

IMPROVING ZINC PHOSPHATING TECHNIQUE USING CALCIUM OXIDE AND MAGNESIUM OXIDE

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ABSTRACT

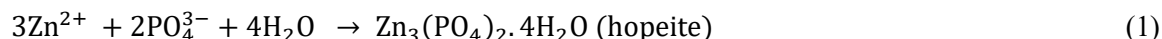
This study aims to improve the zinc phosphating technique, an industrial conversion coating technique, by investigating the performance of both calcium oxide and a combination of calcium oxide and magnesium oxide as particle modifiers in the zinc phosphating process. Mild steel samples were subjected to chemical pretreatment (degreasing, pickling, and activation) before being subjected to a zinc phosphate bath with process variables of phosphating temperatures (65°C and 80°C), phosphating time (40, 60, and 80 minutes) and additive concentrations (calcium oxide and a combination of calcium oxide and magnesium oxide) of 0.9 g/L and 1.8 g/L. The SEM/EDX analysis of the coated samples was carried out before the sample weight loss test. For the calcium-modified phosphating process, bath conditions of 65 °C and 1.8 g/L produce a more uniform coating formation, with SEM/EDX analysis. A very high average inhibition efficiency of 54.11% was obtained for the coated mild steel at 65°C and 1.8 g/L for calcium calcium-modified zinc phosphating process. For the calcium-magnesium additive-modified phosphate process, conditions of 80°C and 1.8 g/L concentration gave the best coating. That is, the MgO and CaO-modified zinc phosphating process had a better synergetic and compatibility behavior at temperatures of 80°C and increased additive concentration, with an inhibition efficiency of 32.68%. Based on the values of K_{ads} and ΔG_{ads} obtained, both the calcium additive adsorption process and calcium-magnesium additive adsorption process can be described by Langmuir and Freundlich isotherms. In each case, the adsorption process was physical adsorption and the process was exothermic, as justified by ΔH_{ads} .

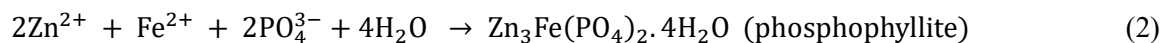
Keywords: Calcium Oxide, Coating, Corrosion, Magnesium Oxide, Zinc Phosphating.

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INTRODUCTION

Metals, especially mild steels, have wide areas of industrial applications but very susceptible to corrosion to form compounds.¹⁻⁵ This is because metals are thermodynamically more stable in their compound state than their elemental state.⁶⁻⁹ The phosphating technique of mild steel is a reliable corrosion prevention phenomenon that causes metal steel surfaces to be electrically non-conductive through the formation of a thin and highly adhesive insoluble phosphate (coating) on the surface.^{10,11} Phosphating is an electrochemical process. Phosphate solution, which is essentially a phosphoric acid-based solution, reacts electrochemically with steel when it comes into contact with it. At the anodic site, Fe^{2+} begins to dissolve and release electrons, while at the cathodic site, H^+ is reduced.¹² The three main types of phosphate coatings are iron phosphate coating, manganite phosphate coatings, and zinc phosphate coatings.¹³ Zinc phosphate coating which can be applied to mild steel is adjudged as having excellent corrosion and wear resistance, good lubrication, adhesion, and affordable process; hence it is being used extensively.¹⁴ As a result of chemical interactions between Zn^{2+} and PO_4^{3-} ions in the coating solution, hopeite ($Zn_3(PO_4)_2 \cdot 4H_2O$) is precipitated when hydrogen evolution causes pH values at the metal-bath contact to rise noticeably into the fundamental region.¹⁵⁻¹⁷ Phosphophyllite is produced when iron ions and other essential ions present in the phosphating bath interact, to form insoluble phosphate depositions on mild steel surface, as shown in Eqs.-1 and 2.¹⁸





Several research on how to improve zinc phosphating effectiveness has been carried out through the introduction of different compounds such as accelerators (e.g. NO_3^- , NO_2^-), activators (e.g. Cl^- , F^-), stabilizers, additives (Mn^{2+} , Mo^{2+} , Cu^{2+} , Ca^{2+} , Ni^{2+}).¹⁹ The focus of this research work is to investigate and compare the effects of Ca^{2+} and a combination of Ca^{2+} and Mg^{2+} , as additives in the preparation of zinc phosphating bath, at different concentrations (0.9 g/L and 1.8 g/L), different phosphating times (40, 60 and 80 minutes) and temperatures (65 °C and 80 °C). And to subject the coated samples to a weight loss test, to establish the adsorption isotherm for the coating process, and to determine the thermodynamics parameters of the adsorption process.

