microorganisms.

The XRD analysis of the samples from the surface of coated and acid sprayed concrete blocks led to conclusions about gypsum formation and the coatings' consumption (brucite interaction). Nevertheless, under the above conditions, this method cannot determine the water-soluble magnesium sulfate that was produced. The results were quantified using the Rietveld refinement, in order to evaluate them as weight percentage of brucite and gypsum. Figure 5 shows that M3m and M3mc coatings had smaller amount of brucite on their surface than the other coatings, while they presented increased gypsum formation. M1mc and M2mc coatings exhibited gypsum formation before their coating was consumed.

5. Conclusions

Coatings with different celluloses and different cellulose amounts were evaluated for their corrosion protection on concrete specimens. Three coatings were synthesized with methyl-cellulose (M1m, M2m, M3m) and three coatings were synthesized with a mix of methyl-cellulose and carboxymethyl-cellulose (M1mc, M2mc, M3mc).

Coatings with MC exhibit better adhesion ability and bond strength, than the coatings with the mix of celluloses. In particular, M1m showed the best adhesion properties with concrete. The amount of celluloses seemed to affect the rate of consumption, since the increase of celluloses in the coating, led to an increase of the consumption duration. Moreover, thick coatings seemed to provide longer protection. The surface pH of coatings was above value eight in all cases. The XRD analysis showed that, in some cases, gypsum was formed before the majority of the coating was consumed. In the cases with the lowest cellulose amount, there was consumption of the coating and more gypsum formation.

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