Zinc phosphate and vanadate for corrosion inhibition of steel pipelines transport of CO$_2$ rich fluids

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Abstract

The economic transport of CO$_2$ rich fluids, both in the case of carbon capture and sequestration and in transport of natural gas from CO$_2$ rich fields requires the development of economical coatings for pipeline steel. A possible system is sodium orthovanadate (Na$_3$VO$_4$) embedded in a zinc phosphate coating. The effect of that coating on the inhibition of the oxygen reduction reaction on a mild steel surface was investigated at different pH and vanadate concentration. Weight loss and electrochemical polarization methods were applied to evaluate the corrosion rate and inhibition efficiency ($\eta$). Mild steel and zinc phosphate coated steel were immersed in slightly acidic de-ionized water (HCl/H$_2$O) (pH 4) containing different sodium vanadate concentrations (0.0005, 0.001, 0.005 M). Vanadate-plus-zinc phosphate coating has high inhibition efficiency ($\eta$) of 99% by immersion in 0.001 M sodium vanadate at pH 4. As the vanadate concentration increases (> 0.001 M VO$_4^{3-}$) the inhibition efficiency decreases to 25% at 0.005M sodium vanadate. The polarization of steel was performed at pH range of 1-9. The effect of adding sodium orthovanadate on the polarization behavior of steel at high pH was investigated. At high pH (>7) the inhibition efficiency of vanadate ions increases as the VO$_4^{3-}$ concentration dropped to 10 mg/l$^{-1}$. The effect of zinc phosphate aging time in the vanadate inhibitor on the corrosion rate was also investigated.

Keywords: Zinc phosphate, CO$_2$ corrosion, pipelines, Vanadate, Inhibitors, corrosion protection
1. Introduction

Both in carbon sequestration and capture (CCS) and in transport of natural gas from CO$_2$ rich fields economical coatings are required to protect steel pipelines. The fundamental chemistry and electrochemistry is similar in both cases (given that a separate aqueous phase exists in the fluid being transported in CCS).

CO$_2$ impurities such as sulfide compounds are chemically dissolved in the phase and react carbonic acids (and sulfuric) according to the following reaction:

$$\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \quad (1)$$

These corrosive species attack the steel surfaces and create cathodic and anodic galvanic cells. At pH 6 the main corrosion process can be summarized by three cathodic (Eqs. (2a), (2b) and (2c)) and one anodic (Eq. (3)) reactions [Ogundele et al., 1986; Damiań et al., 2003; Nesic et al., 2001].

$$2\text{H}_2\text{CO}_3 + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{HCO}_2^- \quad (2a)$$
$$2\text{HCO}_2^- + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{CO}_3^- \quad (2b)$$
$$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \quad (2c)$$
$$\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^- \quad (3)$$

CO$_2$ corrosion, usually referred to as sweet corrosion, is one of the most severe forms of attack in the oil and gas production and transportation [Kermani et al., 2003; Lopez et al., 2003]. Carbonic acid (H$_2$CO$_3$) is a weak acid which has a strong base that oxidize ferrous cations (Fe$^{2+}$) to form iron carbonate (FeCO$_3$) or bicarbonate (Eqs. 4-6). Iron carbonate (FeCO$_3$) is commonly related with the formation of protective layers on the steel surface [Videm et al., 1989; Videm et al., 1989; Heuer et al., 1999].

$$\text{Fe}^{2+} + \text{CO}_3^{2-} \rightarrow \text{FeCO}_3 \quad (4)$$
$$\text{Fe}^{2+} + 2\text{HCO}_3^- \rightarrow \text{Fe} (\text{HCO}_3)_2 \quad (5)$$
$$\text{Fe} (\text{HCO}_3)_2 \rightarrow \text{FeCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \quad (6)$$
The iron activity may be attributed to the instability of oxides and carbonate formation, and to the support of cathodic reaction (Glezakou et al., 2009) induced by the high hydrogen ion concentration.