EXPERIMENTAL

Physical Treatment/Preparation of Mild Steel Samples

Mild steel was cut into smaller samples of the dimensions 250 mm by 250 mm. A soft cup brush attached to a hand-grinding machine was then used to polish the surfaces of the metal samples before the application of emery papers (of different sizes) to achieve the smooth surfaces required for efficient coating. A small hole was made on each sample of the mild steel so as to ensure suspension of the sample (using thread) during the pre-treatment stage and the phosphating process.

Chemical Treatment of Mild Steel Samples

Chemical pre-treatment operations on the surface of mild steel are essential requirements for an effective phosphating process. These operations include metal degreasing, pickling, activation, and drying. Rinsing with distilled water was done at the end of each operation before the commencement of the next pretreatment operation. During degreasing, each sample was dipped into 1.0 M NaOH solution for a minute. This was followed by pickling in a weak 0.5 M HCl solution and then activated in an H_2O_2 solution.

Preparation of Zinc Phosphating Bath

Table-1 shows the reagent concentrations utilized for the preparation of the phosphating bath.

| Reagents | Chemical Formula | Concentration (g/L) |
|-----------------|----------------------------|---------------------|
| Zinc Oxide | ZnO | 5.0 |
| Zinc Nitrate | $\text{Zn}(\text{NO}_3)_2$ | 0.2 |
| Sodium Nitrite | NaNO_2 | 0.1 |
| Additives | CaO and MgO | 0.9, 1.8 |
| Phosphoric acid | H_2PO_3 | 30 mL |

Experimental Design for Metal Sample Phosphating

Table-2 reveals the design of the experiment adopted during the phosphating (coating) of the metal samples. The varied reagents are the additives (CaO and MgO) of concentrations 0.9 g/L and 1.8 g/L. CaO additive was used separately and a combination of CaO and MgO additives (in 50:50) was also considered. And there was a control experiment in which no additive (C_0) was utilized. The phosphating temperature of $T_1 = 65^\circ\text{C}$ and $T_2 = 80^\circ\text{C}$, as well as three phosphating time of $t_1 = 40$ minutes, $t_2 = 60$ minutes and $t_3 = 80$ minutes were considered.

Table-2: Design of Experiment for the Phosphating Process

| Temperature | C_0 | C_1 | C_2 |
|-------------|-------|-------|-------|
| T_1 | t_1 | t_1 | t_1 |
| | t_2 | t_2 | t_2 |
| | t_3 | t_3 | t_3 |
| T_2 | t_1 | t_1 | t_1 |
| | t_2 | t_2 | t_2 |
| | t_3 | t_3 | t_3 |

$T_1=65^\circ\text{C}$, $T_2=80^\circ\text{C}$, $C_0=0\text{g/L}$, $C_1=0.9\text{ g/L}$, $C_2=1.8\text{ g/L}$
 $t_1 = 40$ minutes, $t_2 = 60$ minutes, $t_3 = 80$ minutes

SEM/EDX Analysis of the Coated Samples

In order to determine the morphology of the phosphate metal surface, SEM analysis involving scanning the metal surface to generate images (using Jeol JSM – 7600F UHR Analytical FEG SEM) and EDX analysis involving the elemental composition of the surface coatings were determined.

Corrosion (Gravimetric) Tests

The strength of the phosphating process was evaluated by subjecting the coated surfaces to a gravimetric (weight loss) test. The coated mild steel samples were immersed in 3.5 wt% NaCl solution and left for 10 days. The weight loss (W) was measured every 2 days using Eq. 3.

$$W = W_1 - W_2 \quad (3)$$

Where W_1 is the weight of the coated metal before the corrosion experiment and W_2 is the weight of the coated metal after corrosion.

Adsorption on the Mild Steel Surface

The adsorption mechanism of calcium and calcium-magnesium-modified zinc phosphate coating on mild steel was determined by considering both the Langmuir and Freundlich adsorption isotherms, using Eqs. 4 and 5.

$$\frac{C}{\theta} = \frac{1}{K_{ad}} + C \quad (4)$$

$$\log \theta = \log K_{ads} + n \log C \quad (5)$$

Where n is an empirical constant, θ is the surface coverage, C is the inhibitor (additive) concentration, and K_{ads} is the adsorption equilibrium constant.

