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CORROSION PROTECTION OF CARBON STEEL IN RO WATER BY SODIUM GLUCONATE-Zn^{2+} SYSTEM

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ABSTRACT

The Protection Efficiency (PE) of sodium gluconate (SG), in controlling corrosion of carbon steel in Reverse Osmosis (RO) water in the absence and presence of Zn^{2+} has been evaluated by mass-loss method. The formulation consisting of 150ppm SG and 10ppm Zn^{2+} has 87% PE. It is found that the protection efficiency of SG increases with the addition of Zn^{2+}ion. A synergistic effect exists between SG & Zn^{2+}. Polarization and surface characterization analysis studies confirm the protection of the carbon steel surface by inhibitive film. A suitable mechanism for corrosion inhibition has been proposed based on the results obtained from the above studies.

Keywords: Carbon Steel, Corrosion protection, sodium gluconate, RO Water.

INTRODUCTION

Corrosion is the slow and continuous destruction of a metal or alloy by the environment. Corrosion is the cancer of metals due to thermodynamic instability.[1] Metals and alloys are generally used as fabrication or construction materials. If the metal or alloy structures are not properly maintained, they deteriorate slowly by the action of atmospheric gases, moisture and other chemicals. Due to low cost, availability etc., steel is considered in wide area of practical applications such as water pipelines[2,3], cooling water systems[4], RO water[5], boilers etc., However they are susceptible to different forms of corrosion inducted by many factors. One of the most important methods in corrosion protection is to use inhibitors. Inhibitors should be of low toxicity and easily biodegradable in order to meet environmental protection requirements.

Corrosion of carbon steel is a subject of fundamental, academic and industrial concern and has received a considerable attention during the last few decades[6]. Corrosion, scale and fouling problems can appear when water containing chlorides is used as thermal fluid. This problem can occur jointly, reducing the thermal efficiency of the cooling circuit with the significant social-economic repercussions. Many inhibitors have been used in cooling water systems in order to solve these problems.[7,9] Carbon steel is an important material for construction of cooling water systems and heat exchangers used in industries. The use of water as thermal fluid in cooling water system usually leads to three forms of inconvenience namely: scale, corrosion and biological fouling processes. There is a colossal economic loss to limit the damage, many formulations have been developed to protect circuits, piping and material structures.[10] Particularly several phosphonic acids have been used as corrosion inhibitors due to their ability to from complexes with metal ions and hydrolytic stability.[11]

The RO product water in pipelines, when comes into contacts with pumps, valves or other metallic components, has the capability to corrode these Components. A survey of the literature indicates that although numerous references are available on corrosion resistant materials but only limited references are available on carbon steel related to RO product water.[12-14]

The formulation based on chromates, nitrites, etc. are replaced by phosphonate based formulations which have been used as corrosion inhibitors, since the past three decades.[15-20] Phosphonates in combination with Zn^{2+} ions have proved to be a valuable corrosion inhibitor for carbon steel. However higher

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concentrations of both phosphonate and zinc ions are required for an effective inhibition. Though SG and Zn^{2+} ion crystal used as corrosion protection in many cases like cooling water systems, no study can explained about the binary system present in RO water. So we selected in our project.
The present work was designed to study the corrosion inhibition of carbon steel in RO water by Sodium gluconate (SG) and Zn^{2+} as corrosion inhibitors using three different techniques: mass-loss, electrochemical studies, surface analysis techniques, hoping to get some general ideas to guide the composing of inhibitor in reality.

EXPERIMENTAL

Preparation of the Specimen

Carbon steel specimens (0.026% S, 0.6% P, and 0.4 % Mn, 0.1% C, and rest iron) of the dimensions 1.0 cm X 4.0 cm X 0.2 cm were polished to a mirror finish and degreased with trichloroethylene and used for the mass- loss method and surface examination studies.
A stock solution of 1000 ppm of SG was prepared in bidistilled water and the desired concentration was obtained by appropriate dilution. The concentration of SG used for the study ranges from 10 to 200ppm. All solutions were prepared using RO water (Karur, Tamil Nadu, India). The study was carried out at room temperature. The physico-chemical parameters of RO water is given in Table-1.

