International Journal of Engineering Research and General Science Volume 3, Issue 5, September-October, 2015
ISSN 2091-2730

Effect of Induced Stress on the Corrosion Rate of Medium Carbon Steel in Saline Environment

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Abstract-This study investigated how 0.33% medium carbon steel is affected by induced stress in a saline environment. Three geometries namely U-bend, C-ring and I-shape samples were formed representing varying degrees of stress level induced on the samples. The test specimens were subjected to static loading in saline environment containing 15.0 wt.%, 10.0 wt.% and 3.5 wt.% of sodium chloride (NaCl) for a typical exposure time of 31 days at ambient conditions of temperature and pressure. Weight loss method was used to estimate the corrosion rate in mils per year (mpy). The results of the experiment show that corrosion rate is maximum in samples with the highest stress level and in medium containing highest amount of dissolved chloride ions. The least corrosion rate occurred in samples with the least amount of chloride ions and in a non-stressed condition. It was inferred that the corrosion rate of 0.33 %C steels increased with increasing tensile stress and chloride ions content of the medium.

Key words: Stress corrosion cracking, medium carbon steel, saline environment, corrosion rate, chloride ion, induced stress, protective films

INTRODUCTION

Corrosion has persistently become a major problem and has attained a global nature in which there is no facet of human endeavour where its impact is not felt and recognized. Corrosion problems in production plants can increase substantially the operation and maintenance cost. For example, one of the most costly problems facing the oil companies is corrosion in crude oil systems. In their report, SPE stated that in the Nigeria oil and gas industry, the total pipeline breakage loss figure due to corrosion in 2004 alone is 396,000 metric tons while the financial losses is estimated to be 19.66 billion naira (#19.66billion) equivalent to US $154.4 million [1]. Generally, the shutdowns resulting from the failures of components due to corrosion are extremely expensive thus creating a great need for in-depth understanding of this insidious phenomenon.

Carbon steel is by far the most important alloy used as structural members [2]. Its behavior is a fundamental parameter in the design and application of structural steel such as reinforcement members in structures. This is because they can be readily bent or prestressed. They can also be used where small radii bend are necessary. Its high tensile strength, yield strength, percentage elongation and ductility are of great advantage in these applications. Unfortunately, corrosion has proved to be a major threat to its favourable mechanical properties.

Various studies have been carried out to investigate the corrosion mechanism and factors affecting the corrosion rates of steel alloys. For example, Ikpeseri [2] investigated the corrosion behaviour of mild steel in 0.5M H_2SO_4 and 3.5% NaCl solutions. His results showed that corrosion rate is higher in 0.5M H_2SO_4 environment than 3.5% NaCl throughout the entire period of investigation reaching a maximum of 22.2 mm/yr and 0.158 mm/yr respectively.

Stress corrosion cracking (SCC) is the cracking indicated from the combined influence of tensile stress and a corrosive environment [3]. The required tensile stresses may be in the form of directly applied stress or in the form of residual stress [4]. It has been reported that one of the most accepted mechanisms of SCC (*i.e.*, the “dissolution-repassivation” mechanism) requires recurrence of the steps of: (a) the stress-assisted disruption of the passive film at the crack-tip; (b) localized crack-tip dissolution at a high rate; and (c) repassivation at the crack-tip [5]-[7].

In the past it was thought by several investigators that SCC of a given alloy occurs only in limited range of specific environments [8]. However, subsequent researches have revealed that SCC occurs in wide range of environments including pure water [9]-[10]. It has been reported that the carbon steels are prone to SCC in carbonate, bicarbonate, acetates, phosphate and chloride environments [11-[12]. For example, studies on J-55 and N-80 steels have shown that H_2S containing chloride solutions promote SSC [13]. Also, synergistic effect of low concentration chloride in bicarbonate solutions and low concentration of sulfate causing SCC in low alloy steels has also been reported [14]-[15].

