

SYNERGISTIC INHIBITIVE EFFECT OF AMMONIUM PHOSPHATE (AMP) – Al^{3+} SYSTEM FOR CARBON STEEL IN GROUND WATER

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Abstract

The inhibition efficiency (IE) of Ammonium Phosphate (AMP) 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 100ppm AMP and 25 ppm of Al^{3+} has 90% IE. Polarization study reveals that AMP- 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 analyzed by FT-IR and optical microscope studies. It is found that the protective film consists of Fe^{2+} -AMP complex. 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, Ammonium Phosphate



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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. Aluminium ions have long been considered as valuable corrosion inhibitors for protection afforded by a cathodic polarization mechanism [3-4]. Speller [5-7] reported

that "Compound films" formed by phosphate – chromate mixture are more effective than those of either alone.

The synergistic effect of halides and organic compound inhibitors are reported often in the literature [8-11]. Several inhibitors such as phosphonic acid [12, 13], Thiourea [14], carboxy methyl cellulose [15], Sodium dodecyl sulphate [16] 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 [17] have been reported.

The corrosion inhibition of carbon steel in ground water by adipic acid and Al^{3+} system has been reported [18]. Existence of synergism between succinic acid and Al^{3+} in controlling corrosion of carbon steel in well water has been investigated [19]. Inhibitors such as benzoate, phthalate and other carboxylates [20-22] 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 [23]. In present study synergistic effect of Ammonium Phosphate (AMP) and Al^{3+} in corrosion inhibition of carbon steel in ground water has been investigated in detail. Ammonium Phosphate is an environment friendly inorganic compound $[(NH_4)_3PO_4]$ 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.

1. 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 near Madurai, Tamilnadu, India. Corrosion behaviour of carbon steel in this water was evaluated.

1.2. 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 three 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[24]. The inhibition efficiency (IE) was then calculated using the equation

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

Where,

w_1 = Corrosion rate (mdd) in absence of inhibitor

w_2 = Corrosion rate (mdd) in presence of inhibitor

1.3. Surface examination study

The carbon steel specimens were immersed in various test solutions for a period of three days. After three 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.

1.4. 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.

1.5. 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.

1.6. 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_{ct} (charge transfer resistance) and C_{dl} (double layer capacitance) values were calculated.

2. RESULTS AND DISCUSSION

The various parameters of Ground water are given in Table 1. The inhibition efficiencies (IE) of AMP in controlling corrosion of carbon steel in ground water, for a period of three days in the absence and presence of Al^{3+} by weight loss method are given in Tables 2 to 6. 100 ppm of AMP alone has some 64% IE, whereas 25 ppm of Al^{3+} has 20% IE. In the absence of AMP, the rate of transport of Al^{3+} from the bulk of the solution towards the metal surface is slow. A similar observation has already been reported [30-31]. When AMP is combined with Al^{3+} ions it is found that the IE also increases to 90%. This suggests a synergistic effect between AMP and Al^{3+} ions; AMP is able to transport Al^{3+} towards the metal surface.

3.1. Analysis of the results of potentiostatic polarization study for the AMP- 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 – 455mV Vs saturated calomel electrode (SCE). The formulation consisting of 100ppm of AMP and 25 ppm of Al^{3+} shifts the corrosion potential to -496mV Vs SCE. This suggests that the cathodic reaction is controlled predominantly; since more AMP is transported to the cathodic sites in the presence of Al^{3+} . This result suggests that the AMP– Al^{3+} formulation functions as a cathodic inhibitor. The corrosion current for ground water is $5.29 \times 10^{-3} \text{ A/cm}^2$. It is decreased to $0.064 \times 10^{-3} \text{ A/cm}^2$ by 100ppm of AMP and 25ppm of Al^{3+} system. This indicates that a protective film is formed on the metal surface.

