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Effect of Corrosion Inhibitors on the Corrosion Rate of Refinery Boiler Components

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Abstract This research work investigated the corrosion rates in six boiler component parts in the absence and presence of corrosion inhibitors. The investigations were based on tested mathematical model equations derived from ordinary differential equation. For the period of four years the corrosion of the boiler component tubes in the absence of inhibitors ranged between 0.54-1.80mm in the fan suction air duct, 0.05-0.2mm in the bank tubes, 0.4623-2.15mm in the desuperheater coil, 0.2125-0.75mm in the baffle wall tube, 0.175-0.60mm in the vapourizing tube bank and0.11-0.4mm in the superheater coils. While in the presence of inhibitors, the corrosion rate in the four-year period ranged between 0.27-0.60mm in the fan suction air duct, 0.035-0.0874mm in the bank tubes, 0.2835-0.706mm in the desuperheater coil, 0.1295-0.32mm in the baffle wall tube, 0.103-0.256mm in the vapourizing tube bank and 0.0685-0.1705mm in the superheater coils. The percentage efficiency of the inhibitors, were between 41-66.67% for the fan suction air duct, 30-95.62% for the bank tube, 38.68-67.16% for the desuperheater coil, 39.06-57.33% for the baffle wall tube, 41.14-57.33% for the vapourizing tube bank and 37.73-57.38 for the superheater coils. In comparing the corrosion rates in the absence and presence of inhibitors, it showed clearly that the presence of inhibitors in the boiler produced reduction in the rate of deterioration of the walls of the boiler component parts.

Keywords boiler components, corrosion inhibitors, suction air duct, bank tubes, desuperheater coil, baffle wall tube, vapourizing tube bank, superheater coils

Introduction

Corrosion which is the degradation, deterioration and disintegration of materials is multifaceted in nature and produces adverse effect on metals through the process of oxidation and reduction reactions. Corrosion constitute a major challenge in the petrochemical, chemical and petroleum processing plants. The corrosion process in industrial plants bring about failure in equipment and account for huge financial losses due to equipment and spares replacements [1]. Corrosion which bring about the wearing, tearing breaching and final failure of equipment is produced as a result of these reactions [3]

$Fe + 2H_2O \rightarrow Fe(OH)_2 + H_2$ (1)

$Fe + (OH)_3 \rightarrow Fe^{2+} + 3OH^-$ (2)

$4Fe + 6H_2O + 3O_2 \rightarrow 2Fe(OH)_3 + Fe_2O_3 + 3H_2O$ (3)

Corrosion is a predominant issue in boilers, which is a steam generating equipment in the refinery. The different compartments of the boiler suffer great metal losses due to the high temperature requirement of about 110 ^oC and above in the various steam lines and condensate systems, especially when it comes in contact with water [4-5]. The boiler is prone to serious corrosion attack since the water passing through it is influenced by high temperature, and the materials are made of carbon steel [6]. The flow accelerated corrosion predominant in the boiler system is also a factor that help in influencing the rapidity of corrosion attack.

The electrochemical reaction and process depends on temperature (90-120^{o}C), which indicated that increased temperature produces increased electrochemical reaction thereby resulting in increased rate of corrosion of carbon steel (boiler) [7]. Boiler tubes are associated with corrosion cracking, erosion-corrosion fatigue, pitting corrosion, steam cycles and general corrosion due to the concentration of salts, hydroxides and acids, which bring about challenges due to corrosion of plant equipment of the refinery. The presence of impurities of salts and acids in water and steam of the boiler component parts produces enormous corrosion results [8].

Several methods of reducing corrosion attack, which is caused by certain factors like environment, type of metal involved, corrosion species and agents, in order to effectively minimize the rate of corrosion and thereby giving longer life to the equipment and plant [9]. One of the ways to effectively reduce and mitigate the wear and tear (corrosion) of these equipment is the use of corrosion inhibitors [10], which are substances when added to corrosive environment in small quantity produces significant decrease in the rate of corrosion of the metallic materials exposed to such environments [11].

