Synergistic Inhibitive Effect of Sodium Gluconate (SG) – Al^{3+} System for carbon steel in ground water

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ABSTRACT

The inhibition efficiency (IE) of Sodium Gluconate (SG) in controlling corrosion of carbon steel immersed in ground water in the absence and presence of Al^{3+} has been evaluated by weight loss method. It is observed that the synergistic formulation consisting of 50ppm SG and 200 ppm of Al^{3+} has 96.55% IE. Polarization study reveals that SG- Al^{3+} system functions as a cathodic inhibitor. AC impedance study reveals that a protective film is formed on the metal surface.

The protective film has been analysed by FT-IR and scaning electron microscope (SEM) studies. It is found that the protective film consists of Fe^{2+}-SGcomplex. On the basis of all the above studies, a suitable mechanism of corrosion inhibition is proposed.

Key words: *Carbon steel, corrosion inhibition, Synergistic effect, Cathodic inhibitor, Sodium Glugonate*

1. INTRODUCTION

The usage of ground water is common in all industries. The role of dissolved oxygen in ground water is the predominant factor to cause mild steel corrosion [1-2]. Depending upon the metal /environment combinations different types of inhibitors are used in suitable concentrations. The inhibition efficiency [3-15] organic inhibitors such as carboxylates, gluconates, gluconic acids, amines[16] are explained by the adsorption of organic molecules on the metal surface incorporation into the oxide film. They can be adsorbed on the metal surface through hetero atoms such as nitrogen, oxygen, sulphur and phosphorous, multiple bonds with aromatic rings and block the active sites, thus decreasing the corrosion Rates. Several inhibitors such as phosphonic acid[17-18], Thiourea[19], carboxy methyl cellulose[20], Sodium dodecyl sulphate[21] have been used to control corrosion of carbon steel. Inhibitors for carbon steel in near neutral, aqueous solutions are soluble chromates, dichromates nitrates, borates, benzoates and salts of carboxylic acids. Corrosion inhibition due to the formation of oxide layer on Cu metal surface in concentrated propionic acid and dilute citric acid [22] have been reported. The corrosion inhibition of carbon steel in ground water by adipic acid and Zn^{2+} system has been reported [23]. Existence of synergism between succinic acid and Zn^{2+} in controlling corrosion of carbon steel in well water has been investigated [24]. Inhibitors such as benzoate, phthalate and other carboxylates [25-27] stabilize the oxide film on iron surface presumably. Their inhibitive action results from the bonding of the O^- ion. Carboxylates are anodic inhibitors. The corrosion inhibition of steel by salicylic acid in acidic media has been investigated [28]. In present study synergistic effect of Sodium Gluconate SG and Al^{3+} in corrosion inhibition of carbon steel in ground water has been investigated in detail. Sodium Gluconate is an environment friendly organic compound of molecular formula is $[CH_2OH(CHOH)_4\ COO]Na$. While the inhibition efficiencies have been evaluated by the weight loss method, the mechanistic aspects are based upon the results of potentiostatic polarization, AC impedance studies and also by the surface examination such as FT-IR, and optical microscopy.

2.EXPERIMENTAL

2.1. Preparation of the specimens

Carbon steel specimens (0.025% S, 0.06% P, 0.4% Mn, 0.15%C and the rest iron) of the dimension 1.0 x 4.0 x 0.2cm were polished to a mirror finish and degreased with trichloroethylene and used for the weight loss method and surface examination studies. Ground water was collected from Nilaiyur village in Madurai, Tamilnadu, India. Corrosion behaviour of carbon steel in this water was evaluated.

