

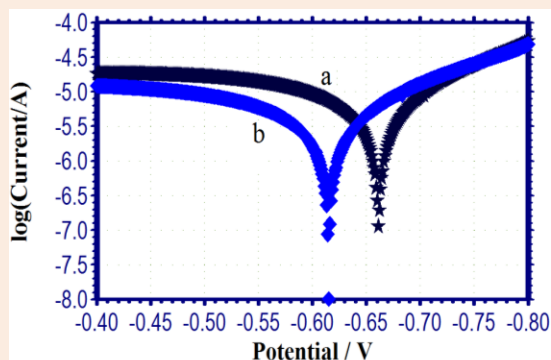
Research Article

Influence of Potassium Permanganate-Zn²⁺ System on Inhibition of Corrosion of Mild Steel in Simulated Concrete Pore SolutionM. Pandiarajan*¹ S.Rajendran^{1,2} J.Sathiyabama¹, N.Vijaya³ and P.Shanthya⁴¹Corrosion Research Centre, PG and Research, Department of Chemistry, GTN Arts College, Dindigul, India²Corrosion Research Centre, Department of Chemistry, RVS School of Engineering and Technology, Dindigul, India³Department of Chemistry, Vellalar College for Women, Thindal, Erode.⁴Department of Chemistry, Kunthavai Naachiar Government Arts College, Thanjavur.**Abstract**

The inhibition efficiency (IE) of Potassium Permanganate - Zn²⁺ system in controlling corrosion of mild steel in Simulated Concrete Pore Solution (SCPS) prepared in well water in the absence and presence of Zn²⁺ has been investigated by mass loss study. It can be seen from the data obtained that formulation consisting of 100 ppm of KMnO₄ and 50 ppm of Zn²⁺ provides 96% of inhibition efficiency. Inhibition was found to increase with an increasing concentration of Zn²⁺. Polarization study confirms the formation of inhibitor film formed on the mild steel surface. FTIR spectral study leads to the conclusion that the Fe²⁺ - MnO₄ complex, formed on anodic sites of the mild steel surface, controls the anodic reaction. Zn(OH)₂ formed on the cathodic sites of the mild steel surface controls the cathodic reaction. The nature of the protective film formed on the mild steel surface was examined by SEM analysis.

Keywords: Concrete corrosion, Simulated concrete pore solution, Mild steel, Potassium Permanganate, Well water.

The results obtained show that the KMnO₄ could serve as an effective inhibitor for the corrosion of mild steel in Simulated Concrete Pore Solution.

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Introduction

Corrosion is a naturally occurring phenomenon commonly defined as the deterioration of a substance (usually a metal) or its properties because of a reaction with its environment. Like other natural hazards such as earthquakes or severe weather disturbances, corrosion can cause dangerous and expensive damage on everything from automobiles, home appliances, and drinking water systems to pipelines, bridges, and public buildings.

Corrosion of reinforcing steel produces important damage to concrete structures in coastal, urban, and industrial zones. This damage has increased in recent years in all countries when concrete is a regular construction material, no matter if it is a technologically advanced country or it is in the process of being one. Reinforcing steel is initially protected by concrete alkaline reserve which helps to maintain the reinforcing steel passive layer. However, chlorides from salty water (i.e., marine water and/or de-icing salts) or CO₂/SO₂ present in urban/industrial environment accumulate on the concrete surface and then move towards the rebar by known transport mechanisms like diffusion. When the chloride or CO₂ threshold is exceeded, depassivation occurs and a corrosion products layer is formed in the rebar perimeter. The volume of this layer is bigger than the original steel consumed; thus, tensile stresses develop and produce concrete cover cracking and spalling. Besides being aesthetics, cracking decreases steel/concrete adherence and, potentially, the structural capacity of the affected structural element. Then, corrosion of reinforcing steel can

produce significant damage affecting the whole structural behaviour. Several research groups in the world has been working in the past five decades to determine possible actions to increase the service life of concrete structures, especially the initiation period (time when the aggressive elements such as chlorides and/or CO_2 penetrates into the concrete cover until reaching the reinforcing steel and depassivation occurs). Many are the approaches that can be used to mitigate corrosion of reinforcing steel, among which, protective coatings and sealers, cathodic protection, concrete realkalinization and corrosion inhibitors are commonly employed.

