Corrosion Co-inhibition of Sodium Tungstate with Sodium Nitrate and Sodium Silicate on Low Carbon Steel in HCl

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Abstract: This study has investigated the co-inhibitive potentials of sodium tungstate with sodium nitrate and sodium silicate on low carbon steel immersed in 0.085 M hydrochloric acid. This was done with a view to determining which of the oxidizing inhibitors will give better co-inhibition efficiency (IE) with sodium tungstate. The study was carried out using the gravimetric technique. The uninhibited solution of 0.085 M hydrochloric acid served as the control. The results obtained have shown that 71% IE was produced by co-inhibiting sodium tungstate with sodium silicate and 54% IE produced by co-inhibiting with sodium nitrate after 336 hours of exposure. This was due to a greater oxidizing condition produced by the former. Sodium tungstate alone gave 47% IE and sodium nitrate produced 57% IE when used alone, and sodium silicate showed 18%IE after 336 hours of exposure.

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Introduction

Corrosion is an electrochemical process involving the oxidation of a metal and the corresponding reduction reactions (Simpson, 1997). Inhibitors are substances added in small concentrations to particular environments with the aim of slowing down the rate of corrosion at such sites. Co-inhibition is achieved when two or more inhibitors are used at the same time to give better inhibition efficiency than single inhibitors used separately.

The major use of inhibitors in acid solutions is in pickling processes, oil well cleaning, descaling and industrial acid cleaning (Saeed, 2004). Anodic inhibitors such as sodium tungstate are found to be the most effective and readily available but for its low oxidizing potential and high cost (Shibli and Saji, 2003). This is due to the fact that tungstate ions alone cannot shift the potential of the metal into the passive region substantially (Shibli and Saji, 2003, Saji and Shibli, 2002, Azambuja et al, 2003). This fact justifies the small quantity of sodium tungstate (50 ppm) used throughout this work. Hence, its inhibitive potential can be fully maximized when used in the presence of oxidizing inhibitor such as sodium nitrate, sodium silicate, sodium chromate and sodium nitrite.

Co-inhibitive effects have been investigated on molybdate and phosphate in synthetic tap water environments (Li et al, 2002) and on potassium permanganate with sodium tungstate for the protection of carbon steel (Saeed, 2004). The similarity in chemical structure and periodicity between chromates and other group VI ions has made molybdate, phosphate and tungstate to be reliable replacement. Among the non –oxidizing passivating inhibitors, tungstate seems to be better than molybdate in terms of its inhibition efficiency and applicability under wide experimental condition, including pH (Shibli and Saji, 2003, Saji and Shibli, 2002). However, tungstate has been adjudged to be highly effective even in highly reducing environment as reported by Azambuja et al, 2003 and Pu and Wu, 2003. Robertson in his study concluded that molybodate ions could deliver comparable effects to those achieved using chromate and nitrite ions. Li et al (2002) stated that to improve the inhibitive capacity of molybdate, it must be in co-inhibition with other inhibitors which may be organic or inorganic.

The use of small concentrations of inhibitors in this work was borne out of the studies carried out by researchers like Shreir (1979), Shibli & Saji (2003), and Saeed, (2004) in order to accommodate small amount of acid such as 0.085M Hcl.

This work aimed at investigating corrosion co-inhibitive characteristics of sodium tungstate with sodium nitrate and sodium silicate in metal cleaning and pickling processes.

Experimental Procedure

A locally made low carbon steel sheet was used for this research work it was obtained commercially and it was spectrometrically analyzed at the Materials laboratory, Ajaokuta Steel Complex Limited, Ajaokuta, Nigeria. The weight percent of the constituent elements is as presented in Table 1.

One hundred and seventy five coupons were cut from the low carbon steel sheet using the cutting saw into 50 X 30 X 0.5mm each, and a hole of 4mm diameter was drilled at the center top of each coupon so as to facilitate its suspension. The samples were mechanically polished using emery papers with 240, 320, 400 and 600 grits. This was to eliminate scaling, surface contaminant and oxide film on the surface of the metal. This was followed by degreasing with acetone to remove grease, dirt or dust to avoid error in experimentation and subsequent corrosion rate measurement. The degreased surface is then air-dried.

