SYNERGISTIC EFFECT OF AMINOTRIMETHYLENE PHOSPHONIC ACID (ATMP) – Al^{3+} SYSTEM FOR CARBON STEEL IN GROUND WATER

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ABSTRACT

The inhibition efficiency (IE) of AminoTrimethylenephosphonic acid (ATMP) in controlling corrosion of steel immersed in ground water within the absence and presence of Al^{3+} has been evaluated by weight loss method. It is observed that the synergistic formulation consisting of 150ppm ATMP and 50 ppm of Al^{3+} has 98% IE. Effect of immersion period and pH on IE has also been studied. Polarization study reveals that ATMP- Al^{3+} system functions as a mixed inhibitor. AC impedance study reveals that a protective film is made on the metal surface. The protective film has been analysed by FT-IR and optical microscope(SEM) studies. It is found that the protective film consists of Fe^{2+} -ATMP complex. On the basis of all the above studies, a suitable mechanism of corrosion inhibition is proposed.

KEYWORDS: Carbon Steel, Corrosion Inhibition, Synergistic Effect, Cathodic Inhibitor, Aminotrimethylenephosphonic Acid

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1. INTRODUCTION

The usage of ground water is common in all industries. The role of dissolved oxygen in ground water is that the predominant factor to cause low carbon steel corrosion [1-2]. Depending upon the metal /environment combinations different types of inhibitors are used in suitable concentrations. Speller [3-5] reported that "Compound films" formed by phosphate – chromate mixture is more effective than those of either alone.

The synergistic effect of halides and organic compound inhibitors are reported often in the literature [6-9]. Several inhibitors such as phosphonic acid [10-11] Thiourea [12], carboxy methyl cellulose [13], Sodium dodecyl sulphate [14] 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 [15] have been reported.

The corrosion inhibition of steel in ground water by adipic acid and Zn^{2+} system has been reported [16]. Existence of synergism between succinic acid and Zn^{2+} in controlling corrosion of carbon steel in well water has been investigated [17]. Inhibitors such as benzoate, phthalate and other carboxylates [18-20] stabilize the oxide

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film on iron plane 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 [21]. In present study synergistic effect of AminoTrimethylene phosphonic acid (ATMP) and Al^{3+} in corrosion prevention of carbon steel in ground water has been investigated in detail. AminoTrimethylene phosphonic acid is an environment friendly organic compound, $C_3H_{12}P_3O_9N$. Which is mainly used in open water circulation cooling system, petroleum pipelines and boilers? 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 specimen (0.025% S, 0.06% P, 0.4% Mn, 0.15% C and the rest iron) of the measurement $1.0 \times 4.0 \times 0.2$ cm were polished to a reflect finish and degreased with trichloro ethylene and used for the weight loss method and surface examination studies. Ground water was collected from Ramanathapuram (near sea shore area) in the state of Tamil Nadu, India.

2.2. Weight Loss Method

The parameters of ground water used in the at hand study are given in Table-1. 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 [22]. The inhibition efficiency (IE) was then calculated using the equation

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

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 a range of test solutions for a period of three days. After three days, the specimens were full out and dried. The nature of the film formed on the surface of metal specimens was analysed by various surface analysis techniques, namely FT-IR spectra and Optical Microscopy (SEM) studies.

2.3.1. FT-IR Spectra

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

2.3.2. Potentiostatic Polarization Study

This study was carried out using CHI 66A Electrochemical Workstation model. A three-electrode cell gathering was used.

The working electrode was used as a rectangular specimen of carbon steel with one look of the electrode of constant 1 cm² 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} and E_{corr} 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.

2.3.3. AC Impedance Measurements

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

2.3.4. Surface Analysis by Optical Microscopy (SEM)

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

2.4. Influence of Duration of Immersion on the IE

The power of duration of immersion on the IE of the ATMP- Al³⁺ system has been studied for 1,3,5 and 7 days.

2.5. Influence of pH on the IE of ATMP- Al³⁺ System

Influence of pH on the IE of ATMP- Al³⁺ System has been analysed various from 6 to 12.

2.6. Synergism Parameters (S_1)

The synergism parameter (S_1) is measured using the relation as stated below

$$S_1 = \frac{1 - I_{1+2}}{1 - I'_{1+2}}$$

Where,

$$I_{1+2} = (I_1 + I_2) - (I_1 \cdot I_2)$$

I'_{1+2} = combined inhibition efficiency of substance 1 and substance 2.