Table-1: Physico- chemical parameters of RO water used to prepare solutions

S.No.	Parameters	Level of content
1	Appearance	Colorless and clear
2	Odour	None
3	TDS	200 ppm
4	pH	7.5
5	Total hardness as $CaCO_3$	200 ppm
6	Chloride as Cl	200 ppm
7	Fluoride as F	Nil
8	Sulphate as SO_4	Nil
9	Phosphate as PO_4	Nil

Mass-loss method

Carbon steel specimens were immersed in 100ml of the RO water, containing various concentration of the inhibitor in the absence and presence for 7 days. The weight of the specimens before and after immersion were determined using a digital balance model AUY 220 SHIMADZU. The corrosion products were cleaned with Clarke's solution.
The Corrosion PE was then calculated using the equation:
% of IE = 100 [1-(W_2 / W_1]

Where W_1 is the corrosion rate in the absence of inhibitor and W_2 is the corrosion rate in the presence of inhibitor. Corrosion rate was calculated using the above formula.

Corrosion rate = 87.6 W / DAT mmy^{-1} [21]
W = Mass- loss, milligrams
D = density of specimen, g / cm^3
A= area of specimen, cm^2
T = exposure, hours = 168 hrs

Potentiodynamic Polarization Technique

Polarization studies were carried out in a CHI – electrochemical workstation with impedance model 660 A. It was provided with IR facility. A three electrode cell assemble was used and the working electrode was carbon steel. A SCE was the reference electrode. Platinum was the counter electrode. From

polarization study, corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}) (Tafel slopes anodic = β_a and cathodic = β_c) were calculated and a linear polarization study was done. The scan rate (V /S) was 0.01. Hold time at E_{fcs} was zero and quit time (s) was two.

AC Impedance technique

Electrochemical impedence spectra in the form of Nyquist plots were recorded at OCP in the frequency range from 60 KHz to 10MHz with 4 to 10 steps per decade. A sine wave, with 10mV amplitude, was used to perturb the system. The impedence parameters viz., charge transfer resistance (R_{ct}), double layer capacitance (C_{dl}) were obtained from the Nyquist plots.

Surface examination techniques

The carbon steel specimens were immersed in blank as well as inhibitor solutions, for a period of 7 days. After the immersion period is over, the specimens were taken out and dried. The nature of the thin film formed on the surface of the metal specimen analyzed by various surface analysis techniques. The morphology of carbon steel specimen surface (corroded and inhibited) was studied by recording SEM images of the corresponding samples using OXFORD Instruments analytical scanning electron microscope.

RESULTS AND DISCUSSION

Mass–loss method

Weight-loss measurements of the carbon steel in RO water in the absence and presence of different concentrations of the inhibitors were carried out and the results are reported in Table-2. When the concentration of SG increased from 10ppm to 200ppm, P.E increases from 30 to 87 %. The formulation 10ppm Zn^{2+} + 150ppm SG shows the maximum P.E. Beyond the Concentration of 150ppm SG, P.E decreases due to the desorption of inhibitor molecules into bulk of the solution from the metal surface. When 10 ppm Zn^{2+} was used alone, protection efficiency is 5.5% and 150ppm SG alone, protection efficiency is 23 % only. When all the above was combined, the protection efficiency is 87 %. From below results, it is clear that there exists a synergism.

Table-2: Corrosion Rates of Carbon steel in RO water in the absence and presence of SG and Zn^{2+} ions

Concentration (ppm)		Corrosion Rate (mmy^{-1})	Protection efficiency (%)
Zn^{2+}	SG		
Blank	-	171.5	-
10	-	162	5.5
-	150	132.6	23
10	10	120.5	30
10	50	115.6	32.5
10	75	85.5	50
10	100	50	71
10	125	34	80
10	150	22	87
10	175	26.5	84.5
10	200	30	82.5

Analyses of Polarization Curves

Polarization study has been used to confirm the type of inhibition during corrosion inhibition processes[22-25].The potentiodynamic polarization curves of carbon steel immersed in RO water in the absence and presence of inhibitors are shown in Fig1. The corrosion parameters are given in Table-3.