The dimension of each coupon sample was carefully taken and recorded in order to take care of minutest difference in the exposed surface area. Since exposed area is involved in the calculation of corrosion rate, its accuracy determines accurate corrosion rate. The initial weights were obtained using the mettler balance. They were stored in a dessicator prior to immersion to avoid reaction with the environment.

Seven samples were immersed completely in each of the 0.085 M HCl already prepared in a large labeled plastic bowl by suspending them on thread and rack. The coupons in each medium were to cater for the fourteen days (336 hours) duration of the experiment. A coupon was removed from each solution medium at intervals of two days (48 hours). After elapsed time, a coupon was removed, held under a stream of tap water and the surface was scrubbed with a rubber stopper to remove the corrosion product. This was followed by cleaning with acetone to halt the minute electrochemical reactions and form a barrier against atmospheric corrosion. The coupon was then air-dried completely, re-weighed and recorded in order to determine the weight loss (ASTM G 1-90, 1993).

Results

Fig.1 shows the results of corrosion rates for the low carbon steel in 0.085 M hydrochloric acid inhibited with sodium tungstate at 50 ppm, 100 ppm and 200 ppm concentrations. It was observed that the corrosion rates of the coupon increased with an increase in concentration of sodium tungstate. When 50 ppm of sodium tungstate was added, a corrosion rate of 21 mpy was obtained while with 200 ppm sodium tungstate addition, a corrosion rate of 27 mpy was obtained after 336 hours of exposure in both cases. This may be due to the tungstate ions that were adsorbed onto the steel specimen's surface and forms diffusion barrier against metal dissolution, thereby reducing anodic reaction as observed in the uninhibited acid medium. It was observed that the corrosion rate increased with increasing concentration.

Table 1: Chemical Composition of experimental low carbon steel

Element	Fe	C	Si	Mn	P	S	Co	Mo	Ni	Al	Cu
% Wt	99.00	0.117	0.033	0.011	0.0258	0.014	0.005	0.014	0.19	0.59	0.055

The result in Fig. 2 shows that increasing the sodium nitrate concentration causes a decrease in the rate of the anodic dissolution reaction. It was also observed that the inhibition efficiencies increase with increase in concentration. In Fig. 3, the results of corrosion rates (mpy) and percent efficiencies are presented for low carbon steel immersed in 0.085 M hydrochloric acid inhibited with sodium silicate. It was observed that 50 ppm of sodium silicate offered significant corrosion inhibition (slightly above 60%IE) as shown in Fig. 3 after 336 hours. However, the sodium silicate at 100 ppm and 200 ppm was observed to produce about 4%IE and 9%IE respectively after 336 hours. Hence, 50 ppm sodium silicate was the best inhibitor when compared with sodium tungstate and sodium nitrate used separately.

The highest inhibition efficiency was as demonstrated in Fig. 4 with concentrations of 100 ppm sodium nitrate in 50 ppm sodium tungstate. The corresponding percent inhibition efficiencies were shown in Fig. 4. The use of sodium nitrate to co-inhibit sodium tungstate has resulted into much lower corrosion rate values compared to the inhibitor used separately (see Figs. 1 and 2). In Fig 5, it was observed that co-inhibition with 100 ppm sodium silicate provided 71% inhibition efficiency after 336 hours while with 150 ppm sodium silicate, above 60 %IE was observed at the same time.

The corroded samples were evaluated micrographically after 336 hrs of exposure in the 0.085M HCl, however prior to this the uninhibited samples were observed visually. It was noted that the sample was severely attacked with large magnitude of pits and holes such that the mild steel is subjected to near – tearing. Plate 1 shows the micrograph of the uninhibited sample immersed in the medium and it was observed that the attack is severe, widespread and highly localized and those attacks exist in the form of pits and cavities. The corrosion products are found to be minimal uniformly distributed. The sample inhibited with 150 ppm Na_2WO_4 is as shown in plate 2. There is presence of corrosion products which is also uniform and the attack is then that less severe. The corrosion attacks are reducing more uniformly.