3 RESULTS AND DISCUSSIONS

3.1. Parameters of Ground Water

Corrosion behavior of carbon steel in ground water was evaluated and a variety of parameters are given in Table 1.

3.2. Analysis of the Results of Weight Loss Method

The inhibition efficiencies (IE) of ATMP in controlling corrosion of carbon steel in ground water, for a stage of three days in the absence and presence of Al³⁺ by weight loss method are given in Tables 2 to 6. ATMP alone has some 70% IE, whereas Al³⁺ has 12% IE. In the absence of ATMP, the rate of transport of Al³⁺ from the mass of the solution towards the metal surface is slow. Similar observations have already been reported [23-24]. When ATMP is joint with Al³⁺ ions it is

found that the IE also increases. For example, 150 ppm ATMP has only 70% IE and 50 ppm of Al^{3+} has only 12%. Interestingly their mixture shows 98% IE. This suggests a synergistic effect between ATMP and Al^{3+} ions; ATMP is able to transport Al^{3+} towards the metal surface.

3.3. Analysis of the Results of Potentiostatic Polarization Study for the ATMP- Al^{3+} System

The corrosion parameters of carbon steel immersed in a variety of 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 150ppm of ATMP and 50 ppm of Al^{3+} shifts the corrosion potential to -457mV Vs SCE. This suggests that the cathodic reaction is controlled predominantly which is further conformed by more shifted in the cathodic Tafel slope as shown in Table 7. This result suggests that the ATMP– 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 $0.315 \times 10^{-5} \text{ A/cm}^2$ by the 150ppm of ATMP and 50 ppm of Al^{3+} system. This shows that a protective film is formed on the metal surface.

3.4. Analysis of the Results of AC Impedance Spectra

The AC impedance spectra of carbon steel in a variety of solutions were regarded (Fig. 2). The AC impedance parameters, namely, charge transfer resistance (R_{ct}) 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 ATMP and Al^{3+} are added to ground water, R_{ct} value increases from $5.06 \Omega \text{ cm}^2$ to $68.25 \Omega \text{ cm}^2$. The C_{dl} decreases from $1.6 \times 10^{-2} \text{ Fcm}^2$ to $1.1 \times 10^{-4} \text{ Fcm}^2$. These suggest that a protective film is formed on the surface of the metal. This accounts for the very high IE of ATMP– Al^{3+} system.

3.5. Analysis of FT-IR Spectra

The FT-IR spectrum of pure ATMP is given in Fig.3. The P=O stretching frequency occurs at 945, C-N stretching frequency 1102 cm^{-1} . The FT-IR spectrum of the film scratched from the surface of the metal immersed in ground water, 150 ppm of ATMP and 50ppm of Al^{3+} is given in Fig.3. It is seen from the spectrum that P=O stretching frequency of ATMP in the free state has shifted from 945 cm^{-1} to 1010 cm^{-1} , C – N stretching frequency changes from 1102 cm^{-1} to 1129 cm^{-1} . This shift indicates that the oxygen and nitrogen atoms of phosphonic acid are co-ordinated to from Fe^{2+} -ATMP complex on the anodic sites of the metal surface [25-27]. The band at 1350 cm^{-1} is due to $\text{Al}(\text{OH})_3$ [28-29]

3.6. Analysis of Optical Microscopes

The photo micro graphs of dissimilar 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, shows the rough film that indicates the corrosion products spread on the mild steel surface in groundwater and the smooth film that shows the effect of inhibitor system on the mild steel surface.

3.7. Influence of Duration of Immersion on the IE of the ATMP – Al^{3+} System

The influence of duration of immersion on the IE of the ATMP- Al^{3+} system is given in Table 9.

It is found that as the duration of immersion increases with the inhibition efficiency found to decrease. When the immersion period is 1day IE=97%, when the immersion period is 3 days IE =98%. When immersion period is 5 days

IE=87%, when the immersion period is 7 days IE = 73%. This may be due to the fact that as the period of immersion increases the protective film formed on the metal surface namely Fe²⁺ - ATMP Complex is broken by the aggressive chloride ion present in ground water and hence IE decreases.