Due to the complex nature and operating conditions of the refinery boiler, different types of inhibitors are used in order to combat the high corrosion rate associated with it. Such inhibitor types include film forming inhibitors with neutralizing amines (methylketoxime) added as oxygen scavenger, diethyleneamine, a neutralizing type amine and helps in the control of pH between 8.5-9.5 in the condensate line. Trisodium phosphate is used in the boiler to increase the pH and it is a good film former that prevents and controls the formation of scales in the boiler and also a useful softener. These inhibitors are readily soluble in water and hence produces effective check on the high corrosion rate of the material [12].

The investigation of this work is to ascertain the effectiveness of the corrosion inhibitors in the refinery boiler system in reducing or mitigating the high rate of corrosion associated with its various component parts.

Materials and Methods

Ultrasonic thickness scanning method of metal loss in a boiler was used to ascertain the amount of metal lost by the refinery boiler compartments (internal tubes or parts) yearly for a period of four years. The corrosion data obtained was subjected to ordinary differential equation (first order), through the framework of mass balance equation [13-15]. The corrosion rate equation obtained, $C_R = C_{R0}e^{KcT}$, where C_R = corrosion rate of the boiler component parts, Kc =corrosion rate constant, T = time (years), and C_{R0} = initial corrosion rate (metal loss of the first year). The equation was then modified by the application of a modified type of Langmuir adsorption isotherm to derive a mathematical representation of boiler corrosion in the presence of the different types of inhibitors, thus giving rise to the equation $C_{Ri} = C_{R0}e[\frac{Cinh\Theta}{1-\Theta} x\ t]$ [13-14, 16]. Where, C_{inh} = inhibitor concentration (assumed to be = 0.5 mols/dm in the boiler system), Θ = degree of inhibitor coverage (0.75 in the scale of 1) and t = time (years).

Boiler Corrosion Inhibitors Efficiency Calculations

The inhibitors efficiency was calculated from the formula

% Efficiency = $\frac{CR-CRi}{CR}\ x100,$ for each of the various component parts to see the effectiveness of the inhibitor application for the period of four years as applied in the model equation for the corrosion of the boiler component parts in the presence of the various of inhibitors present in the boiler.

Results and Discussion

Corrosion of Refinery Boilers during Operation

Metal losses that brought about reduction in the thickness of the boiler component parts (compartments) due to the effect of corrosion and the effect of inhibitor applications are shown in Figures 1-6. The metal loss increases as the year progresses from the first to the fourth year, resulting in the thinning of the walls of the tubes of the boiler component parts. The results revealed that the degree of metal loss vary from one component to the other [17]. This was made possible due to the configurations and the turbulence associated with the different parts and within the tubes of the boiler [17].

Taking the variations in metal loss in the boiler component parts from 1 to 4 years, metal loss increased from 0.54-1.80mm in the fan suction air duct, 0.05-0.2mm in the bank tubes, 0.4623-2.15mm in the desuperheater coils, 0.2125-0.75mm in the baffle wall tube, 0.175-0.6mm in the vapourizing tube bank and 0.11 -0.4mm in the superheater coils. The investigation revealed that the rate of metal loss (corrosion) in the four years was in the order, desuperheater coil > fan suction air duct > baffle wall tube >vapourizing tube bank >superheater coils > bank tubes, which confirmed that metal loss that bring about thinning of the boiler walls vary from component to component in the boiler [17].

Internal corrosion of boiler components parts is due primarily to the presence of dissolved gasses such as oxygen and carbon dioxide in the feed water and being released into the boiler and transported through the various parts during operation [16]. The high metal losses observed from Figures 1-6 come as a result of the feed water undergoing dissociation reaction such as,

$$H_2O \rightarrow H^+ + OH^- \qquad (4)$$

Despite the dissociation degree being very small, it produces H^+ ions which are reduced in the corrosion process. Carbonic acid is produced when CO_2 is dissolved in water and results in the equation,

$$CO_2 + H_2O \rightarrow H_2CO_3 \qquad (5)$$

Which breaks down into two steps

$$HCO_3 \rightarrow H^+ + HCO_3^- \qquad (6)$$

$$HCO_3^- \rightarrow H^+ + CO_3^{2-} \qquad (7)$$

The more carbonic acid present in the boiler system gives an extra source of H^+ ions. The reduction reaction due to the hydration of ions is

$$H^+ + e^- \rightarrow H \qquad (8)$$

The reaction in equation (8) gives the diffusion rate of H^+ ions due to hydrogen reduction from the bulk solution where electrons are transferred to the surface due to the presence of plenty H^+ ions and as the transfer occurs the H ions are being consumed.