Various findings have also been reported on some variables affecting SCC of metallic materials in many media [16]-[18]. Also, Afolabi *et al*. [19] studied the stress corrosion cracking and microstructural analysis of a mild steel immersed in orange juice medium using weight loss technique and SEM analysis. Their results showed that SCC relative to mild steel is mainly a function of the acidity of the medium under study, and the corrosion rate increases with increase in exposure time throughout the exposure time. The SEM analysis revealed that the trans granular and inter granular attacks were visibly responsible for the corrosion of this material in this medium. Singh Raman and Wai [20] investigated the SCC of an austenitic stainless steel in nitrite-containing chloride solutions.

Their results showed that additions of NO_2 (1400–5600 ppm) accelerate susceptibility to chloride SCC. With increasing NO_2 content, SCC susceptibility increases in the order, 1400 ppm > 2800 ppm > 5600 ppm. This behaviour has been attributed to the increasing passivation characteristic with increasing NO_2 content. This work is concerned with the study of the effect of induced stress in the corrosion rate of 0.33% medium carbon steel in a saline environment.

MATERIALS AND METHODS

Materials for testing

The steel product (ST 44-2 plain) used in this study was a medium carbon steel in hot rolled condition of 0.33% C. The chemical composition of the steel is shown in Table 1. Table 2 shows the mechanical properties of the steel sample. The steel was obtained from Osogbo Steel Rolling Company (OSRC) in Osogbo, Nigeria

Table 1: Chemical Composition of Steel Sample (ST 44-2 plain)

Element	C	Mn	P	S	Ni	Cr	Mo	Sn	Fe	Others
Composition (%)	0.33	0.09	0.02	0.02	0.03	0.45	0.02	0.01	98.63	0.05

Table 2: Mechanical Properties of As-rolled 0.33%C Steel Sample

U.T.S (N/mm^2)	**Yield Strength (N/mm^2)**	**Elongation (%)**
318.0	258.0	26.0

Saline environment

The environment used for the corrosion testing was a saline-based one simulated in the laboratory. The saline environment was made up of three different compositions of sodium chloride (NaCl); 3.5 wt.%, 10.0 wt.% and 15.0 wt.% NaCl.

Sample preparation

One hundred and eight (108) medium steel samples were cut into three different geometries: 36 were cut into I-shape of 6 cm long, 36 cut into a U-bend of 12 cm long of small anchorage radius and the remaining 36 cut into a C-ring shape. Figures 1-3 shows the geometries of the samples. The radius of curvature (anchorage radius) distinguished the U- bend from the C-ring. The anchorage radius for the U-bend, C-ring and I-shape are 0.6 mm, 0.9 mm and 0 mm respectively. The I-shape samples were annealed between 650 °C – 670 °C for about 30 minutes and furnace cooled to room temperature in order to relieve internal stresses developed during solidification, rolling or machining and hence serve as control samples. The samples used have cylindrical geometry and each has a total surface area given by equation 1.

$$A = 2\pi rl + 2\pi r^2 \qquad \ldots\ldots\ldots\ldots\ldots\ldots 1$$

Quantifiable amount of tensile stress was induced in the samples by plastic deformation at various stress levels below the yield strength of the material. The expression to estimate the induced stress is given in equation 2.

$$L = \frac{0.95fy_{\emptyset}}{4f_{bu}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

Where L = anchorage radius in mm, f_y = characteristic strength of steel = tensile strength in N/mm^2, ϕ = diameter of the bar in mm, f_{bu} = induced stress in N/mm^2.

The calculated value for the induced stress for the U-Bend, C-Ring and I-Shape samples are 755.25 N/mm^2, 503.50 N/mm^2 and 0 N/mm^2 respectively. The U-bend and C-ring samples were statically loaded in such a way that a metal holder was placed through the legs of the samples which prevents stress-relaxation in the samples during corrosion process. The sample surfaces were then ground and polished to remove scales and oxide deposits on the steel surfaces. The I-shape samples were drilled in the center in other to make holes in them for proper suspension in the medium.

Measuring and weighing

After surface preparation, the specimens were carefully measured to permit calculation of the surface area needed in the formula for calculation the corrosion rate.