In plate 3, the microstructure of the sample inhibited with 100 ppm sodium nitrate was shown and it was seen that the attack is nonuniform but localized. The attacks exist in the form of cavities and pits which are highly severe but the corrosion products and the attacks are almost equal. The micrograph of the sample inhibited with 100 ppm Na_2SiO_3 is as shown in plate 4. It revealed a uniform, widespread but less severe corrosion attacks. This may be attributed to the presence of corrosion products. The corrosion products are observed around the edges of the localized attacks which may aggravate the localized attack due to galvanic action of varying potentials.

Plate 5 is the micrograph showing the effect of co-inhibition of 50 ppm Na_2WO_4 and 50 ppm Na_2NO_3. It revealed a less pronounced and highly distributed localized corrosion attack in size, shape and severity and also the corrosion products are uniform and widespread. The micrograph of the sample co-inhibited with 50 ppm of Na_2WO_4 and Na_2SiO_3 is as shown in Plate 6. The microstructure shows few localized attacks but the attacks are uniform and it exists in form of general corrosion. The corrosion product is also more uniform and widespread.

Discussion

It is observed that for sample inhibited with Na_2WO_4 the corrosion rate increases with increase in concentration of the inhibitors and as such the sample inhibited with low concentration of Na_2WO_4 gives the highest inhibition efficiency. Hence it is recommended that sample with 50 ppm Na_2WO_4 will provide better cover for the low carbon steel in the medium. This can be attributed to adsorption of inhibitor species at low coverage being more effective in producing inhibition than adsorption at high surface coverage. Consequently, inhibition efficiencies were highest with 50 ppm sodium tungstate. Saheed,(2004) stated that as the corrosion rate of materials increases it implies the effectiveness and efficiency of the inhibitor in the environment becomes poor. He also assumed that the tungstate ions were adsorbed onto the sample surfaces and formed diffusion barrier against the metal dissolution. Though the corrosion attacks is as observed in Plate 1 is severe and localized their effects on the corrosion rate was nullified by the presence of uniform corrosion products. This is still in concordance with earlier position of Saeed (2004) that localized attacks increase with the concentration of Na_2WO_4. From the electrochemical point of view the probable chemical reactions taking place in the medium are given by the equations below:

$$Fe + 2HCl = FeCl_2 + H_2 \quad \text{-----------} \quad (1)$$

$$FeCl_2 + 2NaWO_4 = 2NaCl + FeWO_4 \text{-----------} (2)$$

It was suspected that iron tungstate was adsorbed to the anodic sites on the steel surface thereby blocking off the corrosion areas. This is as a result of film formation by the adsorbed iron tungstate over the specimen (Ogungare et al, 2009).

The inhibition efficiencies of sodium nitrate on mild steel in 0.085M HCl increases with increase in concentration which is the reversal of the tendency observed for Na_2WO_4. This implies that the concentration of $NaNO_3$ is inversely related to the inhibition efficiencies and hence the rate of corrosion at 50 ppm of $NaNO_3$ is higher than that at 200 ppm. According to Pu & Wu (2003) the adsorption effect and the inhibitive tendencies of the nitrate ions become greater with the increase in concentration of participating inhibitor species.

The results as obtained in Fig. 2 it was shown that increasing the sodium nitrate concentration causes a decrease in the rate of the anodic dissolution reaction. This implies that the presence of inhibitor brought about a decrease in the rate of hydrogen evolution reaction, and consequently the rate of the overall corrosion reaction is reduced. This is similar to the submission of Abdallah et al (2003) who studied the effect of nickel alloys as inhibitors in sulphuric acid. Also it was observed from Fig. 2 that the inhibition efficiencies increase with increase in concentration. Azambuja et el (2003) in his study of corrosion behaviour of iron and AISI 304 Stainless Steel in Tungstate aqueous solution containing chloride showed that the adsorption effect and inhibitive tendencies of the nitrate ions become greater with increase in concentration of participating inhibitor species. Hence, sodium nitrate used alone, with better oxidizing ability, exhibited better inhibitive efficiency than sodium tungstate used alone. The decreasing corrosion rate values at increasing levels of concentrations shown in Fig. 2 are an indication of the continuous weakening of the medium by the corrosion process. The work of Loto and Mohammed (2000) showed a decrease in corrosion rate due to increasing weakness of the medium with time.

