International Journal of Environmental Sciences
ISSN: 2229-7359
Vol. 11 No. 22s, 2025
https://theaspd.com/index.php

Investigation of Nickel Carbonate as a Functional Accelerator in Zinc Phosphating: Corrosion Behavior and Electrochemical Insights

Suraj dabhekar[1], Dr. Sunil kahar[2]
[1]PhD Scholar, The Maharaja Sayajirao University of Baroda, Vadodara, Gujarat, India
[2]Assitant Professor, The Maharaja Sayajirao University of Baroda, Vadodara, Gujarat, India
CORRESPONDING AUTHOR:
2120suraj@gmail.com

Abstract
The inherently slow reaction kinetics of zinc phosphating—primarily due to polarization caused by hydrogen evolution during the cathodic process—can be enhanced through various chemical, mechanical, and electrochemical strategies. This study investigates the role of nickel carbonate ($NiCO_3$) as an accelerator in improving the corrosion resistance and structural compactness of zinc phosphate coatings. Zinc phosphate layers were successfully deposited on low carbon steel substrates, both in the presence and absence of the accelerator. Nickel carbonate was added to the phosphating solution in concentrations of 0.6%, 1.2%, and 1.8%. Corrosion behavior was analyzed using potentiodynamic polarization tests in a 3.5% NaCl medium. Furthermore, Electrochemical Impedance Spectroscopy (EIS) was conducted to evaluate the compactness of the coatings in the same environment. The results demonstrated that incorporating nickel carbonate significantly improved the performance and density of the phosphate coatings. The inherently slow reaction kinetics of zinc phosphating—primarily due to polarization caused by hydrogen evolution during the cathodic process—can be enhanced through various chemical, mechanical, and electrochemical strategies. This study investigates the role of nickel carbonate ($NiCO_3$) as an accelerator in improving the corrosion resistance and structural compactness of zinc phosphate coatings. Zinc phosphate layers were successfully deposited on low carbon steel substrates, both in the presence and absence of the accelerator. Nickel carbonate was added to the phosphating solution in concentrations of 0.6%, 1.2%, and 1.8%. Corrosion behavior was analyzed using potentiodynamic polarization tests in a 3.5% NaCl medium. Furthermore, Electrochemical Impedance Spectroscopy (EIS) was conducted to evaluate the compactness of the coatings in the same environment. The results demonstrated that incorporating nickel carbonate significantly improved the performance and density of the phosphate coatings.
Keywords: Zinc phosphating, corrosion resistance, Nickel carbonate, potentiodynamic test

1. INTRODUCTION

Metals have played a crucial role in the advancement of human civilization; however, once extracted from their ores, they tend to revert to their more stable oxide states, resulting in considerable economic losses caused by corrosion [1–3]. To mitigate corrosion, surface modification remains the most effective strategy. This generally involves forming a protective layer that acts as a physical shield between the metal surface and its corrosive surroundings [4,5]. Among the various surface treatments, phosphate coating (or phosphating) is widely adopted. This process creates a layer of insoluble crystalline metal-phosphate compounds through chemical or electrochemical interaction between the base metal and a phosphoric acid solution enriched with metal ions such as zinc, iron, or manganese [6].

Phosphating stands out as a widely adopted metal pretreatment technique, extensively used for surface preparation and finishing of both ferrous and non-ferrous substrates [7]. The phosphate layer produced during this process plays a critical role in enhancing paint adhesion and in preventing the onset and spread of corrosion [8]. This treatment promotes the growth of numerous crystals of varying dimensions, which form at nucleation sites, then expand, coalesce, and ultimately blanket the entire metal surface [9]. A significant limitation of phosphating baths lies in their requirement for high operating temperatures, generally between 90 and 98°C [10–12]. Such temperature demands often cause overheating of the bath, leading to operational challenges such as scale buildup on heating coils. As a result, inefficient heating

necessitates more frequent replacement of the bath solution, thereby complicating the maintenance and overall operational efficiency of the process [13–16].

Research Significance

The limitations associated with conventional phosphating methods can be mitigated by enhancing the rate of the phosphating reaction [17]. In real-world applications, this process frequently suffers from slow kinetics due to polarization effects resulting from hydrogen evolution at the cathodic sites [18]. To ensure timely formation of phosphate coatings, the use of accelerators becomes crucial [19]. Acceleration techniques for promoting phosphate layer development are generally classified into three main types: chemical, mechanical, and electrochemical methods [20].