RESULTS AND DISCUSSION

XRF Analysis of the Plain Mild Steel Sample

Table-3 shows the results obtained from the XRF content evaluation of the plain mild steel sample. Iron (Fe) accounted for 88% of the mild steel, which accounts for 88.10% of the sample.

Table-3: Mild Steel Composition

| Element | (%) |
|---------|-------|
| Si | 0.70 |
| Fe | 88.10 |
| Al | 0.14 |
| Mn | 0.30 |
| Ca | 0.80 |
| P | 0.01 |
| K | 0.02 |
| Ti | 0.02 |
| Mg | 0.50 |
| Na | 0.002 |
| Sn | 4.67 |
| Cl | 0.04 |
| Cu | 4.80 |
| Total | 100 |

Surface Characterization of the Coated Mild Steel Samples

Figure-1(i–ii) shows the results from the SEM analysis and the corresponding EDX analysis of the mild steel sample coated with calcium oxide additive at 65 °C. The metal surface experienced fair surface coverage, as characterized by roughness and pores especially at 0.9 g/L concentration of calcium additive (Fig.-1(i)). The surface coating was relatively more compact and uniform with a 1.8 g/L concentration of calcium additive (Fig.-1(ii)). Also, the EDX result revealed an increase in calcium composition on the metal surface from 5.40% in Fig.-1(i) to 26.33% in Fig.-1(ii). Hence, an increase in the concentration and content of calcium

enhanced a better distribution of particles on the metal surface, as justified by an enlargement of the coating coverage. That is, an increase in the concentration of calcium ions (from 0.9 to 1.8 g/L calcium additive) in the phosphating bath at 65°C showed a decrease in the surface porosity and a more uniform coating.

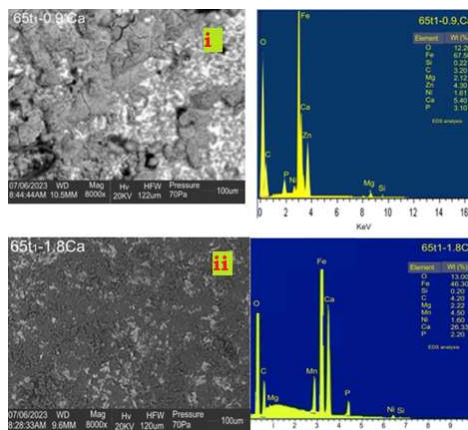


Fig.-1(i-ii): SEM/EDX Analysis of the Mild Steel Sample Coated with Calcium at 65°C

The results of SEM/EDX analysis of the phosphate mild steel samples that are laden with calcium additive at 80°C are shown in Fig.-2(i-ii). The coating was fairly more compacted at 1.8 g/L calcium additive (Fig.-2(ii)) compared to the result obtained at 0.9 g/L calcium additive concentration (Fig.-2(i)). Also, the EDX analysis revealed an increase in Fe content (from 50.50% to 60.50%) as the concentration of calcium additive increased. The results of better coating at 1.8 g/L calcium additive at 80°C corroborate the results obtained at 65°C phosphating temperature. This further established the literature findings of good phosphating at high calcium concentration as an excellent grains distributor.^{20,21}

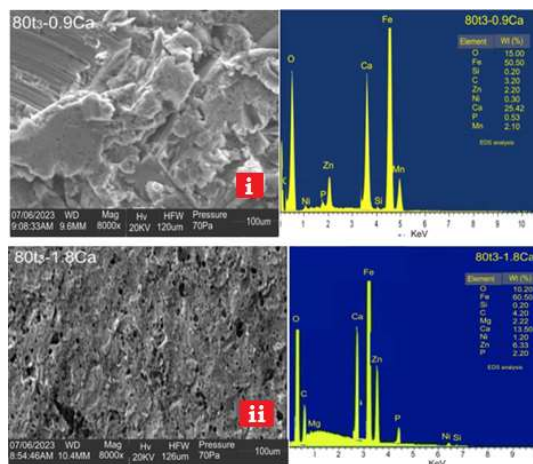


Fig.-2(i-ii): SEM/EDX Analysis of the Mild Steel Sample Coated with Calcium at 80°C