In CO₂ capture and storage (CCS), in order to avoid two-phase flow, CO₂ need to be transported either in the supercritical or the liquid state-at pressures ranging from >5 to >10MPa. At these pressures, the solubility of water is limited (0.3-0.4 x 10⁻² mole fraction) (Spycher et al., 2003). The pH value is changed depending on the water mole fraction and other additives (H₂S, SO₂, NO₃⁻) in CO₂ transport. Free water condition is the ideal in CO₂ transport where the pH is >4. As the water contaminant mole fraction increase, the tendency of carbonic acid formation increase that drop the pH value to 3.3. In presence of other contaminants (H₂S, SO₂, NO₃⁻) pH value is dropped to<3 with a recent review indicating that high corrosion levels occur (Cole et al. 2010). Appropriate gas cleaning prior to transport may be able to limit the level of additional contaminates (Cole et al. 2010), however as indicated above if an aqueous phase exists that aqueous phase will have a pH between 3 and 4. Thus for both CCS and for transport of oil or gas a coating that can protect steel at acid pH values below 4 is required.

Corrosion inhibition of steel pipelines in oil and fuel transport is usually performed by incorporating inhibitors in petroleum based oils during transports. The inhibitors, organic materials with amine groups, are often fed with the oils or gases under transport in the pipelines. The inhibitors are usually adsorbed on the steel surface through their active functional group and form a protective film that inhibits the oxygen-reduction reaction. Severe corrosion may occur when film forming inhibitors are removed from the steel by high liquid shear forces [Gerretsen et al., 1993]. Organic inhibitors such as benzimidazole and its derivatives have been employed to protect steel surfaces against corrosion and their inhibition mechanisms were investigated [Kuznetsov et al., 1970; Makovei et al., 1983; Makovei et al., 1985; Voloshin et al., 1988; Popova et al., 1996].

Zinc phosphate conversion coatings are an economical and environmentally friendly process to protect steel, Al and Mg alloys surfaces against corrosion in many industries such as automotive, steel forming, and as a primer for steel and aluminium paint for many years because they enhance the adhesion of the paint to the substrates [Sun et al., 2002; Zimmermann et al., 2003; Li et al., 2004; Akhtar et al., 2006]. Zinc phosphates have a unique crystal structure that is able to carry and store organic and inorganic inhibitors due to their porous structure. A lubricant such as soap (pH > 7) or mineral oil increases the corrosion resistance efficiency of zinc phosphate [Farias et al., 2009]. With the economy of production, environmentally friendly coating, speed of operation and ability to afford excellent corrosion
resistance, wear resistance, adhesion and lubricative properties, zinc phosphate plays a significant role in
the automobile, process and appliance industries [Lorin et al., 1974; Freeman et al., 1986; Rausch et al.,
1990; Rajagopal et al., 2000]. The advantages of phosphate coatings make them suitable to protect steel
pipelines at moderate pH level of >3.3 in oil transport.

Vanadium compounds were reported as effective corrosion inhibitors in a number of anti-
corrosion applications of aluminium [Buchheit, 1995; Guan et al., 2004; Seth et al., 2004; Schem et al.,
2009; Wang et al., 2010]. Vanadium compounds inhibition is due to the formation of an insoluble oxide
thin film (500 nm) over a wide range of pH and environmental conditions [Livage, 1996; Iannuzzi et al.,
2007; Cuevas-Arteaga, 2008; Pulvirenti et al., 2009]. Monovanadate (V1), divanadate (V2),
tetravanadate (V4) and pentavanadate (V5) are different vanadates species that change their electronic
state in different pH. Polymerization of these oligomers to form orange decavanadates (V10) occurs
during acidification [Heath et al., 1981; Larson, 1995; Tracey et al., 1995; Gorzsas et al., 2004;
Aureliano et al., 2005]. At pH 4, only a signal from V10 is detected by $^{51}$V NMR, indicating complete
polymerization of V1–V5. At pH 8.71 V10 partially de-polymerizes to give V2, V4, and V5 species.

For carbon steel pipelines corrosion protection, zinc phosphate coating is an economic,
environmentally friendly and easy to apply. In addition, the phosphate-plus-inhibitor system can
enhance the corrosion protection even more through the unique microstructure of the phosphate crystals
that can absorb and store the different kinds of inhibitors. This article focuses on the surface protection
of steel pipelines at moderate condition (pH 4) using zinc phosphate coating and vanadates inhibitor.
The preparation and testing of the corrosion performance of zinc phosphate layer-plus-vanadate inhibitor
on mild steel by means of chemical and electro-chemical methods were investigated. The effect of
vanadate concentration, aging time and pH on inhibition efficiency was assessed.