It was found that the values of corrosion current density (I_{corr}) of carbon steel in the presence of inhibitor were smaller than without addition of inhibitor (Fig.-1). Furthermore, as presented in Fig.1b the addition

of 10ppm Zn^{2+} + 150ppm SG shifts the corrosion potential (E_{corr}) value (from -593.466mV to -509.144mV) in studied inhibitor system. According to Ferreira and W.H. Li, if the displacement in corrosion potential is more than 85mVwith respect to the corrosion potential of the blank, the inhibitor can be seen as cathodic or anodic type [26-27]. The corrosion potential shift in more anodic mode and maximum displacement was <85mV which indicated that the studied inhibitor system can be classified as anodic inhibitor.

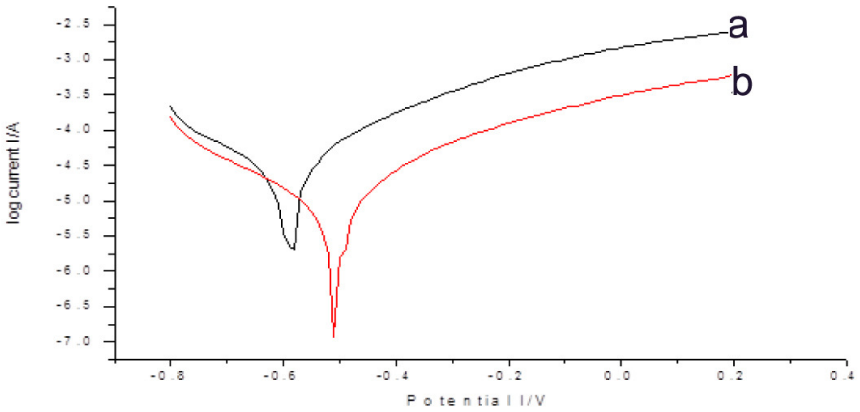
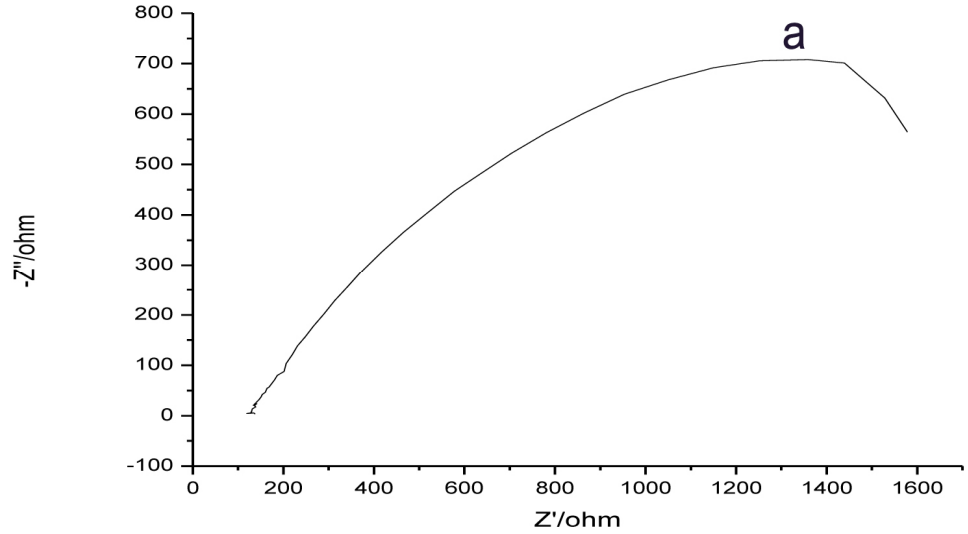