The rate of corrosion can also be reduced by using corrosion inhibitors. These inhibitors are chemical compounds that reduce the corrosion rate of metals existing in actively corrosive environments. Using corrosion inhibitors on embedded steel is difficult. There are corrosion inhibitors known to protect bare steel, but some of these compounds have ill effects on the properties of hardened concrete. Setting time, strength, and durability are key elements that can be affected by the corrosion inhibitors. Few commercial corrosion inhibitors are available for concrete due to the stringent requirements that must be met for concrete. To increase the service life of steel imbedded in concrete, some form of corrosion protection must be provided. This is accomplished by using corrosion inhibitors or reducing the rate of chloride ingress to the steel reinforcement. The ideal protection would accomplish both of these.

The use of corrosion inhibitors is probably more attractive from the point of view of economics and ease of applications [1] Reviews of the most commonly used inhibitor types in concrete repair systems [2] and the various possible mechanisms of inhibition have been recently published [3]. There is a wide range of available inhibitors for steel in reinforced concrete [4-14].

The present work in undertaken

- 1) To evaluate the inhibition efficiency of Potassium manganate - Zn^{2+} system in controlling corrosion of mild steel in SCPS prepared in well water in the absence and presence of Zn^{2+} using mass-loss method.
- 2) To study the mechanistic aspects of corrosion inhibition by polarization technique.
- 3) To analyze the inhibitor film by FTIR spectroscopy and scanning electron microscope
- 4) To propose the mechanism of corrosion inhibition based on the above results.

Material and Methodology

Preparation of Simulated Concrete pore solution (SCPS):

Simulated concrete pore solution is mainly consisted of saturated calcium hydroxide ($\text{Ca}(\text{OH})_2$), sodium hydroxide (NaOH) and potassium hydroxide (KOH) with the pH ~ 13.5[15]. However in numerous studies of rebar corrosion, saturated $\text{Ca}(\text{OH})_2$ has been used as a substitute for pore solution[16]. A saturated calcium hydroxide solution is used in present study, as SCP solution with the pH ~ 12.5.

Table 1 Physico- chemical parameters of well water

Parameters	value
pH	8
Conductivity	$1770\mu\Omega^{-1}\text{cm}^{-1}$
Chloride	665 ppm
Sulphate	214 ppm
Total dissolved solids	1204 ppm
Total hardness	402 ppm
Total Alkalinity	390 ppm
Magnesium	83 ppm
Potassium	55 ppm
Sodium	172 ppm
Calcium	88 ppm

Preparation of the specimens:

Mild steel specimen was used in the present study. Composition (wt %): 0.026 S, 0.06 P, 0.4 Mn, 0.1 C and balance iron. The dimension of the specimen was 1 x 4 x 0.2cm were polished to a mirror finish and degreased with trichloroethylene and used for the mass-loss method and surface examination studies. The environment chosen is well water and the physico-chemical parameter of well water is given in **Table 1**.

Mass Loss Method

Determination of Surface Area of the specimens:

The length, breadth, and the thickness of mild steel specimens and the radius of the holes were determined with the help of vernier calipers of high precision, and the surface areas of the specimens were calculated.

Weighing the specimens before and after Corrosion:

All the weighing of the mild steel specimens, before and after corrosion, was carried out using Shimadzu balance, model AY62.