2. Experimental procedure

2.1. Materials and Chemicals

Mild steel specimens of chemical composition C-0.13, Si-0.03, Mn-0.31, S-0.05, P-0.2, Ni- 0.01,
Cu-0.01, Cr-0.01 and Fe-Balance (Wt. %) were used. Weight loss method was carried out to evaluate
the inhibition performance of sodium vanadate on mild steel and zinc phosphate coated steel corrosion.
Steel specimens of dimension 50x50x2 mm³ were ground to a 600 grit finish, degreased with ethanol, washed in double distilled water and finally dried with compressed air. The cleaned steel specimens and zinc phosphate coated steel were weighed before and after immersion in chlorinated de-ionized water (H₂O + HCl) at pH4 for 2h in the absence and presence of various concentrations of sodium orthovanadate (0.0005, 0.001, 0.005 M) at room temperature. After immersion the samples were cleaned de-ionized water and ethanol and dried with compressed air. The weight loss measurements were performed using 4 digit electric balance and the inhibitor efficiency was calculated by applying the following formula:

$$\eta(\%) = \frac{W_{u} - W_{i}}{W_{u}} \times 100$$

where, $\eta$ is the inhibitor efficiency, $W_{u}$ and $W_{i}$ are the average weight-losses of test sample after immersion in acidic solution without and with inhibitor respectively.

2.2. Zinc Phosphate Treatment

Zinc phosphate bath was prepared by dissolving approximately 3.1 g zinc oxide in 2.7ml nitric acid (C: 61%) and 3ml phosphoric acid (C: 85%) in 100 ml de-ionized water. 0.01 g MnCO₃ and 0.05 MgCO₃ were dissolved in the concentrated bath to prepare Zn-Mn-Mg phosphate bath. Mn phosphate bath was prepared by dissolving 3.7 g MnCO₃ in 12 ml phosphoric acid in 100 ml de-ionized water. The phosphate bath was diluted to 1 litre with de-ionized water. The bath acidity was adjusted at pH at 2.5 using sodium hydroxide. Upon immersion in the phosphate bath, steel panels chemically react with primary zinc phosphate (Zn(H₂PO₄)₂) solution and insoluble zinc phosphate crystals (hopite-Zn₃(PO₄)₂·4H₂O) of grey color are grown and adhere to the surface. In Mn phosphate bath the steel reacts with primary manganese phosphate and a dark grey layer of manganese tertiary phosphate is grown.

The surface of steel specimens was polished (emery grade: 180 and 400), degreased with ethanol and rinsed with deionized water before immersion in diluted zinc phosphate bath at 60 °C. The immersion time is 5 min followed by rinsing with deionized water and drying with compressed air.

The surface morphology of zinc phosphate crystals was observed using a Philips XL30 FE-SEM with a LinkISIS X-ray analysis system (Oxford Instruments).
A JEOL JDX-3530M X-ray diffractometer system was employed to analyse the phase structure of the zinc phosphate coatings.

2.3. Electrochemical Polarization Measurements

For electrochemical polarization investigations, both the zinc phosphate coated steels and mild steel strips of the same composition were cleaned as mentioned in the previous section and fixed in a perspex electrochemical cell with an exposed area of 3.14 cm$^2$. The electrochemical measurements were carried out in a conventional three-electrode cell. The working electrode was the mild steel specimen (coated or uncoated). A saturated calomel electrode (SCE) and a titanium mesh were used as the reference and counter electrodes respectively. All polarization measurements were carried out at room temperature. The specimens were immersed in the electrolyte for a period of 30 min to allow them reach the equilibrium state before running the polarization measurements. Electro-chemical polarization studies were carried out using a Solartron potentiostat / galvanostat- model 1280B unit. The polarization measurements were carried out at different pH (1-9) by changing the pH of double ionized water (>10 MΩ) using hydrochloric acid and sodium hydroxide solutions. All the measurements were made in a 200 ml working solution.

The potentiodynamic polarization measurements were carried at a potential range of -0.8 to -0.2V vs. reference electrode. The sweep rate was 0.2mVs$^{-1}$. The Tafel method was adopted to acquire the values of the corrosion current ($I_{corr}$). The inhibition efficiency ($\eta$) was calculated from the corrosion current by the following formula:

$$\eta = \frac{I_{corr} - I_{corr}^i}{I_{corr}} \times 100$$

where $I_{corr}^i$ and $I_{corr}$ are the corrosion current densities in the absence and presence of inhibitor respectively.

2.4. ICP-AES Analysis
An Agilent 730 Simultaneous Axial atomic emission spectrophotometric ICP-AES system was applied to detect and evaluate the elemental metal ions concentration (Fe, V, Zn) in the solutions after immersion of the steel and zinc phosphate coated steel in the mild acidic de-ionized water at pH4 for 2 hours. The solutions were diluted to 1:50 by deionised water.