The inhibitive tendencies of sodium silicate follows the same pattern as that of sodium tungstate in that the efficiencies decreases as the concentration of the Na_2SiO_3 inhibitor increases but the corrosion rate have a linear relationship with the concentration of the inhibitors. According to Shreir (1979) Na_2SiO_3 is regarded as a precipitation inhibitor which is able to form precipitates on the metal surface at a low concentration. They easily form films over the entire metal at low surface coverage but breaks as the concentration increases. The electrochemical reactions are:

$Fe + 2HCl = FeCl_2 + H_2$ ----------- (3)

$FeCl_2 + Na_2SiO_3 = 2NaCl + FeSiO_3$ -------- (4)

Ogundare et al (2009) reported that iron silicate ions are expected to give a more adherent and protective film at high concentration. They also suspected that the precipitate is enough at concentration of 50 ppm while at high concentrations such as 100 ppm and 200 ppm, the precipitate formed may be too thick and may fall off the surface of the specimen as the film thickness increases. This is expected to invariably exposed them to a fresh attack.

The microstructure of the corroded sample shows that the attack is uniform and it is not localized but it has corrosion products. It is generally known that uniform attack is preferred than localized because localized attack is insidious and this is one of the reasons that is accountable for the higher efficiencies associated with 50 ppm Na_2SiO_3 inhibitor in the medium. The presences of the corrosion products also minimize the corrosion attacks although the corrosion products are observed around the transgranular areas. These effects are offset by the low presence of localized attacks. It is also observed that localized corrosion attacks increase with the concentration Na_2SiO_3 and it is assumed that adsorption of inhibitor species at low coverage is more effective in producing inhibition than adsorption at high surface coverage.at a ratio of 1:3.It is found out that a low dosage must be applied and in this study the concentration is 50 ppm. It is also observed that the efficiencies of the co-inhibitive effects of sodium nitrate and even that of Na_2SiO_3 are found to be very high at a concentration ratio of 1:3.

In the case of sodium tungstate and sodium nitrate, it is noted that the corrosion rate decreases as the concentration of the $NaNO_3$ increases until it get to around 150 ppm but at a greater concentration than this the percent inhibition efficiencies decreases. It is assumed that the formation of film over the surface of the sample may be attributed to the inhibition. Also it can be asserted that the oxidizing power of the medium has been altered in such a manner that the tungstate ions cannot act as diffusion barrier against metal dissolution.

It is realized that the behaviour of samples co-inhibited by Na_2WO_4 and Na_2SiO_3 follows the same trend as that of sodium tungstate with sodium nitrate. The %IE increases until 150 ppm of Na_2SiO_3 after which it decreases such that the concentration ratio is 50 ppm Na_2WO_4 and 150 ppm Na_2SiO_3. Electrochemically, the following rections were suspected to have taken place:

$Fe + 2HCl = FeCl_2 + H_2$ --------------- (5)

$2FeCl_2 + Na_2WO_4 + Na_2SiO_3 = 4NaCl + FeWO_4 + FeSiO_3$ ------- (6)

The iron tungstate and silicate formed were regarded to form film over the surface of the specimen. It isrealised that the combining effects of the anodic property of the tungstate ions and precipitating capacity of the silicate ions comes into play (Ogundare et al, 2009). The micrograph shows a uniform corrosion attacks and the corrosion products are uniform with wide coverage. It is known that uniform or general form of corrosion is better than that of localized corrosion attacks. This may be attributed to the better performance of the samples co-inhibited by Na_2WO_4 and Na_2SiO_3. This can be attributed to the oxidizing ability of sodium tungstate being enhanced by sodium silicate at the concentration of 100 ppm. This observation is not surprising because the inhibition efficiency of sodium silicate alone when used was found to be high.

