Nanotechnology Perceptions
ISSN 1660-6795
www.nano-*ntp.com*

Synergistic Corrosion Inhibition of Carbon Steel in Groundwater by an Ammonium Phosphate (AMP)–Mg^{2+} System

Angel J.B. Ponmalar[†] and S. Sudha Kumari

Department of Chemistry, S.T. Hindu College, Nagercoil, Tamil Nadu – 629 002
[†] (Reg. number: 21113152032011)
(Affiliated to Manonmaniam Sundaranar University, Tirunelveli-12, Tamil Nadu, India)

Received: 12-03-2024 *Accepted: 28-03-2024* *Published: 07-04-2024*

The synergistic corrosion inhibition of carbon steel in groundwater by an ammonium phosphate (AMP)–Mg^{2+} system was investigated using weight-loss measurements, potentiostatic polarization, AC impedance spectroscopy, FT-IR analysis, and surface morphology examination. Carbon steel specimens were exposed to groundwater containing different concentrations of AMP and Mg^{2+}. The optimum formulation, 100 ppm AMP with 50 ppm Mg^{2+}, produced an inhibition efficiency of 95% after three days of immersion. Electrochemical measurements indicated a marked decrease in corrosion current and a substantial increase in charge-transfer resistance in the presence of the inhibitor system, confirming the formation of a protective surface film. FT-IR analysis was consistent with the formation of an Fe^{2+}–AMP complex, while the surface studies supported the presence of a protective film containing $Mg(OH)_2$. The inhibition efficiency was also dependent on immersion time and pH. The results demonstrate a strong synergistic interaction between AMP and Mg^{2+} and indicate the potential usefulness of this formulation for corrosion control in cooling-water environments.

Keywords: ammonium phosphate; magnesium ions; carbon steel; groundwater; corrosion inhibition; synergistic effect.

1. Introduction

Groundwater is widely used in industrial operations, and dissolved oxygen is an important factor contributing to the corrosion of mild and carbon steels [1,2]. Depending on the metal–environment combination, different corrosion inhibitors are employed at suitable concentrations. Metal ions have long been recognized as effective corrosion inhibitors, particularly through cathodic polarization mechanisms [3,4]. Previous studies have shown that compound films formed by phosphate–chromate mixtures can be more effective than those produced by either component alone [5-7]. Synergistic effects involving halides and organic inhibitors have also been widely reported [8-11]. Various compounds, including phosphonic acids [12,13], thiourea [14], carboxymethyl cellulose [15], and sodium dodecyl sulphate [16], have been investigated for controlling the corrosion of carbon steel. In near-neutral aqueous

media, soluble chromates, dichromates, nitrates, borates, benzoates, and carboxylate salts are among the commonly used inhibitors. 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].

The stabilization of oxide films by benzoates, phthalates, and other carboxylates has also been reported. In the present study, the synergistic effect of ammonium phosphate (AMP), an environmentally friendly inorganic compound [$(NH_4)_3PO_4$], and Mg^{2+} ions on the corrosion inhibition of carbon steel in groundwater was investigated in detail. Inhibition efficiencies were evaluated by the weight-loss method, while the inhibition mechanism was examined using potentiostatic polarization, AC impedance spectroscopy, FT-IR spectroscopy, and surface morphology studies. Recent studies further confirm the importance of phosphate-containing formulations, magnesium-modified phosphate systems and synergistic inhibitor combinations in improving the corrosion resistance of carbon steel and related steels in aqueous chloride-containing and water-based environments [24–33].

2. Experimental

2.1. Materials and specimen preparation

Carbon steel specimens containing 0.025% S, 0.06% P, 0.40% Mn and 0.15% C, with the balance iron, were used. Rectangular specimens of dimensions 1.0 × 4.0 × 0.2 cm were prepared for the corrosion studies. Before each experiment, the specimens were polished to a mirror finish, degreased with trichloroethylene and dried. Groundwater collected from Tirunelveli, Tamil Nadu, India, was used as the corrosive medium, and its physicochemical characteristics are listed in Table 1. Ammonium phosphate (AMP) was investigated as the primary inhibitor and Mg^{2+} as the synergistic component. Different concentrations of AMP and Mg^{2+}, both individually and in combination, were examined under identical conditions to establish their individual and combined inhibition effects.