Results and Discussions

3.1. Phosphate Microstructure

Figure 1 shows the scanning electron microscope images of Zn, Zn-Mn-Mg and Mn-phosphate coatings. The different phosphate coatings have different crystal morphologies such as needles, flowers, and scale shapes. The crystals morphology is related to the nucleation and growth mechanism of phosphate crystals on the steel surface. Bath acidity, type of metal-ion (Mn, Mg, Ni,…), and metal surface pretreatment affect the crystal morphology. Mn and Mg metal ions in the phosphate bath have a positive effect on refining and improvement of the phosphate crystal structure as shown in Fig. 1. In zinc phosphate free Mn-Mg bath the crystal size is bigger (Fig. 1a) compared to zinc phosphate bath with Mn-Mg and Mn-phosphate bath (Fig. 1b and1c). This is attributed to the activity of metal ions (Mn and Mg) that creates huge numbers of active sites on the steel surface to initiate the phosphate crystal growth.

The cross-section observed by SEM (Fig. 2) provides information about the phosphate layer thickness (500- 2000 nm) as well as the growth mechanism of the phosphate layer. It was concluded that the phosphate layer is composed of huge numbers of phosphate crystals which grew on the active sites of the steel surface. The growth mechanism of phosphate crystals is affected by many factors including: steel surface roughness, surface chemical activation, type of phosphate bath, and steel microstructure. However, the crystals grow from nano-size to micron size during growth and as a result, overlapping of crystals may occur during growth. The crystals overlapping can be observed in the cross-section SEM micrograph. Overlapping creates channels among the phosphate crystals that host inhibitors, organic paint, minerals oils that inhibit the corrosion by preventing the oxidation reaction of Fe from occurring.

Hopeite (Zn$_3$(PO$_4$)$_2$·4H$_2$O) is the phase structure of the zinc phosphate coating deposited on the steel surface as analysed by X-ray diffraction (Fig. 3). Hopeite is a hydrated zinc phosphate with crystals in
the orthorhombic system. The chemical reaction involved in phosphate deposition is the transfer of primary phosphate salt into tertiary phosphate salt according to the following formula:

\[
3Zn(H_2PO_4) \rightarrow Zn_3(PO_4)_2 + H_3PO_4 + H_2↑
\]

(Primary phosphate) (Tertiary phosphate) (Free acid)

### 3.2. Polarization of Mild Steel and Zinc Phosphate at different pH

Figure 4 shows the polarization behaviour of mild steel and zinc phosphate coated steel at different pH. The corrosion current \(i_{corr}\), and corrosion potential \(E_{corr}\) of mild steel and zinc phosphate on mild steel are listed in Table 1, along with the calculated inhibition efficiency of the zinc phosphate coating. Zinc phosphate and mild steel have similar polarization behaviour at different pH. At low pH (1-3) there is a negative shift of polarization potential from -500 to -650 mV as the pH increases from 1 to 3. A typical feature of these polarization curves was that the hydrogen evolution reaction (cathodic curve) was remarkably accelerated by lowering the pH (increasing HCl concentration). However, the anodic curves obtained showed very similar current densities, regardless of the HCl concentration. At pH 4, the polarization potential of mild steel is significantly shifted towards positive direction that recorded the highest potential value of -159 mV. On the other hand, zinc phosphate coated steel recorded a potential range of -320 to -430 mV at pH range of 4-9. The matching of corrosion potential values of the mild steel and zinc phosphate coated steel at pH 1-3 indicate an erosion of zinc phosphate coating by the acidic electrolyte during the relaxation period (30 min). For steel and zinc phosphate, the corrosion current decreases obviously as the pH increases, indicating a decrease in corrosion rate (Table 1). Erosion of zinc phosphate coating is significantly higher at low pH as the inhibition efficiency of zinc phosphate is nil at pH range of 1-3. The inhibition efficiency of zinc phosphate increased to nearly 70% at pH>3. The results revealed an enhancement in corrosion resistance by applying zinc phosphate coating on mild steel.