Chemical accelerators are instrumental in improving the chemical, metallurgical, and mechanical characteristics of phosphated surfaces [21]. Frequently employed oxidizing agents include nitrites, chlorates, nitrates, peroxides, and various organic nitro compounds, used either alone or in combination. Typical formulations consist of mixtures such as nitrite-nitrate, nitrite-chlorate-nitrate, and chlorate with nitrobenzene sulfonic acid. In recent studies, compounds like nickel carbonate have also been explored for their potential as alternative accelerators to enhance coating performance. These additives significantly contribute to the acceleration of the phosphate layer formation through specific mechanisms [22–23]. Oxidizing agents function by depolarizing the cathodic half-cell, thereby inhibiting hydrogen buildup at the cathode sites. Concurrently, noble metal ions promote metal dissolution by depositing on the surface and creating cathodic sites with lower over-potentials. This combined effect leads to improved phosphating kinetics and enhanced coating quality [24].

Nickel-based additives have proven to be effective accelerators in zinc phosphating baths, with nickel carbonate ($NiCO_3$) offering a gradual and controlled release of Ni^{2+} ions that play a crucial role in influencing the coating development process [25]. Unlike traditional studies that primarily rely on microscopic evaluation techniques, the present research emphasizes corrosion rate measurements and electrochemical impedance spectroscopy (EIS) to assess the coating's performance [26]. According to previous literature, nickel ions not only enhance the initiation of phosphate crystal formation but also promote the development of denser, less porous coatings [27]. For example, Abdalla et al. (2013) reported a significant decrease in corrosion current density (I_corr) with the inclusion of nickel, suggesting a strong link between Ni^{2+} ions and improved corrosion resistance [28]. In support of this, Lee et al. (2016) demonstrated that nickel-based accelerators increase the charge transfer resistance (R_ct) observed in EIS analyses, indicating the formation of more compact and protective phosphate layers—without the need for SEM or other microscopy-based techniques [29].

In the present work, nickel carbonate is added to a zinc phosphating solution at different concentrations to study its impact on coating density and corrosion protection for low carbon steel (AISI 1020) [30]. The electrochemical behavior is evaluated through EIS, where larger R_ct values and greater capacitive arc diameters signify enhanced coating compactness [31]. Corrosion rates are determined using Tafel extrapolation, enabling a comparative analysis across the varied nickel levels [32]. This approach allows for a robust, microscopy-independent evaluation of the phosphating bath, establishing a direct relationship between nickel carbonate content, corrosion inhibition efficiency, and coating quality. The findings aim to optimize the dosage of nickel carbonate, contributing to the advancement of more efficient and user-friendly phosphating systems [33].

2. MATERIAL AND METHODS

2.1 Process of the Coating

A steel specimen of grade AISI 1020, with dimensions 40 × 30 × 3 mm, was used as the base material for applying the zinc phosphate coating. The coating process employed the immersion technique, which involved a sequence of four treatment baths: degreasing, pickling, acid activation, and finally, zinc phosphating. The specific compositions of each bath along with their respective immersion durations are summarized below [34].

Table 1: Sequence of phosphating

Sequence of pretreatment	Details of Bath Composition	Time
1	Degreasing solution: NaOH= 10%	10 minutes

2	Water rising: distilled water	2 minutes
3	Pickling solution: HCl= 0.1 M	8 minutes
4	Water rising: distilled water	2 minutes
5	Acid Activation solution: $H_2 SO_4$ = 10%	2 minutes

After pretreatment, sample were carried out to phosphating bath with and without addition of Nickel carbonate as per following table.

Table 2: Details of phosphating bath composition

Exp No	Details of Bath Composition	Accelerator addition
1	Zinc Phosphating $NaNO_2$ = 5g/L, ZnO= 20g/L, $H_3 PO_4$ = 15g/L	0%
2	Zinc Phosphating $NaNO_2$ = 5g/L, ZnO= 20g/L, $H_3 PO_4$ = 15g/L	0.6% ($NiCO_3$)
3	Zinc Phosphating $NaNO_2$ = 5g/L, ZnO= 20g/L, $H_3 PO_4$ = 15g/L	1.2% ($NiCO_3$)
4	Zinc Phosphating $NaNO_2$ = 5g/L, ZnO= 20g/L, $H_3 PO_4$ = 15g/L	1.8% ($NiCO_3$)

(a) (b) (c)

(d)

Figure 1: Various stages of treatment (a) Degreasing in NaOH (b) Pickling in HCL (c) Acid Activation in H2SO4 (d) phosphating in ZnO+NaNO2+H3PO4 (e) Hot water Rinsing

