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Performance of seawater-derived $Mg(OH)_2$ as an alternative coating solution for hydrogen sulfide-induced corrosion in concrete pipes

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ABSTRACT

Inadequate wastewater treatment facilities have raised concerns about improper disposal, posing a significant threat to bodies of water. In the Philippines, 90% of generated wastewater is released untreated into waterways, putting nearby concrete pipe networks at risk for hydrogen sulfide-induced corrosion – a type of biogenic acid corrosion resulting from the anaerobic decomposition of organic materials. To address this issue, this study evaluates the effectiveness of a sustainable concrete surface coating material derived from seawater as an alternative to commercially available magnesium hydroxide ($Mg(OH)_2$). A total of six (6) distinct mixtures were prepared, with varying proportions of seawater-derived and commercially available magnesium hydroxide ranging from 0%, 25%, 50%, 75%, and 100%. Four (4) concrete specimens were cast for each experimental setup. These specimens were placed in a testing chamber and sprayed with 4 mol/L of sulfuric acid solution for four days. The compressive strength of each sample was tested. Response Surface Methodology (RSM) was employed to optimize the combination of seawater-derived and commercially available $Mg(OH)_2$. Based on the generated RSM Model, the optimal coating was determined to contain 61% seawater-derived and 39% commercially available $Mg(OH)_2$, indicating that the utilization of seawater-derived $Mg(OH)_2$ serves as a potential solution to mitigate hydrogen sulfide-induced corrosion in concrete pipes.

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1. INTRODUCTION

In the Philippines, the continuous improper disposal processes of wastewater facilities have detrimentally affected nearby bodies of water. Over 90% of such effluents are released untreated into proximate concrete pipe systems (Domingo & Manejar, 2021). As these wastewaters are mainly characterized by high volumes of organic matter and pathogens, constant exposure to anaerobic systems, such as the inner portions of concrete pipes, results in the proliferation of sulfate-reducing bacteria (SRB). As these microbes facilitate the production of sulfuric acid, infrastructures are rendered vulnerable to hydrogen sulfide-induced corrosion (Bagheri Novair et al., 2024). Current conventional solutions to such challenges include the application of protective coatings mainly composed of epoxy tar coal and commercially available magnesium hydroxide. However, various analyses have observed that continuous application of such methods detrimentally affects the environment. Moreover, modern research has also presented the viability of naturally sourcing magnesium hydroxide from seawater. This extraction process is perceived to result in an overall lower environmental impact than traditional commercially sourced methods (Gong et al., 2018). As such, this study aimed to evaluate the optimal coating ratio of seawater-derived and commercially available magnesium hydroxide to mitigate hydrogen sulfide-induced corrosion in concrete pipes effectively.

2. METHODOLOGY

2.1 Concrete Specimens

Concrete specimens, each with dimensions of 100 mm x 100 mm x 100 mm, were utilized in this study. Four trials were conducted for each coating ratio, resulting in 24 specimens, including control samples.

The concrete mix design followed the specifications of the Department of Public Works and Highways (DPWH) for non-reinforced concrete sewers, storm drains, and culvert pipes. The composition of the mix per cubic meter of concrete is detailed in Table 1. The mix was prepared using a concrete mixer and subsequently cured in water for 28 days.

Table 1. Concrete mix design

Concrete Mix (per 1 cu.m. of concrete)	
Water	216.00 kg/m³
Cement	451.88 kg/m³
Coarse Aggregates	984.30 kg/m³
Fine Aggregates	650.25 kg/m³

2.2 Extraction of Seawater-derived Magnesium Hydroxide Coating

The amount of magnesium hydroxide ($Mg(OH)_2$) coating necessary to cover a single face of a 100 mm x 100 mm x 100 mm x 100 mm concrete specimen was calculated using the stoichiometric relationships of the equations outlined in Eq. (1) and Eq. (2). A basis of 0.002 g/mm² was applied, resulting in a requirement of 20 g of $Mg(OH)_2$ coating per face of the specimen.

$$CaO + H_2O \rightarrow Ca(OH)_2 \tag{1}$$

$$Ca(OH)_2 + Mg^{2+} \rightarrow Mg(OH)_2 \downarrow + Ca^{2+} \tag{2}$$

2.3 Formulation of Magnesium Hydroxide Coating

This study used five varying coating ratios: 100% SW - 0% CA, 75% SW - 25% CA, 50% SW - 50% CA, 25% SW - 75% CA, and 0% SW - 100% CA. The commercially available (CA) component was obtained through the hydration of store-bought magnesium oxide in a process represented by the following Eq. (3):

$$MgO + H_2O \rightarrow Mg(OH)_2 \tag{3}$$

On the other hand, the seawater-derived (SW) components of the mix ratios were extracted from seawater through a series of chemical processes. The desired final product is $Mg(OH)_2$ in precipitate form, as shown in Eq. (2).