2.2. Weight loss method

Carbon steel specimens in triplicate were immersed in 100ml of ground water containing various concentrations of the inhibitor in the absence and presence of Al^{3+} for five days. The weights of the specimens before and after immersion were determined using a balance, Shimadzu AY62 model. The corrosion products were cleaned with Clarke's solution [29]. The inhibition efficiency (IE) was then calculated using the equation

$$\mathbf{IE = 100\ [1-(w_2/w_1)]\ \%} \quad \mathbf{(1)}$$

Where,

w_1 = Corrosion rate (mdd) in absence of inhibitor

w_2 = Corrosion rate (mdd) in presence of inhibitor

2.3. Surface examination study

The carbon steel specimens were immersed in various test solutions for a period of five days. After five days, the specimens were taken out and dried. The nature of the film formed on the surface of metal specimens was analyzed by various surface analysis techniques, namely FT-IR spectra and Optical Microscopy Studies.

2.4. FT-IR spectra

These spectra were recorded in a Perkin – Elmer 1600 spectrophotometer. The film was carefully removed, mixed thoroughly with KBr and made into pellets and the FT-IR spectra were recorded.

2.5. Potentiostatic polarization study

This study was carried out using CHI 66A Electrochemical Workstation model. A three-electrode cell assembly was used. The working electrode was used as a rectangular specimen of carbon steel with one face of the electrode of constant 1 cm^2 area exposed. A saturated calomel electrode (SCE) was used as reference electrode. A rectangular platinum foil was used as the counter electrode. The results such as Tafel slopes, I_{corr}(corrosion current) and E_{corr} (corrosion potential) were calculated.

Tangents were drawn on the cathodic and anodic polarization curves. From the point of intersection of the two tangents I_{corr} and E_{corr} were calculated.

2.6. AC impedance measurements

The CHI 66A Electrochemical Workstation model was used for AC impedance measurements. The cell set up was the same as that used for polarization measurements. The real part (Z') and imaginary part (Z") of the cell impedance were measured in ohms for various frequencies. The R_t (charge transfer resistance) and C_{dl} (double layer capacitance) values were calculated.

2.7. Surface analysis by optical microscopy

Samples for SEM analysis were mounted directly on scotsch double adhesive tape and analysed in a Hitachi scanning electron microscope model s-450 operated at 15 Kv and photographed.

3. RESULTS AND DISCUSSION

3.1. Analysis of the results of weight loss method

. The various parameters of ground water are given in Table 1. The inhibition efficiencies (IE) of SG in controlling corrosion of carbon steel in ground water, for a period of five days in the absence and presence of Al^{3+} by weight loss method are given in Tables 2 to 6. SG alone has some 26 % IE, whereas Al^{3+} has 81% IE. In the absence of SG, the rate of transport of Al^{3+} from the bulk of the solution towards the metal surface is slow. Similar observations have already been reported [30-36]. When SG is combined with Al^{3+} ions it is found that the IE also increases. For example, 50 ppm SG has only 19% IE and 200 ppm of Al^{3+} has only 81%. Interestingly their combination shows 97% IE. This suggests a synergistic effect between SG and Al^{3+} ions; SG is able to transport Al^{3+} towards the metal surface.

3.2. Analysis of the results of potentiostatic polarization study for the SG - Al^{3+} system.

The corrosion parameters of carbon steel immersed in various test solutions obtained by polarization study are given in Table 7. The polarization curves are shown in Fig.1.When carbon steel is immersed in ground water, the corrosion potential – 4550mV Vs saturated calomel electrode (SCE). The formulation consisting of 200ppm of Al^{3+} and 50 ppm of SG shifts the corrosion potential to -488mV Vs SCE. This suggests that the cathodic reaction is controlled predominantly, since more SG is transported to the cathodic sites in the presence of Al^{3+}. The Tafel Slopes (b_a and b_c) are also shifted in the presence of inhibitor. These results suggest that the SG– Al^{3+} formulation functions as a cathodic inhibitor. The corrosion current for ground water is 5.291 x 10^{-3} A/cm^2. It is decreased to 0.116 x 10^{-3} A/cm^2 by the 50ppm of SG and 200 ppm of Al^{3+} system. This indicates that a protective film is formed on the metal surface.