2.2 Corrosion Studies

Corrosion studies on the phosphated samples were conducted in a 3.5% NaCl solution, prepared by dissolving analytical-grade sodium chloride in distilled water. Electrochemical evaluations were carried out using a Gamry Reference 600 system equipped with a standard three-electrode setup, wherein the phosphated specimen functioned as the working electrode, graphite as the counter electrode, and a calomel electrode as the reference. The DC potentiodynamic polarization test, performed according to

the ASTM G5 standard, is a widely accepted technique for investigating corrosion behavior. It provides quantitative data on corrosion potential and current density, helping to estimate corrosion rates. The Tafel extrapolation method was employed to interpret the polarization curves, allowing the calculation of both anodic and cathodic corrosion current densities. In addition to polarization testing, Electrochemical Impedance Spectroscopy (EIS) was conducted following ISO 16773:2016 guidelines over a frequency range of 100 kHz to 0.01 Hz using a 10 mV sinusoidal perturbation. EIS offers insight into the electrochemical processes occurring at the metal–solution interface, such as coating resistance, charge transfer behavior, and double-layer capacitance. Together, potentiodynamic polarization and EIS provided a comprehensive understanding of the corrosion resistance and coating compactness of the phosphate layers [35–37].

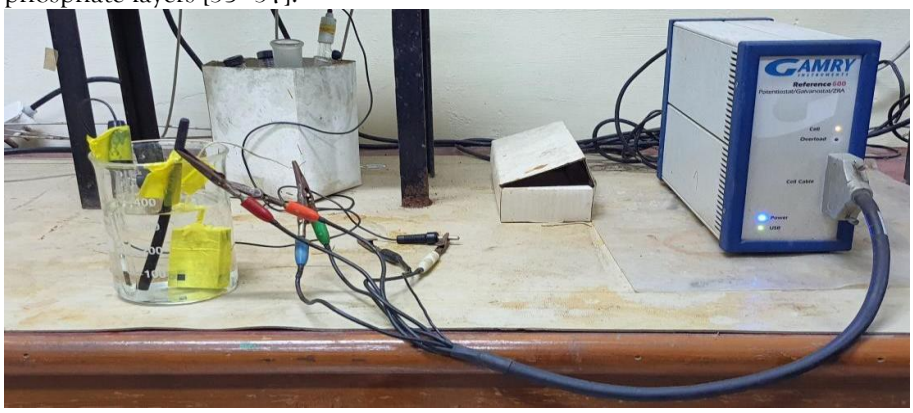

Figure 2: Experimental setup of Potentiodynamic and EIS test

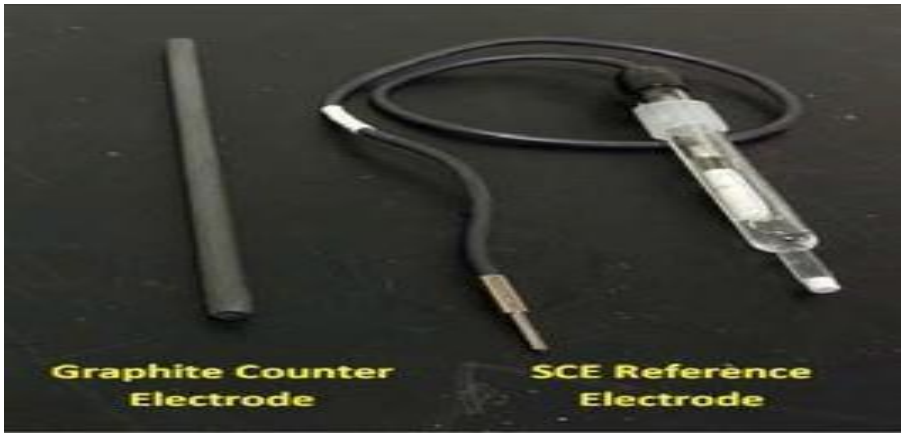

Figure 3: Graphite and SCE electrode

3. RESULTS AND DISCUSSION

3.1Potentiodynamic test

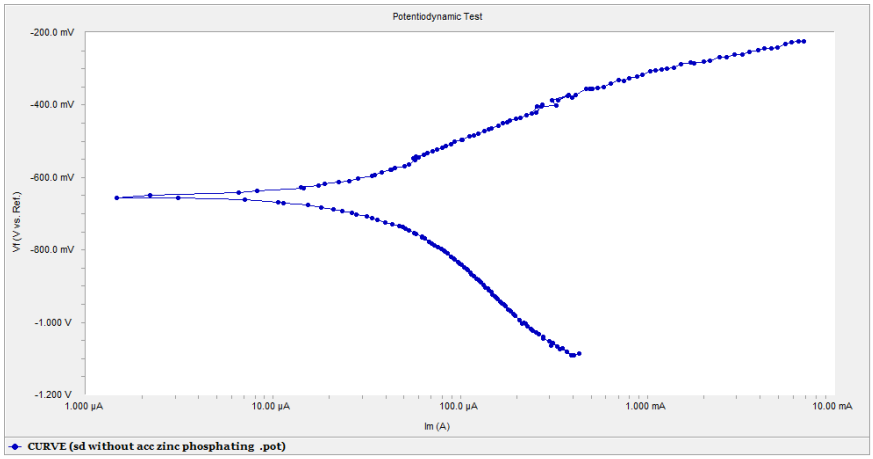

Figure 4: corrosion behaviour of Zinc Phosphate coating without accelerator in 3.5 % NaCl solution