According to Gong et al. (2018), seawater contains significant amounts of magnesium, approximately 1.29 g/L. Thus, seawater was expected to provide the magnesium necessary for this reaction. The calcium hydroxide reactant was derived experimentally by hydrating calcium oxide (CaO) as shown in Eq. (1). The water-to-quicklime ratio was determined in accordance with Australian Standard AS 4489.3.1 for lime testing, which recommends adding water at four times the weight of quicklime. The resulting slurry was then sieve-washed through a 100 μm mesh to minimize the presence of insoluble solids and foreign materials that could negatively affect the downstream processes of producing the final magnesium hydroxide precipitate. Once dried calcium oxide (CaO) was obtained, it was reacted with the stoichiometrically determined amount of seawater based on the literature value of the approximate magnesium ion concentration in seawater. This reaction produced magnesium hydroxide precipitate and dissolved calcium ions. The magnesium precipitate was then subjected to sedimentation, double filtration, and oven-drying to obtain the powdered form. The obtained commercial and seawater-derived $Mg(OH)_2$ precipitates were combined according to the weight ratios specified for testing.

The design of the protective coating was based on the study conducted by Merachtsaki et al. (2021), which recommended a solid weight ratio of 57.5% for the overall mixture, with the remaining 42.5% comprising deionized water. This corresponds to 11.30 g of magnesium hydroxide precipitate and 8.5 mL of deionized water per specimen face.

To prepare the coating, 8.5 mL of deionized water was first heated to 90°C to improve the solubility and reaction rates of the subsequent solutes. Once the water reached a stable temperature, 0.2 grams of methyl-cellulose (MC) was added as an adhesive, and the mixture was stirred continuously until it cooled to room temperature. Following this, 11.3 g of magnesium hydroxide, measured according to the required proportions, was gradually incorporated and mixed thoroughly until a homogeneous slurry was obtained. The coating was then applied to the concrete surfaces using a trowel and spatula and left to dry for 24 hours before the initiation of sulfuric acid exposure.

2.4 Exposure to Sulfuric Acid

The concrete specimens were placed in an improvised testing chamber (Fig. 1) and manually sprayed on the top with sulfuric acid, using 12.11 mL of 4M sulfuric acid for each specimen face for four days. This totaled 290.7 mL of 4M sulfuric acid for all 24 specimens per day.

Fig. 1. Improvised testing chamber

This amount was determined using Eq. (4), which indicates that theoretically, 48.45 mL of sulfuric acid is needed to remove the coating from each concrete specimen.

$$Mg(OH)_2 + H_2SO_4 \rightarrow MgSO_4 + 2H_2O \tag{4}$$

2.5 Compressive Strength Testing

To evaluate the effectiveness of the various coating ratios, the compressive strength of each concrete specimen was measured following exposure to sulfuric acid. This assessment was carried out using a Universal Testing Machine (UTM), as seen in Fig. 2, at a load rate of 140 kg/cm^2.

Fig. 2. Universal testing machine (UTM)

An acceptance criterion of 24.5 MPa was adopted for this study in accordance with the standards set by the American Concrete Institute (ACI). According to ACI guidelines, the compressive strength of a concrete specimen is considered satisfactory when test values exceed the specified compressive strength (fc'). Additionally, no individual test result should fall below 3.5 MPa if the specified fc' is 35 MPa or less or more than 10% below the specified fc' value if it exceeds 35 MPa (ACI, 1999). Since this study used a target strength of 28 MPa for all concrete specimens, the acceptance criterion for the compressive strength after exposure to sulfuric acid should not be more than 3.5 MPa below the target strength or 24.5 MPa.