Determination of Corrosion Rate: The weighed specimens in triplicate were suspended by means of glass hooks in 100mL SCPS prepared in well water containing various concentration of potassium chromate in the presence and absence of Zn^{2+} for 24 hours, the specimen were taken out, washed in running water, dried, and weighed. From the change in weights of the specimens, corrosion rates were calculated using the following relationship:

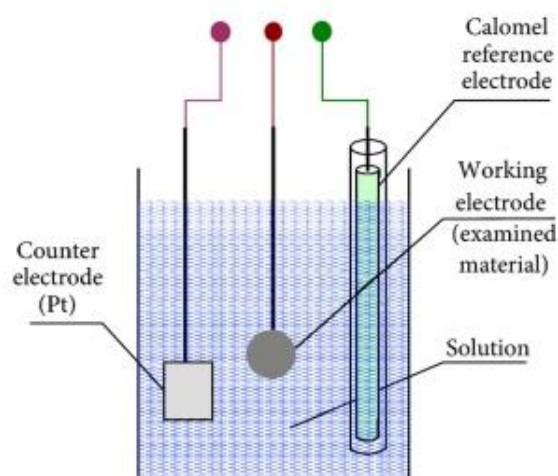
$$CR = [(Weight\ loss\ in\ mg) / (Area\ of\ the\ specimens\ in\ dm^2 \times Immersion\ periods\ in\ days)]\ mdd \quad (1)$$

Corrosion inhibition efficiency (IE %) was then calculated using the formula:

$$I.E = 100[1 - (W_2/W_1)] \% \quad (2)$$

where, W_1 and W_2 are weight losses of steel in uninhibited and inhibited solutions.

Surface Examinations study: The mild steel specimens were immersed in various test solutions for a period of 24 hours, After 1 day the specimens were taken out and dried. The nature of the film formed on the surface of mild steel specimen was examined by various surface analysis techniques.



Scheme 1 Circuit diagram of three- electrode cell assembly

Potentiodynamic Polarization: Polarization studies were carried out in a CHI – Electrochemical workstation with impedance, Model 660A. A three-electrode cell assembly was used. The three electrode assembly is shown in **Scheme 1**. The working electrode was mild steel. A saturated calomel electrode (SCE) was the reference electrode and platinum was the counter electrode. From the polarization study, corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}) and Tafel slopes (anodic = ba and cathodic = bc) and Linear polarization resistance (LPR) were calculated. The scan rate (V/S) was 0.01. Hold time at (E_{ics}) was zero and quit time(s) was two.

Fourier Transform Infrared Spectra: These spectra were recorded in a Perkin-Elmer -1600 spectrometer using KBr pellet. The spectrum of the protective film was recorded by carefully removing the film, mixing it with KBr and making the pellet.

Scanning Electron Microscopic Studies (SEM): The mild steel immersed in blank solution and in the inhibitor solution for a period of 24 hours was removed, rinsed with double-distilled water, dried, and observed in a scanning electron microscope to examine the surface morphology. The Surface morphology measurements of mild steel were examined using Tescan, Vega 3, and USA computer -controlled scanning microscope. The elements analysis of the mild steel surface at the same condition was carried out using an energy dispersive X-ray analyzer unit attached to the SEM machine.

Results and Discussion

Mass loss method

Table 2 Corrosion rates (CR) of mild steel immersed in Simulated Concrete Pore Solution (SCPS) prepared in well water and the inhibition efficiency (IE) obtained by Mass loss method.

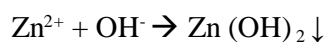
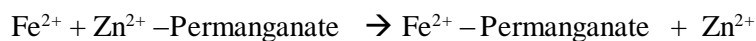
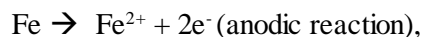
System	IE %	CR (mdd)
Well Water	-----	25
SCPS	68	8
SCPS + KMnO ₄ 50 ppm	88	3
SCPS + KMnO ₄ 100 ppm	92	2
SCPS + KMnO ₄ 50 ppm + Zn ²⁺ 50 ppm	94	1.5
SCPS + KMnO ₄ 100 ppm+Zn ²⁺ 50 ppm	96	1

CR =Corrosion Rate; mdd = milligram per square decimetre per day.