3.3. Analysis of the results of AC impedance spectra

The AC impedance spectra of carbon steel in various solutions were regarded (Fig. 2). The AC impedance parameters, namely, charge transfer resistance (R_t) and double layer capacitance (C_{dl}) are given in Table 8. When carbon steel is immersed in ground water R_{ct} value is 5.06 Ω cm^2 and C_{dl} value is 1.62 x 10^{-2} F cm^{-2}. When SG and Al^{3+} are added to ground water, R_{ct} value increases from 5.06 Ω cm^2 to 187.92 Ω cm^2. The C_{dl} decreases from 1.62 x 10^{-2} Fcm^{-2} to 2.1 x 10^{-5} Fcm^{-2}. This suggests that a protective film is formed on the surface of the metal. This accounts for the very high IE of SG– Al^{3+} system.

3.4. Analysis of FT-IR spectra

The FT-IR spectrum of pure SG is given in Fig. 3. The C=O stretching frequency occurs at 1585cm^{-1}. The FT-IR spectrum of the film scratched from the surface of the metal immersed in ground water, 50 ppm of SG and 200ppm of Al^{3+} is given in Fig. 3. It is seen from the spectrum that C=O stretching frequency of SG in the free state has shifted from 1585 cm^{-1} to 1565 cm^{-1}. This shift indicates that the carbonyl oxygen atom is co-ordinate to from Fe^{2+}-SG complex on the anodic sites of the metal surface[37-39]. The band at 1428 cm^{-1} is due to Al $(OH)_3$[40-41]

3.5. Analysis of optical microscopes

Giacomelli [42] and Jagdheesh[43] studied the inhibitor effect of succinic acid on the corrosion resistance of mild steel by optical microscopic studies and established the protective layer formation from photographic images. The photo micro graphs of different magnification (120, 600 times) of mild steel specimen immersed in the groundwater for 5 days in the absence and presence of inhibitor system are shown in Fig 4, shows the rough film that indicates the corrosion products spread on the mild steel surface in groundwater and the smooth film that indicates the effect of inhibitor system on the mild steel surface.

3.8. Mechanism of corrosion inhibition

The results of the weight loss study show that the formulation consisting of 50ppm of SG and 200 ppm of Al^{3+} has 97% IE in controlling corrosion of carbon steel, in ground water. A synergistic effect exists between Al^{3+} and SG. Polarization study reveals that the formulations functions as mixed inhibitor. AC impedance spectra reveal that the protective film is formed on the metal surface. FT-IR spectra study reveals that the protective film consists of Fe^{2+} – SG complex and Al $(OH)_3$. In order to explain these facts the following mechanism of corrosion inhibition is proposed.

- When the solution containing ground water, 200 ppm of Al^{3+} and 50ppm of SG is prepared, there is formation of Al^{3+} -SG complex in solution.
- When carbon steel is immersed in the solution, the Al^{3+} -SG complex diffuses from the bulk of the solution towards metal surface.
- On the metal surface, Al^{3+} - SG complex is converted in to Fe^{2+} - SG complex on the anodic sites. Al^{3+} is released.
- Al^{3+} -SG+ Fe^{2+} -----------> Fe^{2+}-SG+ Al^{3+}
- The released Al^{3+} combines with OH^- form $Al(OH)_3$ on the cathodic sites.
- Al^{3+} + $3OH^-$ -------------> $Aln(OH)_3\downarrow$
- Thus the protective film consists of Fe^{2+}–SG complex and $Al(OH)_3$.

4. Conclusions

The present study leads to the following conclusions

- A synergistic effect exists between Sodium Gluconate SG and Zn^{2+} in controlling corrosion of carbon steel immersed in ground water.
- The formulation consisting of 200ppm of SG and 10 ppm of Zn^{2+} has 96% IE.
- Polarization study reveals that SG–Zn^{2+} system functions as a cathodic inhibitor.
- AC impedance spectra reveal that a protective film is formed on the metal surface.
- FT-IR spectra reveal that the protective film consists of Fe^{2+}-SG complex and $Zn(OH)_2$
- This formulation may find application in cooling water system.
- Optical micro graphic images and AFM images confirm the formation of protective layer on the metal surface with its surface morphology.
- The synergistic formulation with 100 ppm of CTAB has 96% corrosion inhibition efficiency and 100% biocidal efficiency.

