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Corrosion Evaluation and Corrosion Inhibitors Influence in the Furnace Internal Wall Tubes of the Refinery Boiler

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Abstract

This work evaluated the rate at which metal walls of the tubes of the furnace internal tubes of the refinery boiler were corroded due to the harsh environment in which it is operated. The rate of corrosion was investigated in the absence and presence of corrosion inhibitors with the use of a material balance equation of the boiler system where a mathematical model was derived using first order differential equation. The results obtained during the four years period under review were between 0.1425-0.5550mm, 0.1250-0.5000mm, 0.1125-0.4650mm, 0.2250-0.8000mm and 0.1700-0.6000mm in the absence of corrosion inhibitors in the FWT, EWT, IWT, ITURB AND ETURB respectively. The results also revealed that in the presence of corrosion inhibitors under the same period were 0.0945-0.2345mm, 0.0860-0.2135mm, 0.0775-0.1920mm, 0.1375-0.3415mm and 0.1035-0.2560mm in the FWT, EWT, IWT, ITURB AND ETURB respectively. The metals gained during the period under evaluation ranged between 0.0480-0.3205mm, 0.0490-0.2865mm, 0.0350-0.2730mm, 0.0875-0.4585mm and 0.0665-0.3440mm in the FWT, EWT, IWT, ITURB AND ETURB respectively. The resultant percentage efficiencies recorded during the period under review were in the range of 33.68-57.75%, 36.30-57.30%, 31.11-58.71% 38.89-57.31% and 39.12-57.33% in the FWT, EWT, IWT, ITURB AND ETURB respectively. The corrosion evaluation in the furnace internal wall tubes showed that there was a remarkable decrease in corrosion rate due to the application of corrosion inhibitors.

Keywords: Furnace internal wall, corrosion rate, high temperature corrosion, corrosion inhibitors, furnace tubes, boiler tube failure, inhibitor efficiency.

INTRODUCTION

The boiler used in the production of heat through fuel combustion in a closed vessel, and at certain temperature and pressure conditions transfer water into steam (Reynolds, 1961). Different boiler types are, fire tube boilers, waste heat boilers, packaged boilers, water tube boilers and pulverized fuel boilers. Boilers find its usefulness in the refinery, petrochemical industry, sugar industry, waste incinerators, building materials and food industry (Nielson et al., 2000). For these industries to be managed efficiently, depends practically on how the boiler is working effectively so that sudden shutdown in the industry will be avoided due to the failure of the boiler and its components (Singh et al., 2018). The tubes of the various boiler compartments are regularly exposed to damaging conditions because of the high temperature requirement involved in its operation. One of the most damaging instruments in the boiler compartments' tubes is corrosion (Bozorgian and Ghazinezhad, 2018). The corrosion effect leads to degradation of the tubes which then results in the failure of the boiler leading to undue shutdowns in the refinery, petrochemical and other plants that made use of boilers (Jonas, 2000; Noori et al., 2011; Ameri and Shamshirgaran, 2018).

The refinery furnaces' walls consist of various tubes within the furnace box and due to the high temperature involved in the operation of the boiler; the compartment undergoes several corrosion problems. The corrosion attack on the metal walls of the furnace wall tubes often accumulates corrosion deposits (Edori et al., 2014). The presence of carbon monoxide within the tubes of the furnace wall at high concentrations which is as a result of low oxygen content in the system results in the corrosion of the furnace walls which is even aggravated with the high temperature within the system. The fabrication of refinery furnace tubes which are made of different grades of steel to accommodate the high temperature in the system. These materials are used because of their resistance to rupture and the ability to resist corrosion (API 530, 2008; Shalaby et al., 2017). The furnace tubes are prone to failure and degradation that may result in problems during the operational processes. The inside of the tubes and surfaces may become damaged due to the aggressiveness of the feed introduced into the boiler. The presence of sulphides and chlorides can lead to stress corrosion cracking in the walls of the tubes of the furnace internal walls of the boiler. This may occur within the boundary of the water wall and the metal of construction (Gutzeit, 1986; Shalaby et al., 2017).