The presence of H_2CO_3 in the boiler water also results in increased corrosion rate in two ways as depicted in equations (6) and (7). Equation 6 is the cathodic reaction which causes the carbonic acid in the boiler to be more corrosive than a completely dissociated acid [18]. This reaction is under activation control. Electrochemically iron dissolves as

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad (9)$$

But at the point when both concentrations of Fe^{2+} and CO_3^{2-} ion has exceeded the limit of solubility, they combine together to form iron carbonate ($FeCO_3$) which is solid in nature and form films according to equation (9) which is the most significant factor that controls the corrosion rate,

$$Fe^{2+} + CO_3^{2-} \rightarrow FeCO_3(s) \qquad (10)$$

The application of corrosion inhibitors to the boiler system actually reduced the rate at which metal was lost to the environment and hence a reduction in the thinning of the walls of the boiler tubes of the different compartments. The results from Figures 1-6 also showed the variation in the effect of corrosion inhibitors in mitigating against the rapid loss of metals to the environment due to the operating conditions of the boiler. The metal loss when the corrosion inhibitor model was applied showed metal loss between 0.27-0.6mm in the fan suction air duct, 0.035-0.087mm in the bank tubes, 0.2835-0.706mm in the desuperheater coil, 0.1295-0.32mm in the baffle wall tube, 0.103-0.256mm in the vapourizing tube bank and 0.0685-0.1705mm in the superheater coils. The recorded loss of metal from the boiler between the first year to the fourth year revealed that metal loss that resulted in the thinning of the walls reduced in the presence of the corrosion inhibitors in the boiler [13-17], and hence elongated the life span of the boiler.

The corrosion inhibitors added to the refinery boiler to reduce the effect of corrosion ranged from film formers with neutralizing agents, oxygen scavengers, pH controlling inhibitors, inhibitors for effective deaeration, softeners etc. The solubility of these inhibitors in the water help effectively in corrosion check as regards the refinery boiler compartments. The presence of corrosion inhibitors in the boiler water enhances the reduction in the rate of thinning of the walls of the boiler tubes in the various compartments or component parts under the same operating conditions.

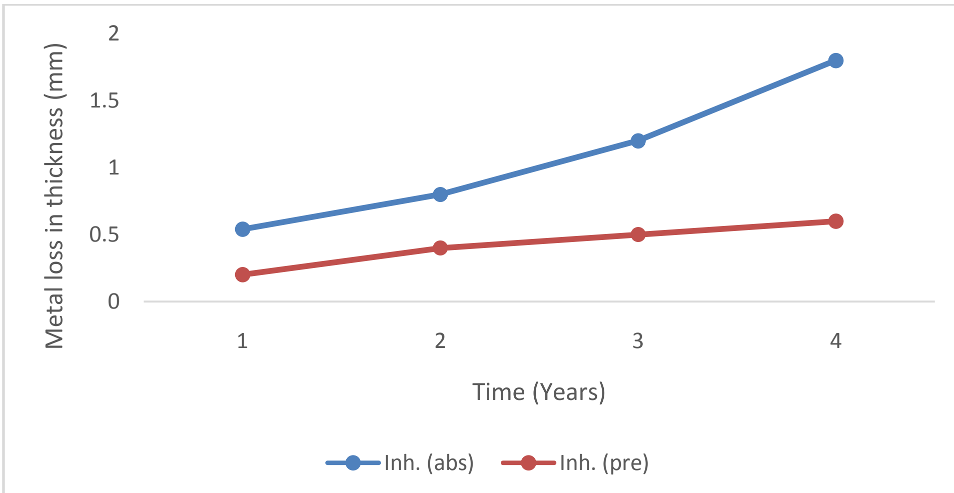

Figure 1: Metal loss due to the absence and presence of inhibitors in the fan suction air duct

