American Journal of Engineering Research (AJER)
e-ISSN : 2320-0847 p-ISSN : 2320-0936
Volume-03, Issue-05, pp-329-334
www.ajer.org

Research Paper Open Access

Mathematical Model for Predicting Corrosion Rates in Furnace Internal Wall Tubes of The Refinery Boiler

Edori, E. S[1]; Edori O. S[2]; Igwe, P. U.[3]

1. Community Secondary School Akinima, Ahoada West, Rivers State, Nigeria.
2. Department of Chemistry, Ignatius Ajuru University of Education, PMB 5047 Rumuolumeni, Port Harcourt, Nigeria.
3. HSE Department, ALCON, Nigeria Limited, Plot 17 Trans-Amadi Industrial Layout, P. O. box 4616 Port Harcourt, Rivers State, Nigeria.

Abstact: - A model for predicting the corrosion rates in the furnace internal wall tubes of the refinery boiler was resolved, using the first order differential equation derived from the material balance equation of the system. The mathematical model was able to predict the metal loss recorded by ultrasonic thickness scanning technique (UTS), and the results shows an agreement. The results from both the model and UTS shows that in the various tubes of the furnace, internal wall of the refinery boiler were between the same range. The percentage deviation which was calculated to ascertain the acceptability of the model result as compared to that from UTS proved that the model is effective. The inhibitor model result show that corrosion will drastically reduce in the presence of corrosion inhibitors under proper chemical treatment and management. The model developed can be used to monitor furnace internal wall corrosion even when the system is in operation by extrapolating the result to further years.

***Keywords**: - Furnace internal wall, metal loss, prediction of corrosion rates, first order differential equation, material balance, ultrasonic thickness scanning technique.*

I. INTRODUCTION

The boiler is an important equipment in the Engineering process unit in the generation of steam for their turbines, so it needs to be prevented from corrosion attack in order to minimize corrosion rate. Corrosion attack in the boiler compartments may be external or internal. Internal corrosion is caused by fluids being transported, stored or processed while External attack is caused by the corrosive species in the ambient environment. As a result of these attacks effects of corrosion must be incorporated into components remaining life assessment and aging management programs of the boiler life (Koch and Jaske, 1991; Shah and Macdonald, 1993).

The furnace wall is a compartment in the refinery boiler hence the various tubes in the furnace box are subjected to severe corrosion attack as a result of the high temperature experienced in the internal wall tubes. According to Farrell and Robins (2002), Furnace wall corrosion is a problem with long history and that boiler wall tubes can suffer considerable corrosion when exposed to the boilers harsh internal environment. Lees and White head (1983) found out that under highly reducing conditions corrosion rates may increase to values as high as 9mm/yr.

The corrosion of metals exposed to high-temperature gaseous environment as in the case of the furnace internal wall, frequently in the presence of deposits, has long been a problem in industrial process plants and furnaces (Halstead, 1970), and furnace wall corrosion is generally considered to result from low excess oxygen level leading to high concentrations of carbon monoxide around furnace tubes (Davis et al 1997).

Hence it is necessary to monitor corrosion in the furnace internal wall in order to minimize boiler shut down and also to improve the efficiency of a boiler without causing undue corrosion on the furnace wall, and since low corrosion rate may be acceptable as long as the tubes lost between shut down and boiler outages.

The boiler operating conditions are important variables when considering the role they play in corrosion of the fireside walls of the boiler. The boiler chemistry also plays significant part in fireside corrosion and must be considered in the internal corrosion of the boiler, since corrosion contributes to deposits and also results in metal damage. Management of corrosion in high temperature gases includes prediction of sound metal losses for a range of conditions (John *et al* 2000). In predicting corrosion rates in the boiler (Furnace internal wall), the problem of agreement is generating the high temperature corrosion data to ascertain the lifetime of the equipment and the combinations of alloys in the boiler and the ambient corrosion environment is there to contend with.

This paper seeks to describe a mathematical model that predicts the corrosion rates of the various locations of the tubes of the refinery boiler, measured by Ultrasonic Thickness Scanning Technique (UTS) of the tubes. First order differential equation will be used in interpreting the rates through a material balanced equation developed for the boiler compartment. It will seek to see correlation between the model results and that from the ultrasonic thickness scanning technique.