Fig.-1: Tafel plots of carbon steel immersed in a) Blank b) Presence of binary inhibitor system

Table-3: Tafel corrosion parameters for carbon steel in RO water in the absence and presence of the binary inhibitor formulations

Concentration ppm		E_{corr} mV vs SCE	β_a mV/dec	β_c mV/dec	I_{corr} µA/cm^2	PE %
Zn^{2+}	SG					
Blank	-	-593.466	649.068	91.98	190.397	-
10	150	-509.144	492.289	786.506	26.995	86

Analyses of Electrochemical Impedance Spectroscopy



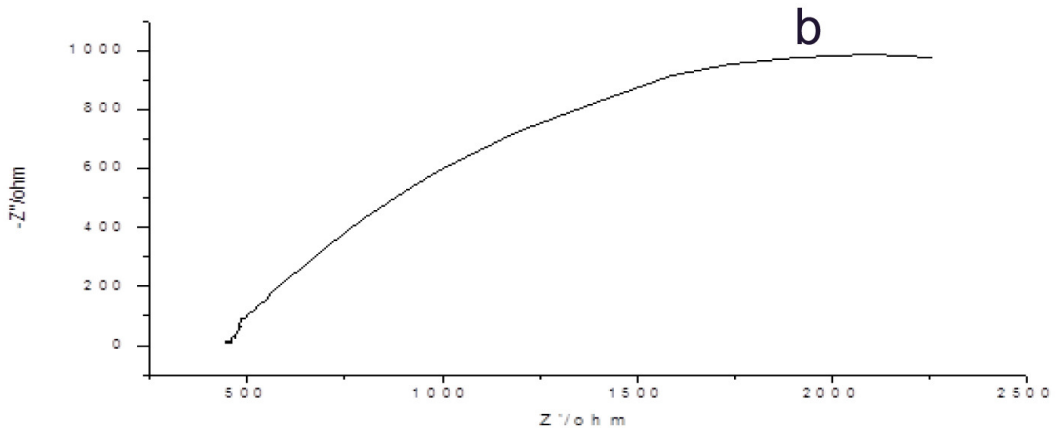


Fig.-2: Nyquist plots of carbon steel immersed in (a) Blank ;(b) Presence of binary inhibitor system

Figure-2 (a-b) shows in it is clear that the impedance curves are significantly changed with the presence of inhibitor. It is also found that from the Nyquist plot, even with the addition (or) absence of inhibitor does not alter the style of impedance curves, thus proposing a similar mechanism of inhibition is involved. It can be seen from the figure, that the obtained Nyquist curves is due to the charge transfer process, mostly control the corrosion of carbon steel. The low frequency inductive loop is owing to the growth and dissolution of the surface layer [28-29]. The impedance parameters derived from these plots are given in Table 4. As noted from Table 4, the charge transfer resistance values (R_{ct}) substantially increased, and double layer capacitance (C_{dl}) decreased when 10ppm Zn^{2+} and 150ppm SG added as inhibitors.

Table-4: Impedance parameters for carbon steel in RO water in the absence and presence of the binary inhibitor formulation

Concentration (ppm)		Charge transfer resistance R_{ct} (Ω)	Double layer Capacitance (C_{dl}) $\mu F/cm^2$	I.E %
Zn^{2+}	SG			
Blank	-	950	$7.3x10^{-5}$	-
10	150	4000	$1.1x10^{7}$	76.25