2.6 Response Surface Methodology

The compressive strength data were input into Design-Expert software, which can perform Response Surface Methodology (RSM) based on input parameters, variables, and constraints. RSM uses statistical techniques to create models that optimize independent parameters for a desired response. It establishes a relationship between the dependent variable y and independent variables x_1, x_2, …, x_n, which is then used to predict theoretical values based on these independent parameters. This relationship is represented by Eq. (5).

$$y = f(x_1 + x_2 + \dots) + \varepsilon \tag{5}$$

Where:

y = Dependent variable, response

x_n = Independent variable

bicarbonate (HCO_3^-), and chloride (Cl^-), which are introduced during the material's derivation from seawater (Gaofeng et al., 2009). These additional ions may interfere with the neutralization reaction between H_2SO_4 and $Mg(OH)_2$, potentially impacting the effectiveness of the coating in mitigating hydrogen sulfide-induced corrosion.

Despite this decreasing trend, the coating ratios 75% SW - 25% CA, 50% SW - 50% CA, and 25% SW - 75% CA were still able to meet the acceptance criterion. This indicates that incorporating seawater-derived magnesium hydroxide is a viable alternative concrete coating to mitigate hydrogen sulfide-induced corrosion.

To further illustrate, Fig. 3 displays the box-and-whisker plot for the compressive strength data of each coating ratio.

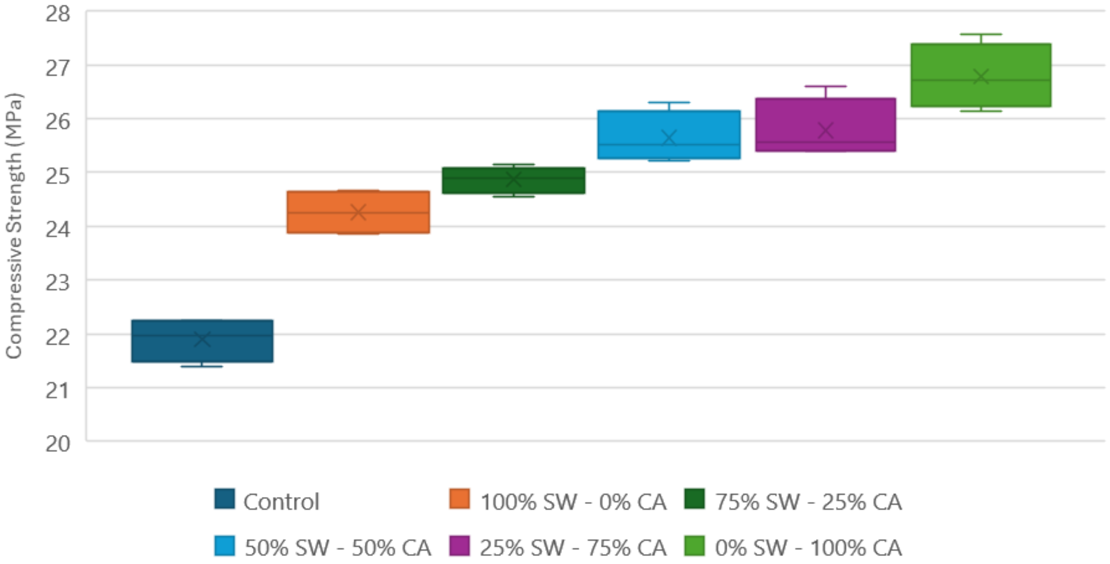

Fig. 3. Box-and-whisker plot for compressive strength

As seen in Fig. 3, the compressive strength of the concrete specimens all falls within the interquartile ranges. This indicates no outliers in the data set, signifying consistency in the results for the compressive strength for each ratio.

3.2 Response Surface Methodology

The experimental data were analyzed to optimize compressive strength in this study. An RSM model was developed using the best-fitting interaction equation to represent the system. The models were compared using Design-Expert software, specifically evaluating linear and 2-factor interaction models. This study set a two-tailed 95% confidence interval, with a significance level of 0.05 as the basis for the generated model. Table 4 presents the p-values and R^2 values for each model.

Table 4. P-value and R^2 of models generated

Model	**P-value**	**Adjusted R^2**	**Predicted R^2**

Linear	<0.0001	0.9213	0.9061
2 Factor Interaction	0.8702	0.9175	0.8956

A comparison of both models shows that the p-value for the linear model is less than 0.0001, which is below the significance level of 0.05. In contrast, the 2-factor interaction model has a p-value of 0.8702, exceeding the significance level. This suggests that the linear model provides a better fit and is more representative of the experimental data. Additionally, the linear model's adjusted and predicted R^2 values are closer to 1. Therefore, the linear model equation was chosen to represent the data as shown in Eq. (8).

$$CS = 21.895 + 0.023815\, SW\ Mg(OH)_2 + 0.047635\, CA\ Mg(OH)_2 \tag{8}$$

Where:

CS = Compressive strength (f'c)

SW $Mg(OH)_2$ = Seawater-derived magnesium hydroxide coating

CA $Mg(OH)_2$ = Commercially available magnesium hydroxide coating

Based on Eq. (8), a surface plot was developed to illustrate the relationship between the three variables. Fig. 4 displays this surface plot for compressive strength.