International Journal of Environmental Sciences
ISSN: 2229-7359
Vol. 11 No. 22s, 2025
https://theaspd.com/index.php

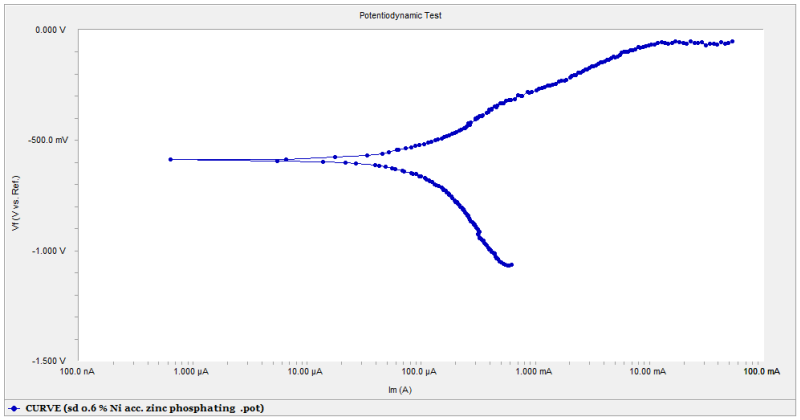

Figure 5: Corrosion behaviour of Zinc Phosphate coating with 0.6 % Nickel accelerator addition in 3.5 % NaCl solution

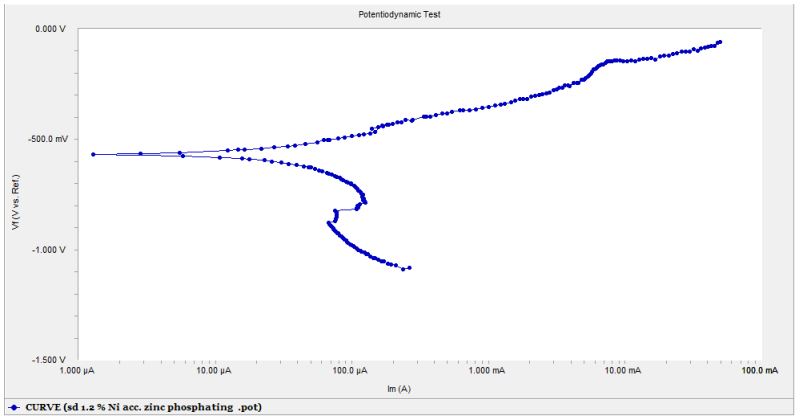

Figure 6: Corrosion behaviour of Zinc Phosphate coating with 1.2 % Nickel accelerator addition in 3.5 % NaCl solution

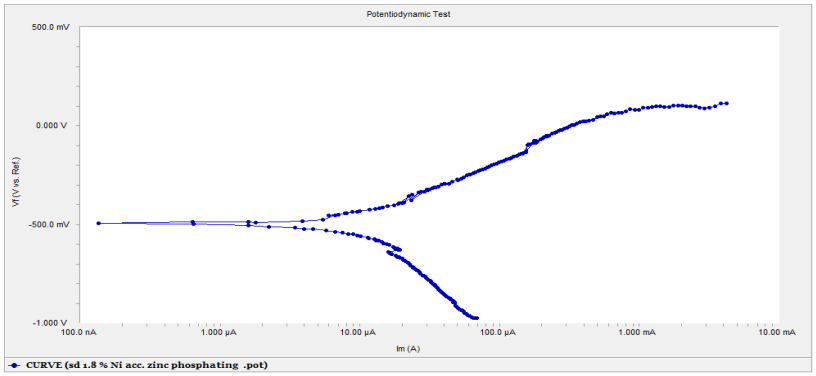

Figure 7: Corrosion behaviour of Zinc Phosphate coating with 1.8 % Nickel accelerator addition in 3.5 % NaCl solution