Figure-3(i-ii) shows the results from the SEM analysis and the corresponding EDX analysis of the mild steel sample coated with calcium-magnesium additive at 65 °C. In general, uniform coating was observed with calcium-magnesium additive at 65 °C phosphating temperature. A more perfect coating was noticed with 0.9 g/L calcium-magnesium additive compared to the result from 1.8 g/L calcium-magnesium additive. EDX analysis showed no significant difference in calcium and magnesium contents in Fig.-3(i) and Fig.-3(ii), despite an increase in additive concentration from 0.9 g/L to 1.8 g/L. It could be inferred that there was a synergetic performance of calcium and magnesium (as excellent coating agents), and the optimum condition for the performance is at 0.9 g/L calcium-magnesium. Also, the synergetic behavior of the combined calcium and magnesium produced a far better coating in relation to the effect of calcium additive only (Fig.-2).

Figure-4(i-ii) shows the results from the SEM analysis and the corresponding EDX analysis of the mild steel sample coated with calcium-magnesium additive at 80 °C. The coating was better at 1.8 g/L calcium-

magnesium additive compared to the results at 0.9 g/L calcium-magnesium additive. The general observation was that coating with calcium-magnesium additive gave a more reliable coating compared to the ones from calcium additive.

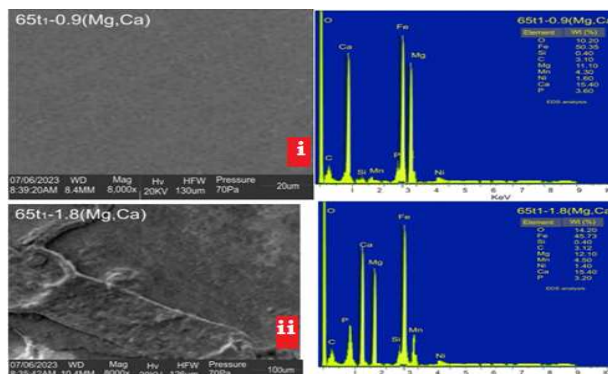


Fig.-3(i-ii): SEM/EDX Analysis of the Mild Steel Coated with Calcium-Magnesium at 65°C

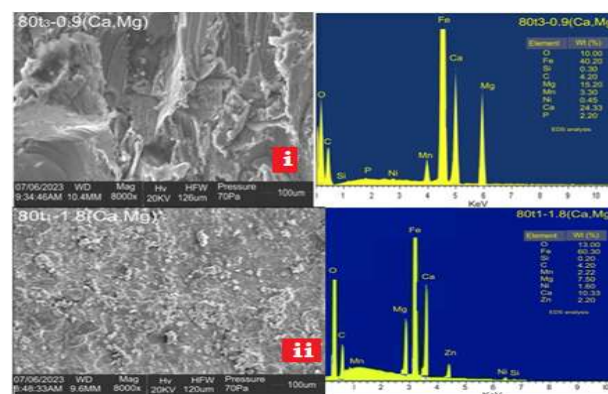


Fig.-4(i-ii): SEM/EDX Analysis of the Mild Steel Coated with Calcium-Magnesium At 80°C

The Coating Thickness of Calcium and Calcium-Magnesium Modified Samples

Figure-5 shows the coated mild steel samples' coating thickness. In general, coated samples but with no additive (65t₁-C0 and 80t₁-C0) had the least level of coating thickness of approximately 0.01mm. Considering the categories of the phosphating samples modified with calcium oxide additive, sample 65t₁-1.8 Ca (prepared at a phosphating temperature of 65 °C and calcium oxide concentration of 1.8g/L) was observed to have the highest coating thickness of 0.09 mm. This was followed by 80t₃-0.9 Ca. In the categories of the sample modified with calcium-magnesium additive, the 80t₁-1.8 MgCa sample had the highest coating thickness of 0.03 mm.