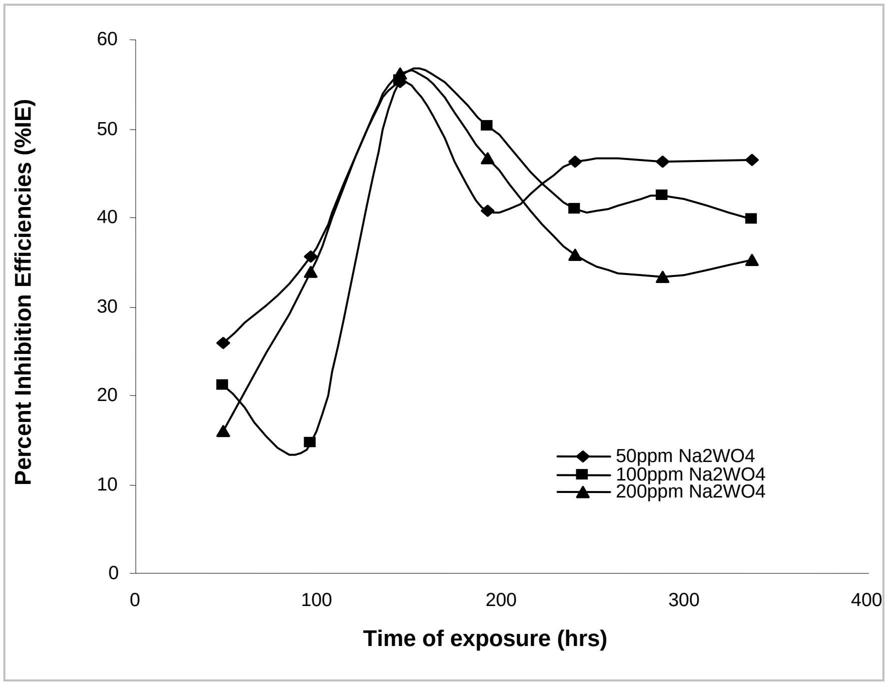

Fig.1: Percent Inhibition Efficiencies of low carbon steel immersed in 0.085 M hydrochloric acid inhibited with sodium tungstate

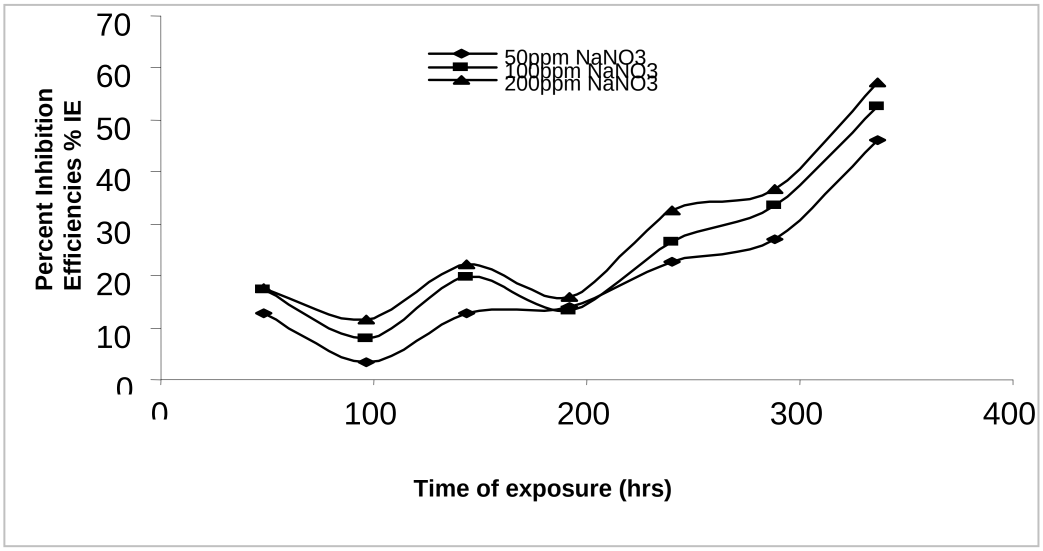

Fig.2: Inhibition efficiencies of low carbon steel immersed in 0.085 M hydrochloric acid inhibited with sodium nitrate.