2.2. Weight-loss and electrochemical measurements

For gravimetric measurements, three carbon-steel specimens were immersed in 100 mL of groundwater containing the required concentration of AMP, Mg^{2+} or AMP–Mg^{2+} formulation. Unless otherwise stated, the immersion period was three days. After exposure, the specimens were removed, cleaned with Clarke's solution [34,35] to eliminate corrosion products, washed, dried and weighed. The corrosion rate was determined from the mass loss, and the inhibition efficiency (IE) was calculated from the corrosion rates in the uninhibited and inhibited solutions using Eq. (1):

$$IE = 100\left[1 - \left(\frac{w_2}{w_1}\right)\right]\% \quad (1)$$

where w_1 is the corrosion rate (mdd) in the absence of inhibitor and w_2 is the corrosion rate (mdd) in the presence of inhibitor. Potentiostatic polarization measurements were performed using a CHI 66A electrochemical workstation with a three-electrode cell. A rectangular carbon-steel specimen with an exposed area of 1 cm² served as the working electrode; a saturated calomel electrode (SCE) was used as the reference electrode and a rectangular platinum foil as the counter electrode. The anodic and cathodic polarization branches were obtained, and tangents to the two branches were extrapolated to determine the corrosion current (Icorr) and corrosion potential (Ecorr). The polarization parameters were used to determine the predominant mode of inhibition.

AC impedance measurements were performed using the same workstation and cell arrangement. The real (Z′) and imaginary (Z″) components of impedance were measured over the experimental frequency range. The charge-transfer resistance (Rct) and double-layer capacitance (Cdl) were evaluated from the impedance response. Changes in Rct and Cdl were used to assess formation of a protective film at the metal/solution interface.

2.3. Electrochemical and surface characterization

Carbon-steel specimens were immersed in the test solutions for three days, removed, dried and examined for the protective film formed on the surface. FT-IR spectra were recorded using a Perkin–Elmer 1600 spectrophotometer. The film formed on the metal surface was carefully removed, thoroughly mixed with KBr, pressed into pellets and analysed to identify functional groups and bonding changes associated with inhibitor–metal interaction. Surface morphology was examined by scanning electron microscopy (SEM). The specimens were mounted directly on Scotch double-sided adhesive tape and examined using a Hitachi S-450 SEM operated at 15 kV. The SEM micrographs were used to compare the uninhibited and inhibited surfaces and to assess the development of a protective layer.

FT-IR spectra were recorded using a Perkin–Elmer 1600 spectrophotometer. The film formed on the metal surface was carefully removed, thoroughly mixed with KBr, pressed into pellets, and subjected to FT-IR analysis. 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.

Samples for scanning electron microscopy (SEM) were mounted directly on Scotch double-sided adhesive tape and examined using a Hitachi S-450 scanning electron microscope operated at 15 kV. The resulting micrographs were used to assess the surface morphology of carbon steel in the absence and presence of the inhibitor formulation.

2.4. Immersion period, pH and synergism calculations

The influence of immersion duration was investigated after 1, 3, 5 and 7 days of exposure using the same gravimetric procedure. The effect of pH was examined over the range pH 6–12; where required, the pH was adjusted using dilute H_2SO_4. The inhibition efficiency was determined under each condition so that the effects of exposure time and solution pH could be compared directly. The synergistic interaction between AMP and $Mg^{2+}$was quantified using

the synergism parameter S_1. The theoretical combined inhibition efficiency of substance 1 and substance 2 was calculated from $I'_{1+2} = (I_1 + I_2) - (I_1.I_2)$ and S_1 was evaluated from the experimentally observed combined inhibition efficiency.

The synergism parameter $(S_1)^{26}$ is calculated using the relation as stated below

$$S_I = \frac{1 - I_{1+2}}{1 - I'_{1+2}} \qquad (2)$$

A value of S_1 greater than unity indicates synergistic interaction between the two inhibitor components.

3. Results and Discussion

The relevant physicochemical parameters of the groundwater are presented in Table 1. The inhibition efficiencies of AMP for carbon steel in groundwater, both in the absence and presence of Mg^{2+}, were evaluated by the weight-loss method after three days of immersion. AMP alone at 200 ppm produced an inhibition efficiency of 74%, whereas 50 ppm Mg^{2+} alone produced an inhibition efficiency of 25%. In the absence of AMP, transport of Mg^{2+} from the bulk solution toward the metal surface appears to be slow which is analogous to the earlier observations [36]. When AMP was combined with Mg^{2+}, the inhibition efficiency increased to 95%, indicating a pronounced synergistic effect. The results suggest that AMP facilitates the transport of Mg^{2+} toward the metal surface.

