Algorithmic Models On Chemo-Statistics Corrosion Rate Data of a Nitrogenous Fertilizer Plant, South-South Niger Delta.

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ABSTRACT

Corrosion rate trend of the High-Pressure Carbamate Condenser, in a Nitrogenous Fertilizer plant was simulated from an existing Field Data Initially in Place (FDIIP), using the sequence algorithm to establish the corrosion pathways and failure analysis in the plant. The tube material is made up of: A213M16L: X2CrN M017132 urea grade (BC.01), (Ike et al, 2021). The tube dimensions: OD20, 12163mm. The tube number: 2353 with a minimum overlay thickness of 8mm and 5mm liner material. This study further highlights chemical process plat corrosion statistics (Chemo-statistics) in the tubular High Temperature, High Pressure (HTHP) equipment over a period of ten active production year where the temperature of the liquids ranges from 183-195oC. Carbon dioxide gas while the pressure of the system is kept at about 163kgf/cm2 after the ammonia flow has been discharged. The data sets were carried out as part of the preliminary field investigation on the plat and is useful for planning and good decision-making. The simulation was done using computer program in Visual Basic with two major assumptions on Percentage counting process (pica) and Random counting process (Racop). These results obtained quite contradict field report of the technical partner which indicated that corrosion rate was within the maximum tolerable limit value. The total Td accounted for 15% of the population predicting CR at tp =1.8years above MTLV (O.064mpy). These are responsible for the rapid drop in tensile properties of the tubes and hence increase CR along Td $\leq 2.40mm$*. Also, increased CR directly increased the heavy metal and chloride ion (Cl-) concentrations in process waters which enhanced pressure drop in the tubes due to severe leakages. This work is useful for good decision making and for forecasting in oil and gas chemical corrosion data statistics for strategic administration.*

Keywords: *Nitrogenous Fertilizer, Corrosion Rate Data, Algorithmic Models, Chemo-statistics.*

1.0: INTRODUCTION:

The rate of failure of the High-Pressure Carbamate Condenser (H.P.C.C). tubes in the Nitrogenous Fertilizer Plant located in the lower Niger Delta, and the frequent plant shutdown up to the point of abandonment triggered this research. It is a simulation method aimed at determining the actual corrosion rate in the equipment at the point of abandonment, with reference to the experimental data from STAMICABON, (Neeka, 2012). Obviously, corrosion failure analysis is dependent on the nature and quality of data available. Such data could be generated through experiment, correlated from past experiment, or simulated based on prevailing conditions and assumptions. Sometimes, time factor and cost implication in acquiring data call for economic consideration in corrosion analysis. This research has been carried out in three phases of complex mathematical analysis. Each phase reflects a comparative approach between the test data of STAMICABON and the simulated data obtained. In the first phase a time response study of an NDT test data generated on the high-pressure tubes were carried out, and the simulated data obtained through an incremental random sampling at each time interval corresponding to the period of test equally done. The analysis of both data was through a mathematical model equation describing weight loss in the tubes. The second phase is based on the use of statistical tools such as test of hypothesis, regression, and correlation coefficient to test the significance in value between the two data sets. The third phase involves the introduction of the concept of cost to corrosion failure analysis. Of more importance here is the use of the equation on time value of money in predicting the actual corrosion rate at the point of abandonment. Economics in general and cost are of importance to the corrosion engineer especially in decision making. Hence it has been treated universally so that corrosion is basically an economic problem and the duty of the corrosion engineer in achieving optimum production through smooth operation is to minimize cost. The entire work was done using computer software in Visual Basic developed for fast, detailed, and easy analysis of the data. Certain fundamental assumptions have been made to help in the analysis as well as provide directions in this study. However, the choice of the right approach to corrosion forecast from a variety of possible options requires the right statistical tools, economic factors as well as understanding the actual technology in data generation. This is because data acquisition on fertilizer production in Nigeria is difficult as the industry is not many in the country. Again, certain raw materials used in fertilizer manufacturing process are highly corrosive. Therefore, materials selection, design, construction, and maintenance operations require the expertise of experienced corrosion engineer whose services may not be readily available. In the face of the foregoing, there is the need to evolve a more realistic and practicable approach toward solving corrosion problems. That approach is the simulation method adopted in this work leveraging on statistics and computing skills in the absence of adequate and relevant tools for an in-situ measurement. The overall goal is to enable the corrosion engineer proffer acceptable solutions for decision-making to forestall damages on equipment and personnel. Hence, statistical approach to corrosion failure has been useful and necessary in this work as a basis for the analysis, discussions, and conclusions on test data from the NDT experiments and simulations.