The corrosion resistance of mild steel immersed in SCPS prepared in well water in the absence and presence of potassium permanganate and Zn²⁺ are given in **Table 2**. It is observed that when 50 ppm of potassium permanganate is added to SCPS the inhibition efficiency increases from 68% to 88%. Similarly when 100 ppm potassium permanganate is added the inhibition efficiency increases from 68% to 92%.

Influence of Zn²⁺ on the corrosion inhibition efficiency: It is observed that when 50 ppm Zn²⁺ is added, the inhibition efficiency increases in the both the cases. The formulation consisting of SCPS + 100 ppm of potassium permanganate and 50 ppm of Zn²⁺ has 96% corrosion inhibition efficiency. In presence of Zn²⁺ more amount potassium permanganate is transported towards mild steel surface. On the mild steel Fe²⁺- permanganate complex is

formed on the anodic sites of the mild steel surface. Thus the anodic reaction is controlled. The cathodic reaction, the generation of OH^- is controlled by the formation of $\text{Zn}(\text{OH})_2$ on the cathodic sites of the mild steel surface. Thus, the anodic reaction and cathodic reaction are controlled effectively.



Analysis of Polarization Curves

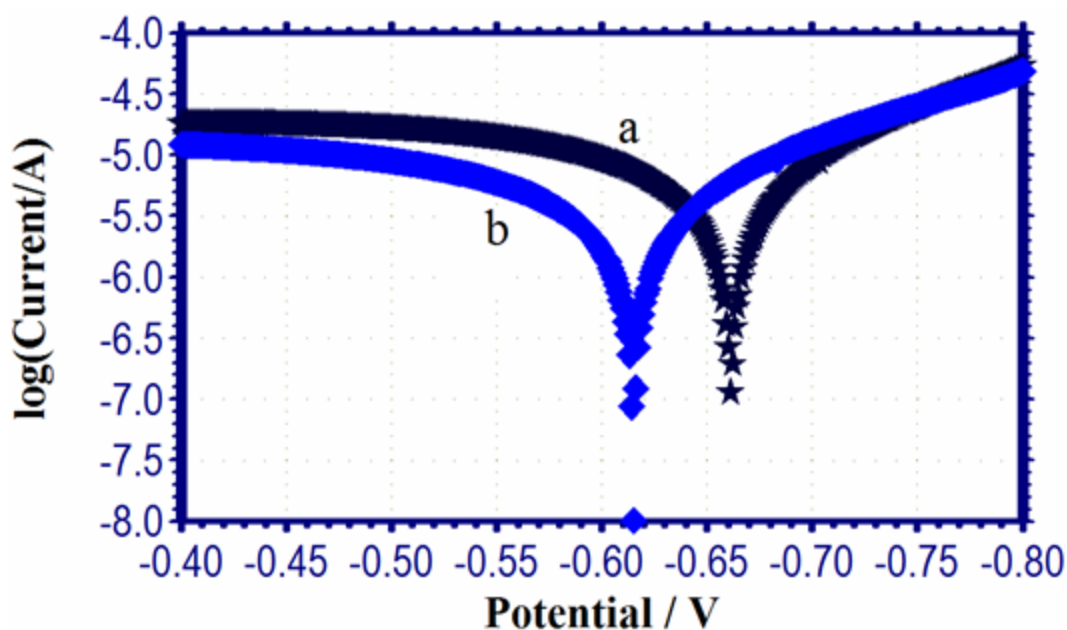


Figure 1 Polarization curve of mild steel immersed in SCPS prepared in water a) SCPS; b) KMnO_4 100 ppm+ Zn^{2+} 50 ppm