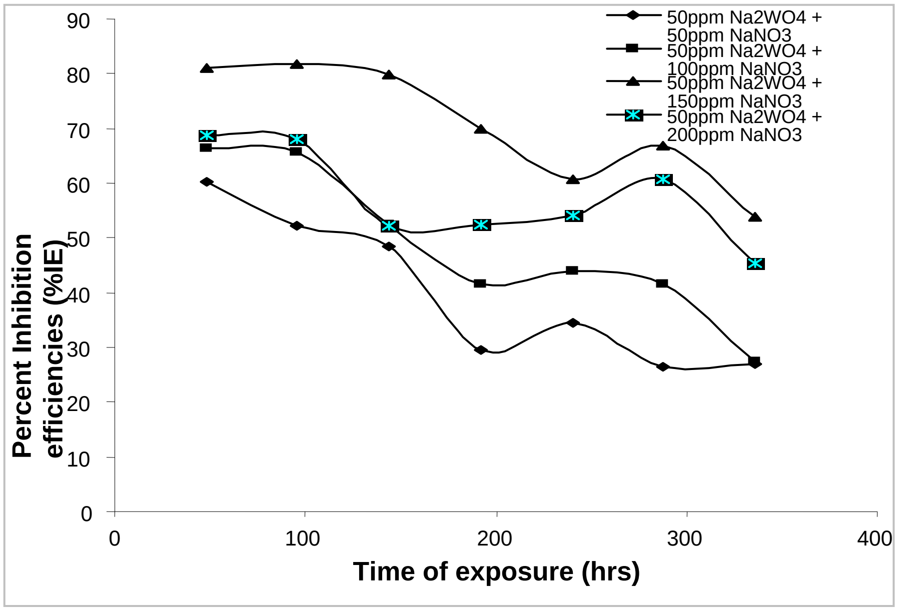

Fig.3: Inhibition efficiencies of low carbon steel immersed in 0.085 M hydrochloric acid co-inhibited with sodium tungstate and sodium nitrate.

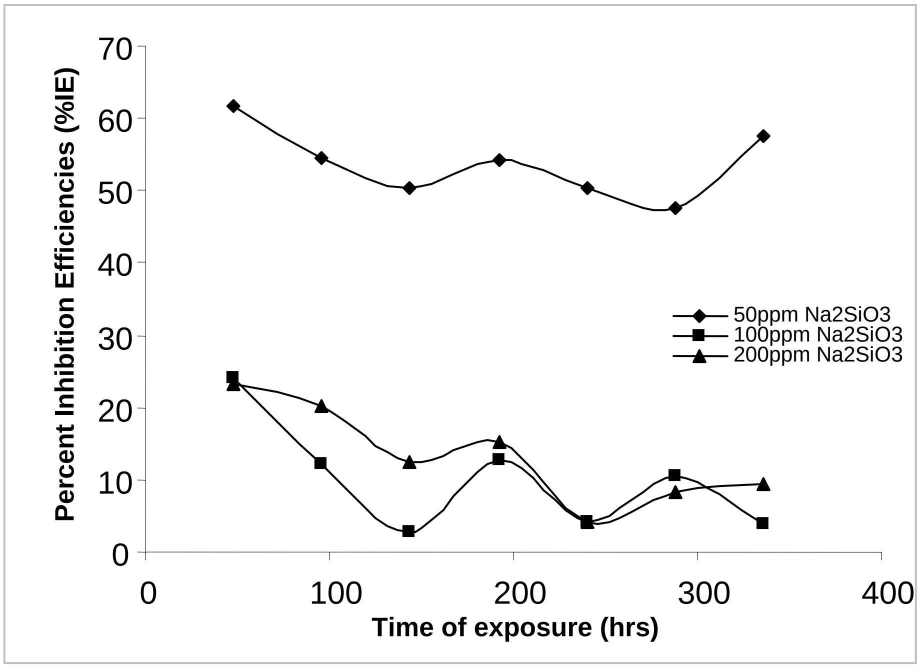

Fig 4: Percent Inhibition Efficiencies of low carbon steel immersed in 0.085 M hydrochloric acid inhibited with sodium silicate