Table 1. Physicochemical parameters of the groundwater used in the investigation.

Parameter	Value
pH	8.0
TDS	810 mg/l
Alkalinty	389 mg/l
Chloride	15 mg/l
Sulphate	17 mg/l
Calcium	82 mg/l
Magnesium	92 mg/l
Barium	14mg/l

Table 2. Corrosion rate (CR) and inhibition efficiency (IE) of carbon steel in groundwater in the presence of AMP–Mg^{2+} (0 ppm Mg^{2+}), after 3 days of immersion.

Inhibitor system: AMP + Mg^{2+} (0 ppm) Immersion period –3 days

Ammonium phosphate ppm	Mg^{2+} 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**

Table 3. Corrosion rate (CR) and inhibition efficiency (IE) of carbon steel in groundwater in the presence of AMP–Mg^{2+} (5 ppm Mg^{2+}), after 3 days of immersion.

Inhibitor system: AMP + Mg^{2+} (5 ppm) Immersion period –3 days

Ammonium phosphate	Mg^{2+} ppm	CR mdd	IE %
0	0	13.64	-----
0	5	12.28	10
50	5	6.82	50
100	5	6.14	55
150	**5**	**2.73**	**80**
200	5	2.05	85

Table 4. Corrosion rate (CR) and inhibition efficiency (IE) of carbon steel in groundwater in the presence of AMP–Mg^{2+} (10 ppm Mg^{2+}), after 3 days of immersion.

Inhibitor system: AMP + Mg^{2+} (10 ppm) Immersion period –3 days

Ammonium phosphate ppm	Mg^{2+} ppm	CR Mdd	IE %
0	0	13.64	----
0	10	10.91	20
50	10	3.41	75
100	**10**	**3.00**	**78**
150	10	6.14	55
200	10	4.77	65

Table 5. Corrosion rate (CR) and inhibition efficiency (IE) of carbon steel in groundwater in the presence of AMP–Mg^{2+} (25 ppm Mg^{2+}), after 3 days of immersion.
Inhibitor system: AMP + Mg^{2+} (25 ppm) Immersion period –3 days

Ammonium phosphate ppm	Mg^{2+} ppm	CR mdd	IE %
0	0	13.64	------
0	25	12.28	10
50	25	6.82	50
100	**25**	**3.82**	**72**
150	25	5.46	60
200	25	4.09	70

Table 6. Corrosion rate (CR) and inhibition efficiency (IE) of carbon steel in groundwater in the presence of AMP–Mg^{2+} (50 ppm Mg^{2+}), after 3 days of immersion.
Inhibitor system: AMP + Mg^{2+} (50 ppm) Immersion period –3 days

Ammonium phosphate ppm	Mg^{2+} ppm	CR mdd	IE %
0	0	13.64	----
0	50	10.23	25
50	50	5.46	60
100	**50**	**0.68**	**95**
150	50	2.73	80
200	50	3.41	75

3.1. Weight-loss and electrochemical corrosion studies

The physicochemical characteristics of the groundwater are presented in Table 1. The weight-loss measurements show that AMP alone provides measurable protection to carbon steel, whereas Mg^{2+} alone gives comparatively lower protection. The combined AMP–Mg^{2+} formulation produces a substantially higher inhibition efficiency, demonstrating a synergistic effect. Among the formulations investigated, 100 ppm AMP with 50 ppm Mg^{2+} gave an inhibition efficiency of 95% after three days of immersion and was therefore selected for detailed electrochemical and surface investigations.

The corrosion parameters obtained from potentiostatic polarization are given in Table 7 and the corresponding curves are shown in Fig. 1. For carbon steel in groundwater, the corrosion potential was approximately −0.465 V versus SCE. In the presence of 100 ppm AMP and 50 ppm Mg^{2+}, the corrosion potential shifted to approximately −0.502 V versus SCE,

accompanied by a pronounced decrease in corrosion current. The predominant change in the cathodic branch indicates that the AMP–Mg^{2+} formulation functions mainly as a cathodic inhibitor [37]. The corrosion current density decreased from 4.98 × 10^{-3} A cm^{-2} in groundwater to 0.052 × 10^{-3} A cm^{-2} in the inhibited solution.