Table 3 Corrosion parameters of mild steel immersed in SCPS prepared in well water in the absence and presence of inhibitor system obtained from Potentiodynamic Polarization Study

System	E_{corr} mV vs SCE	b_c mV/ decade	b_a mV/ decade	LPR ohm cm^2	I_{corr} Acm^{-2}
SCPS	-661	143	313	5103.1	8.389×10^{-6}
SCPS + KMnO_4 100 ppm + Zn^{2+} 50 ppm	-615	151	284	8727.1	4.91×10^{-6}

When mild steel is immersed in simulated concrete pore solution prepared in well water the corrosion potential was -661 mV vs SCE (saturated calomel electrode). When KMnO_4 (100 ppm) and Zn^{2+} (50 ppm) were added to the above system the corrosion potential shifted to the anodic side -615 mV vs SCE; that is noble side. This reveals that the KMnO_4 - Zn^{2+} system controls anodic reaction predominantly. This indicates that the passive film is formed on the metal surface in presence of inhibitor [17-24]. The shifting of corrosion potential towards anodic side in presence of inhibitors has been reported by several researchers. Further, the LPR value increases from 5103.1 ohm cm^2 to 8727.1 ohm cm^2 ; the corrosion current decreases from 8.389×10^{-6} A/ cm^2 to 4.91×10^{-6} A/ cm^2 . When an inhibitor film formed on mild steel surface, in presence of inhibitor system, the electron transfer from the metal surface towards the bulk of the solution is difficult and prevented. So rate of corrosion decreases and hence corrosion current decreases in presence of inhibitor system.

Analysis of FTIR spectra: Earlier researchers have confirmed that FTIR spectrometer is a powerful instrument that can be used to study inhibitors adsorbed on the metal surface. FTIR spectra were used to analyze the inhibitor film formed on mild steel [25-30].

The FTIR (KBr) spectrum of pure potassium permanganate is shown in figure 2(a). The MnO_4^- stretching frequency appears at 903.38 [31]. The FTIR spectrum of the film formed on the mild steel surface after immersion in SCPS prepared in well water containing 100 ppm of KMnO_4 and 50 ppm of Zn^{2+} is shown in figure 2(b). It is seen from the spectrum that the MnO_4^{2-} stretching frequency of KMnO_4 shifted from 903 to 813 cm^{-1} . This confirms that the oxygen atom of the permanganate has coordinated with Fe^{2+} resulting in the formation of Fe^{2+} - permanganate complex on the mild steel. Also there is possibility of anchoring of Permanganate on the layer consisting of CaO , $\text{Ca}(\text{OH})_2$, CaCO_3 .

The Peak appearing at 1382 cm^{-1} is due to Zn-O stretching. The -OH stretching frequency appears at 3430.39 cm^{-1} . These observations indicate the presence of $\text{Zn}(\text{OH})_2$ formed on the metal surface. Peak appearing at 1593, 765 and 1349 cm^{-1} . These peaks confirm the presence of calcium carbonate, calcium oxide, calcium hydroxide and on the mild steel surface [32].