3.2. 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 $5.06 \Omega \text{ cm}^2$ and C_{dl} value is $1.6 \times 10^{-2} \text{ F cm}^{-2}$. When AMP and Al^{3+} are added to ground water, R_{ct} value increases from $5.06 \Omega \text{ cm}^2$ to $381 \Omega \text{ cm}^2$. The C_{dl} decreases from $1.6 \times 10^{-2} \text{ F cm}^{-2}$ to $5.8 \times 10^{-6} \text{ F cm}^{-2}$. This suggests that a protective film is formed on the surface of the metal. This accounts for the very high IE of AMP– Al^{3+} system.

3.3. Analysis of FT-IR spectra

The FT-IR spectrum of pure AMP is given in Fig.3. The C=O stretching frequency occurs at 1560 cm^{-1} . The FT-IR spectrum of the film scratched from the surface of the metal immersed in ground water, 100 ppm of AMP and 25ppm of Al^{3+} is given in Fig.3. It is seen from the spectrum that C=O stretching frequency of AMP in the free state has shifted from 1560 cm^{-1} to 1570 cm^{-1} . This shift indicates that the carbonyl oxygen atom is coordinated to from Fe^{2+} -AMP complex on the anodic sites of the metal surface [32-34]. The band at 1430 cm^{-1} is due to $\text{Al}(\text{OH})_3$ [35-37].

3.4. Analysis of optical microscopes

Giacomelli[32] Jagdheesh [33] 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 photomicro graphs of different magnification (120, 600 times) of mild steel specimen immersed in the groundwater for three days in the absence and presence of inhibitor system are shown in Fig 4. It shows the rough film that indicates the corrosion products spread on the mild steel surface immersed in groundwater and the smooth film that indicates the effect of inhibitor system on the mild steel surface.

3.5. Mechanism of corrosion inhibition

The results of the weight loss study show that the formulation consisting of 100ppm of AMP and 25 ppm of Al^{3+} has 90% IE in controlling corrosion of carbon steel, in ground water. A synergistic effect exists between Al^{3+} and AMP. 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+} – AMP complex and $\text{Al}(\text{OH})_3$. In order to explain these facts the following mechanism of corrosion inhibition is proposed.

- 1) When the solution containing ground water, 25 ppm of Al^{3+} and 100ppm of AMP is prepared, there is formation of Al^{3+} -AMP complex in solution.
- 2) When carbon steel is immersed in the solution, the Al^{3+} -AMP complex diffuses from the bulk of the solution towards metal surface.
- 3) On the metal surface, Al^{3+} – AMP complex is converted in to Fe^{2+} – AMP complex on the anodic sites. Al^{3+} is released.
- 4) Al^{3+} -AMP+ Fe^{2+} -----> Fe^{2+} -AMP+ Al^{3+}

- 5) The released Al^{3+} combines with OH^- form $\text{Al}(\text{OH})_3$ on the cathodic sites.
- 6) $\text{Al}^{3+} + 3\text{OH}^- \text{-----} \rightarrow \text{Al}(\text{OH})_3 \downarrow$
- 7) Thus, the protective film consists of Fe^{2+} -AMP complex and $\text{Al}(\text{OH})_3$.

3. CONCLUSIONS

The present study leads to the following conclusions

- 1) A synergistic effect exists between Ammonium Phosphate (AMP) and Al^{3+} in controlling corrosion of carbon steel immersed in ground water.
- 2) The formulation consisting of 100ppm of AMP and 25 ppm of Al^{3+} has 90% IE.
- 3) Polarization study reveals that AMP- Al^{3+} system functions as a cathodic inhibitor.
- 4) AC impedance spectra reveal that a protective film is formed on the metal surface.
- 5) FT-IR spectra reveal that the protective film consists of Fe^{2+} -AMP complex and $\text{Al}(\text{OH})_3$
- 6) This formulation may find application in cooling water system.
- 7) Optical micro graphic images confirm the formation of protective layer on the metal surface with its surface morphology.