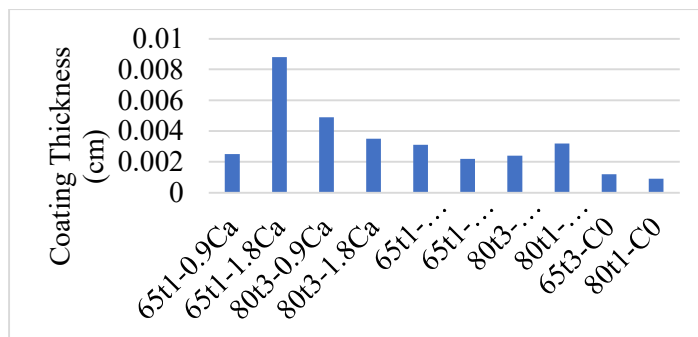


Fig.-5: Coating Thickness of Mild Steel Samples

Weight Loss Test and Inhibition Efficiency of the Coated Mild Steel Samples

Figure-6 depicts the results obtained when the coated samples were subjected to a weight loss test in a solution of 3.5 wt% NaCl for 10 days (at a 2-day interval evaluation). Plain mild steel (uncoated and unmodified

control sample) suffered the highest level of weight loss and this was followed by the unmodified samples (65t₁-C0 and 80t₁-C0), while 65t₁-1.8Ca had the least weight loss.

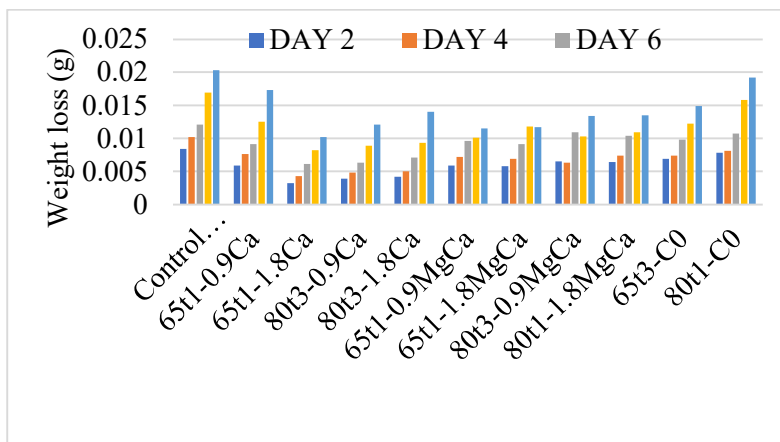


Fig.-6: Mild Steel Sample Weight Loss at Two-Day Intervals

Table-4 displays the coating samples' corrosion-inhibition efficiency after having been examined in a 3.5 wt% NaCl solution. The lowest efficiency was recorded for the unmodified samples (65t₁-C0 and 80t₁-C0), while 65t₁-1.8Ca had the highest average efficiency of 54.11%. The results of inhibition efficiency confirmed the same results obtained from the weight thickness and weight loss.

Table-4: Inhibition Efficiency of Mild Steel Samples

| Sample | Day 2 | Day 4 | Day 6 | Day 8 | Day 10 | Average Inhibition Efficiency (%) |
|---------------------------|-------|-------|-------|-------|--------|-----------------------------------|
| 65t ₁ -0.9Ca | 29.76 | 25.49 | 24.79 | 26.04 | 14.78 | 24.17 |
| 65t ₁ -1.8Ca | 61.90 | 57.84 | 49.59 | 51.48 | 49.75 | 54.11 |
| 80t ₃ -0.9Ca | 53.57 | 52.94 | 47.93 | 47.34 | 40.39 | 48.43 |
| 80t ₃ -1.8Ca | 50.00 | 50.98 | 41.32 | 44.97 | 31.03 | 43.66 |
| 65t ₁ -0.9MgCa | 29.76 | 29.41 | 20.66 | 40.24 | 43.35 | 32.13 |
| 65t ₁ -1.8MgCa | 23.81 | 27.45 | 14.05 | 35.50 | 33.50 | 26.86 |
| 80t ₃ -0.9MgCa | 22.62 | 38.34 | 9.92 | 39.05 | 33.99 | 28.76 |
| 80t ₁ -1.8MgCa | 30.95 | 32.35 | 24.79 | 30.18 | 42.36 | 32.68 |
| 65t ₃ -C0 | 17.86 | 27.45 | 19.01 | 27.81 | 26.60 | 23.75 |
| 80t ₁ -C0 | 7.14 | 20.59 | 11.57 | 6.51 | 5.42 | 10.25 |

Adsorption Isotherms and Thermodynamics Parameters

Figure-7 and 8 show the Langmuir adsorption plot of calcium and calcium-magnesium additives on mild steel samples respectively, while Fig.-9 and 10 show the Freundlich adsorption plot of calcium and calcium-magnesium additives on mild steel samples respectively.