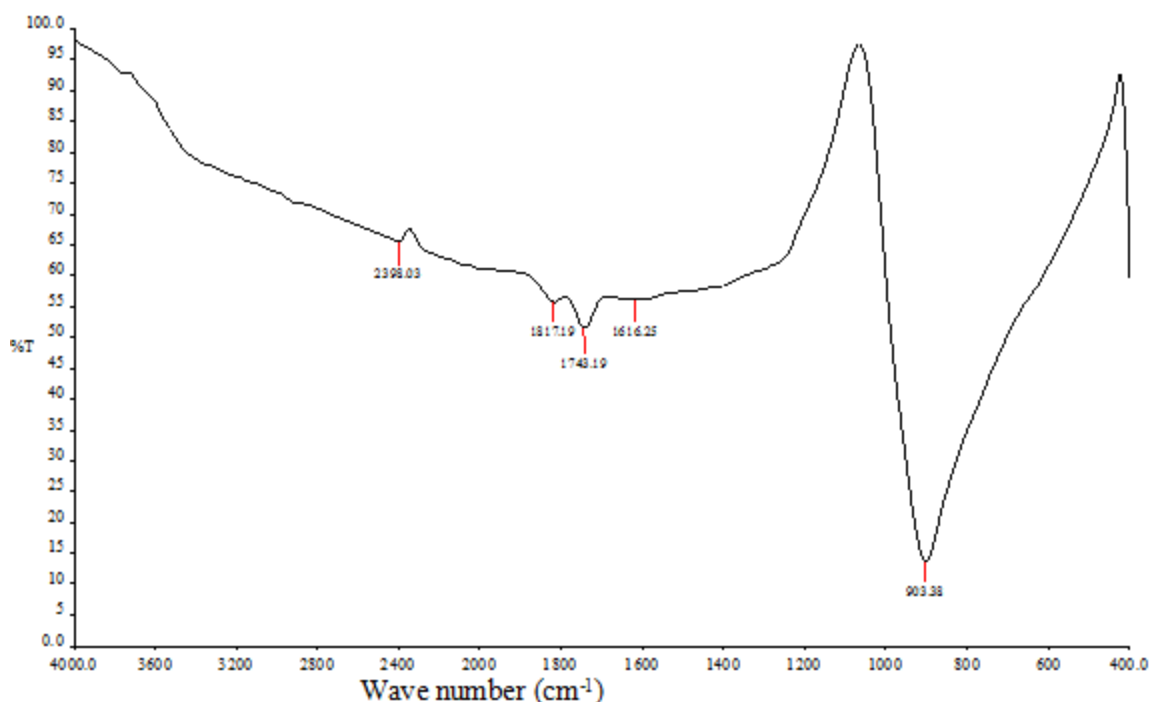


Figure 2(a) FTIR spectrum of Pure Potassium Permanganate

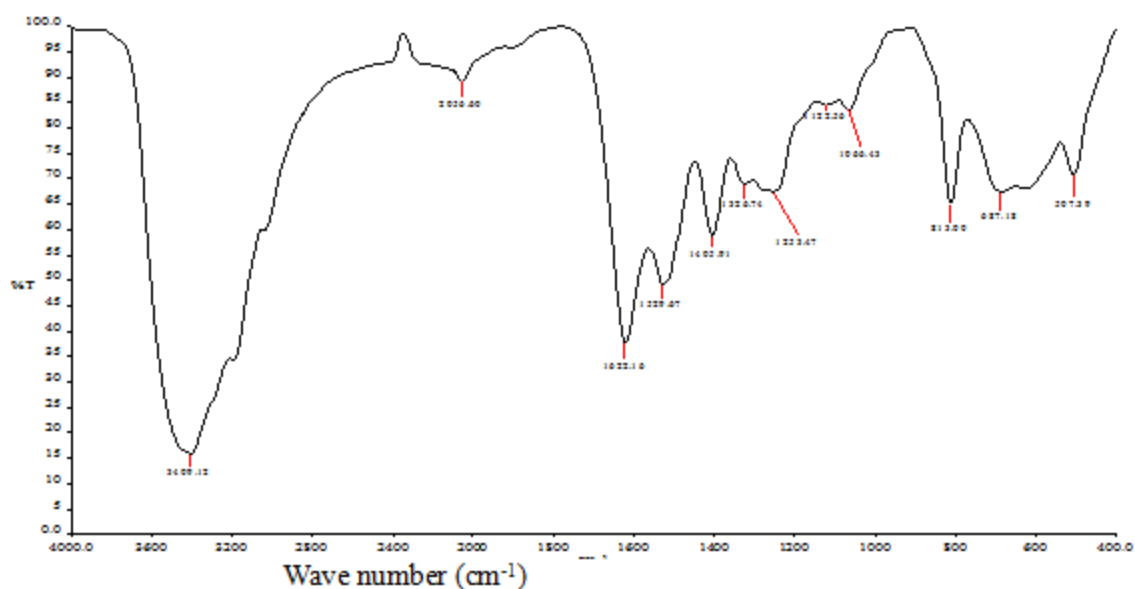


Figure 2(b) FTIR spectrum of inhibitor film formed on the mild steel after immersion in SCPS prepared in well water containing 100 ppm of KMnO_4 and 50 ppm of Zn^{2+}