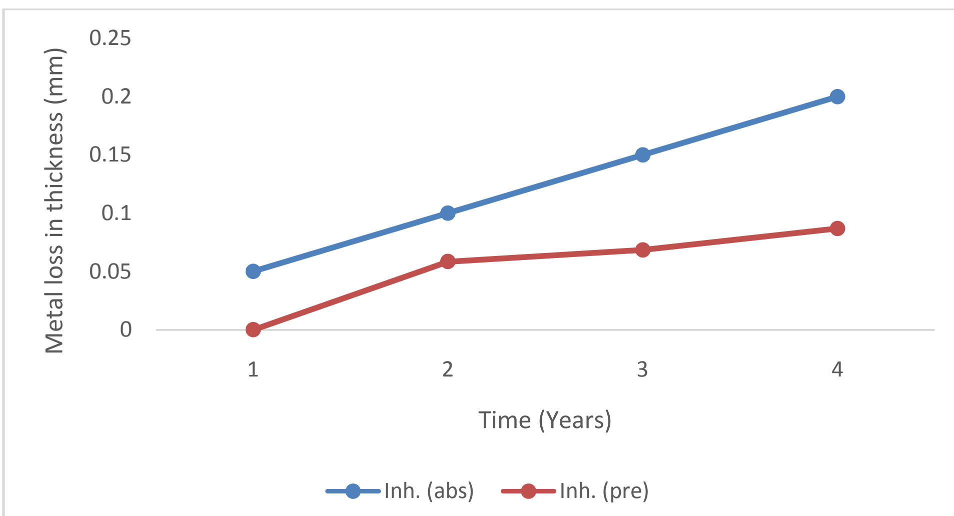

Figure 2: Metal loss due to the absence and presence of inhibitors in the bank tubes

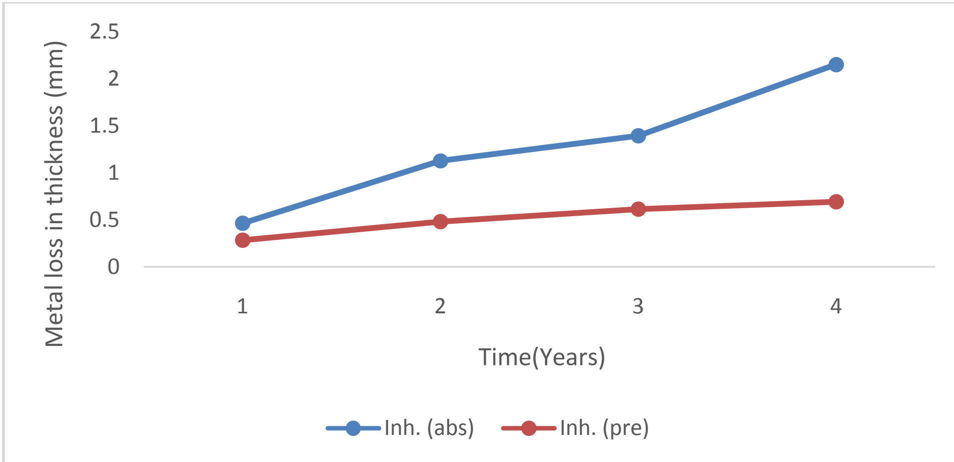

Figure 3: Metal loss due to the absence and presence of inhibitors in the desuperheater coil

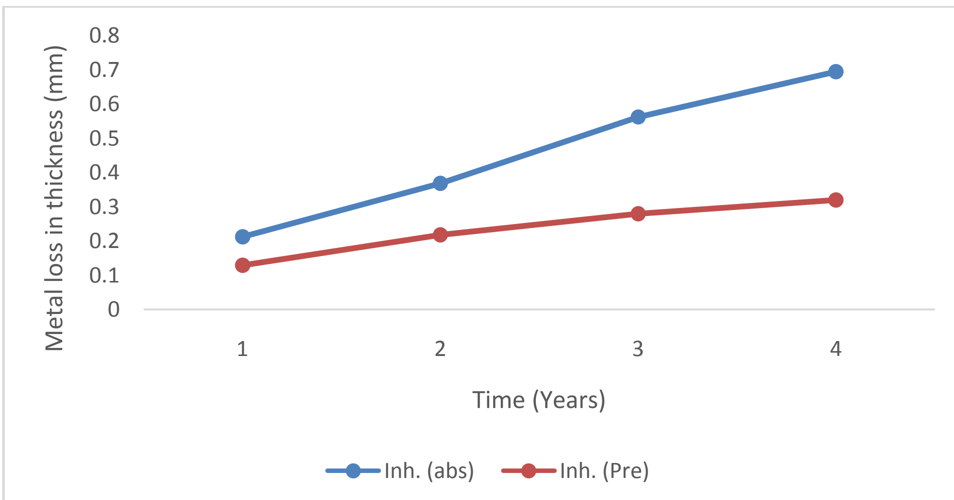

Figure 4: Metal loss due to the absence and presence of inhibitors in the baffle wall tube