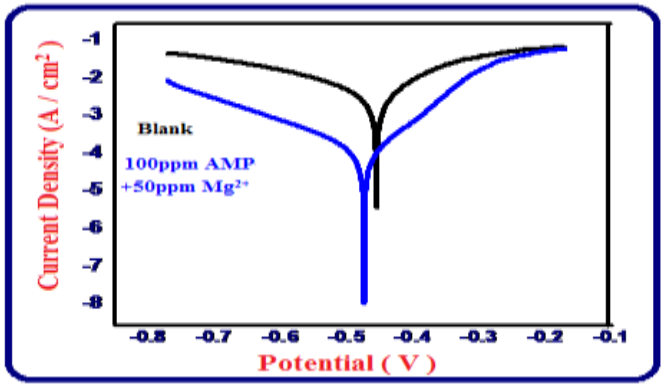
The AC impedance spectra are presented in Fig. 2 and the corresponding parameters are listed in Table 8. The charge-transfer resistance increased from 5.12 Ω cm^2 in groundwater to 369 Ω cm^2 in the presence of AMP and Mg^{2+}, while the double-layer capacitance decreased from 1.7×10^{-2} to 4.3×10^{-3} F cm^{-2}. The increase in Rct and decrease in Cdl are consistent with the formation of a protective film and a reduction in the rate of charge transfer at the metal/solution interface [38].

When carbon steel is immersed in ground water, the corrosion potential – 465mV Vs saturated calomel electrode (SCE). The formulation consisting of 100ppm of AMP and 50 ppm of Mg^{2+} shifts the corrosion potential to -502 mV Vs SCE. This suggests that the cathodic reaction is controlled predominantly; since more AMP is transported to the cathodic sites in the presence of Mg^{2+}. This result suggests that the AMP– Mg^{2+} formulation functions as a cathodic inhibitor [39]. The corrosion current for ground water is 4.98 x 10^{-3} A/cm^2. It is decreased to 0.052 x 10^{-3} A/cm^2 by 100ppm of AMP and 50ppm of Mg^{2+} system. This indicates that a protective film is formed on the metal surface.

Table 7. Corrosion parameters obtained from potentiostatic polarization measurements

System	E_{Corr}	I_{Corr}	b_c	b_a	R_p	% I.E
Blank	-0.465	4.98×10^{-3}	186.85	153.55	9	------
AMP 100 ppm + Mg^{2+} 50 ppm	-0.502	0.052×10^{-3}	149.74	102.20	350	95

Fig. 1. Polarization curves of carbon steel immersed in groundwater in the presence and absence of inhibitors

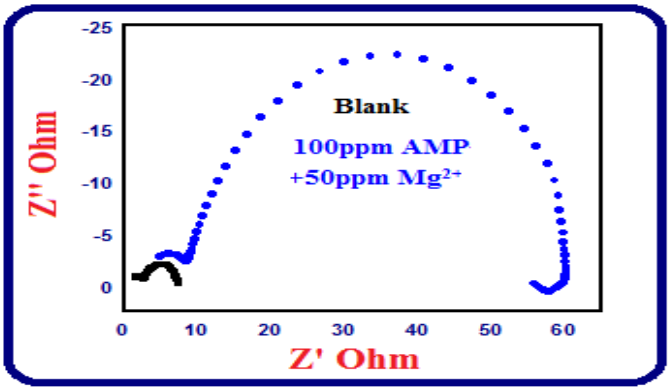


The AC impedance spectra of carbon steel in the different test solutions are presented in Fig. 2, and the corresponding impedance parameters are listed in Table 8. In groundwater, the Rct value was 5.12 Ω cm² and the Cdl value was 1.7×10^{-2} F cm^{-2}. Upon addition of AMP and Mg^{2+}, Rct increased to 369 Ω cm², while Cdl decreased to 4.3×10^{-8} F cm^{-2}. The increase in charge-transfer resistance and decrease in double-layer capacitance indicate the formation of a protective film on the metal surface and account for the high inhibition efficiency of the AMP–Mg^{2+} system.