### 3.2. Vanadate inhibition and weight loss test

The effect of vanadate concentration on the inhibition of mild steel and zinc phosphate coated steel studied by immersion in mild acidic de-ionized water at pH 4 containing different sodium vanadate
concentrations: 0.0005, 0.001, and 0.005 M. The inhibition efficiency and change in weight loss of steel strips and zinc phosphate coated steel at different vanadate concentration are shown in Fig. 5. Based on the weight loss data, it is observed that zinc phosphate coatings exhibit high inhibition performance ($\eta$) of 86% and 99% in mild acidic solution containing 0.0005 and 0.001 M vanadate, respectively. On the other hand, the vanadate has a lower inhibition performance of 25 and 55% on the corrosion of steel at vanadate concentration of 0.0005 and 0.001 M respectively. Vanadate with molar concentration of 0.001 M has effective inhibition efficiency for both zinc phosphate coated steel and steel corrosion. As the vanadate concentration increases to >0.001M, the inhibition performance decreases. At vanadate concentration of 0.005M, the steel weight increased after immersion, indicating a growth of a film on the surface. Vanadate ions ($\text{VO}_4^{3-}$) probably react with the steel surface by chemical reaction to form an iron vanadate layer on the steel surface that reduces the rate of dissolution of iron in HCl.

ICP-AES Atomic emission spectrophotometric analysis of the acidic solutions containing 0.005M vanadate after immersion of steel and zinc phosphate coated steel samples are listed in Table 2. Fe metal ions were found in the solution used for steel immersion, indicating the reaction of steel surface with the vanadates acidic solution. The zinc phosphate layer prevented the dissolution of iron because there was no iron detected in the solution used for immersion of zinc phosphate coated steel. Also, zinc has not been detected which confirms the stability of the zinc phosphate layer in the acidic solution.

Figure 6 shows SEM and EDS elemental analysis for a layer deposited on the steel surface after immersion in the acidic solution with 0.005M sodium vanadate for 2 hours. An increase in the weight after immersion of the mild steel sample in the acidic solution contains 0.005M sodium vanadates for 2 hours was measured, indicating the development of a layer on the surface. EDS analysis of this layer showed the presence of V, Fe, and oxygen. From the results of atomic analysis and SEM, it was concluded that a vanadate conversion reaction occurred on the steel surface during immersion. The vanadate ions are converted to vanadium pentoxide by consumed the electron released by anodic desolving of iron. A thin layer of vanadium oxide was detected by XRD, EDS and atomic analysis. The reactions involved in vanadate conversion coating are iron dissolution (anodic reaction) and cathodic conversion of vanadate anions (cathodic reaction) into vanadium pentaoxide. The possible reactions are:

$$
\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad (\text{iron dissolution})
$$

$$
\text{VO}_4^{3-} + 2e^- \rightarrow \text{V}_2\text{O}_5 \quad (\text{Vanadium pentaoxide})
$$
3.3 Aging time and Vanadate Concentration

The potentiodynamic polarization curves for zinc phosphate in alkaline-ionized water containing 5, 10 and 20 mg vanadate at pH 9 are shown in Fig. 7. The potential shifted to positive value and the corrosion current density decreased as the vanadate concentration reduced from 20 to 5 mg\textsuperscript{l}\textsuperscript{-1}. The inhibition performance of zinc phosphate coatings increased as the aging time of the zinc phosphate samples in vanadate solution was increased from 1 to 2 hours. The results indicated a higher corrosion protection at low concentration of vanadate inhibitor. The zinc phosphate coating has two advantages in steel protection: as a solid anti-corrosion inhibitor and as a carrier for vanadate inhibitor or any other effective inhibitors. Phosphate crystals adhere well with the steel surface and that prevents the loss of inhibitor film from the surface by gas or liquid shear forces during CO\textsubscript{2} transport. Although there is no available evidence of the presence of vanadate ions attached to zinc phosphate crystals yet, it is likely that vanadate ions are adsorbed and adhered onto the phosphate crystals and steel surface through the channels of the phosphate structure. For high inhibition performance, the optimum concentration for vanadate is 5 mg\textsuperscript{l}\textsuperscript{-1} in alkaline medium and 15-20 mg\textsuperscript{l}\textsuperscript{-1} in acidic medium. At present, it is not known why the inhibitor is working effectively at very low concentration.

3.4 Applicability to CCS or oil and gas applications

A requirement of a coating for both the CCS and the oil and gas transport application was good corrosion protection at moderately acidic pH values. The results in this paper have shown that the combination a zinc phosphate coating and a 0.001 M vanadate solution can lead to 99% efficiency of corrosion inhibition in a saline solution at pH of 4. Thus it is suggested is a good system for future exploration. Such future exploration would need to consider:

1. How to embed the vanadate in the zinc phosphate coating
2. How the system performed under a wider range of acid pH’s
3. How the system performed under supercritical CO\textsubscript{2} at the pressures likely in CCS.