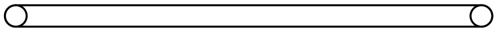

Figure 1: I-shape sample

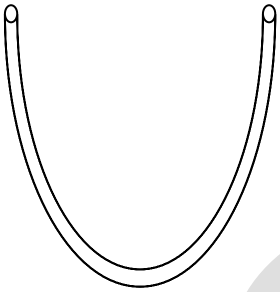

Figure 2: U-bend sample

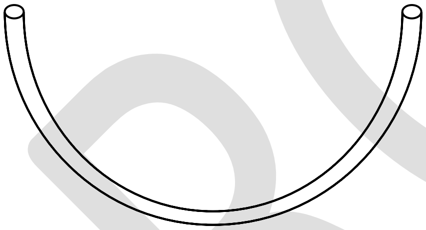

Figure 3: C-ring sample

After measuring, the specimens were cleaned by washing in acetone and alcohol, then degreased in petroleum ether, dried in air and weighed. This was recorded as the initial weight of the specimen. The specimens were then stored in a desiccator before exposure to the corrosion environment to prevent reaction with the environment.

Immersion in saline environment

The I-shape samples were fully immersed in the medium while the U-bend and C-ring samples were partially immersed. The U-bend and C-ring samples were suspended in the medium through the holes bore in the metal holder. Partial immersion was adopted for the U-bend and C-ring in order to eliminate galvanic or two-metal corrosion as a result of a different metal used as the sample holder.

Determination of corrosion rate

The time of exposure to the corrosion medium during the experiment was 31 days (744 hours). However, after every 48 hours, samples were taken out of the environment, cleaned by holding under a stream of water, and scrubbing the surfaces with rubber stopper to remove corrosion products. They were then dried in warm air and re-weighed. The weight was recorded as the final weight. The weight loss was calculated using equation 3:

$W = W_o - W_f$ …………………………3

Where W = weight loss, W_o = initial weight and W_f = final weight

The change in weight of the specimens was then used to calculate the corrosion rate. The corrosion rate was determined through the mils per year method using equation 4:

Corrosion rate = $\frac{534W}{DAT}$ …………....4

Where W = weight loss in mg, D = density of specimen in g/cm^3, A = area of specimen in in^2 and T = exposure time in hours.

RESULTS

The variation of corrosion rate of I-shape, C-ring and U-bend samples at different concentrations of sodium chloride (NaCl) with increasing exposure time respectively is given in Figure 4-6.

Figures 7, 8 and 9 respectively show the corrosion behavior of the samples under varying stresses at 3.5 wt.%, 10.0 wt.% and 15.0 wt.% NaCl with increasing exposure time.

DISCUSSION OF RESULTS

The corrosion rate

As in all the figures, the corrosion rate of the samples in the saline environment increases as the experiment progresses over time. The graphs show that the samples underwent high corrosion rate in the first 48 hours of the corrosion testing period (Fig. 4-9). This may be due to the fact that the samples just like any other metals are unstable at high energy state; consequently, the metals want to achieve rapid change to the low energy state where they become stable.

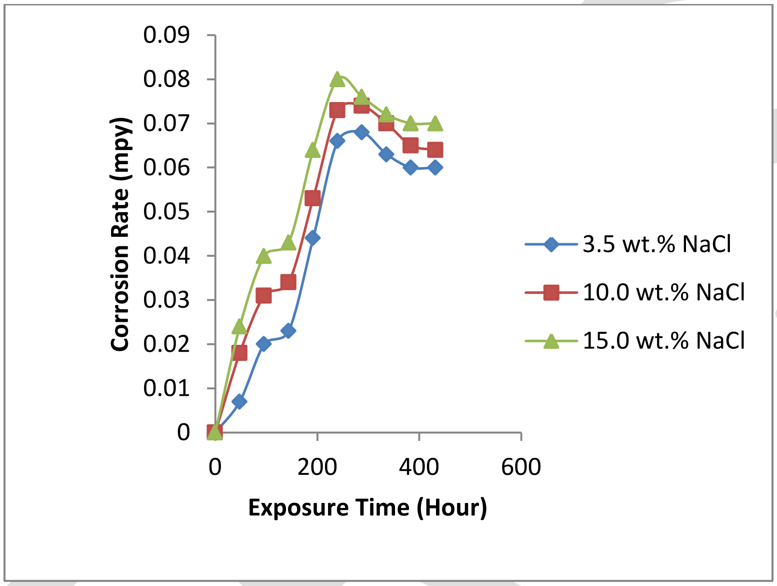

Fig. 4: Corrosion rate of I-shape samples at different concentration of sodium chloride (NaCl) with increasing exposure time