Scanning Electron Microscopy (SEM): SEM analysis was carried out for characterizing the inhibitive film formed on the mild steel surface. SEM microscope of a polished mild steel surface (control) in Figure 3(a) shows the smooth surface of the mild steel and thus the absence of any corrosion products formed on the mild steel. The SEM micrographs of mild steel immersed in SCPS prepared in well water for 24 hours in the absence and presence of inhibitor system are shown Figures 3(b),3(c) respectively. The SEM micrograph of mild steel immersed in SCPS prepared in well water shows the roughness of the metal surface which indicates the corrosion of mild steel in SCPS prepared in well water. The figure (c) shows that in presence of 100 ppm of KMnO_4 and 50 ppm of Zn^{2+} mixture in SCPS, the surface coverage increases which in turn results in the formation of insoluble complex on the metal surface (Permanganate- Zn^{2+} complex). In the presence KMnO_4 and Zn^{2+} , the surface is covered by a thin layer of inhibitors which effectively control the dissolution of mild steel. Such results have been reported earlier [33-34].

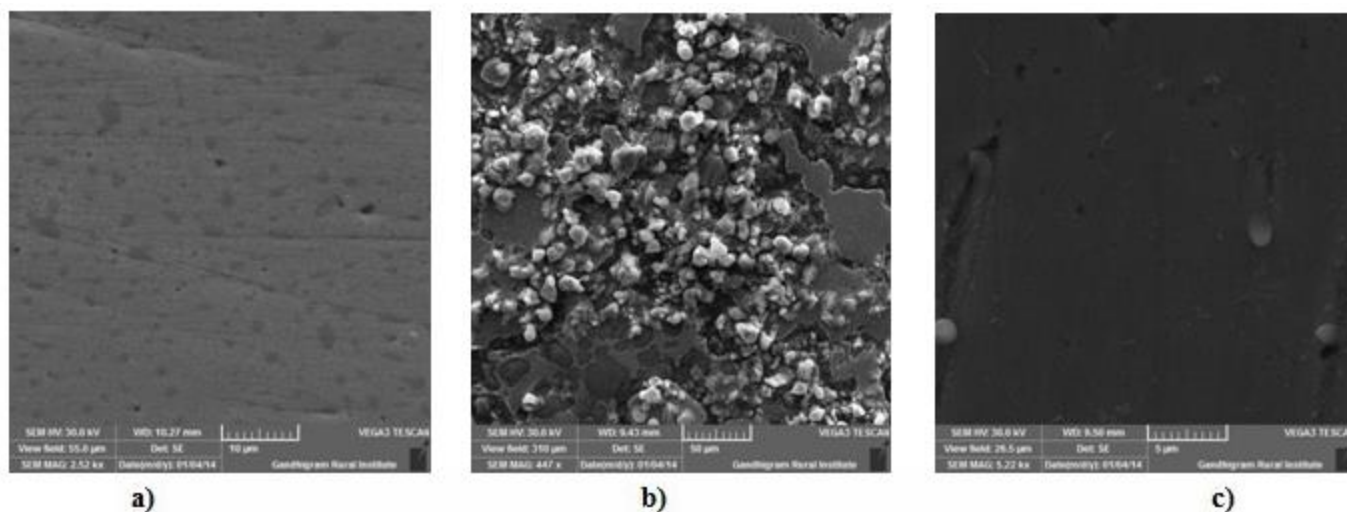


Figure 3 a) Polished mild steel (control); b) mild steel immersed in SCPS (blank); c) mild steel immersed in SCPS+ KMnO_4 100 ppm and Zn^{2+} 50 ppm