The undue attack of corrosion is a major problem in boilers and has resulted in costing the world over billions of dollars every year. The high temperature obtained in the boiler is also associated with corrosion rates facilitated by flow accelerated corrosion. This brings in localized corrosion attack on the components of the boiler which finally results in the failure of the tubes and pipings (Diden and Buet, 2003)). The flow accelerated corrosion dissolves the protective layer of magnetite (Fe_3O_4) in the flowing water of the boiler. The dissolution of the protective layer removes the steel material and results in metallurgical failure. The flow accelerated corrosion rapidly wears the boiler walls of the furnace internal tubes to 3mm/yr in some cases (Attebery and Hing, 2004). The flow accelerated corrosion coupled with the high temperature leads to increased oxidation of the materials of construction and forming deposits on the sides of the boiler compartments' tubes. The deposited contaminants on the boiler internal tubes are as a result of the oxidation of the materials of construction (Geobel et al., 1973; Singh et al., 2018).

The application of chemical treatment in the boiler to contain corrosion attack to a minimum level and prevent the deposition of contaminants will help in prolonging the lifespan of the boiler and its compartments. Such corrosion problems associated with the boiler include microbial activities, fouling and scaling where the water comes in contact with the metal surfaces the boiler tubes (Loretitsh, 2005). Such chemical treatment programmes include the use of corrosion inhibitors, which are substances when added to any given environment in little quantity reduce the rate at which corrosion of the metal(s) take place. Corrosion inhibitors are used in the refinery boiler and other extraction and processing systems due to their ability to militate against corrosion. They are the most useful agents for the defense of corrosion (Sastri, 2012; Javaherdashti, 2008). These corrosion inhibitors can effect positive changes on the corrosiveness of the boiler environment by altering the nature of the boiler environment.

This research work provides the rate of corrosion of the furnace internal wall tubes considering the various locations of the internal wall tubes of the refinery boiler through ultrasonic thickness scanning method and the application of corrosion inhibitors to effectively curtail the rate at which the boiler walls deteriorates and degrades.

MATERIALS AND METHODS

The rates at which the different location wall tubes found in the furnace inter al wall tubes of the refinery boiler disintegrates due to corrosion were measured using ultrasonic thickness scanning method annually for four years. Metal losses leading to thinning of the wall tubes were recorded yearly during the period and the data obtained were subjected to differential equation using first order principle expressed mathematically as $\frac{dCR}{dt} = Fso + Gs - Cs - Fs$. Where; CR = corrosion rate, dt = change in time, Gs = rate of chemical reaction generated during operation, Cs = rate at which corrosion inhibitors are consumed within the system and Fso = inflow rate of feedwater into the system (Edori et al., 2014). The mode of flow in a closed system like the boiler was used in the development of the first order differential equation by applying a material balanced equation. The material balance equation has been previously applied by Edori et al., (2014); Edori et al., (2018). The rate of thinning of the wall tubes by corrosion attack in the furnace internal wall tubes were then calculated using the equation $C_R = C_{R0}e^{KcT}$, developed from the first order differential equation, where C_R = final corrosion C_{R0} = initial corrosion rates, Kc = corrosion rate constant and T = time in years. The equation was further modified the application of Langmuir adsorption isotherm resulting int he equation, $C_{Ri} = C_{R0}\, e\, [\frac{Cinh\theta}{1-\theta} x\, t]$ (Edori and Bekee, 2014, Edori et al., 2014). Where C_{Ri} = rate of corrosion due to the presence of inhibitors, $C_{inh.}$ = inhibitors concentration in the system (0.5mols/dm3), ϴ = inhibitor coverage of the wall tubes which is taken as 0. 75 in a unit (1) scale and t is the time in years. The equation that was modified was then applied in calculating the corrosion rate in the presence of inhibitors in the different wall tubes of the furnace internal wall to verify the possibility of reduction in the reduction of the walls of the tubes in the furnace internal wall due to corrosion attack. The rate at which the thinning of the walls occurs in the boiler system as a result of the presence of the different types of inhibitors dosed into the boiler system within the period of operation.

