Appraisal of Different Inorganic Inhibitors Action on the Corrosion Control Mechanism of Mild Steel in HNO₃ Solution

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Abstract

Effects of eco-friendly inorganic inhibitors (i.e., calcium nitrate, zinc sulfate, sodium hexametaphosphate and sodium tetra-borate or borax) for the mild steel corrosion control in 1 M HNO₃ solution open to air at 28±1 °C were studied using corrosion, inhibition efficiency, and corrosion potential tests. The corrosion rate of the mild steel is increased with increasing the concentrations of HNO₃ solution from 0.01 M to 1 M. The uses of 200-2400 ppm of these inhibitors enhanced the corrosion resistance properties of the mild steel in 1 M HNO₃ solution. The corrosion resistance property of the mild steel is generally decreased with increasing the concentration of all corrosion inhibitors used here. The most efficient corrosion inhibitor is found to be calcium nitrate and it is followed by zinc sulfate, sodium hexametaphosphate, and borax subsequently. Adsorption of these inorganic salts inhibitors on the mild steel surface obeyed Langmuir adsorption isotherm. Consequently, the corrosion inhibition mechanism of the four inorganic salts for the mild steel corrosion control can be explained based on the formation of the passive film. It is found from the corrosion potential measurement that the cathodic type of corrosion inhibition action was by calcium nitrate, whereas zinc sulfate, sodium hexametaphosphate, and borax are acted as a mixed type of the inhibitors in 1 M HNO₃ solution. In summary, all four inorganic inhibitors utilized in the present study can be applied as an environmentally friendly inhibitor to control the corrosion of the mild steel in aggressive HNO₃ solutions.

Keywords: Corrosion inhibitor, inorganic salts, mild steel, nitric acid, immersion tests

Introduction

Different types of iron and iron-containing alloys (for example, steels) are world-widely used as structural materials. Material scientists, technologists, and chemical engineers are facing a problem of the untimely degradation of such structural materials due to the unwanted and unavoidable corrosion processes, mainly in slightly basic, neutral or acidic solutions [1]. The iron and steels are generally passive at a pH higher than 9.6, even though the passivity decreases in very strong alkaline solutions (i.e., >13.5 pH) where it tends to dissolve to form a highly corrosive product of hypo-ferrite (HFeO²⁻) in aqueous solution [2].

Hence, the uses of different corrosion control approaches are becoming an important subject in the field of different types of unwanted destruction/damages of such structural materials mainly in aggressive acidic solutions. Corrosionists need to understand what can be done to reduce such type of corrosion problems of the structural materials like mild steel in various acidic environments to ensure its durability for long periods although corrosion prevention techniques were constantly reviewed and discussed by various research groups in the past [3-6]. In particular, nitric acid is used as pickling solution to remove rust formed on the surface of different types of steels and iron. On the other hand, the passivation
of numerous steel-made structures and equipment is generally practiced in nitric acid by the USA DoD (Department of Defense) and NASA (National Aeronautics and Space Administration) [7].

In this context, it became a fundamental research concern of corrosion scientists, engineers, and technologists to control the corrosion of such metallic materials in aggressive acidic electrolytes using eco-friendly corrosion inhibitors. It is purposeful to highlight the corrosion inhibitor (CI) which is a chemical substance that when added in a very small concentration to an aggressive electrolyte like nitric acid, effectively controls the corrosion damages of the metallic materials in the corrosive media [8].

The highly toxic nature of the widely used chromium-containing organic and inorganic corrosion inhibitors (CIs) in the early stage has motivated now to look the eco-friendly corrosion inhibitors [9,10], because such CIs are quite toxic with their direct impacts on human health, and do not fulfill completely the requirements imposed by the environmental protection standards. Therefore, nowadays, the corrosion control method of metallic materials using various eco-friendly CIs to prevent metallic corrosion is becoming a fundamental research concern of corrosionists, and chemical engineers [11-19], because the eco-friendly corrosion inhibitors generally impose zero or negligible toxicity to the environment and human beings.