Table 8. Corrosion parameters obtained from AC impedance measurements

System	R_s (ohm cm^{-2})	R_{ct} (ohm cm^{-2})	C_{dl} (F/cm^2)	% I.E
Blank	2.568	5.12	1.7×10^{-2}	-----
AMP 100 ppm + Al^{3+} 25 ppm	-54.201	369	4.3×10^{-6}	95

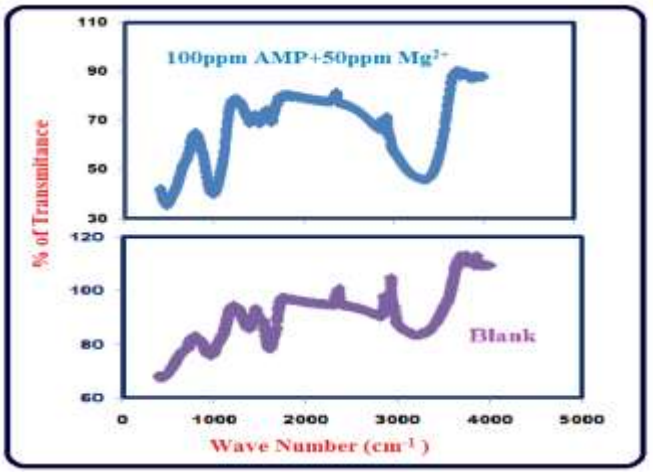
Fig. 2. AC impedance spectra of carbon steel immersed in groundwater in the presence and absence of inhibitors



3.2. FT-IR and surface morphology studies

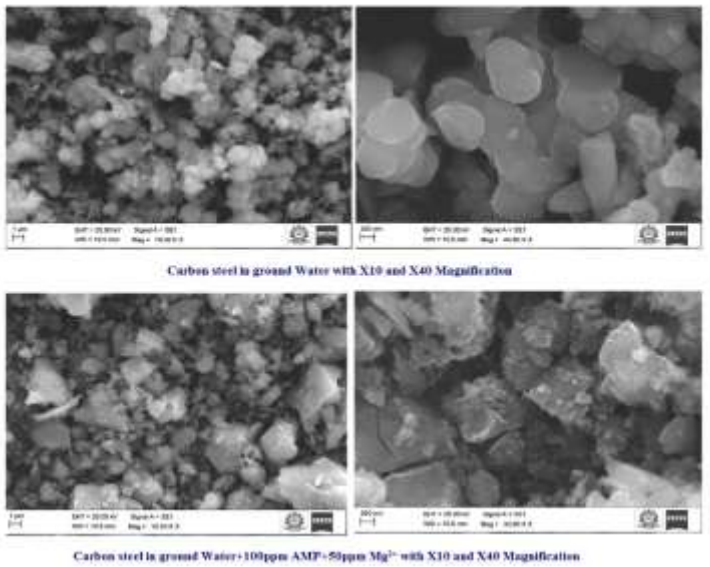
The FT-IR spectra of AMP and the film formed on carbon steel in groundwater containing 100 ppm AMP and 50 ppm Mg^{2+} are shown in Fig. 3. The C=O stretching band of AMP at about 1540 cm^{-1} shifted to about 1560 cm^{-1} in the film, indicating interaction of AMP with Fe^{2+} and supporting formation of an Fe^{2+}–AMP complex [40]. The band near 1430 cm^{-1} is attributed to $Mg(OH)_2$. These spectral features support the proposed composition of the protective film. The SEM images in Fig. 4 show that the uninhibited carbon-steel surface is comparatively rough and covered with corrosion products, whereas the inhibited surface is smoother and more compact. The morphological observations therefore provide additional evidence for formation of a protective layer by the AMP–Mg^{2+} formulation [41].

Fig. 3. FT-IR spectra of carbon steel in groundwater in the presence and absence of inhibitors



Previous optical and microscopic studies have been used to establish the formation of protective films on corroding metal surfaces. The surface images of carbon steel immersed in groundwater for three days in the absence and presence of the inhibitor system are shown in Fig. 4. The uninhibited specimen exhibits a rough surface associated with corrosion products, whereas the inhibited specimen shows a comparatively smoother morphology, consistent with the formation of a protective layer.

Fig. 4. SEM images of carbon steel in groundwater in the presence and absence of inhibitors



3.3. Effect of immersion period, pH and synergism

The influence of immersion period is presented in Table 9. The inhibition efficiency was 92% after one day and reached a maximum of 95% after three days, followed by a decrease to 87% after five days and 73% after seven days. The decrease at prolonged exposure may be associated with deterioration of the protective Fe^{2+}–AMP film by aggressive chloride ions present in groundwater. Competition between the formation of iron chlorides and the Fe^{2+}–AMP complex may also contribute to the reduction in protection.