Inhibitors' efficiency calculation in the furnace internal wall tubes

The efficiency due to the addition of multiple corrosion inhibitors into the boiler system in curtailing the corrosion rate within the furnace internal wall tubes was obtained by applying the formula, % Efficiency =

$\frac{CR-CRi}{CR}$ x100, (Edori et al., 2020), where C_R = corrosion rate in the absence of corrosion inhibitors and C_{Ri} = corrosion rate in the presence of inhibitors. The equation was applied in evaluating the efficiency of the corrosion inhibitors used in the system for the period of four years under review in the furnace internal wall tubes of the refinery boiler.

RESULTS AND DISCUSSION

The corrosion processes in the boiler is highly non-linear and the physics and chemistry involved in controlling the process exposes the boiler and the various compartments to conditions that are unusual and dominates the overall loss of metals from the boiler (Edori et al., 2014), the furnace internal wall tubes also inclusive. The rate of deterioration and disintegration of the different location tubes in the furnace internal wall tubes in the refinery boiler are shown in Figures 1-5, in the absence and presence of corrosion inhibitors and the thickness of metals that was gained due to the addition of corrosion inhibitors.

The metal loss obtained in the front wall tubes were 0.1425, 0.2750, 0.4130 and 0.5550mm, in the external wall tubes, 0.1350, 0.2500, 0.3750 and 0.500mm, in the internal wall tubes, 0.1125, 0.2250, 0.3325 and 0.4650mm, in the internal tube under refractory blocks, 0.2250, 0.4000, 0.6000 and 0.8000mm and in the external tube under refractory blocks, 0.1700, 0.3000, 0.4500 and 0.6000mm for the 1^{st}, 2^{nd}, 3^{rd} and 4^{th} year respectively. The results indicated that the metal lost to the environment due to the operational process increased as the year progressed. The results obtained due to the application of corrosion inhibitors through the proposed model was also obtained in Figures 1-5. The results revealed that there was a noticeable reduction in the rate at which metals were lost from the various locations of the furnace internal wall tubes. The results were, 0.0945, 0.1595, 0.2040 and 0.2345 mm in the front wall tubes, 0.0860, 0.1450, 0.1855 and 0.2135mm in the external wall tubes, 0.0775, 0.1305, 0.1670 and 0.1920mm in the internal tube under refractory blocks and 0.1035, 0.1740, 0.2225 and 0.2560mm in the external tube under refractory blocks for the 1^{st}, 2^{nd}, 3^{rd} and 4^{th} year respectively. Furthermore, the metals gained in terms of wall thickness due to the application of corrosion inhibitors within the system as shown in Figures 1-5 were 0.0480, 0.1155, 0.2030 and 0.3245mm in the front wall tubes, 0.0490, 0.1050, 0.1895 and 0.2865mm in the external wall tubes, 0.0350, 0.0945, 0.1655 and 0.2730mm in the internal wall tubes, 0.0875, 0.1680, 0.3030, and 0.4585mm in the internal tube under refractory blocks and 0.0665, 0.1260, 0,2275 and 0.3440mm in the external tube under refractory blocks. The gain in metal loss actually preserved the boiler given it a longer life in the thinning process of the boiler parts and hence an enhancement in production processes and economic gain to the industry.

Corrosion in refinery boiler (furnace wall tubes) associated with operating conditions

The water in the boiler flows through all the components including the furnace internal wall tubes and the various location boxes in it. The heated water flows round the tubes with combustion gases and produces steam (Singh et al., 2018). The feedwater that was converted to steam comes with dissolved gases like oxygen, carbon dioxide, H_2S and other gases that were dissolved during the operation process which then resulted in the corrosion of the boiler and its components. Corrosion in the boiler results primarily due to the presence of these dissolved gases (Adekoya and Osiberu, 1990). The boiler is a closed system, and it is being constructed with carbon steel, and the presence of oxygen in a closed system facilitates the rate of corrosion. The affinity of iron towards oxygen is very high and easily forms Fe_2O_3 or Fe_3O_4 which increases the rate of corrosion within the system. Furthermore, the boiler components are made of carbon steel and when it is associated with water under high velocity, it is prone to flow accelerated corrosion attack. The turbulent water-steam combination when in contact with carbon steel surfaces results in flow accelerated corrosion and leads to quick disintegration of the steel material through the falling off and spalling of iron particles in to the stream of flowing water (Carvalho, 2005).