3.8. Influence of pH on the IE of ATMP- Al³⁺ System.

pH is a crucial factor for the determination of corrosion inhibition efficiency. This inhibition efficiency on mild steel is dependent on concentration of inhibitor and also the efficiency increases with the increasing concentration of acids. Lowering or raising the pH brings down the value of IE.

The influence of P^H on the IE of ATMP- Al³⁺ system is given in Table. 10. It is found from Table.10 that when P^H is decreased from 8 to 6 (by addition of dil. H₂SO₄) the IE decreases from 98% to 87%. This is due the attack of H⁺ ion of the H₂SO₄ on the metal surface and hence increases in corrosion rate and decrease in IE. When P^H is increased from 8 to 10 (by addition of dil NaOH) the IE decrease from 98% to 88%. This is due to the fact when NaOH is added Al³⁺ is precipitated as Al(OH)₃ in the bulk of the solution so the transport of inhibitor towards the metal surface decreases and hence the IE decrease when P^H is increased from 10 to 12 (by addition of dil. NaOH) the IE increases from 88% to 91%. This is due to the fact that further addition of NaOH converts Al(OH)₃ precipitate into soluble sodium aluminate (NaAlO₂)) now the transport of inhibitors towards the metal surface is favoured. Hence the IE increases.

3.9. Synergism Parameters (S₁)

The synergism parameters are given in Table.11. The joined impact effect is called synergistic effect. The synergism boundaries (S₁) determined from surface inclusion was seen as more than unity. This outcome unmistakably shows the synergistic impact among ATMP and Al³⁺

3.10. Mechanism of Corrosion Inhibition

The consequences of the weight reduction study show that the definition comprising of 150ppm of ATMP and 50 ppm of Al³⁺ has 98% IE in consumption corrosion of carbon steel, in ground water. A synergistic impact exists among Al³⁺ and ATMP. Polarization study uncovers that the definitions capacities as blended inhibitor. Air conditioning impedance spectra uncover that the defensive film is shaped on the metal surface. FT-IR spectra study uncovers that the defensive film comprises of Fe²⁺ – ATMP complex and Al (OH)₃. So as to clarify these realities the accompanying instrument of erosion hindrance is proposed

- When the arrangement containing ground water, 50 ppm of Al³⁺ and 150 ppm of ATMP then there is a development of Al³⁺-ATMP complex in arrangement.
- When carbon steel is immersed in the solution, the Al³⁺-ATMP complex diffuses from the bulk of the solution towards metal surface.
- On the metal surface, Al³⁺ – ATMP complex is converted in to Fe²⁺ – ATMP complex on the anodic sites. Al³⁺ is released.
- $\text{Al}^{3+}\text{-ATMP} + \text{Fe}^{2+} \longrightarrow \text{Fe}^{2+}\text{-ATMP} + \text{Al}^{3+}$
- The released Al³⁺ combines with OH⁻ form Al(OH)₃ on the cathodic sites.
- $\text{Al}^{3+} + 2\text{OH}^- \longrightarrow \text{Al(OH)}_3 \downarrow$

- Thus the protective film consists of Fe^{2+} – ATMP complex and $\text{Al}(\text{OH})_3$.

4. CONCLUSIONS

The present study leads to the following conclusions

- A synergistic effect exists between AminoTrimethylenePhosphonic acid (ATMP) and Al^{3+} in controlling corrosion of carbon steel immersed in ground water.
- The formulation consisting of 150ppm of ATMP and 50ppm of Al^{3+} has 98% IE.
- Polarization study reveals that ATMP– Al^{3+} system functions as a mixed 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+} -ATMPcomplex and $\text{Al}(\text{OH})_3$
- This formulation may find application in cooling water system.
- Optical micro graphic images confirm the formation of protective layer on the metal surface with its surface morphology.