II. MATHEMATICAL MODEL DEVELOPMENT

In developing the mathematical model used in this paper, a material balanced equation of the boiler is used. The mathematical model is based on first order differential equation. The material balance equation is given as:

Corrosion Rate = Rate of inflow of material into the system + Rate of generation of chemical reaction within the system. - Rate of consumption of corrosion inhibitors - Rate of outflow of materials from the system ----(1)

Mathematically represented as

$$\frac{dC_R}{dt} = F_{S0} + G_S - C_s - F_S \text{ ------------------------ } (2)$$

Where

C_R = Corrosion rate of the system (mm/yr)
F_{S0} = Rate of inflow into the system (m3/s)
G_S = Rate of generation of chemical reaction within the system (m3/s)
C_s = Rate of consumption of corrosion inhibitors (Mol.dm3/s)
F_S = Rate of outflow from the system (Mol/dm3/s)
dt = change in time (years)

But rate of inflow into the system is equal to rate of outflow
$F_{So} = F_s$ therefore $F_{S0} = F_S = 0$
Hence

$$\frac{dC_R}{dt} = G_S - C_s \text{ ------------------------------ } (3)$$

But Gs = $K_c C_R$ and $C_S = C_R - C_{Ro}$ hence

$$\frac{dC_R}{dt} = C_s - C_{R0} + K_C C_R \text{ --------------------------- } (4)$$

When we assume no consumption of corrosion inhibitors
$C_R - C_{R0}$ = o, therefore $C_R = C_{R0}$
Then equation (4) now becomes

$$\frac{dC_R}{dt} = K_c C_R \text{ ------------------------------------ } (5)$$

Separating the variables in equation (5) yields

$$\frac{dC_R}{C_R} = K_C dt \text{------------------------------------}(6)$$

Integrating both sides of equation (6) and taking the limits from θ to t yields

$$In \frac{C_R}{C_{R0}} = K_C t \text{------------------------------------}(7)$$

Taking exponential on both sides of equation (7) gives

$$C_R = C_{RO} \ell^{kcT} \text{------------------------------------}(8)$$

C_{R0} = initial corrosion rate (corrosion rate of the first year)
Equation (8) will predict the corrosion rates of the furnace wall tubes of the refinery boiler at any given time as compared to the ones measured by the ultrasonic thickness scanning technique.
The system uses inhibitors; hence the effect of corrosion inhibitors will be solved by modifying $K_{c,}$ (corrosion rate constant) by introduction of an adsorption isotherm equation.

$$1 - \theta = \frac{1}{1 + K_{inh} C_{inh}} \text{------------------------------}(9)$$

Which is a modification of langmuir type adsorption isotherm
Where
K_{inh} = Adsorption constant for the combined effect of the corrosion inhibitors
C_{inh} = concentrations of the inhibitors
θ = degree of inhibitor coverage/protection.
From equation (9)

$$(1-\theta)(1+K_{inh}C_{inh}) = 1 \text{ ---}(10)$$

$$\therefore K_{inh} = \frac{C_{inh}\,\theta}{1-\theta} \text{-------------------------------}(11)$$

Putting equation (11) into equation (8) yields

$$C_R = C_{R0}\ \ell \left[\frac{C_{inh}\,\theta}{1-\theta}\ t\right] \text{----------------------------}(12)$$

Equation (12) predicts corrosion rates in the presence of inhibitors, to see how addition of inhibitors affects the corrosion rates of the furnace internal walls.

III. DETERMINATION OF CORROSION RATE CONSTANT ($_{KC}$) AND PERCENTAGE DEVIATION CALCULATION

Corrosion rates were measured by the ultrasonic thickness scanning technique for a period of four years. A graph is drawn from each of the various tubes in furnace internal wall and a slope is got from the graph. The slope is plotted mathematically as C_{R2} - C_{R1}/t_2-t_1 to give the curve of the graph. Where C_{R2} and C_{R1} are final and initial corrosion rates and t_1 and t_2 are final and initial time in years. The corrosion rate is then calculated to see if it agrees with the one measured by ultrasonic thickness scanning.
The percentage deviation of the results was then calculated from the formula % deviation = $\frac{Model\ data - UTS\ data}{UTS\ data} x\,100$, to show if there is any correlation between the results obtained from the ultrasonic thickness scanning technique and that from the model equation.

IV. RESULTS

The results shown in the table below were obtained from ultrasonic thickness scanning (UTS) measurement of the furnace internal wall tubes of the refinery boiler, the model equation and the inhibitor model equation developed from the first order differential equation for the boiler system, and also a percentage deviation equation.