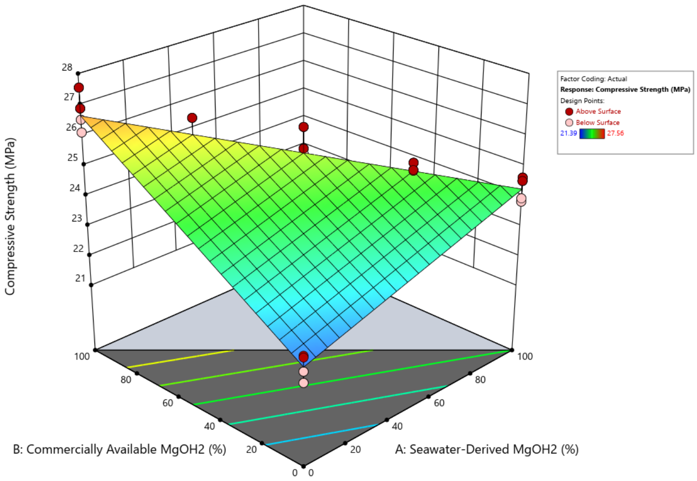

Fig. 4. Surface plot of compressive strength for commercially available $Mg(OH)_2$ vs. seawater-derived $Mg(OH)_2$

The surface plot shows that as the percentage of both commercially available $Mg(OH)_2$ and seawater-derived $Mg(OH)_2$ coatings increase, the compressive strength improves compared to the control (without coating). This suggests that a coating significantly increases the concrete's ability to mitigate corrosion. However, the surface plot also shows that the compressive strength decreases as seawater-derived $Mg(OH)_2$ increases while the proportion of commercially available $Mg(OH)_2$ decreases. Therefore, the optimal coating ratio can be identified by locating the point on the plot where the compressive strength reaches the target value of 24.5 MPa.

The target value and constraints of the data were considered to determine the optimal coating ratios. Table 5 presents a summary of the optimization constraints for compressive strength.

Table 5. Optimization Constraints

Parameter	Goal	Lower Limit	Target	Upper Limit
Compressive Strength	Target	21.39	24.5	27.56

Table 6 presents the top three solutions generated by the RSM model. The model produced multiple solutions based on the provided data and constraints. To achieve the target compressive strength, various coating ratios were suggested. The RSM model provided a theoretical compressive strength value for each specified coating ratio of seawater-derived (%) and commercially available (%).

Table 6.RSM optimization solutions

Solution	1	2	3
SW%	62	61	60
CA%	38	39	40
Compressive Strength (MPa)	24.5	24.5	24.5
Desirability	1.000	1.000	1.000

Based on the solutions obtained, the optimal coating ratio for achieving a compressive strength of 24.5 MPa falls within the 60% to 62% SW range. Since all solutions had a desirability value of 1.000, the identified coating ratios precisely meet the target compressive strength of 24.5 MPa. As this study aims to maximize the use of seawater-derived magnesium hydroxide while still meeting the target strength, the coating ratio of 62% SW - 38% CA was selected.

4. CONCLUSIONS

The compressive strength results indicated that all coating ratios, except for the 100% seawater-derived magnesium hydroxide (SW) and 0% commercially available magnesium hydroxide (CA) ratio, achieved a compressive strength of at least 24.5 MPa after exposure to sulfuric acid. Moreover, all coated specimens outperformed the non-coated control specimens, demonstrating the potential of combining seawater-derived magnesium hydroxide with its commercially available counterpart to enhance the sustainability of the coating.

Using the compressive strength test data, an RSM model was generated with Design-Expert software to determine the optimal coating ratio of seawater-derived to commercially available magnesium hydroxide, with an acceptance criterion of 24.5 MPa. The best-fit model was linear, with a predicted R^2 of 0.906. The optimal coating ratio was 62% SW and 38% CA. This finding illustrates the effectiveness of integrating seawater-derived magnesium hydroxide in mitigating hydrogen sulfide-induced corrosion while meeting the acceptable compressive strength value.

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