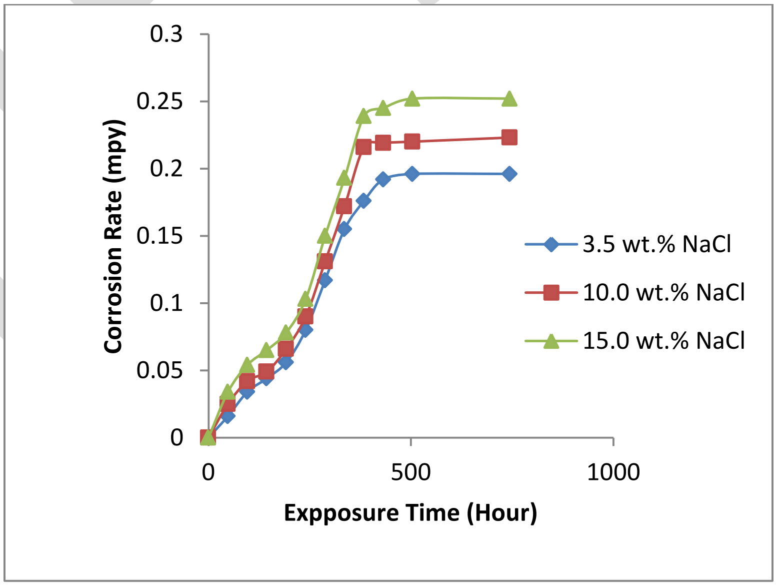

Fig 5: Corrosion rate of C-ring samples at different concentration of sodium chloride (NaCl) with increasing exposure time

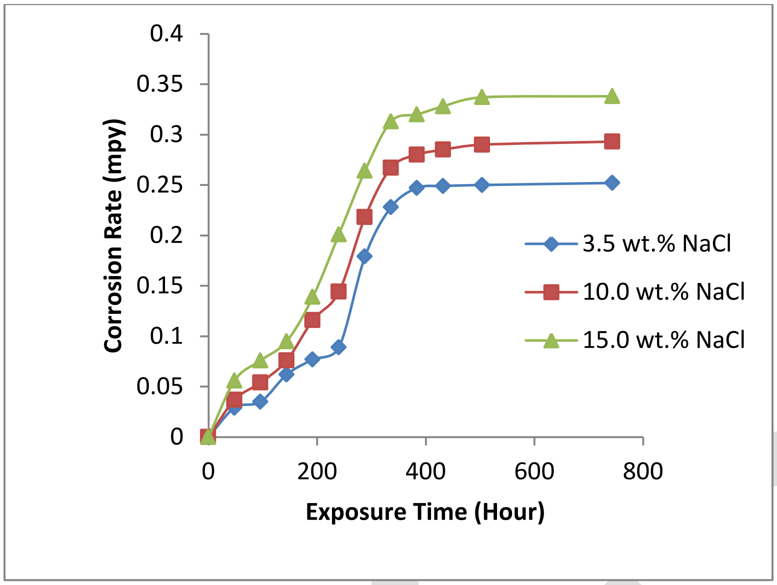

Fig. 6: Corrosion rate of U-bend samples at different concentration of sodium chloride (NaCl) with increasing exposure time