In general, the eco-friendly inhibitors restrict the rate of anodic or/and cathodic reactions involved in the corrosion damages by blocking active sites of the corroded metal/alloy surfaces. On the other hand, the corrosion inhibition mechanism occurs through the adsorption of the inhibitors ions/molecules on the corroding metal/alloy surfaces to form more stable films. Past researches had reported that some organic [20-25] and inorganic [26-30] compounds were used as eco-friendly corrosion inhibitors because they form complexes with metal ions on metal/alloy surface. Investigations of corrosion-inhibiting ability of inorganic radicals or ions, e.g., nitrites, molybdates, tungstates, polyphosphates are now being increasingly used as eco-friendly inhibitor due to their zero-toxic nature [10,31-36]. It was reported that calcium nitrite [37] because it is also cheaper, less harmful and more available [38]. Similarly, sodium polyphosphate, zinc sulfate, borate etc. are widely used as the corrosion controller for different metals and alloys mostly in chloride containing neutral solutions [39-41], although these inorganic salts are rarely used as corrosion retarder in acidic media.

Extensive research has led to the discovery of a new class of corrosion inhibitors that are eco-friendly. Previous studies were reported about the corrosion behavior of different ferrous structural materials used in Nepal in different corrosive environments [42-51], although a few studies were focused on the effects of eco-friendly plant-extracted green inhibitors on the mild steel corrosion [14,15,18]. In this context, the present work was aimed to study the effects of four inorganic compounds; Ca(NO$_3$)$_2$, ZnSO$_4$, (NaPO$_3$)$_6$ and Na$_2$[B$_4$O$_5$(OH)$_4$]·8H$_2$O as eco-friendly inhibitors for the mild steel corrosion prevention in 1 M HNO$_3$ solution open to air at 28±1 °C using immersion tests, inhibition efficiency, and corrosion potential measurements.

**Materials and Methods**

**Preparation of mild-steel coupon**

The mild steel coupons having a dimension of (2 cm × 3 cm × 0.5 cm) were used for both corrosion inhibition and electrochemical tests. The approximate chemical constituents of the mild steel coupons were reported as in wt. (%); C = 0.17, P = 0.05, Si = 0.04, Mn = 0.90, S = 0.05 and balanced by iron as described elsewhere [15,16]. The surface of each sample coupon was mechanically polished with different grades (200-1500 grit) SiC paper using ethanol, rinsed with acetone, and dried by air blowing until the surface exhibited mirror-like reflection to obtain reproducible results from the corrosion as well as the electrochemical tests.

**Corrosion test**

The corrosion test of the mild steel coupons was carried out after immersion for 240 hours in 1 M HNO$_3$ solution open to air at 28±1 °C in absence and presence of different concentrations (i.e., 200, 400, 800, 1200, 1600 & 2400 ppm) of calcium nitrate, zinc sulfate, sodium hexametaphosphate and borax as eco-friendly corrosion inhibitors. Besides, comparative
studies on the corrosion tests of the mild steel coupons in different concentrations of nitric and hydrochloric acids were also estimated. Weight-loss method was used to estimate the average corrosion rate of the mild steel coupons using the equation 1 [52].

\[
\text{Corrosion Rate (mm.y}^{-1}\text{)} = \frac{87600 \times \Delta w}{d \times A \times t} \tag{1}
\]

Where, \(\Delta w\) is the weight loss of the mild steel sample in gram (g), \(d\) is the density of the steel sample (=8.76 in g/cm\(^3\)), \(A\) is the area of the sample in cm\(^2\), \(t\) is the immersion time in hour, and 87600 is the conversion factor as described elsewhere [2].