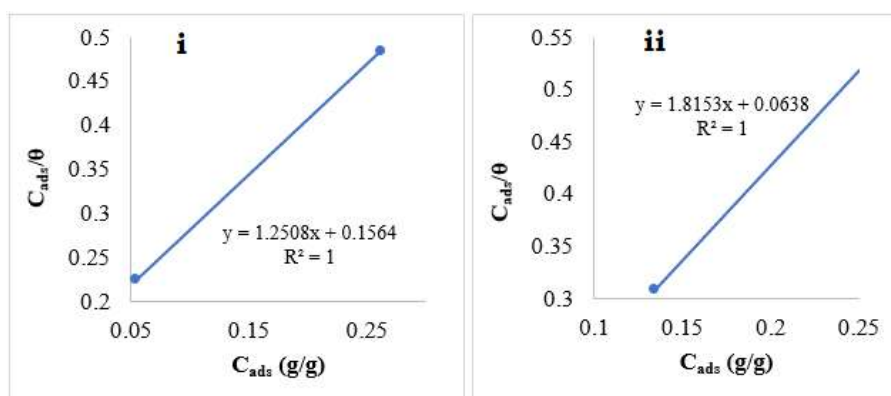


Fig.-7: Langmuir Adsorption Plot of Calcium Additive on Mild Steel Sample at (i) 65°C (ii) 80°C

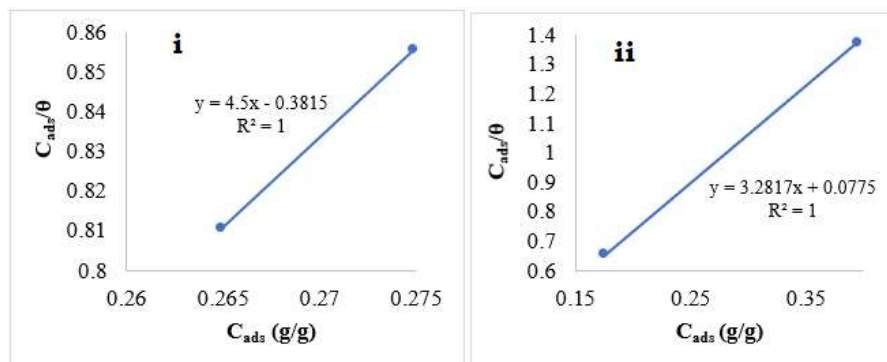


Fig.-8: Langmuir Adsorption of Calcium-Magnesium Additive on Mild Steel at (i) 65°C (ii) 80°C

The corresponding values of the K_{ads} and ΔG_{ads} parameters obtained for both Langmuir and Freundlich adsorption isotherms (at different temperatures of 65°C and 80°C) are presented in Tables 5–6. These results of the positive value of K_{ads} and negative of ΔG_{ads} revealed that both Langmuir and Freundlich adsorption isotherms could be considered for the description of the two forms of additives on the surface of the metal. In addition, the negative values to the change in Gibbs free energy (ΔG_{ads}) implied a spontaneous and physical adsorption process of the additives on the surface of the metal.²²⁻²⁶ Tables-7 revealed the calculated ΔS_{ads} and ΔH_{ads} of the modified zinc phosphating process (using calcium and calcium-magnesium additives at different temperatures). The negative values of ΔS_{ads} indicated that an increase in temperature (from 65 °C to 80 °C) reduced the degree of randomness of the adsorption process of the additives. The negative values of ΔH_{ads} proved that the process of coating was an exothermic process.

Table-5: K_{ads} and ΔG_{ads} Parameters Determined from the Langmuir Plot

| Temperature | Additive | K_{ads} | ΔG_{ads} (kJ/mol) |
|-------------|-------------------|-----------|---------------------------|
| 338K (65°C) | Calcium | 6.3939 | -1.6507 |
| | Magnesium-Calcium | 2.6121 | -0.2580 |
| 353K (80°C) | Calcium | 15.6740 | -1.9873 |
| | Magnesium-Calcium | 12.9032 | -1.9301 |