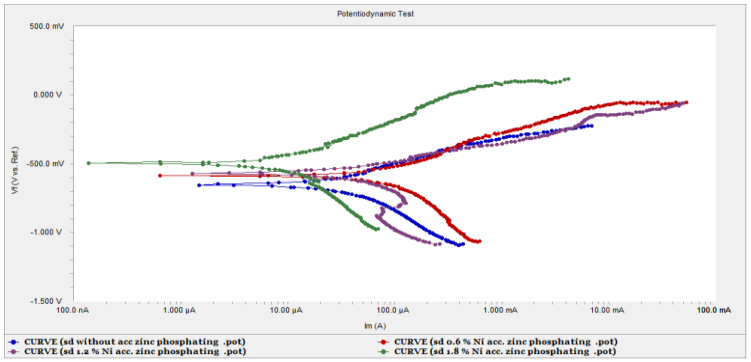

Figure 8: Comparison of Corrosion behavior of Zinc Phosphate coating with Nickle accelerator addition in 3.5% NaCl solution

Table 3: Potentiodynamic test result value in 3.5% NaCl solution

Details of coating	Icorr (µA)	Ecorr (mV)	Corrosion Rate (mpy)
Zinc Phosphate Coating (without accelerators)	124.80	-653.0	181.18
Zinc Phosphate Coating (with accelerators 0.6%)	126.0	-587.0	193.2
Zinc Phosphate Coating (with accelerators 1.2%)	46.80	-567.0	71.94
Zinc Phosphate Coating (with accelerators 1.8%)	24.30	-495.0	37.32

The potentiodynamic polarization tests conducted in 3.5% NaCl solution demonstrated a distinct influence of nickel accelerator concentration on the corrosion resistance of zinc-phosphated low carbon steel. At 0.6% nickel carbonate, a slight increase in corrosion current density (I_corr) was observed compared to the standard zinc phosphated sample. This increase may be attributed to the insufficient availability of Ni^{2+} ions in the bath, which could hinder proper nucleation and growth of the phosphate layer, resulting in a less uniform and less protective coating. Similar behavior has been reported in the literature, where sub-threshold levels of nickel were found to produce irregular or incomplete phosphate coatings with reduced barrier properties [38]. In contrast, samples treated with 1.2% and 1.8% nickel carbonate showed a significant reduction in I_corr, indicating enhanced corrosion resistance. The lowest corrosion rate was recorded at 1.8% nickel, suggesting that higher Ni^{2+} concentrations contribute to the formation of a denser and more protective phosphate layer, consistent with previous findings on the beneficial effects of nickel in zinc phosphating systems [39,40].

3.2Electrochemical Impedance Spectroscopy (EIS) test

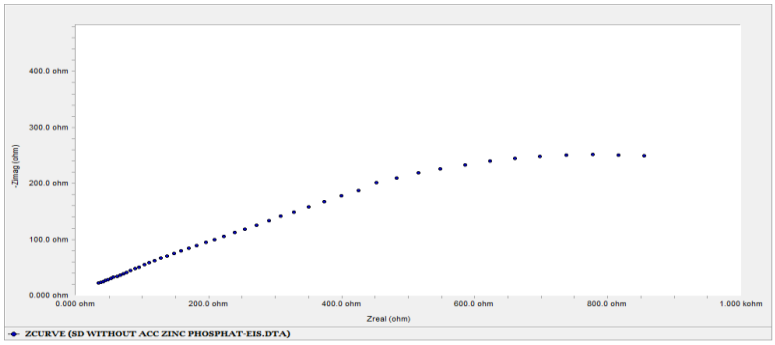

Fig 9. compactness and uniformity of Zinc Phosphate coating without accelerator in 3.5% NaCl solution by EIS Scan

CAPACITANCE VALUE -234.5 ohm

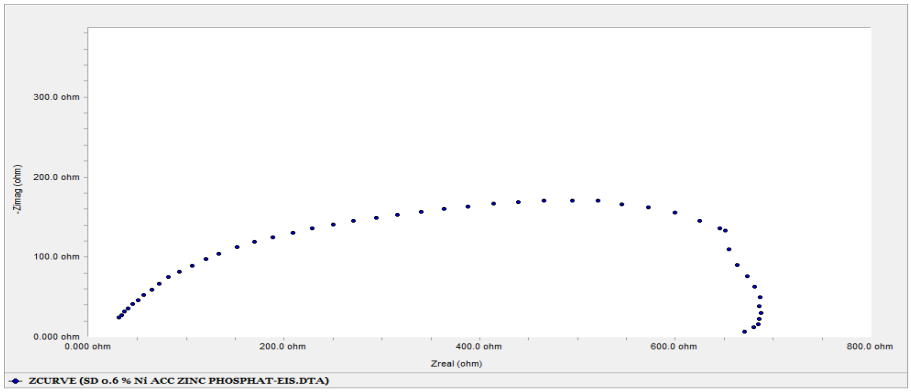

Fig 10. compactness and uniformity of Zinc Phosphate coating with 0.6 % Nickel accelerator in 3.5% NaCl solution by EIS Scan