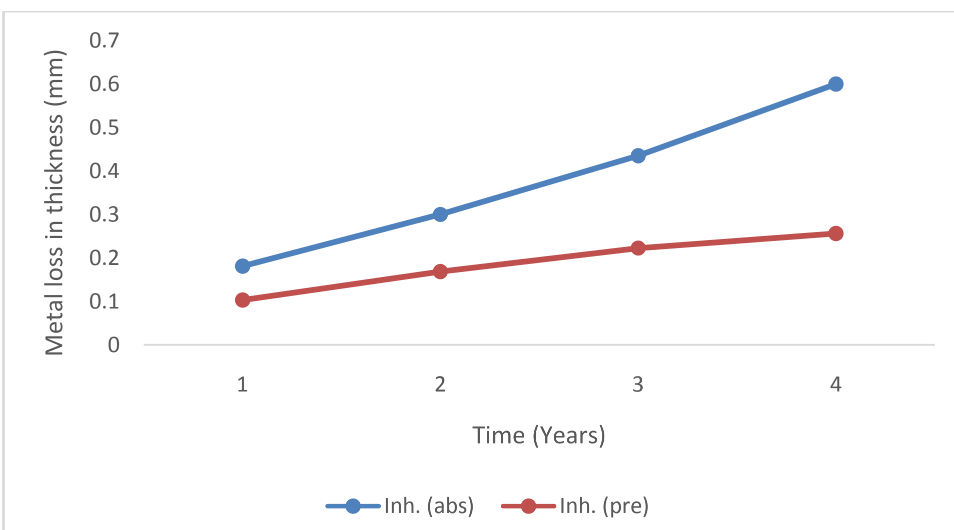

Figure 5: Metal loss due to the absence and presence of inhibitors in the vapourizing tube bank

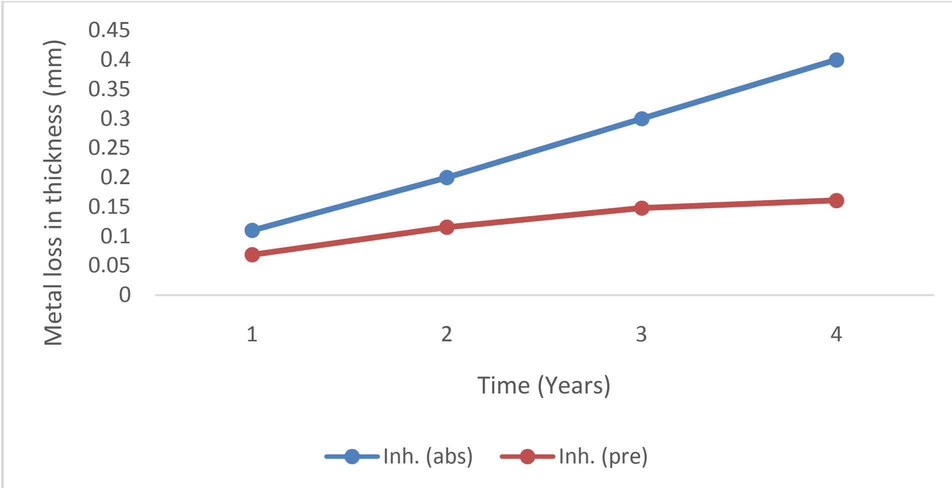

Figure 6: Metal loss due to the absence and presence of inhibitors in the superheater coils

Efficiency of Corrosion Inhibitors in The Boiler

Figure 7, is an illustration of the efficiency of the corrosion inhibitors used in the boiler and how they affect the various component parts of the boiler. The percentage inhibition (efficiency) of the inhibitors in the boiler component parts ranged between 50-66.67% in the fan suction air duct, 30-95.63% in the bank tubes, 38.68-67.16% in the desuperheater coil, 39.06-57.33% in the baffle wall tube, 41.14-57.33% in the vapourizing tube bank and 37.73-57.38% in the superheater coils. The results from Figure 7 also showed that the effect of the inhibitor (efficiency) progressed in the various component parts as the years progressed. In the first year, highest efficiency of 50% was recorded in the fan suction air duct, second year in the desuperheater coil of 57.42%, third year in the fan suction air duct of 58.33% and in the fourth year in the bank tubes of 95.63%.