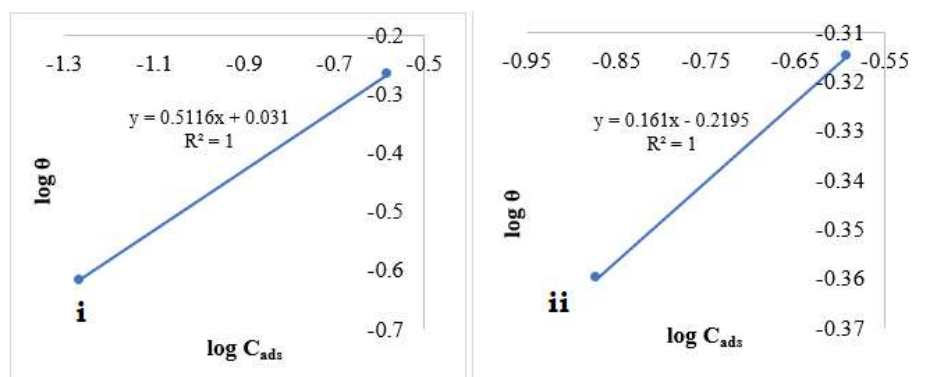


Fig.-9: Freundlich Adsorption Plot of Calcium on Mild Steel Sample at (i) 65°C, (ii) 80°C

Table-6: K_{ads} and ΔG_{ads} Parameters Determined from the Freundlich Plot

| Temperature | Additive | K_{ads} | ΔG_{ads} (kJ/mol) |
|-------------|-------------------|-----------|---------------------------|
| 338K (65°C) | Calcium | 1.0740 | -1.1492 |
| | Calcium-Magnesium | 0.1789 | -6.453 |
| 353K (80°C) | Calcium | 0.6033 | -1.0308 |
| | Calcium-Magnesium | 0.3108 | -8.3600 |

Table-7: ΔS_{ads} and ΔH_{ads} of the Modified Zinc Phosphating Process

| Isotherm | ΔS_{ads} (J mol ⁻¹ K ⁻¹) | ΔH_{ads} (kJ mol ⁻¹) |
|------------|---|--|
| Freundlich | -185.1694 | -57.3474 |
| Langmuir | -90.2480 | -35.32203 |

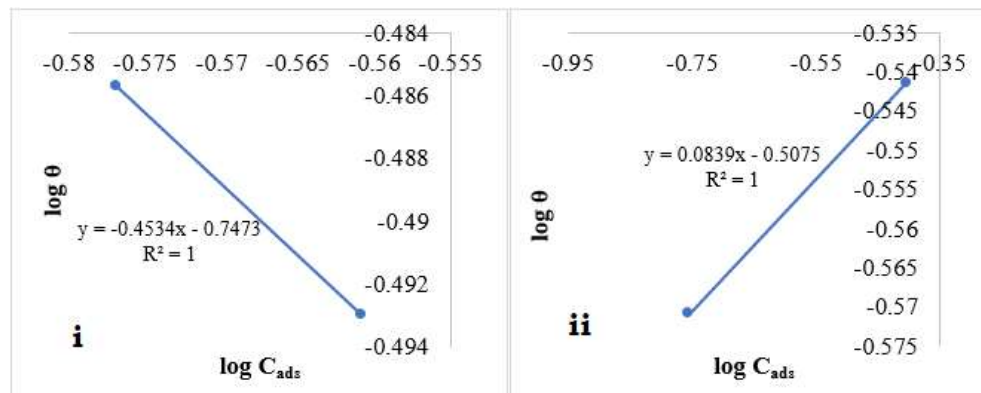


Fig.-10: Freundlich Adsorption of Calcium-Magnesium on Mild Steel at (i) 65°C, (ii) 80°C

CONCLUSION

Zinc phosphate baths modified by calcium oxide as well as the combination of calcium and magnesium oxide were prepared at 0.9 g/L and 1.8 g/L concentrations and a bath temperature of 65°C and 80°C. For the calcium-modified phosphating process, bath conditions of 65°C and 1.8 g/L produce a more uniform coating formation, with good SEM/EDX analysis. A very high average inhibition efficiency of a value of 54.11% was obtained for the coated mild steel at 65°C and 1.8 g/L for calcium calcium-modified zinc phosphating process. For the calcium-magnesium additive-modified phosphate process, conditions of 80 °C and 1.8 g/L concentration gave the best coating. That is, the MgO and CaO-modified zinc phosphating process had a better synergetic and compatibility behavior at increased temperatures of 80°C and increased additive concentration, with a high inhibition efficiency of 32.68%. Based on the values of K_{ads} and ΔG_{ads} obtained, both the calcium additive adsorption process and calcium-magnesium additive adsorption process can be described by Langmuir and Freundlich isotherms. In each case, the adsorption process was physical adsorption and the process was exothermic as well.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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