Surface Examination by EDAX: EDAX is used to analyse corrosion films Fig.4.(a) spectrum shows the EDAX analysis of mild steel surface immersed in SCPS prepared in well water. The analysis shows the presence of corrosion products elements (Fe, O and C) Fig.4.(b) spectrum shows the EDAX analysis of mild steel immersed in SCPS prepared in well water containing 100 ppm of potassium permanganate and 50 ppm of Zn^{2+} . The analysis shows the presence of (K, Mn) which could be attributed to the presence of zinc and potassium permanganate on the mild steel surface. Forming inhibitor film [35]. The elements present on the metal surface were examined using Bruker computer controlled Energy Dispersive Analysis of X-rays (Bruker, Nano, GMBH, Germany).

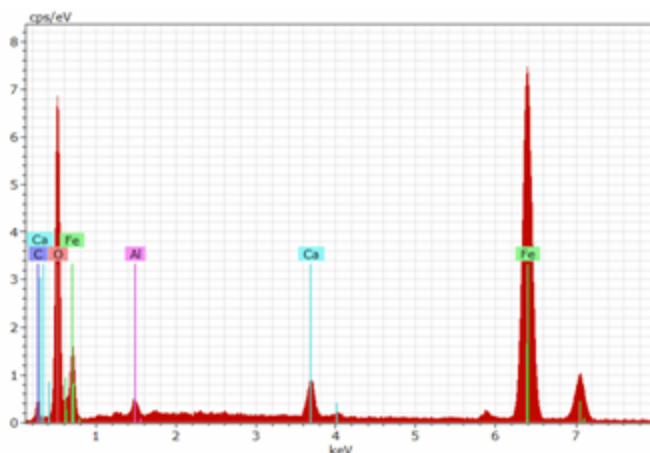


Figure 4(a) EDAX analysis of mild steel immersed in SCPS prepared in well water (blank)

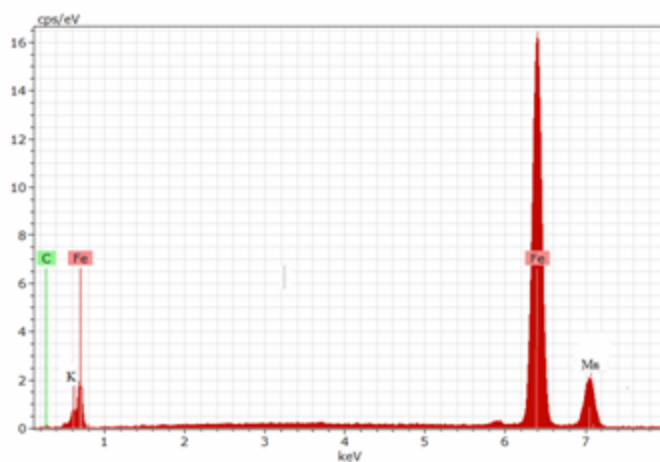


Figure 4(b) EDAX analysis of mild steel immersed in SCPS prepared in well water containing 100 ppm of potassium permanganate and 50 ppm of Zn^{2+}

Conclusions

The present study tells to us the following conclusions:

1. The formulation consisting of 100 ppm of $KMnO_4$ and 50 ppm of Zn^{2+} offers 96% IE to mild steel immersed in simulated concrete pore solution prepared in well water.
2. Polarization study indicates that $KMnO_4$ system controls the anodic reaction.
3. FTIR spectra investigate that the inhibitive film consists of Fe^{2+} - permanganate complex and $Zn(OH)_2$.
4. The surface morphology of the inhibitor film on the mild steel was analyzed by SEM study.

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