CAPACITANCE VALUE -199.5 ohm

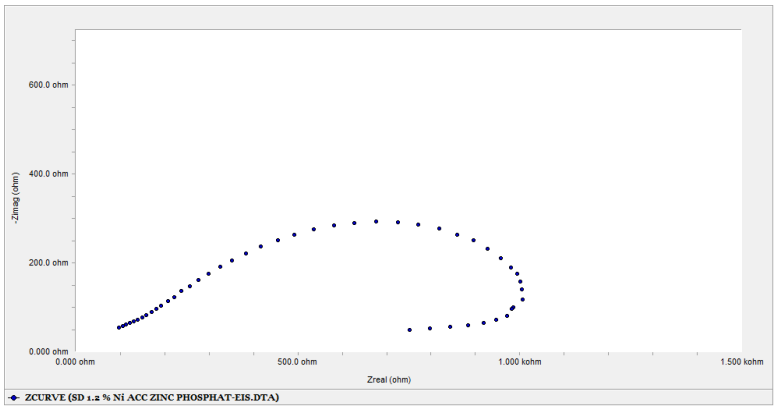

Fig 11. compactness and uniformity of Zinc Phosphate coating with 1.2 % Nickel accelerator in 3.5% NaCl solution by EIS Scan

CAPACITANCE VALUE -302.5 ohm

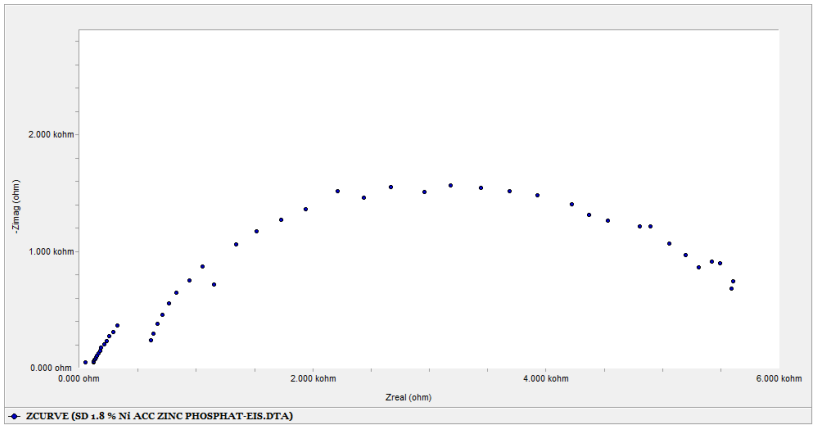

Fig 12. compactness and uniformity of Zinc Phosphate coating with 1.8 % Nickel accelerator in 3.5% NaCl solution by EIS Scan

CAPACITANCE VALUE -1574.5 ohm

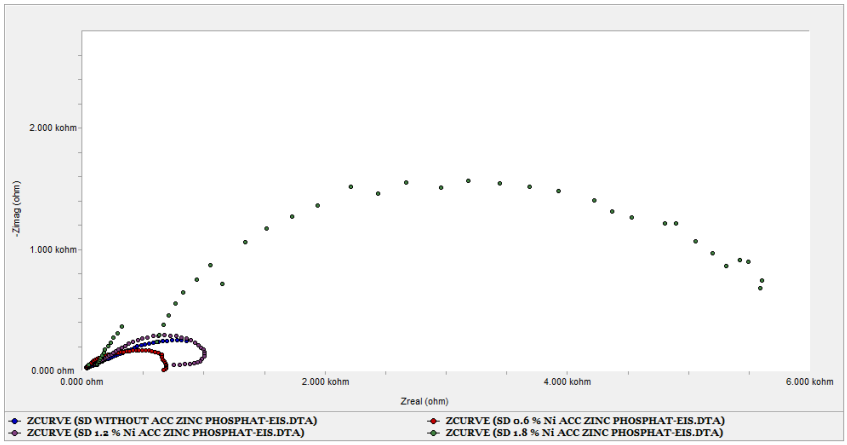

Fig 13 Comparison of compactness and uniformity of Zinc Phosphate coating with and without Nickel carbonate in 3.5% NaCl solution by EIS Scan

Table 5: Electrochemical Impedance Spectroscopy (EIS) test result value in 3.5% NaCl

Zinc Phosphate coating (with & without acceletor)	Capacitance Value
Zinc Phosphate coating (without acceletor)	234.5ohm.
Zinc Phosphate coating (with 0.6 %)	**199.5ohm.**

Zinc Phosphate coating (with 1.2 %)	305.2ohm
Zinc Phosphate coating (with 1.8 %)	1574 ohm