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ANNEXURES:

Table 1 The parameters of ground water which is used for investigation

Parameter	Value
pH	8.0
TDS	790 mg/l
Alkalinty	365mg/l
Chloride	13 mg/l
Sulphate	16 mg/l
Calcium	74 mg/l
Magnesium	86 mg/l
Barium	10mg/l

Table 2 Corrosion rate (CR) of carbon steel in ground water in the presence of inhibitor system and the inhibition efficiency (IE) obtained by weight loss method

Inhibitor system: SG + Al^{3+} (0 ppm)

Immersion period –3 days

SG ppm	Al^{3+} ppm	CR mdd	IE %
0	0	19.52	-
50	0	15.71	19.51
100	0	17.97	7.92
150	0	14.28	26.82
200	0	16.90	13.41

Table 3. Corrosion rate (CR) of carbon steel in ground water in the presence of inhibitor system and the inhibition efficiency (IE) obtained by weight loss method

Inhibitor system: SG + Al^{3+} (50 ppm)

Immersion period – 3 days

SG	Al^{3+} Ppm	CR mdd	IE %
0	50	11.43	41.46
50	50	16.38	16.04
100	50	13.33	31.70
150	50	17.38	10.97
200	50	10.12	48.17

Table 4 Corrosion rate (CR) of carbon steel in ground water in the presence of inhibitor system and the inhibition efficiency (IE) obtained by weight loss method

Inhibitor system: SG + Al^{3+} (100 ppm)

Immersion period – 3 days

SG ppm	Al^{3+} Ppm	CR Mdd	IE %
0	100	11.18	42.68
50	100	13.68	24.87
100	100	20.95	-7.31
150	100	8.21	57.92
200	100	4.88	75.0

Table 5. Corrosion rate (CR) of carbon steel in ground water in the presence of inhibitor system and the inhibition efficiency (IE) obtained by weight loss method

Inhibitor system:SG + Al^{3+} (150 ppm)

Immersion period – 3 days

SG ppm	Al^{3+} Ppm	CR mdd	IE %
0	150	6.9	64.63
50	150	16.9	13.0
100	150	8.93	54.26
150	150	6.43	67.07
200	150	2.62	86.55

Table 6. Corrosion rate (CR) of carbon steel in ground water in the presence of inhibitor system and the inhibition efficiency (IE) obtained by weight loss method

Inhibitor system: SG + Al^{3+} (200 ppm)

Immersion period –3 days

SG ppm	Al^{3+} Ppm	CR mdd	IE %
0	200	3.57	81.70
50	**200**	**0.47**	**97.56**
100	200	13.21	32.31
150	200	4.99	74.39
200	200	1.19	93.90

Table 7 Corrosion Parameters obtained by Potentiostatic Polarization method.

System	E_{Corr}	I_{Corr}	b_c	b_a	R_p	% I.E
Blank	**-0.455**	**5.291×10^{-3}**	**196.85**	**143.55**	**7**	**------**
SG 50 ppm + Al^{3+} 200 ppm	**-0.488**	**0.116×10^{-3}**	**158.60**	**93.70**	**220**	**97.79**

Table 8 Corrosion Parameters obtained by AC Impedance Studies.

System	R_s (ohm cm^{-2})	R_{ct} (ohm cm^{-2})	C_{dl} (F/cm^2)	% I.E
Blank	2.568	5.06	1.6×10^{-2}	-----
SG 50 ppm + Al^{3+} 200 ppm	-25.013	187.92	2.1×10^{-5}	97.30

Fig.1. Polarization curves of carbon steel immersed in ground water in presence and absence of inhibitors