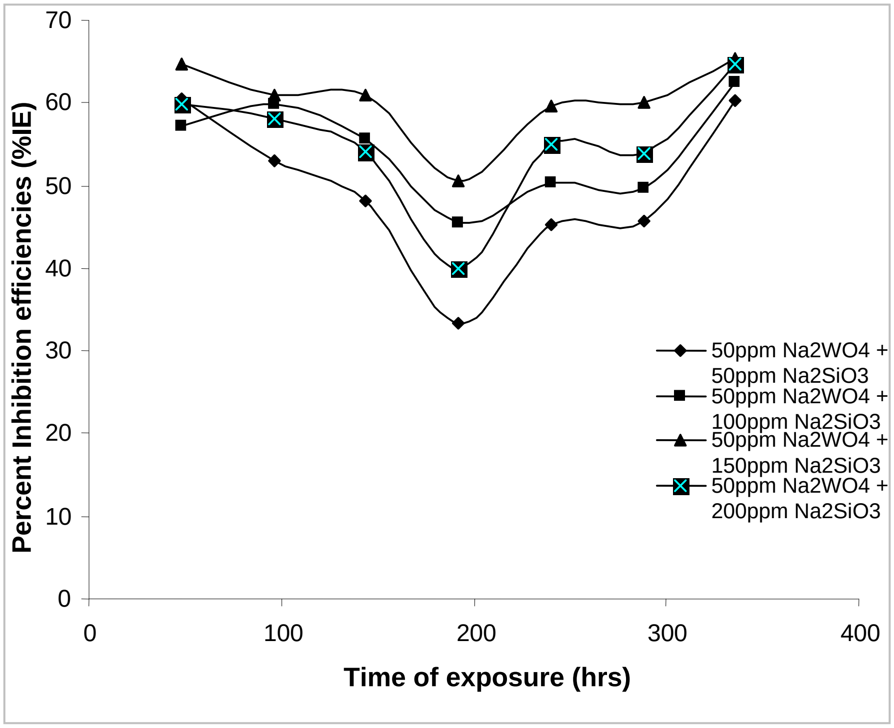

Fig. 5 Percent Inhibition Efficiencies of low carbon steel immersed in 0.085 M hydrochloric acid co-inhibited with sodium silicate

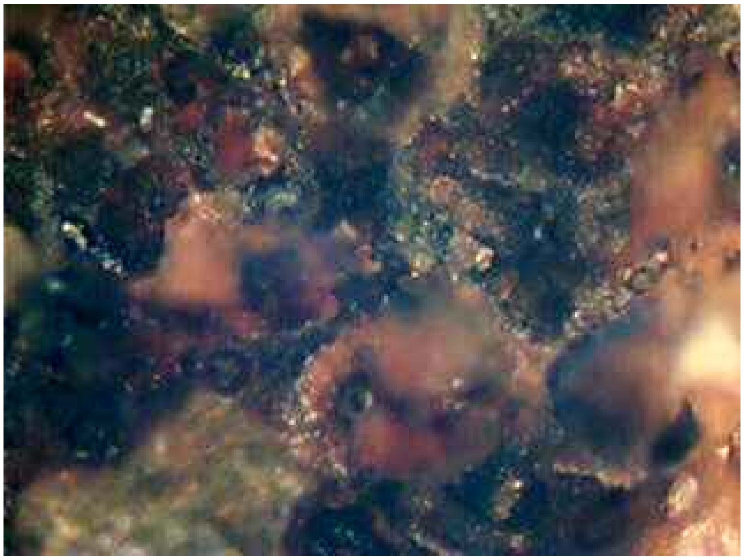

Plate 1: Micrograph of the uninhibited sample immersed after 336 hours of exposure.
X 200

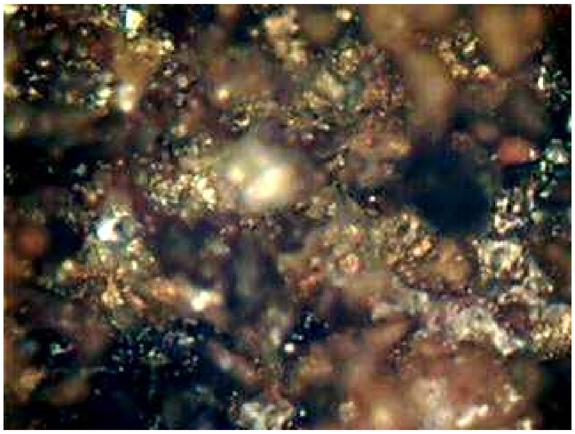

Plate 2: Micrograph of the sample inhibited with 150 ppm Sodium Tungstate after 336 hours of exposure. X 200