The Electrochemical Impedance test results reveal a strong correlation between coating compactness and charge transfer resistance (R_ct), with higher R_ct values indicating superior barrier properties of the phosphate coating [39,40]. In the case of nickel carbonate-accelerated zinc phosphating, the sample without any accelerator exhibited an R_ct value of 234.5 Ω. Interestingly, the 0.6% nickel-treated sample showed a slight reduction in R_ct to 199.5 Ω, indicating a less compact coating likely due to inadequate Ni^{2+} availability. However, a notable improvement was observed at 1.2% nickel concentration, where the R_ct increased to 305.2 Ω. The most significant enhancement in coating compactness was seen at 1.8% nickel, which demonstrated the highest R_ct value of 1574 Ω. These findings are in agreement with the potentiodynamic test results, where the 1.8% nickel sample also exhibited the lowest corrosion current (I_corr), confirming that optimal nickel concentration plays a critical role in achieving maximum corrosion resistance and coating performance.

4. CONCLUSION

The incorporation of nickel carbonate as an accelerator in zinc phosphating baths has shown a significant impact on improving corrosion resistance, as confirmed by potentiodynamic polarization tests. A slight increase in corrosion rate was observed at 0.6% nickel, likely due to insufficient Ni^{2+} concentration to initiate effective crystal growth. However, higher concentrations of 1.2% and especially 1.8% nickel demonstrated a substantial reduction in corrosion current (I_corr), indicating improved protective performance. Electrochemical Impedance Spectroscopy further supported these findings, with the highest charge transfer resistance (1574 Ω) observed in the 1.8% nickel-treated sample, reflecting superior coating compactness. These results affirm that nickel carbonate, when optimized in concentration, can significantly enhance the barrier properties of zinc phosphate coatings. The study provides useful insights for developing effective corrosion mitigation strategies using nickel-based accelerators in phosphating systems.

5. REFERENCE

1. M.G. Fontana,Corrosion Engineering, 3rd Edition (McGraw-Hill Book Company, Singapore, 1987)
2. U.R. Evans, An Introduction to Metallic Corrosion, 3rd Edition (Edward Arnold Publishers Ltd., London, 1981)..
3. H.H. Uhlig, Corrosion and Corrosion Control, 2nd Edition (John Wiley & Sons, Inc., New York, 1971).
4. F.L. La Que, In: Good Painting Practice, ed. by John D. Keane, Vol. 1, 2nd Edition (Steel Structures Painting Council, Pittsburgh, 1973), Chap. 1.1, p. 3.
5. Henry Leidheiser, Jr., In: Metals Handbook, Vol. 13, 9th Edition (American Society of Metals, Ohio, 1987), p. 377.
6. Phosphate Conversion Coating – A Short Review." (June 2023). Archives of Metallurgy and Materials, 68(3), 1029-1034. DOI: 10.24425/amm.2023.145471.
7. Narayanan, T.S.N. Sankara. (2005). National Metallurgical Laboratory, Madras Centre CSIR, Complex, Taramani, Chennai-600 113, India. Received: April 22, 2005.
8. Freeman, D. B. (1986). Phosphating and Metal Pretreatment - A Guide to Modern Processes and Practice. New York: Industrial Press Inc.
9. T.S.N. Sankara Narayanan and M. Subbaiyan. "Trans. Inst. Met. Finish. 70(2) (1992) 81.
10. T.S.N. Sankara Narayanan and M. Panjatcharam and M. Subbaiyan. "Met. Finish. 91 (1993) 65.
11. T.S.N. Sankara Narayanan and M. Subbaiyan. "Trans. Inst. Met. Finish. 71 (1993) 52.
12. American Chemical Paint Co., British Patent, 501,739 (1939)
13. Societe Continentale Parker, French Patent, 849,856 (1939); Pyrene Company Ltd., British Patent 510,684 (1939).
14. B. Mayer, P. Kuhm, P. Balboni, M. Senner, H.D. Speckmann, J. Geke, J.W. Brouwer and A. Willer, U.S. Patent 6,379,474 (2002).
15. K.S. Rajagopalan, B. Dhandapani, and A. Jayaraman, In: Proceedings of the 3rd International Congress on Metallic Corrosion (1966) Vol. 1, p. 365.
16. K.S. Rajagopalan, C. Rajagopal, N. Krithivasan, M. Tajudeen, and M.E. Kochu Janaki // Werkstoffe und Korrosion 23 (1971) 347.
17. R. Murakami, Y. Mino, and K. Saito, European Patent 0,061,911 (1982); U.K. Patent Appl. 2,097,429 (1982)
18. Guy Lorin, Phosphating of Metals (Finishing Publications Ltd., London, 1974).
19. C. Rajagopal and K.I. Vasu, Conversion Coatings: A Reference for Phosphating, Chromating and Anodizing (Tata McGraw-Hill Publishing Company Ltd., New Delhi, 2000).
20. T.S.N. Sankara Narayanan, "Role of surfactants in phosphate conversion coatings," In: Surfactants in Polymers, Coatings, Inks and Adhesives, ed. by D. Karsa (Blackwell Publishers, Oxford, 2003), Chapter 10, p. 227.