The effect of pH is given in Table 10. The inhibition efficiency decreased from 95% at pH 8 to 80% at pH 6 and was about 90% at pH 10–12. This behaviour indicates that the stability and protective action of the AMP–Mg^{2+} system are influenced by the acidity/alkalinity of the medium. The synergism parameters listed in Table 11 are greater than unity, confirming a strong synergistic interaction between AMP and Mg^{2+}. This may be due to the fact that as the period of immersion increases the protective film formed on the metal surface namely Fe^{2+} - AMP Complex is broken by the aggressive chloride ion present in ground water and hence IE decreases [42].

Further there is a competition between the formation of $FeCl_2$ (and also $FeCl_3$ and formation (Fe^{2+} - AMP) complex. It seems that as the immersion period increases the formation of $FeCl_2$ is more favored than the formation of Fe^{2+} AMP complex at the anodic states of the metal. Hence a decrease in inhibition efficiency is noticed as the period of immersion increases.

Table 9. Influence of immersion duration on the inhibition efficiency of the AMP–Mg^{2+} system

Immersion Period Day	1	3	5	7
Blank Corrosion rate mdd	10.32	13.64	15.76	17.86
100ppmAMP+50ppm Mg^{2+}	0.83	0.68	2.05	4.82
IE %	92	95	87	73

Table 10. Influence of pH on the inhibition efficiency of the AMP–Mg^{2+} system

pH	6	8	10	12
Blank Corrosion rate mdd	15.98	13.64	14.78	15.32
100ppmAMP+25ppm Mg^{2+}	3.2	0.68	1.48	0.92
IE %	80	95	90	90

The influence of pH on the IE of AMP- Mg^{2+} system is given in Table 10. It is found from the table that when pH is decreased from 8 to 6 (by addition of dil. H_2SO_4) the IE decreases from 95% to 80%. This is due the attack of H^+ ion of the H_2SO_4 on the metal surface and hence increases in corrosion rate and decrease in IE. When pH is increased from 8 to 10 (by addition of dil. NaOH) the IE decrease from 95% to 90%. This is due to the fact when NaOH is added Mg^{2+} is precipitated as $Al(OH)_3$ in the bulk of the solution so the transport of inhibitor towards the metal surface decreases [43-44] and hence the IE decrease when pH is increased from 10 to 12 (by addition of dil. NaOH) the IE does not change from 90%. This is due to the fact that on further addition of NaOH which do not dissolve $Mg(OH)_2$ precipitate.

The synergism parameters are presented in Table 11. The calculated S_1 values are greater than unity, demonstrating a strong synergistic interaction between AMP and Mg^{2+} in controlling the corrosion of carbon steel.

Table 11. Synergism parameters (S_1) of the inhibitor system

Concn. of AMP ppm	I.E. % I_1	Concn. of Mg^{2+} ppm	I.E. % I_1	Combined I'E. I_{1+2}	Synergism S_1
50	52	50	25	60	20.7
100	55	50	25	95	13.78
150	70	50	25	80	20.9
200	74	50	25	75	23.6

3.4. Mechanism of corrosion inhibition

The proposed inhibition mechanism is based on the combined weight-loss, electrochemical and surface-characterization results. When groundwater containing 100 ppm AMP and 50 ppm Mg^{2+} is prepared, an Mg^{2+}–AMP complex is formed in the bulk solution. After immersion of carbon steel, the complex diffuses towards the metal surface. At anodic sites, the Mg^{2+}–AMP complex is converted into an Fe^{2+}–AMP complex, releasing Mg^{2+}:

$$Mg^{2+}\text{–AMP} + Fe^{2+} \rightarrow Fe^{2+}\text{–AMP} + Mg^{2+}$$

The released Mg^{2+} subsequently combines with hydroxide ions at cathodic sites to form $Mg(OH)_2$. Thus, the protective film is proposed to consist principally of an Fe^{2+}–AMP complex at anodic regions and $Mg(OH)_2$ at cathodic regions [45]. This mechanism is consistent with the predominantly cathodic polarization behaviour, the increased charge-transfer resistance, the FT-IR observations and the smoother SEM morphology.