Analyses of SEM

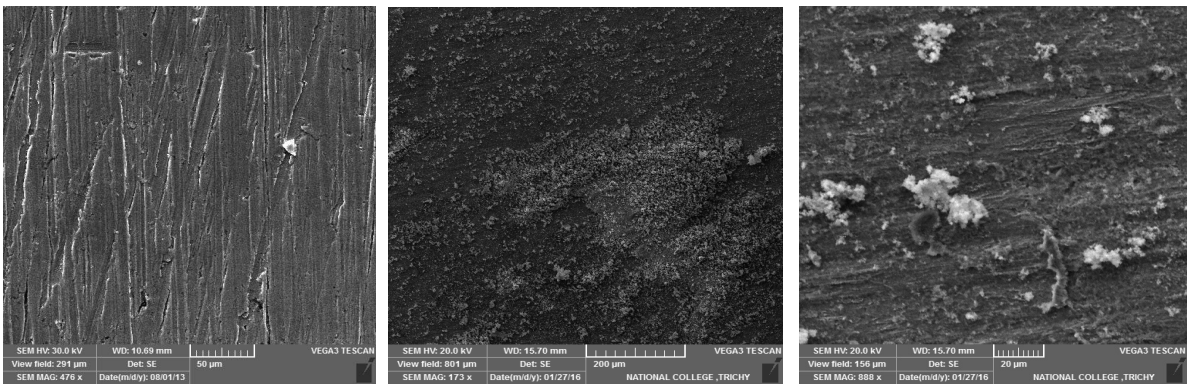


Fig.-3: SEM images of (a) Polished carbon steel; (b) Blank; (c) Presence of binary inhibitor formulation

The scanning electron microscope images further supported the formation of a protective film by the inhibitors and their interaction with surface atoms of carbon steel. The images of carbon steel surface immersed in RO water in the absence and presence of inhibitors are shown in Fig.-3. Figure 3a illustrates the morphology of the polished carbon steel surface before exposure to corrosion environment. The micrograph shows a characteristic inclusion, which is probably an oxide inclusion. Figure-3b shows SEM image of the surface of the studied carbon steel electrode specimen after immersion in RO water. The micrograph reveals that the surface is strongly damaged. The corroded areas are shown as grey and white zones, which correspond to the dandruff of iron oxide. It suggests an uncovered surface of metal electrode severely corroded. The highly oxidized phase has perhaps been formed in air when desiccated under no protection of the surface.
Figure-3c shows SEM image for the surface of another carbon steel specimen after immersion for the same time interval in RO water which contain binary formulation. The micrograph reveals that the inhibited metal surface is smoother than the uninhibited surface because of the presence of a good protective film on the metal surface. This confirms the highest protection efficiency of the inhibitor.

Analysis of Energy Dispersive X-ray (EDX)
The protective film formed on carbon steel surface was analyzed using EDX is shown in Figure-4a shows highly weakened peaks and corrosion products present on to the metal surface.