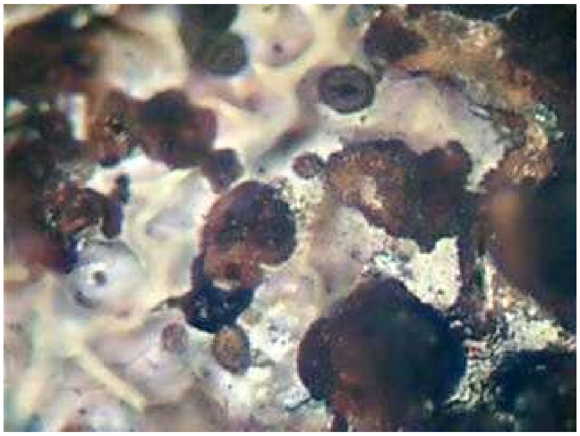

Plate 3: Micrograph of the sample inhibited with 100 ppm Sodium Nitrate after 336 hours of exposure. X 200

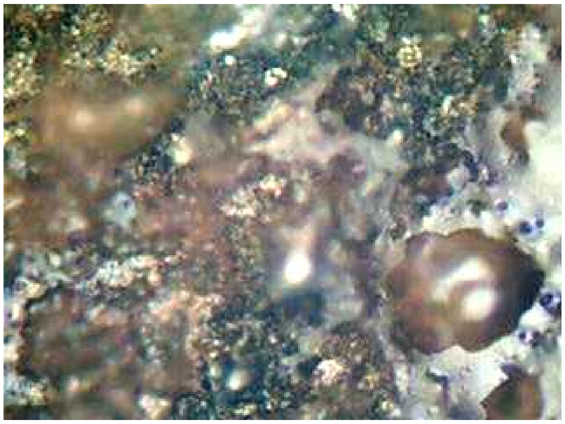

Plate 4: Micrograph of the sample inhibited with 100 ppm Sodium Silicate after 336 hours of exposure. X 200

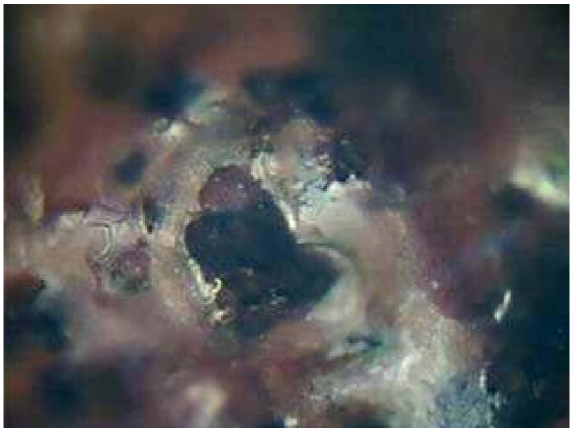

Plate 5: Micrograph of the sample immersed in 50 ppm Sodium Tungstate and 50 ppm Sodium Nitrate after 336 hours of exposure. X 200

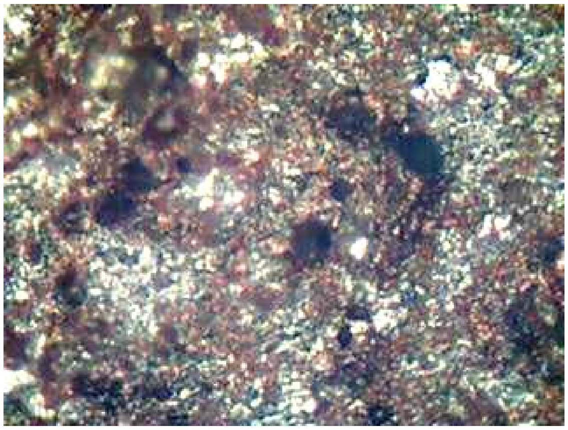

Plate 6: Micrograph of the sample immersed in 50 ppm Sodium Tungstate and 50 ppm Sodium Silicate after 336 hours of exposure. X 200

Conclusions:

Based on the strength of the results obtained it can be concluded that the medium in which $NaSiO_3$ acts as the inhibitor covers the best protection to mild steel in hydrochloric acid medium. The sodium silicate should be applied at a lower concentration and also sodium tungstate but in the case of sodium nitrate the inhibitor should be applied at a higher dosage. This work has been able to establish that sodium silicate can act as better oxidizing co-inhibitor with sodium tungstate. The co-inhibitive efficiencies of the Na_2WO_4 and Na_2SiO_3 gives the optimum performance at a ratio of 1:3.

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