- When a solution containing groundwater, 50 ppm of Mg^{2+} ions, and 100 ppm of AMP is prepared, a Mg^{2+}–AMP complex is formed in the solution.
- When carbon steel is immersed in this solution, the Mg^{2+}–AMP complex diffuses from the bulk solution towards the metal surface.
- At the anodic sites on the metal surface, the Mg^{2+}–AMP complex reacts with Fe^{2+} ions to form an Fe^{2+}–AMP complex, with the simultaneous release of Mg^{2+} ions.

$$\mathbf{Mg^{2+}–AMP + Fe^{2+} \rightarrow Fe^{2+}–AMP + Mg^{2+}}$$

- The released Mg^{2+} ions subsequently react with OH^- ions present at the cathodic sites to form magnesium hydroxide, $Mg(OH)_2$.

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

- Thus, the protective film formed on the carbon steel surface consists of an Fe^{2+}–AMP complex at the anodic sites and $Mg(OH)_2$ at the cathodic sites. The formation of this compact protective film effectively blocks the anodic and cathodic reactions, thereby reducing the corrosion of carbon steel.

4. Conclusions

The present study demonstrates a pronounced synergistic effect between ammonium phosphate (AMP) and Mg^{2+}in controlling the corrosion of carbon steel in groundwater. The principal conclusions are as follows: (i) 100 ppm AMP combined with 50 ppm Mg^{2+} provides an inhibition efficiency of 95%; (ii) potentiostatic polarization measurements indicate predominantly cathodic inhibition; (iii) AC impedance measurements confirm the formation of a protective film on the metal surface; (iv) FT-IR analysis is consistent with an Fe^{2+}–AMP complex and $Mg(OH)_2$ in the protective film; (v) the inhibition efficiency depends on immersion period and pH; and (vi) the formulation may have potential application in cooling-water systems. The microscopic surface images further support the formation of a protective layer.

- A synergistic effect exists between Ammonium Phosphate (AMP) and Mg^{2+} in controlling corrosion of carbon steel immersed in ground water.
- The formulation consisting of 100ppm of AMP and 50 ppm of Mg^{2+} has 95% IE.
- Polarization study reveals that AMP– Mg^{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+}-AMP complex and $Mg(OH)_2$
- 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.

Acknowledgement: The authors are thankful to Dr. R.K. Seenivasan for his help and encouragement.

References

[1] R. T. Foley, Corrosion 26, 58 (1970).
[2] C.P. Dillon, Material Protection and Performance, 12, (1973),18.
[3] W.Chiesa, R.Cigna, I.S.Di Simone, G.Gusmano and G.F.Mazzani, Proc, sixth Europ. Symp.on Corrosion Inhibitors, Ferrara, Italy, 8, (1985), 1295.
[4] Chen. Jiajian and Wang Xiaoming, Proc, seventh Europ.symp.on corrosion Inhibitors, Ferrara, Italy 9, (1990),1049.
[5] F.N. Speller, Proc. ASTM, 36, (1936), 695.
[6] T. Prosek and D. Thierry, Corr, 60, (2004),1122.