The flue gas during the process of operation is allowed to enter boiler at very high temperature of about 1000°C and a pressure of 127 bar (Chen and Yeun, 2003), hence the corrosion rate is affected, for pressure plays a significant role at the rate corrosion takes place in the boiler, for increase in pressure allows molecules to collide frequently at a greater force and hence increasing the rate of reaction (Smith and De Waard, 2005). The corrosion rate becomes higher due to the effectiveness of the collisions coupled with the high partial pressure of oxygen and carbon dioxide in the system (Robinson, 1983). The presence of the combustible gases becomes more aggressive at high temperatures regardless of the chemical nature of the steel used in the construction of the boiler. These outlined challenges during operational processes results in the steel forming iron (III) oxide (Fe_2O_3) which is no more part of the steel and hence reduction of the mass of the tubes (Fontenelle et al., 2017), resulting in the thinning of the furnace internal wall tubes of the refinery boiler.

Minimizing internal corrosion in the furnace internal wall tubes by corrosion inhibitors

The addition of corrosion inhibitors provided a mechanism that reduced the rate of degradation of the furnace internal wall tubes of the refinery boiler. The corrosion inhibitors in the boiler affected the chemical composition of the feedwater by changing the fluid environment, thus enabling the reduction in the rate of thinning of the walls of the tubes (Edori et al., 2020).

The deterioration of the walls in the presence of corrosion inhibitors compared to the deterioration in the absence of corrosion inhibitors revealed that the corrosion inhibitors reduced in the presence of the corrosion inhibitors. The corrosion inhibitors prevented electrochemical reactions from taking place by covering the surface of the wall tubes by adsorbing into the carbon steel walls by the growth of protective films occasioned by corrosion inhibitors (Edori et al., 2014). Corrosion inhibitors in the process helped to protect the boiler and increased the useful life of the wall tubes in the furnace internal walls as seen from Figures 1-5. The metals gained revealed that the thinning of the walls of the tubes was drastically reduced since lesser quantities of metals were lost to the environment during operation. The process of oxidation and reduction was drastically affected due to the application of corrosion inhibitors (Singh et al., 2018). The corrosion inhibitors neutralized the effect of the corrosive agents in the system and prevented and lessened corrosion that will be detrimental (Groysman, 2017) to the furnace internal wall tubes' surfaces. The corrosion inhibitors neutralized the H^+ ions that were generated by the dissolution of CO_2 and other corrosive agents in the boiler. The corrosion inhibitors hydrolyzed the corrosive agents and provided OH^- ions that brought about the neutralization reactions (Duister and Savelkoul, 2005; Boyette and Elliot, 1992).

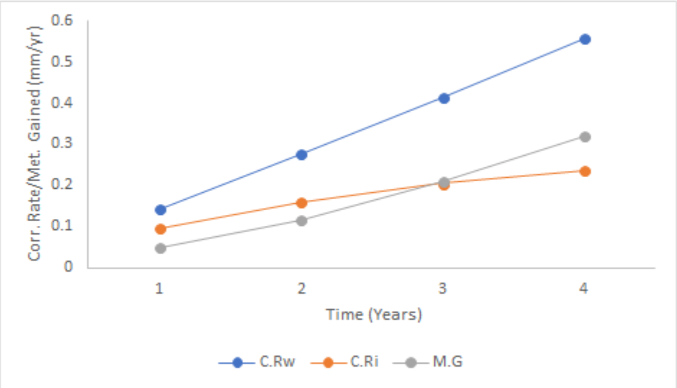

Fig-1: Corrosion rate and metal gained in absence and presence of corrosion inhibitors in the Front wall tubes