21. G. Bikulcius, V. Burokas, A. Martusiene, and E. Matulionis // Surf. Coat. Technol. 172 (2003) 139.
22. D.R. Gabe, K.A. Akanni, and C.P.S. Johal, In: Proceedings of the Interfinish'84, (Tel Aviv, Israel; 1984), p. 474
23. M. Arthanareeswari, P. Kamaraj, M. Tamilselvi, "Anticorrosive performance of zinc phosphate coatings on mild steel developed using galvanic coupling," Journal of Chemistry 673961 (2013).
24. D.P. Burduhos-Nergis, P. Vizureanu, A.V. Sandu, C. Bejinariu, "Evaluation of the corrosion resistance of phosphate coatings deposited on the surface of the carbon steel used for carabiners manufacturing," Applied Sciences 10 (8), 2753 (2020)
25. D.P. Burduhos-Nergiş, C. Nejneru, R. Cimpoeşu, A.M. Cazac, C. Baciu, D.C. Darabont, C. Bejinariu, "Analysis of chemically deposited phosphate layer on the carabiners steel surface used at personal protective equipments," Quality – Access to Success 20, 77-82 (2019).
26. D.P. Burduhos-Nergis, P. Vizureanu, A.V. Sandu, C. Bejinariu, "Phosphate Surface Treatment for Improving the Corrosion Resistance of the C45 Carbon Steel Used in Carabiners Manufacturing," Materials 13, 3410 (2020).
27. C. Bejinariu, D.P. Burduhos-Nergis, N. Cimpoesu, "Immersion Behavior of Carbon Steel, Phosphate Carbon Steel and Phosphate and Painted Carbon Steel in Saltwater," Materials 14, 188 (2021).
28. LeGeros RZ, Bleiwas CB, Retino M, Rohanizadeh R, LeGeros JP. Zinc effect on the in vitro formation of calcium phosphates: relevance to clinical inhibition of calculus formation. Am J Dent. 1999 Apr;12(2):65-71. PMID: 10477985.
29. Intorp, N. B., Kent, G. D., & Springstead, T. H. (1985). Zinc phosphate conversion coating composition. Google Patents.
30. Zurilla, R., & Hospadaruk, V. (1978). Quantitative test for zinc phosphate coating quality. SAE Technical Paper. Google Scholar.
31. Weng, D., Jokiel, P., Uebleis, A., & Boehni, H. (Year not provided). Corrosion and protection characteristics of zinc and manganese phosphate coatings.
32. Munir, S., Pelletier, M. H., & Walsh, W. R. (2016). Potentiodynamic Corrosion Testing. Journal of Visualized Experiments, 2016(115). DOI:10.3791/54351.
33. S. Jegannathan, T.S.N. Sankara Narayanan, K. Ravichandran, S. Rajeswari, "Progress Organic Coatings 57 (2006) 392.
34. K. Ravichandran, T.S.N. Sankara Narayanan, "Trans. Inst. Met. Finish. 79 (4) (2001) 143.
35. S. Jeganathan, T.S.N. Sankara Narayanan, K. Ravichandran, S. Rajeswari, "Surf. Coat. Technol. 200 (2006) 4117.
36. S. Jeganathan, T.S.N. Sankara Narayanan, K. Ravichandran, S. Rajeswari, "Surf. Coat. Technol. 200 (2006) 6014
37. Randviir, E. P., & Banks, C. E. (2013). Electrochemical impedance spectroscopy: An overview of bioanalytical applications. Analytical Methods, 5(5), 1098-1115. DOI: 10.1039/c3ay26476a.
38. Vadhva, P., Hu, J., Johnson, M. J., Stocker, R., Braglia, M., Brett, D. J. L., & Rettie, A. J. E. (2021). Electrochemical Impedance Spectroscopy for All-Solid-State Batteries: Theory, Methods and Future Outlook. ChemElectroChem. Advance online publication. https://doi.org/10.1002/celc.202100108.
39. Barsoukov, E., & Macdonald, J. R. (2005). Impedance Spectroscopy: Theory, Experiment, and Applications. Wiley.
40. Flis, J., Tobiyama, Y., Shiga, C., & Mochizuki, K. (2002). "J. Flis, Y. Tobiyama, C. Shiga and K. Mochizuki." Journal of Applied Electrochemistry, 32(2002), 401.