[7] A.C. Bastos, M.G.S. Ferreira and A.M. Simoes, Prog. in Org.Coatings, 52, 339 (2005).
[8] R.M. Hudson, Q.L. Loony and G.J. Warning, Br. Corr. J. 2, 81 (1967).
[9] R.M. Hudson and G.J. Warning, Corr. Sci., 10, 121 (1970).
[10] R.I. Yurchhenko, S.V.Ivashchenko, T.N.Pillipenko and I.S.Pogrebova, Russian, J. Appl. Chem., 78, 511 (2005).
[11] C.M.V.B. Almedia and B.F. Giannetti, Matls. Chem. & Phy.69, 261 (2001).
[12] A. Veres, G. Reinhard and E. Kalman, Br. Corrosion. J, 27, 147 (1992).
[13] S. Rajendran, B. V. Apparao, N. Palaniswamy, Anticorrosion methods and materials 49, 205 (2002).
[14] J. C. Lin, R. Y. Luem, J. S. Wu and S. L. Lee, Proce. 8th Europ. Symp. Corrosion inhibitors, 1995; 123.
[15] B. V. Meena, Noreen Anthony, K. Mangayarkarasi, S. Rajendran,. J. Electro Chem. Soc. India, 50, (2001),138.
[16] S. Rajendran, S. Mary Reenkala and R. Ramaraj, Corrosion Sci., 44. (2002),2243.
[17] C. A. Baah, J. I. Baah, Anti corrosion methods and materials, 47, (2000),105.
[18] G. Ruba Helen Florence, A. Noreen Anthony, J. Wilson Sahayaraj, John Amal Raj, A. Susai and S. Rajendran, Indian Journal of Chemical Technology, 12, (2005),472.
[19] Felina Rajammal Selvarani, S. Santhamadharasi, J. Wilson Sahayaraj, John Amalraj, A. Susai And S. Rajendran, Bulletin of Electro Chemistry, 20, (2004),561.
[20] I. L. Rosenfield, I. Kuznetsov Yu, Kerbeleva I Ya and V. P. Persianceva, Prot. Met 10, (1974),612.
[21] M Fisher, Z, Phys. Chem. (Leipzig), 260, (1979),93.
[22] J G N Thomas, Proc. Of 5th European Symp Corros. Inhibitors, University of Ferrara, Ferrara, Italy,1980; 453.
[23] S Bilgic & M Sahin Proc. Of 5th European Symp corros Inhibitors, University of Ferrara, Ferrara, Italy, 2000; 771.
[24] R M Silverstein, G C Bassler, T Morril, Spectrometric Identification of organic compounds, John Wiley and Sons, New York, 1981; 95
[25] A D Cross, Introduction to Practical Infrared Spectroscopy Butterworths, Scientific Publication, London, 1960; 73.
[26] Kzauo Nakamoto. Infrared and Raman Spectra of inorganic co-ordination compound Wiley Interscience, New York, 1986; 168.
[27] I Sekine and Y Hirakawa Corrosion, 42, (1986),276.
[28] S Rajendran, B V Apparao & N Palaniswamy, Bulletin of Electrochemistry, 12, (1996),15.
[29] F.C. Giacomelli, C. Giacomelli, M.F. Amadori, V. Schmidt and A. Spinelli, Matls. Chem. And Phy., 83, (2004), 124.
[30] R. Jagdhessh, U. Kamachi Mudali, D. Sastikumar, and A.K. Nath, Proc. Int. Convntion on Surf. Engg., Banglore, India, 2004; 399.
[31] M. Nandhakumaran, R. Pattabiraman, G.S. Saravanan, V. Balusamy, and V. Goplakrishnan, Proc. Int. Convention on Surf. Engg., Banglore, India, 2004; 211.
[32] R.J. Holness, G. Williams, D.A. Worsely and H.N. McMurray, J. Electrochem, Soc., 152, (2005),B73.

[33] Rita Cristina da Silva, Melissa Heinen, Gabriel A. Lorenzi, Demetrius W. Lima, Jo~ao Henrique Lingner Moura, Jamili M. de Freitas, Emilse M.A. Martini, Cesar L. Petzhold, Heliyon, 5, (2019), e01720.
[34] Danial Iravani, Reza Arefinia, Constr. Build. Mater., 233, (2020), 117200.
[35] S. Yin, H. Yang, Y. Dong, C. Qu, J. Liu, T. Guo and K. Duan, Scientific Reports, 11, (2021), 197.
[36] X. Wang, J. Yang, X. Chen, C. Liu and J. Zhao, J. Mol. Liq., 357, (2022), 119140.
[37] Y. Liu, X. Zhou, X. Guan and J. Shi, Corros. Sci., 208, (2022), 110637.
[38] D. Wang, C. Pan, Z. Liu, K. Chen, N. Chen and S. Liu, Constr. Build. Mater., 286, (2021), 122916.
[39] A. Balakrishnan, N. Gopala Krishna, R. Vijay Solomon, T. Nandakumar and J. Philip, J. Environ. Chem. Eng., 11, (2023), 109842.
[40] Q.H. Zhang, B.S. Hou, N. Xu, W. Xiong, H.F. Liu and G.A. Zhang, J. Mol. Liq., 285, (2019), 223.
[41] N. Ferraa, M. Ouakki, K. Alaoui, M. Cherkaoui and M. Bennani Ziatni, J. Mol. Struct., 1348, (2025), 143480.
[42] G. Callaghan, S. Ngo and G. Williams, Prog. Org. Coat., 210, (2026), 109646.
[43] G Wranglen, Introduction To Corrosion And Protection of Metals Chapman & Hall, London, 1985; 236.
[44] S Rajendran, S Shanmugapriya, T Rajalakshmi and A John Amalraj, Corrosion, 61, (2005),685.
[45] S Rajendran, B R E J Peter, A Peter Pascal Regis, A John Amalraj and M Sundaravadivelu, Trans. SAEST 38, (2003),11.