In the front wall tubes, corrosion rates (metal loss) measured by UTS technique ranged from 0.1mm to 0.185mm in the first year and increased to 0.4mm to 0.71mm in the fourth years. This shows that metal loss ranged from between 0.1mm to 0.186mm on yearly bases from the UTS records. The model equation recorded metal loss of 0.11mm to 0.2mm in the first and it increased to 0.35mm to 0.67mm in the fourth year. Thus about 0.1mm to 0.12mm metal was lost on yearly bases according to the model. The percentage deviation calculated decreased from 13.51% in the first year to -5.63% in the fourth year. The inhibitor model equation showed great reduction in the metal loss ranging from 0.069mm to 0.12mm in the first year, and metal loss recorded in the fourth year is between 0.17mm to 0.299mm metal loss (Table 1)..

Table 1: Corrosion rate for the front wall tubes of the furnace internal wall tube of the refinery boiler.

Year	Rate from UTS (mm/yr)	Rate from Model (mm/yr)	% Deviation	Rate from inhibitor model (mm/yr)
1	0.10-0.185	0.11 – 0.21	13.51	0.069 – 0.120
2	0.20-0.35	0.12 – 0.31	-11.43	0.116 – 0.203
3	0.30-0.528	0.23 – 0.48	-8.75	0.148 – 0.26
4	0.40-0.71	0.35 – 0.67	-5.63	0.17 – 0.299

In the internal wall tubes, metal loss from the first year as recorded by UTS is between 0.075mm to 0.15mm and it increased to between 0.32mm to 0.61mm in the fourth year, which shows that about 0.075mm to o.15mm metal was lost in every year in the model equation 0.01mm to 0.17mm metal loss was recorded in the first year, and the loss of metal in this tube increased to between 0.23mm to 0.57mm in the fourth year. The inhibitor model equation recorded about 0.052mm to 0.103mm metal was lost in the first year (initial year) and increased to between 0.128mm to 0.256mm. The percentage deviation calculated for the UTS and model is 13.33% in the first year and decreased to – 6.66% (Table 2).

Table 2: Corrosion rate for the internal wall tubes of the furnace internal wall tube of the refinery boiler.

Year	Rate from UTS (mm/yr)	Rate from Model (mm/yr)	% Deviation	Rate from inhibitor model (mm/yr)
1	0.075 – 0.15	0.081 – 0.17	13.33	0.052 – 0.103
2	0.15 – 0.30	0.087 – 0.28	-6.67	0.087 – 0.174
3	0.225 -0.44	0.094 – 0.39	-11.36	0.111 – 0.223
4	0.32 – 0.61	0.23 – 0.57	-6.66	0.128 -0.256

Considering the External wall tubes, 0.075mm to 0.195mm of metal was lost to corrosion in the first year as recorded by the UTS technique, while in the fourth year, loss of metal increased to between 0.30mm to 0.7mm. This showed that a gradual loss of metal was taken place yearly of about 0.075mm to 0.155mm as a result of the operation of the boiler. The model equation recorded that about 0.081mm to o.21mm metal were lost which showed a percentage deviation of 7.69%, while in the fourth year metal loss recorded in the model equation is between 0.26mm to 0.65mm to 0.65mm and a percentage deviation of -7.14% from the UTS record. The inhibitor model equation showed metal loss of about 0.069mm to 0.12mm in the first year and it increased to between 0.128mm to 0.299mm in the fourth year (Table 3).

Table 3: Corrosion rate for the external wall tubes of the furnace internal wall tube of the refinery boiler.

Year	Rate from UTS (mm/yr)	Rate from Model (mm/yr)	% Deviation	Rate from inhibitor model (mm/yr)
1	0.075-0.195	0.081 – 0.21	7.69	0.052 – 0.120
2	0.15 – 0.35	0.087 – 0.36	2.86	0.087 -0.203
3	0.225 – 0.525	0.094 – 0.49	-6.67	0.111 – 0.26
4	0.30 – 0.7	0.26 – 0.65	-7.14	0.128 – 0.299

In the internal tube under Refractive Blocks, first year metal loss recorded as between o.125mm to 0.325mm by the UTS Technique, while that lost in the fourth year ranged between 0.50mm to 1.10mm. This showed that between 0.125mm to 0.225mm was lost as a result of the system operation yearly. The model equation results showed that about 0.14mm to 0.36mm of metal was lost in the first year with a percentage deviation of 10.79% from the UTS measurements. In the fourth year the percentage deviation became – 10%. The inhibitor model equation results showed 0.086mm to 0.189mm metal loss from the first year and 0.214mm to 0.469mm in the fourth, year which shows a great reduction from the results of the metal loss recorded by the UTS technique and that from the model equation (Table 4).

Table 4: Corrosion rate for the internal tubes under refractory blocks of the furnace internal wall tube of the refinery boiler.