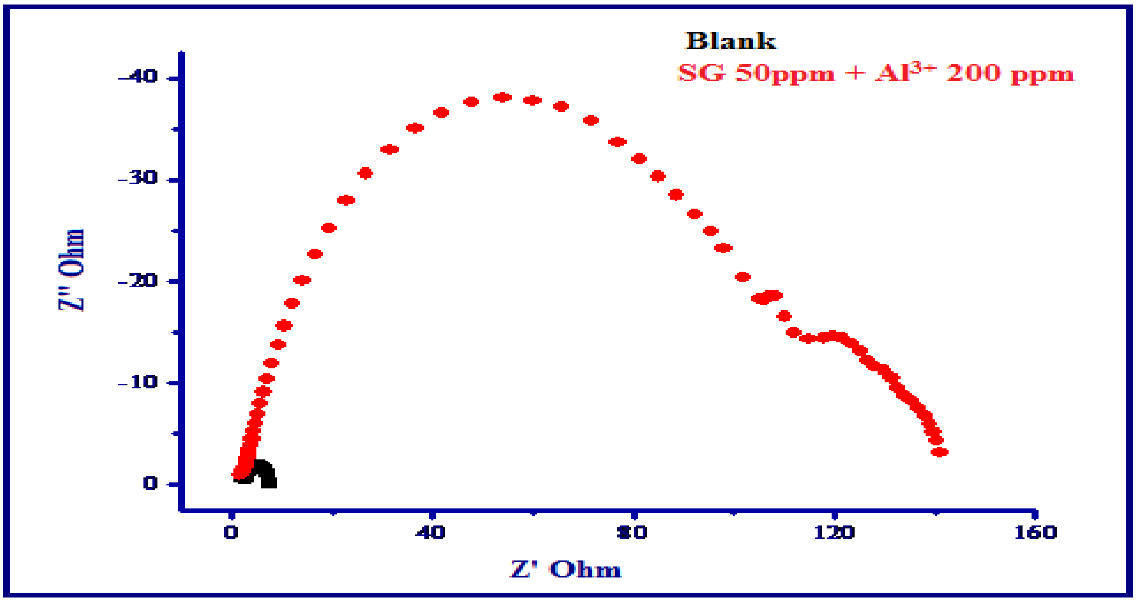

Fig.2. AC impedance study of carbon steel immersed in ground water in presence and absence of inhibitors

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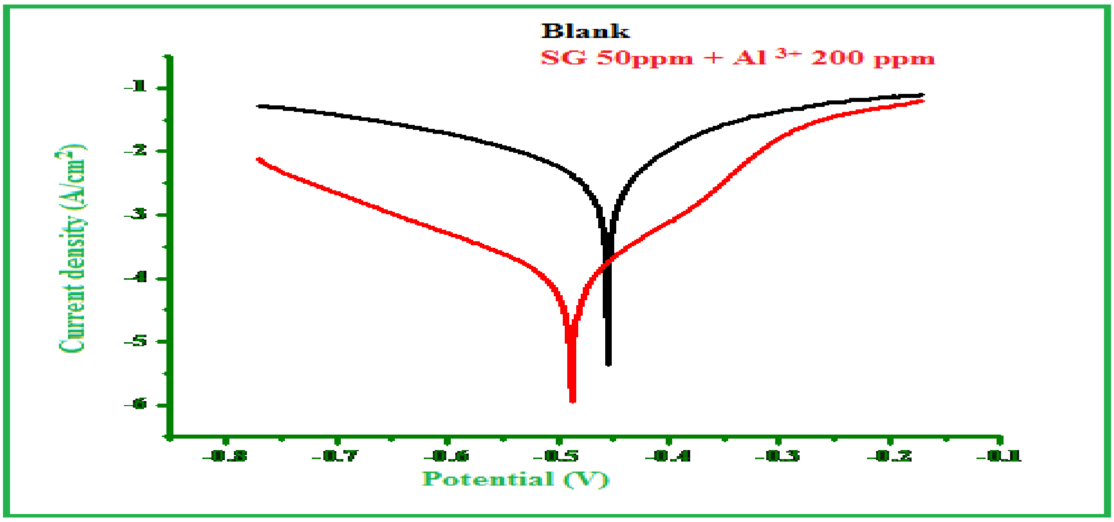