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

Parameter	Value
pH	8.0
TDS	766 mg/l
Alkalinity	380mg/l
Chloride	12 mg/l
Sulphate	18 mg/l
Calcium	70 mg/l
Magnesium	81 mg/l
Barium	11mg/l

Table 2: Corrosion rate (CR) of carbon steel in ground water presence of inhibitor system and the inhibition efficiency (IE) obtained by weight loss Inhibitor system: ATMP + Al³⁺ (0 ppm) Immersion period –3 days

ATMP ppm	Al ³⁺ ppm	CR mdd	IE %
0	0	13.64	--
50	0	6.55	52
100	0	6.14	55
150	0	4.09	70
200	0	3.55	74
250	0	2.73	80

Table 3: Corrosion rate (CR) of carbon steel in ground the presence of inhibitor system and the inhibition efficiency (IE) obtained by weight loss method Inhibitor system: ATMP + Al³⁺ (5 ppm) Immersion period – 3 days

ATMP	Al ³⁺ Ppm	CR mdd	IE %
0	5	13.64	--
0	5	15.00	-10

50	5	6.82	50
100	5	6.14	55
150	5	2.73	80
200	5	2.05	85
250	5	3.0	78

Table 4: Corrosion rate (CR) of carbon steel in ground water in the of inhibitor system and the inhibition efficiency (IE) obtained by weight loss method Inhibitor system: ATMP + Al³⁺ (10 ppm) Immersion period – 3 days

ATMP ppm	Al ³⁺ Ppm	CR Mdd	IE %
0	0	13.64	--
0	10	12.96	5
50	10	2.05	85
100	10	2.59	81
150	10	6.14	55
200	10	4.77	65
250	10	4.22	60

Table 5: Corrosion rate (CR) of carbon steel in ground water presence of inhibitor system and the inhibition efficiency (IE) obtained by weight loss method Inhibitor system: ATMP + Al³⁺ (25 ppm) Immersion period – 3 days

ATMP ppm	Al ³⁺ ppm	CR mdd	IE %
0	0	13.64	--
0	25	12.28	10
50	25	5.45	60
100	25	1.36	90
150	25	4.09	70
200	25	4.77	65
250	25	2.73	80

Table 6: Corrosion rate (CR) of carbon steel in ground water i presence of inhibitor system and the inhibition efficiency (IE) obtained by weight loss method Inhibitor system: ATMP + Al³⁺ (50 ppm) Immersion period –3 days

ATMP ppm	Al ³⁺ ppm	CR mdd	IE %
0	0	13.64	--
0	50	12.00	12
50	50	3.41	75
100	50	2.45	82
150	50	0.27	98
200	50	2.35	85
250	50	1.77	87

Table 7: Corrosion Parameters obtained by Potentiostatic Polarization method

System	E _{Corr}	I _{Corr}	b _c	b _a	R _p	% IE
Blank	-0.455	5.29×10 ⁻³	196.85	143.55	7	-----
ATMP 150 ppm + Al ³⁺ 50ppm	-0.457	0.315×10 ⁻³	183.72	78.28	76	94.02

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}	-----
ATMP 150 ppm + Al ³⁺ 50ppm	-1.157	68.252	1.1×10^{-4}	92.58

Table 9: Influence of duration of immersion on the IE of ATMP (150ppm) +Al³⁺ 50ppm) system

Immersion Period Day	1	3	5	7
Blank Corrosion rate mdd	10.32	13.64	15.76	17.86
ATMP 150ppm + Al ³⁺ 50ppm Corrosion rate mdd	0.27	0.22	2.05	4.77
IE %	97	98	87	73

Table 10: Influence of P^H on the IE of the ATMP (150 ppm) –Al³⁺(50ppm) System.

pH	6	8	10	12
Blank	15.98	13.64	14.78	15.32
ATMP150ppm + Al ³⁺ 50ppm	2.05	0.27	1.77	1.36
IE %	87	98	88	91

Table.11: Synergistic Parameters (S₁) of ATMP-Al³⁺ system

Concn. of ATMP ppm	I.E. % I ₁	Concn. of Al ³⁺ ppm	I.E. % I ₂	Combined I'E. I ₁₊₂	Synergism S ₁
50	52	50	5	85	3.0
100	55	50	5	81	2.7
150	70	50	5	55	5.1
200	74	50	5	65	4.6
250	80	50	5	98	4.0

Figure 1: Polarization curves of carbon steel immersed in ground water in presence and absence of inhibitors

Figure 2: AC impedance study of carbon steel immersed in ground water in presence and absence of inhibitors

Figure 3: FT-IR spectra of carbon steel in ground water in presence and absence of inhibitors

Figure 4: SEM Images of carbon steel in ground water in presence and absence of inhibitors