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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: AMP + Al³⁺ (0 ppm) Immersion period –3 days**

Ammonium phosphate ppm	Al ³⁺ ppm	CR Mdd	IE %
0	0	13.64	---
50	0	5.45	60
100	0	4.87	64
150	0	4.09	70
200	0	3.41	75

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: AMP + Al³⁺ (5 ppm) Immersion period –3 days**

Ammonium phosphate	Al ³⁺ ppm	CR mdd	IE %
0	0	13.64	-----
0	5	12.28	10
50	5	10.23	25
100	5	7.37	46
150	5	5.18	62
200	5	3.55	74

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: AMP + Al³⁺ (10 ppm) Immersion period –3 day

Ammonium phosphate ppm	Al ³⁺ ppm	CR Mdd	IE %
0	0	13.64	----
0	10	12.1	12
50	10	9.55	30
100	10	8.05	41
150	10	6.82	50
200	10	4.23	69

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: AMP + Al³⁺ (25 ppm) Immersion period –3 day

Ammonium phosphate ppm	Al ³⁺ ppm	CR mdd	IE %
0	0	13.64	-----
0	25	14.86	20
50	25	5.46	60
100	25	1.36	90
150	25	1.64	88
200	25	3.68	73

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: AMP + Al³⁺ (50 ppm) Immersion period –3 day

Ammonium phosphate ppm	Al ³⁺ ppm	CR mdd	IE %
0	0	13.64	----
0	50	8.87	35
50	50	8.46	38
100	50	7.37	46
150	50	4.5	67
200	50	2.73	80

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	5.29×10^{-3}	196.85	143.55	7	-----
AMP 100 ppm + Al ³⁺ 25 ppm	-0.496	0.064×10^{-3}	159.74	93.40	400	98.79

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	5.063	1.6×10^{-2}	-----
AMP 100 ppm + Al ³⁺ 25 ppm	-54.201	381.56	5.8×10^{-6}	98.67

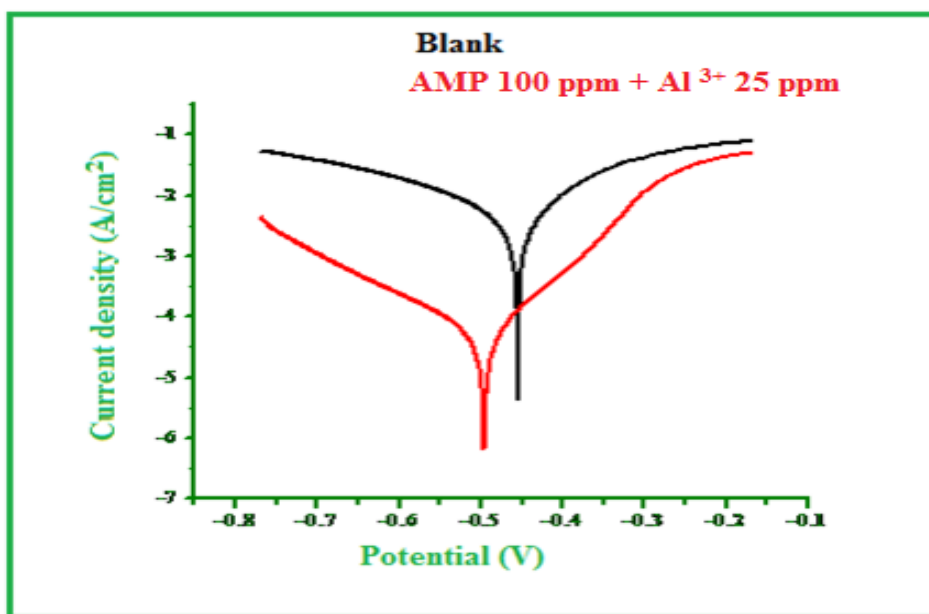


Fig.1. Polarization curves of carbon steel immersed in ground water in presence and absence of inhibitor