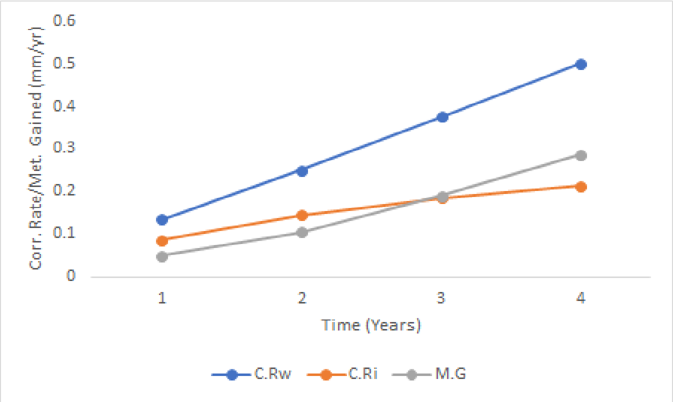

Fig-2: Corrosion rate and metal gained in the absence and presence of corrosion inhibitors in external wall tubes

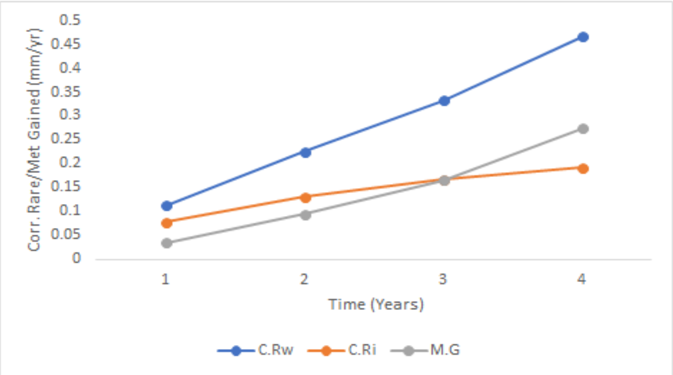

Fig-3: Corrosion rate and metal gained in the absence and presence of corrosion inhibitors in the internal wall tubes

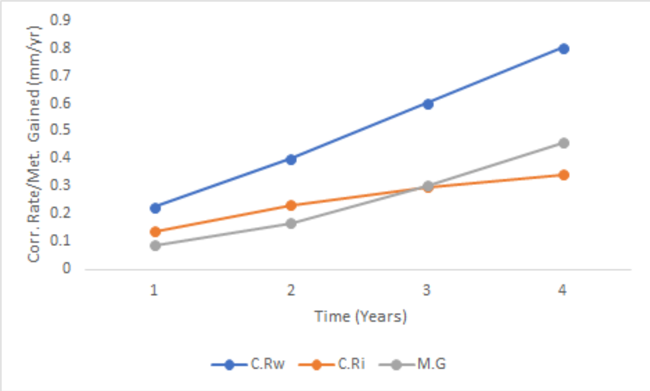

Fig-4: Corrosion rate and metal gained in the absence and presence of corrosion inhibitors in the internal tubes under refractory blocks

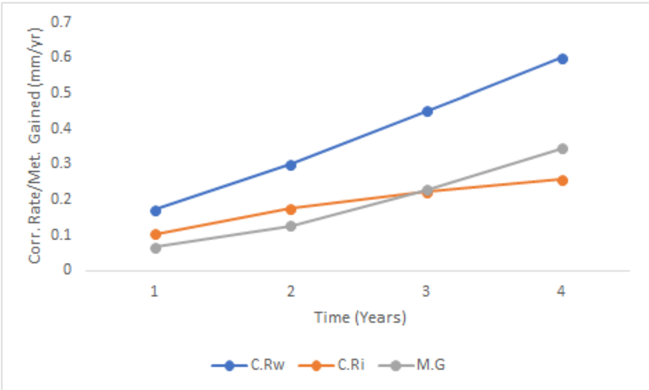

Fig-5: Corrosion rate and metal gained in the absence and presence of corrosion inhibitors in the external tube under refractory blocks

Efficiency of corrosion inhibitors in reducing corrosion in the furnace internal wall tubes