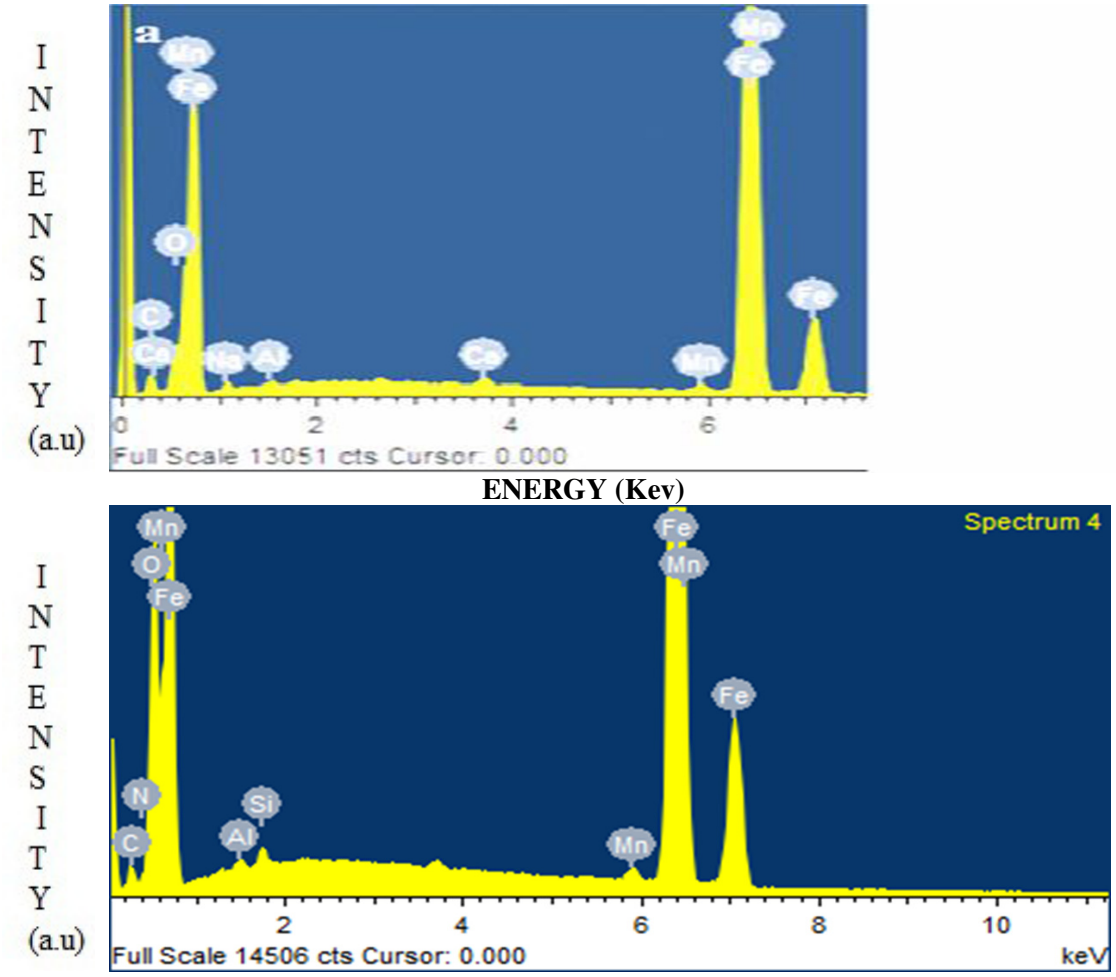


Fig-4: EDX spectra of carbon steel (a) in the absence of inhibitor formulation; (b) in the presence of binary system

Mechanism of Corrosion Inhibition

An analysis of the results of weight- loss method reveals the inhibitor formulation consisting of 10ppm of $Zn^{2+}$and 150ppm of SG offers an IE of 87%. Results of polarization study suggest that the formulation functions as an anodic inhibitor.

From the above observations, the following mechanism of corrosion inhibition is proposed. When carbon steel specimen is immersed in RO water,

The anodic reaction is-

$$Fe \rightarrow Fe^{2+} + 2e^-$$

and the cathodic reaction is-

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$$

When the inhibitor system consisting of 10ppm of $Zn^{2+}$and 150ppm of SG is prepared, there is a formation of Zn^{2+} -SG complex in solution.

$$Zn^{2+} + SG \rightarrow Zn^{2+} - SG$$

When the carbon steel is immersed in the solution, the Zn^{2+} - SG complex diffuses from the bulk of the solution to the metal surface. On the surface of the metal, Zn^{2+} - SG complex is converted into Fe^{2+} - SG complex at the local anodic regions.

$$Zn^{2+} - SG + Fe^{2+} \rightarrow Fe^{2+} - SG + Zn^{2+}$$

The released Zn^{2+} ions combine with OH- ions to form $Zn(OH)_2$ on the anodic sites.

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \downarrow$$

Thus the protective film consists of Fe^{2+} - SG complex, $Zn(OH)_2$ and oxides of Fe.

CONCLUSION

The present study leads to the following conclusions:

1. The Zn^{2+} +SG system shows a synergistic effect in controlling the corrosion of carbon steel immersed in RO water.
2. The binary formulation has good protection efficiency for the corrosion of carbon steel in RO water.
3. Polarization study reveals that the formulation Zn^{2+} -SG functions as an anodic inhibitor.
4. SEM, EDX and AC Impedance study corroborated that the inhibitor molecules are adsorbed onto the metal surface.

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