**Inhibition efficiency test**

The inhibition efficiency (IE\(_{\text{CR}}\)) and the degree of surface coverage (\(\theta\)) of the inhibitor molecule adsorbed on the mild steel surface in 1 M HNO\(_3\) solution open to air at 28±1 °C were estimated using following equations 2 and 3 [53,54], respectively, where, \(CR_{\text{unhib.}}\) and \(CR_{\text{inhib.}}\) are the corrosion rates in absence and presence of the corrosion inhibitors of calcium nitrate, zinc sulfate, sodium hexametaphosphate, and borax, respectively. It is meaningful for citing here that all the calculations of the surface coverage (\(\theta\)) from the corrosion data are based on the assumption that the presently used inhibitors totally prevent the mild steel dissolution from the covered surfaces of it [55].

\[
IE_{\text{CR}} \ (% ) = \frac{CR_{\text{unhib.}}}{CR_{\text{inhib.}}} \times 100 \tag{2}
\]

\[
\theta = \frac{CR_{\text{unhib.}}}{CR_{\text{inhib.}}} \tag{3}
\]

The corrosion inhibition mechanism was studied using the Langmuir adsorption model [56] which is expressed in equation 4.

\[
\frac{C}{\theta} = \frac{1}{K_{\text{ads}}} + C \tag{4}
\]

Where, \(C\) is the inhibitor concentration and \(K_{\text{ads}}\) is the adsorptive equilibrium which is estimated from the intercept of a straight line obtained by plotting \(C/\theta\) vs \(C\). The \(K_{\text{ads}}\) value was used to estimate the standard free energy of adsorption \((\Delta G_{\text{ads}}^0)\) using equation 5 [57].

\[
\Delta G_{\text{ads}}^0 = -RT \ln (55.5 \times K_{\text{ads}}) \tag{5}
\]

Where \(R\) is gas constant, \(T\) is the temperature in Kelvin and the value of 55.5 is the molar concentration of water in solution.

**Corrosion potential measurement**

For understanding the effect of these four eco-friendly inorganic salts on the corrosion inhibition behavior for the mild steel coupons, the corrosion potential of the steel coupons was measured using a two-electrode system potentiometer (Osawa Digital Potentiometer) in 1 M HNO\(_3\) solution open to air at 28±1 °C in absence and presence of different concentrations (i.e., 200, 400, 800, 1200, 1600 & 2400 ppm) of calcium nitrate, zinc sulfate, sodium hexametaphosphate, and borax. A saturated calomel electrode (SCE) and the mild steel sheet were used as reference and working electrodes, respectively. The mechanically polished test coupons were clipped by a sample holder that was made by welding the crocodile pin with a titanium rod. The readings of the corrosion potential were taken immediately after immersion of the coupon in the electrolytic solution until 24 hours at different time intervals as described elsewhere [58]. A saturated calomel electrode (SCE) and the steel coupons were used as the reference and working electrodes, respectively.

**Results and Discussion**

**Corrosion rate in acid solutions**

Figure 1 shows the corrosion rates of the mild steel coupons after their immersion for 240 hours in 0.01

![Figure 1](https://www.nepjol.info/index.php/JNCS)
M, 0.1 M, and 1 M solutions of hydrochloric and nitric acids at 28±1 °C. The corrosion rate of the mild steel is found to be higher in all three concentrations of nitric acid than in hydrochloric acid. Consequently, it can be said that nitric acid seems to be more aggressive to the mild steel than that of hydrochloric acid having the concentration ranges from 0.01 M to 1 M.

**Corrosion inhibition effect**

The corrosion rate of the mild steel coupons was decreased with increasing the concentrations of these four corrosion inhibitors, although it is nearly one order of magnitude lower in 2400 ppm calcium nitrate addition than its absence in 1 M HNO₃ as shown in Fig. 2. The effectiveness of the inhibition activity of the borax for the corrosion prevention of the mild steel in 1 M HNO₃ solution is found to be less among the four eco-friendly inorganic corrosion inhibitors used herein. These results revealed that the use of these four corrosion inhibitors enhanced the corrosion resistance properties of the mild steel in 1 M HNO₃ solution open to air at 28 ± 1 °C.

**Inhibition efficiency and mechanism**

The inhibition efficiency of all four eco-friendly corrosion inhibitors as mentioned above is increased with increasing their concentrations as depicted in Figs. 3 and 4. The maximum inhibition efficiency for each corrosion inhibitor is observed at 1600-2400 ppm and the minimum is observed at 200 ppm addition in 1 M HNO₃ solution.