Year	Rate from UTS (mm/yr)	Rate from Model (mm/yr)	% Deviation	Rate from inhibitor model (mm/yr)
1	**0.125 – 0.325**	**0.14 – 0.36**	**10.79**	**0.086 – 0.189**
2	**0.25 – 0.55**	**0.18 – 0.50**	**-9.10**	**0.145 – 0.319**
3	**0.375 – 0.825**	**0.28 – 0.73**	**-11.52**	**0.186 – 0.408**
4	**0.50 – 1.10**	**0.42 – 0.99**	**-10**	**0.214 – 0.469**

In considering the metal loss recorded in the External tube under refractory blocks, it was observed that first year metal loss as a result of the system operation ranged between 0.075mm to 0.265mm and in the fourth year was between 0.30mm to 0.90mm. In observing through the second and third year it is observed that between 0.075mm to 0.185mm was lost on yearly bases. The model equation gave loss of metal between 0.081mm to 0.28mm in the first year which represents 5.7% deviation and 0.20mm to 0.85mm metal loss in the fourth year which has a percentage deviation of 5.56%. The inhibitor model equation showed that in the first year metal loss to the operation of the boiler system was between 0.052mm to 0.155mm and 0.18mm and 0.18mm to 0.384mm in the fourth year, this showed a great reduction in the corrosion rates as measured the UTS technique and the predictive model equation (Table 5).

Table 5: Corrosion rate for the external tubes under refractory blocks of the furnace internal wall tube of the refinery boiler.

Year	Rate from UTS (mm/yr)	Rate from Model (mm/yr)	% Deviation	Rate from inhibitor model (mm/yr)
1	**0.075 – 0.265**	**0.081 – 0.28**	**5.7**	**0.052 – 0.155**
2	**0.15 – 0.45**	**0.087 – 0.43**	**-4.44**	**0.087 – 0.261**
3	**0.226 – 0.675**	**0.194– 0.592**	**-12.30**	**0.163 – 0.334**
4	**0.30 – 0.90**	**0.20 -0.85**	**-5.56**	**0.18 – 0.384**

V. DISCUSSION

Information on corrosion activity of the furnace internal wall tubes of the refinery boiler will help clear uncertainties in the various tubes in this particular comportment or component of the boiler. A model that will help to evaluate the corrosion activities is required to actually know the amount of metal loss as a result of the operation of the system. According to (Pellegrinetti and Bentsman, 1996) that one of the most effective means of boiler efficiency enhancement is an improvement of the steam generation control system and that an essential tool for such an improvement is a valid boiler model which will be used in predicting remaining wall thickness and the actual metal lost to the system operation. This will help in changing the boiler chemical treatment operation to ascertain longer span of the furnace internal wall and other boiler compartments.

In developing a mathematical corrosion model such as this, the reliability to predict the corrosion rates of the wall is the required goal. Hence the model equation in equation (8) was able to predict metal loss very closely to that recorded by the ultrasonic thickness Scanning (UTS) Technique used in measuring the metal loss of the furnace internal wall in particular and the boiler in general. Since the model could predict closely to that recorded by the recorded by the ultrasonic Thickness Scanning Technique, it can be subsequently used for simulating or forecasting of the remaining wall thickness/metal loss in the furnace internal wall tube in particular and the boiler in general, which will help in identifying the particular time when a particular tube will rupture in the future.

As noted by (Farrel, *et al* 2000), that furnace wall corrosion is a problem with long history and is an issue of on going concern for many boiler operators, there is the need to minimize these problems by providing a model that will help plant personnel to have futuristic overview of the amount of metals that will be lost from the system as a result of the chemical program initiated for the equipment. It will also help in monitoring or inspecting the internal boiler system without boiler downtown or outage.

Human experts can be distracted or rushed and led to incorrect or inconsistent deductions, (Jaffer *et al*, 2003), hence the predictive model will help the expert from being rushed into incorrect and inconsistent deductions, since he has to confirm from the generated values of the model equation, since these values of losses can be shown many years ahead. The model equation develop can also be used to predict corrosion rates in the boiler in general. From the data obtained a reasonable correlation between the Ultrasonic Thickness Scanning Technique and the mathematical model can be established, which can then be used to predict future occurrences as regards metal loss in the boiler system if the operating conditions of the equipment remains the same.

In conclusion, the model have shown the ability to provide information which could have been only been obtained during boiler outage or downtown. The model will assist plant personnel in knowing the time furnace wall tubes could be replaced in advance. It also helps in having increased confidence in understanding how corrosion activity can be for extended periods of boiler maintenance and operation and improving in the chemical program of the boiler.

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