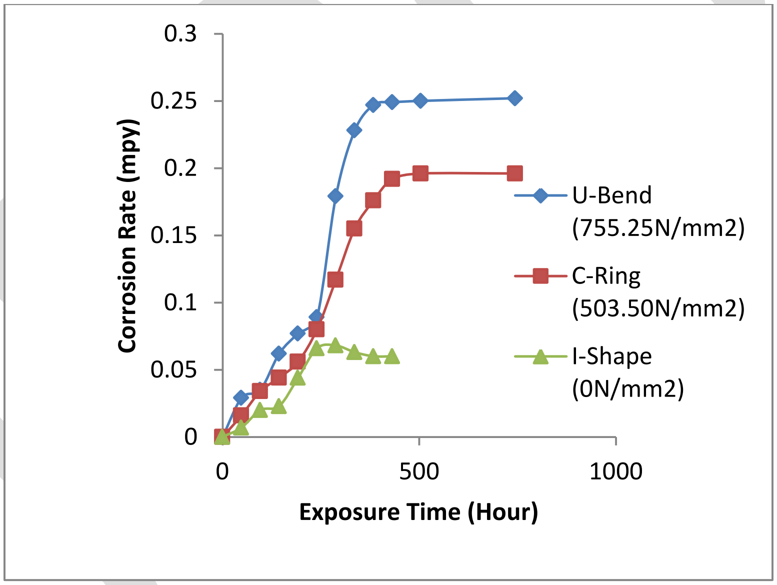

Fig. 7: Corrsosion behavior of the samples under varying tensile stress at 3.5 wt.% NaCl with increasing exposure time

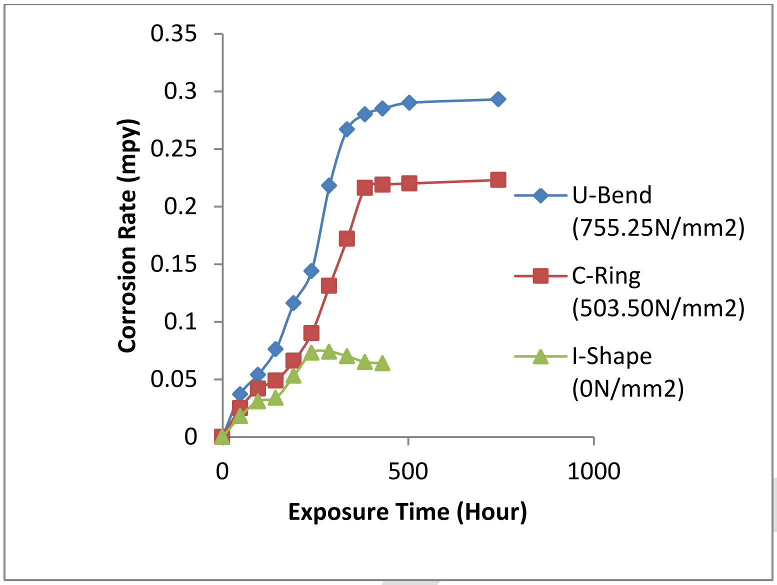

Fig. 8: Corrosion behavior of the samples under varying stress at 10.0 wt.% NaCl with increasing exposure time

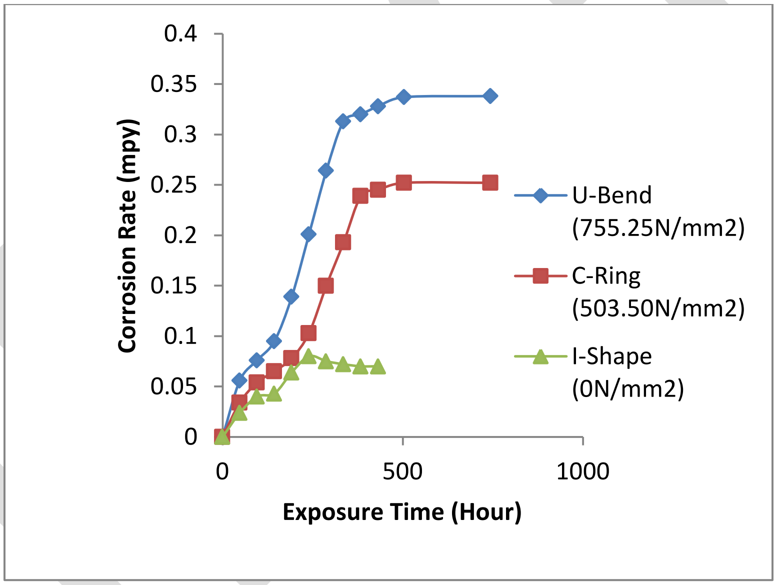

Fig. 9: Corrosion behavior of the samples under varying stress at 15.0 wt.% NaCl with increasing exposure time