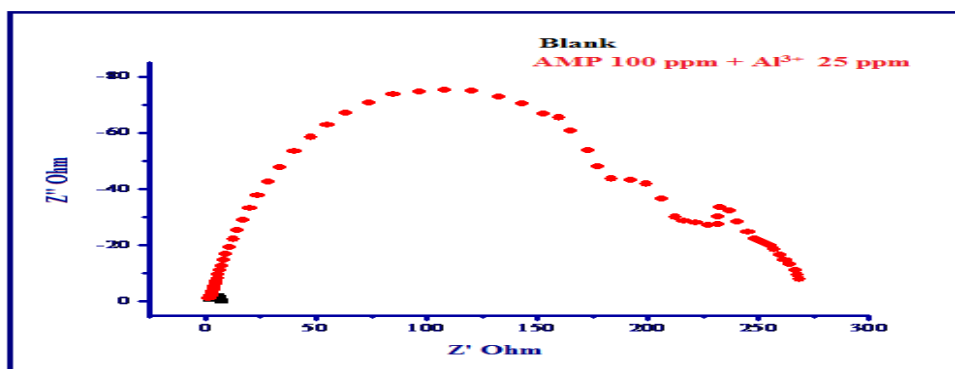


Fig.2. AC impedance study of carbon steel immersed in ground water in presence and absence of inhibitors

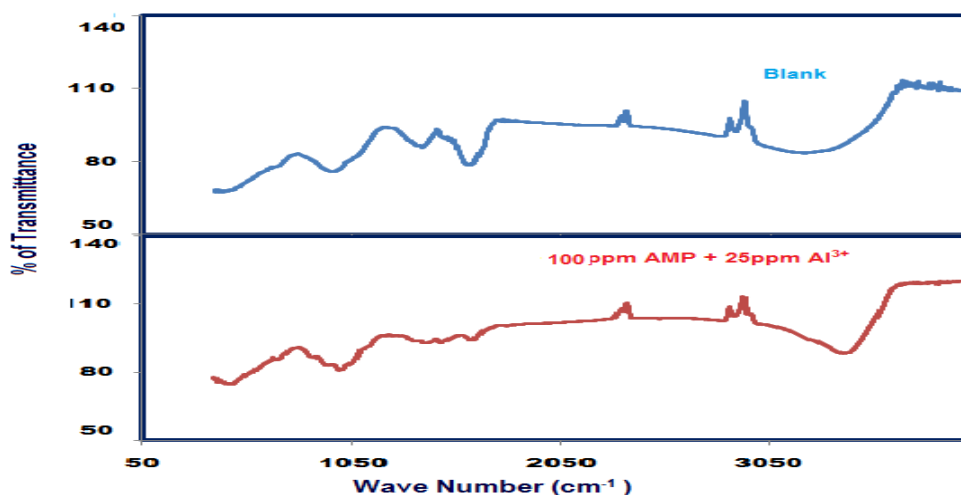


Fig.3. FT-IR spectra of carbon steel in ground water in presence and absence of inhibitors

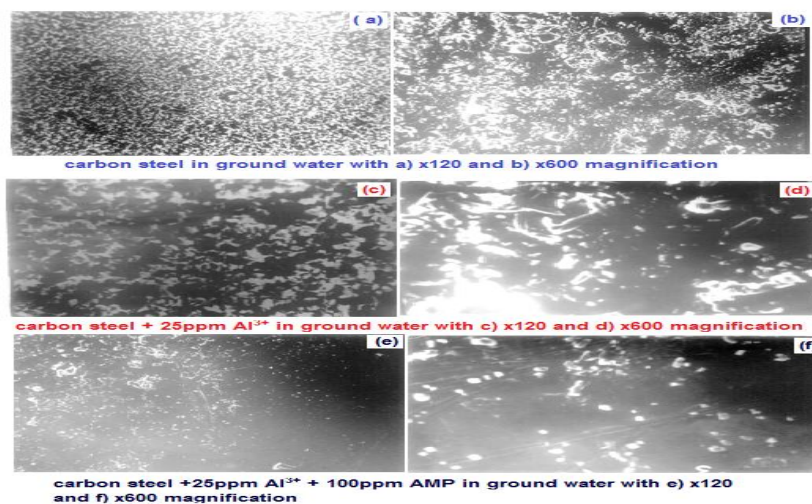


Fig.4. SEM Images of carbon steel in ground water in presence and absence of inhibitors