The efficiency of corrosion inhibitors in the furnace internal wall tubes of the refinery boiler are shown in Figure 6. The efficacy with which the corrosion inhibitors reduced the corrosion of the furnace internal wall tubes lie within 33.68% in the 1st year to 57. 75% in the 4th year in the front wall tubes, 36.30% in the 1st year to 57. 30% in the 4th year in the external wall tubes, 31.11% in the 1st year to 58. 71% in the 4th year in the internal wall tubes, 38.89% in the 1st year to 57. 31% in the 4th year in the internal tube under refractory blocks and 39.12% in the 1st year to 57. 33% in the 4th year in the external tube under refractory blocks. The results from Figure 6 revealed that corrosion inhibitors in the boiler becomes more effective in the system as the years progressed in the different locations of the furnace internal wall tubes. The recorded values of efficiency of the corrosion inhibitors with the wall tubes of the furnace internal walls revealed that the inhibitors within the system checkmated the corrosion rate to an appreciable extent.

The inhibitors' effectiveness within the boiler (furnace internal wall) possibly formed multiple bonds due to the possession of heteroatoms like Sulphur, nitrogen and oxygen. These complex molecules formed adsorbed on the surface of the tubes and prevents corrosion attack (Karthikeyan, 2016). These complex chemicals (corrosion inhibitors) created a barrier between the metal walls and the boiler fluid through desorption process, thereby lowering the rate of dissolution of the surface of the wall tubes in contact with the running fluid (Edori et al., 2020). The formation of a multilayer that covered the surface of the tube walls due to the physical adsorption of the inhibitors to the metal surface led to the formation of film layers that prevented attack from corroding agents in the system (James and Oforka, 2014). The increase in efficiency with time (years) may be as a result of corrosion inhibitors being adsorbed progressively onto the surfaces of the furnace internal wall tubes and reduced the corrosion rate of the tubes and also reduced the reactivity of the corrosive species through chemical reactions and thereby forming coatings on the wall tubes surfaces (Aljbour, 2016). The efficiency of the corrosion inhibitors was achieved through chemisorption and physisorption processes whereby multilayers were formed to give a protective coverage (James et al., 2007) on the surface of the furnace internal wall tubes of the refinery boiler through film formation which blocks the corrosive species from attacking the steel surfaces despite the turbulent flow in the boiler.

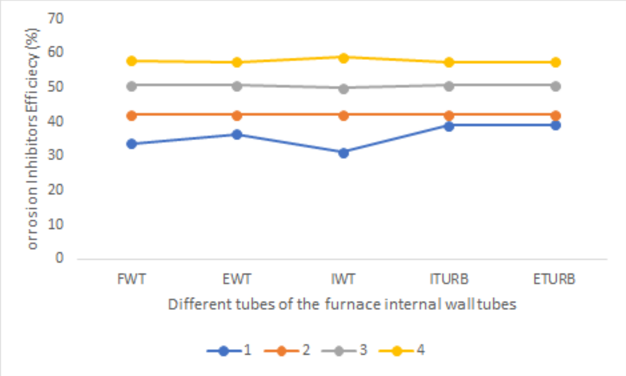

Fig-6: Efficiency of corrosion inhibitors in the different tubes of furnace internal wall tubes

Key: FWT (front wall tubes), EWT (external wall tubes), IWT (internal wall tubes), ITURB (internal tube under refractory blocks), ETURB (external tube under refractory blocks)

CONCLUSION

The reduction in thickness of the location tubes of the furnace internal wall tubes of the refinery boiler were as a result of corrosion that affected the system. The nature of the fluid, the turbulent flow, high pressure, high temperature, heat transfer surface and the material of construction of the boiler were major factors that enhanced the corrosion process. There should therefore be the need to effectively manage and maintain the boiler and its different compartments to ensure it operates under high level energy efficiency to avoid uncertain failure that may lead to increase in energy usage. Corrosion monitoring of the components of the boiler should be enhanced and improved during operation and management of the boiler. The addition of corrosion inhibitors into the boiler at properly calculated doses is very important in elongating the boiler life as was observed in the work. The refinery boiler should therefore be monitored and managed in a proper manner in order to forestall any unprepared failure of the wall tubes occasioned by corrosion leading to process shutdown in the refinery.

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