Fig.3. FT-IR spectra of carbon steel in ground water in presence and absence of inhibitors

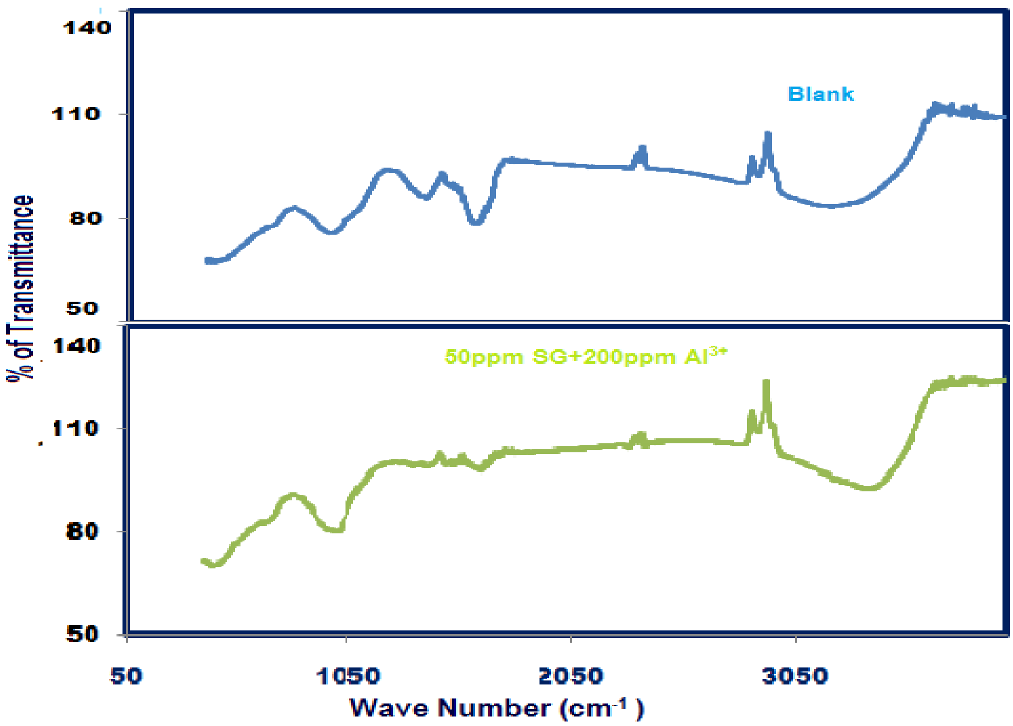
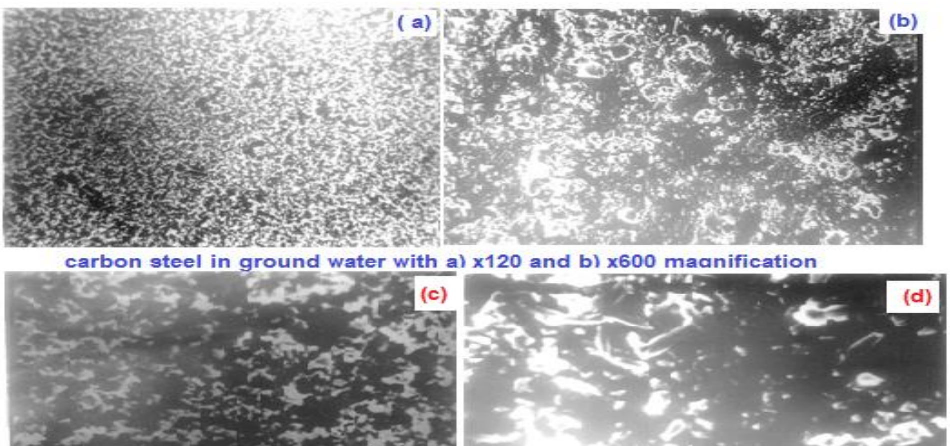


Fig.4. SEM Images of carbon steel in ground water in presence and absence of inhibitors



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