Effect of chloride ions

Figure 4 shows that the corrosion rate of the I-shape medium carbon steel samples increased rapidly in the first 48 hours. The increase in the corrosion rate then became less rapid until it reached a peak and then started to decrease after five hundred and four (504) hours. As pointed out earlier, the initial rapid increase in corrosion rate is due to the rapid change of the metal samples to the low energy state where they become stable. However, the decrease in the corrosion rate at the end of the experiment could be attributed to formation of protective oxide film which shielded the metal from the environment. The corrosion rates of the C-ring and U-bend samples also increased rapidly at the initial stage of the experiment (Fig. 5 and 6). However, towards the end of the experiment, the corrosion rates did not decrease but were almost constant. This could be as a result of the increase in induced stress level in the C-ring and U-bend samples which increased the proneness of the samples to corrosion.

The U-bend samples show the highest corrosion rate throughout the corrosion testing time in all concentrations of NaCl with the highest rate at 15.0 wt.% NaCl (Fig. 6). The C-ring test samples show characteristic corrosion behavior similar to the U-bend as the exposure time increases. In this regard, the highest corrosion rate occurred at 0.252 mpy while that of the U-bend rises up to 0.338 mpy. This behavior is associated with the combined effect of the tensile stress and concentration of corrosion medium being higher in the U-bend samples in 15.0 wt.% NaCl solution.

Chloride ion aggravates the degradation of materials in aqueous environment. It helps in breaking passive oxide layer, leading to localized corrosion [21]. The results of the experiment show that, for a particular level of induced stress, the corrosion rate of 0.33%C steel increases with time when in contact with chloride ions containing environment and the rate increases with increasing concentration of chloride ions, the highest being 15.0 wt.% followed by 10.0 wt.%. 3.5 wt.% NaCl solution shows the least corrosion rate effect (Figures. 4-6). The mechanism responsible for this increase is that there is an increase in the conductivity of the water thereby improving the mobility of ions between the metal/electrolyte interfaces as the chloride content increases.

Effect of induced tensile stress

The role of induced tensile stress could be shown to be important in rupturing protective films. The tensile stress is in fact the result of local corrosion processes in that when a metal is deformed beyond the elastic limit, a permanent or unrecoverable strain occurs in the stressed regions. This permanent plastic deformation causes an onset of plastic strain, thus creating high-energy sites in the microstructures of the metal. The higher the deformation, the higher the strain energy. This energy (strain) varies significantly within the molecules of the metals with the resulting highest energy occurring in the most stressed region (755.25 N/mm^2). Figure 7 shows that in the 3.5 wt.% NaCl solution, the I-shape samples exhibits the least corrosion rate being a non-stressed sample. The corrosion behavior in this case is due to the presence of chloride ions in the medium. The C-ring samples exhibit an increase in corrosion rate with increase in exposure time with the rate reaching a peak at about 0.252 mpy (Fig. 8). As shown in Figure 9, the U-sample shows the highest corrosion rate with a peak at about 0.388 mpy. The U-bend samples being highly stressed regions have the highest energy thereby showing more susceptibility to corrosion attack. This region is then preferentially attacked by the corrosive medium giving a high corrosion rate. The corrosion of the U-bend and C-ring can be attributed to the synergistic effect of induced tensile stress and corrosive medium. Corrosion in this case is seen to increase with increasing dissolved chloride where the medium corresponding to 15,0 wt.% NaCl has the highest corrosion rate and 3.5 wt.% NaCl the least.

CONCLUSION

Induced tensile stress increases the corrosion rate of medium carbon steels when they are in contact with chloride-ion environment. The highest corrosion rate (0.338 mpy) occurred in the U-bend samples, having the highest stress level of 755.25 N/mm^2, at 15.0 wt.% of NaCl which corresponds to the highest dissolved chloride ions concentration. This behavior was followed by the C-ring samples having about 503.5 N/mm^2 stress level and 0.252 mpy as the highest corrosion rate over the exposure time. The least corrosion rate occurred in the I-shape samples in their non –stressed condition. Therefore, the corrosion rate of 0.33 %C steels increased with increasing tensile stress and chloride ions content of the medium.

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