The possible reasons for the inhibition efficiency of the combined inhibitors in the boiler could be that the inhibitors molecules might have desorbed into the walls of the boiler tubes there by creating a barrier between the tube walls and the running boiler water. It can therefore be supposed that both chemical and physical adsorption might have been brought about by the inhibitors present in the boiler [19]. The presence of the inhibitors caused the reduction in the dissolution of the boiler wall tubes and also caused the reduction of reactions involving oxygen (oxidation) [20]. This was made possible through the presence of oxygen scavengers in the boiler. The film formers inhibitors at the surface of the boiler wall form a protective layer through interactions with the metal thereby providing more coverage at the surface and hence reduction in the rate of dissolution of the boiler wall tubes [21]. Also, the thin film produced by the inhibitors interferes with the corrosion process by retarding the progression of the dissolution of the boiler wall tubes. The combination of several mechanisms slowed down the corrosion reaction due to the resistance caused by the film formed on the surface of the boiler walls and thereby reduced the transfer of electrons by diffusion, causing limitation of the electrode potential through the layers of the boiler walls [22].

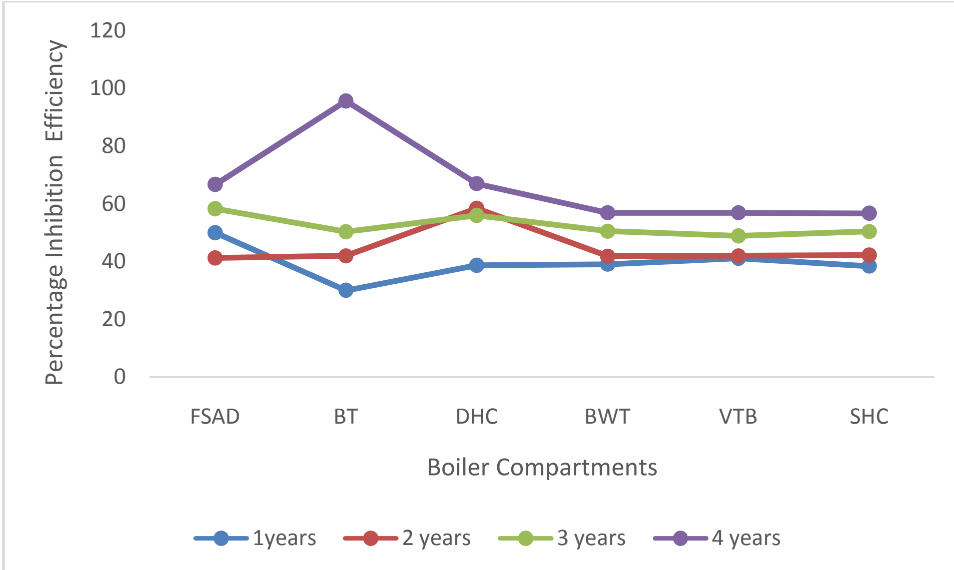

Figure 7 : Inhibitor efficiency in the boiler component parts during the period of four years

Key: FSAD (fan suction air duct), BT (bank tubes), DHC (desuperheater coil), BWT (baffle wall tube), VTB (vapourizing tube bank), SHC (superheater coils)

Conclusion

The study has revealed that the boiler which operates under harsh conditions undergoes severe corrosion attack on the walls of the tubes of the various component parts leading to the thinning of walls of the tubes and a resultant reduction in the lifespan of the boiler. The corrosion of the boiler wall can be greatly reduced by the application of corrosion inhibitors in order to elongate the lifespan of the boiler and also to boost production processes in the refinery in general.

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