4. Conclusions
Zinc phosphate, as solid inhibitor layer for carbon steel surface, has the advantage of the ability to store inhibitors due to the unique structure of the phosphate crystals. The key observations are:

(1) SEM images of different phosphates showed a decrease in phosphate crystal size by adding Mn and Mg metal ions in Zn phosphate bath.

(2) Zinc phosphate layer has a total thickness of 0.5-2 µm under the experimental conditions.

(3) Phosphate crystals are grown from nano-size to micron size and overlap during growth to create channels of unique structure for hosting inhibitors.

(4) Hopeite is the main phase structure of phosphate crystals.

(5) Polarization curves revealed the erosion of zinc phosphate is significantly higher at low pH and the inhibition efficiency of zinc phosphate is nil at pH range of 1-3.

(6) Phosphate crystals are adhered well with the steel surface that may reduce the loss of inhibitor film from the surface by gas or liquid shear forces during oil transport.

(7) Zinc phosphate coatings exhibit high inhibition performance (η) of 86% and 99% in mild acidic solution containing 0.0005 and 0.001 M vanadate, respectively.

(8) The inhibition efficiency of zinc phosphate coatings increased to nearly 70% at pH>3.

(9) Vanadium pentaoxide film is grown on mild steel by immersion in acidic solution containing 0.005M sodium vanadate.

Acknowledgment

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References


Figure Captions

Figure 1 SEM micrographs of different phosphate crystals: a) Zn, b) Zn-Mn-Mg and c) Mn phosphate

Figure 2: SEM micrographs of Zn-phosphate cross-section

Figure 3: X-ray diffraction pattern of zinc phosphate coating on mild steel surface

Figure 4: Potentiodynamic polarization curves of zinc phosphate and mild steel at different pH

Figure 5: Effect of vanadate concentration on the corrosion (weight loss) of mild steel and zinc phosphate

Figure 6: SEM and EDS analysis of deposited layer on mild steel surface after immersion for 2 hours in acidic de-ionized water contains 0.005M vanadate

Figure 7: Effect of immersion time and vanadate concentration on the polarization behaviour of Zn phosphate coatings.
Table 1: corrosion current and inhibition efficiency of Zn phosphate on mild steel at different pH

<table>
<thead>
<tr>
<th>pH</th>
<th>Zinc Phosphate</th>
<th>Mild steel</th>
<th>η, %</th>
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<tr>
<td></td>
<td>$E_{\text{corr}}$, V</td>
<td>$i_{\text{corr}}$, A</td>
<td>$E_{\text{corr}}$, V</td>
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<tr>
<td>1</td>
<td>-0.51</td>
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<td>-0.50</td>
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<td>2</td>
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<td>-0.58</td>
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<tr>
<td>3</td>
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<td>-0.63</td>
</tr>
<tr>
<td>4</td>
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<td>-0.159</td>
</tr>
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Table 2: Atomic analysis data for mild acidic de-ionized water solutions contain 0.005M sodium vanadate at pH 4 (water/HCl) after immersion zinc phosphate coated steel and steel samples for 2hours.

<table>
<thead>
<tr>
<th>Sample Reference</th>
<th>Zinc coated steel, ppm</th>
<th>Steel, ppm</th>
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<tbody>
<tr>
<td>Cu</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
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<td>Fe</td>
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<td>Na</td>
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</tr>
<tr>
<td>V</td>
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</tr>
<tr>
<td>Zn</td>
<td>&lt;0.2</td>
<td>1.6</td>
</tr>
</tbody>
</table>
Figure 1 SEM micrographs of different phosphate crystals: a) Zn, b) Zn-Mn-Mg and c) Mn phosphate.
Figure 3: X-ray diffraction pattern of zinc phosphate coating on mild steel surface
Figure 5: Effect of vanadate concentration on the corrosion (weight loss) and inhibition efficiency of mild steel and zinc phosphate
Figure 6: SEM and EDS analysis of deposited layer on mild steel surface after immersion for 2 hours in acidic de-ionized water contains 0.005M vanadate
Figure 7: Effect of immersion time and vanadate concentration on the polarization behaviour of Zn phosphate coatings.