Furthermore, it is observed that the most efficient corrosion inhibitor among these four inhibitors used here is found to be calcium nitrate with a maximum inhibition efficiency of about 80 % at 2400 ppm at 28±1 °C as shown in Fig. 3(a), whereas the borax is found to be the least efficient inhibitor with about 50 % only in 1 M HNO₃ solution with its 2400 ppm addition at 28 ±1°C as shown in Fig. 4(b).

Likewise, the maximum corrosion inhibition efficiency of 2400 ppm additions of the zinc sulfate and sodium hexametaphosphate in 1 M HNO₃ was found about 60 % for the corrosion control of the mild steel as depicted in Figs. 3(b) and 4(a). Consequently, it can be summarized that the order of the corrosion
inhibition efficiencies of all four inorganic salts in one molar nitric acid solution at 28±1 °C for the mild steel is arranged as follows; \( \text{IE}_\text{Ca(NO}_3\text{)}_2 > \text{IE}_{\text{ZnSO}_4} \geq \text{IE}_{(\text{NaPO}_3)\text{6}} > \text{IE}_{\text{Borax}} \). Therefore, it can be reasoned out from the above-observed results of the corrosion inhibition efficiency that these four inorganic salts can be used as eco-friendly corrosion inhibitors in \( \text{HNO}_3 \) solutions for controlling of its corrosive nature towards the mild steel, and these results are in agreement with the results of corrosion resistance behavior as shown above in Figure 2.

Various adsorption isotherm models are applied for better understanding of such corrosion inhibition mechanism by the additions of such eco-friendly inorganic compounds in aggressive electrolyte for metals/alloys. Langmuir adsorption isotherm is one of the simplest models and it describes the molecular interaction between the inhibitor molecules and the active surfaces of the corroded metallic materials based on the assumption that all adsorption sites are equivalent and the particle binding occurs independently from nearby sites being occupied or not [56,59]. It also shows the relationship between the ratio of inhibitor concentration to surface coverage (C/θ) and the inhibitor concentration (C) as described above in equation (4). To obtain the Langmuir adsorption plot to explain the inhibition mechanism, θ value was estimated from the calculated corrosion rate at different concentrations of all inhibitors used presently in 1 M \( \text{HNO}_3 \) solution at 28±1 °C.

Figure 5 shows a linear relationship between C/θ and C for the mild steel in 1 M \( \text{HNO}_3 \) acid with the additions of different concentrations of all four types of eco-friendly inorganic inhibitors. The linear correlation coefficient (R²) and slope of the straight line were used to choose the isotherm that best fit experimental data because it is almost equal to unity in all cases (Figure 5).

These results indicated that the adsorption process obeyed the Langmuir adsorption isotherm to study the corrosion inhibition mechanism on the surface of the mild steel by the inhibitors of calcium nitrate,
zinc sulfate, sodium hexametaphosphate, and borax in 1 M HNO$_3$ at 28±1 °C. Anions of these inorganic salts are thus adsorbed on the surfaces of the corroded mild steel which prevents their further corrosion by forming a barrier layer.

It was found that the $\Delta G^\circ_{\text{ads}}$ value for the use of calcium nitrate, zinc sulfate, sodium hexametaphosphate and borax as eco-friendly inhibitors in 1 M HNO$_3$ solution at 28 °C for the corrosion control of the mild steel was found to be −25.566, −24.118, −25.116, and −22.634 kJ/mole, respectively, which are consistent with the literature. Hence, authenticate physical adsorption of the inhibitors on the surface of the corroded mild surface by anions of the used four corrosion inhibitors. It is meaningful for mentioning here the fact that there is no interaction between the adsorbed corrosion inhibitor molecules, the energy of adsorption is independent of θ, the metal/alloy surfaces contain a fixed number of adsorption sites and each site holds one adsorbed species according to the Langmuir isotherm model [57,59].

The adsorptive equilibrium constant ($K_{\text{ads}}$) value was higher than 100 mole/g (i.e., between 153 and 493 mole/g) in the present work which attributes to stronger and more stable adsorbed layer formation on the metals or/and alloys surfaces [60]. It is reported that the $\Delta G^\circ_{\text{ads}}$ values of metals/alloys around −25 kJ/mole or lower indicate adsorption of inhibitors onto metals/alloys surface with electrostatic interaction is due to physical adsorption, while those around or higher (more negative) than −40 kJ/mole involve charge sharing between inhibitor molecules and metals/alloys surfaces are of chemisorption [61,62].

Negative values of $\Delta G^\circ_{\text{ads}}$ ensure the spontaneity of the adsorption process and stability of the adsorbed layer of the corrosion inhibitors on the metals/alloys surfaces.

**Corrosion potential**

The corrosion potential measurement was carried out for a better understanding of the corrosion inhibition effect on the mild steel in 1 M HNO$_3$ solution. Figure 6 shows the effects of calcium nitrate, zinc sulfate, sodium hexametaphosphate, and borax in the changes of the corrosion potential of the mild steel after

![Figure 6](https://www.nepjol.info/index.php/JNCS)
immersion for 24 hours in 1 M HNO₃ solution. It is clearly shown that the corrosion potential of mild steel in presence of calcium nitrate [Figure 6(a)] is generally shifted to more negative or less noble direction with increasing their concentrations than in 1 M HNO₃ solution only.

However, its corrosion inhibition effect on the corrosion rate of the mild steel was found to be decreased with increasing concentrations as shown in Figure 2. Consequently, it can be said that calcium nitrate acts as the cathodic type of corrosion inhibitor.

There is no regular trend of corrosion potential change of the mild steel in 1 M HNO₃ solution with the additions of zinc sulfate, sodium hexametaphosphate, and borax as depicted in Figures 6(b), 6(c) and 6(d), respectively. For example, the corrosion potential was reached to the maximum noble potential values of −81 mV vs SCE and −121 mV vs SCE when the additions of 200 and 400 ppm of sodium hexametaphosphate, respectively, in 1 M HNO₃ solution after immersion for 24 hours, although the corrosion potential is shifted to more negative direction with the additions of 800 and 1200 ppm than only in 1 M HNO₃ solution as shown in Figure 6(c). These results indicated that zinc sulfate, sodium hexametaphosphate, and borax are acted as a mixed type of corrosion inhibitor based on corrosion potential measurements.

Conclusions

The effects of four eco-friendly inorganic corrosion inhibitors on electrochemical corrosion control of the mild steel in nitric acid solutions open to air at 28±1 °C were studied using corrosion tests, inhibition efficiency, corrosion mechanism, and open circuit corrosion potential measurements. All the inorganic salts used to study present work are found to be an effective inhibitor to improve the corrosion resistance properties of the mild steel in 1 M HNO₃. The maximum corrosion inhibition efficiencies of calcium nitrate, zinc sulfate, sodium hexametaphosphate and borax for the mild steel are found in order; IE_{Ca(NO₃)₂} = 80% > IE_{ZnSO₄} ≥ IE_{(NaPO₃)₆} = 60% > IE_{Borax} = 50%. The corrosion inhibition mechanism of these inorganic salts on the mild steel was explained by the Langmuir adsorption isotherm model. Experimentally obtained values of the standard free energy of adsorption (ΔG_{ads}^{°}) of these eco-friendly inhibitors on the surface of the corroded mild steel found between about −22 and −26 kJ/mol, suggested that adsorption of the corrosion inhibitors onto alloy surfaces is due to physical adsorption. The corrosion potential and corrosion rate results showed that the calcium nitrate acted as cathodic type inhibitor, while the zinc sulfate, sodium hexametaphosphate, and borax are of mixed type corrosion inhibitors to improve the corrosion resistance property of the mild steel in an aggressive electrolyte of 1 M HNO₃ solution at ambient environment. The used inorganic salts can be used as an efficient and eco-friendly corrosion inhibitor so as to control the corrosion of iron-containing structural materials significantly in very corrosive acidic solutions at room temperature.

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