1.1 Purpose of developing corrosion rate algorithm.

It has become apparent by events of the past decades that most High-Pressure Carbamate Condensers (HPCC) used for the manufacture of nitrogenous fertilizer fail randomly because of corrosion related problems. This is contrary to general engineering ethics of minimizing cost and maximizing profit by producing at an effective and efficient way under safe condition. Therefore, the purpose of this paper includes analyze experimental data based on known mathematical principles; Simulate test data to obtain better results and use the mathematical Algorithmic models to carry out trend analysis to forecast probable conditions of the equipment in the future which will serve to proffer durable practicable solutions for good decision making in fertilizer industries. This research exposes the high level of uncertainty in the Corrosion Failure Trends (CFT) in HPCC and seeks for more satisfactory solutions to the need of the plant and to establish that more reliable results could be obtained from simulation of the test data, which would enable us, predict reliably the expected corrosion outcome in the future. To give valuable practicable recommendations on possible control or preventive measures that could reduce the rate of corrosion attacks on the plant.

1.2 Importance of mathematical algorithm in analytical Work

During equipment failure and down time resulting from corrosion related problems, engineers are face enormous challenges with little or no reference point for current information. Besides, the hope of increase food production calls for the sitting of more fertilizer plant, which as usual most corrode with time. Hence, there must be possible solutions to the corrosion catastrophe in

the industry. This work should therefore be of importance in the following ways: It will add to or provide an entirely new knowledge in statistical modeling to both engineers and industrial scientists. It will help proffer solutions to the problem of frequent equipment failure and downtime thereby saving cost and improving the revenue base of the company. It will also serve as a reference point for further research in statistical data analysis on corrosion failure problems in a nitrogenous fertilizer plant, (Jacob et al; 2006). The high-pressure equipment in urea manufacturing process is a loop for which there exists an interrelated and interdependent reaction. However, for the purposed of this research paper, the H.P.C.C. was isolated for study for which the reaction and chemical activities of the plant are assumed to be at point zero. Besides, the operating conditions of temperature, pressure and chloride ion concentration in-situ remain zero. The effect of microbiologically induced corrosion in process plant corrosion initiation and propagation is considered a limiting factor. It is estimated that this research might contribute significantly to existing problems on the H.P.C.C tubes and that further high-definition simulation in 3D analysis will be needed in the future.

2.0: LITERATURE REVIEW

There are so much to study about the different forms of corrosion in the chemical industry, the nature and purity of feed components that constitute elemental units in fertilizer manufacturing process. More so, the selection of material, design, fabrication, installation, and operations of equipment in the complex fertilizer plant leaves more to be studies than can be imagined.

However, this work is limited to the study of the principle and mechanism of stress corrosion cracking in high pressure equipment, intergranular corrosion, selective attack, and embrittlement as it relates to the high-pressure carbamate condenser.

The nature and purity of the feed stock (starting elemental units) and the operation of the high-pressure equipment are also studied.

According to Malone, et al (1986) raw materials for the process operation are basically from two sources:

(a.): The natural gas containing the methane (CH_4) 90.68 mole percent, ethane (C_2H_6) 4.53 mole percent, propane (C_3H_8) 2.2 mole percent, C_6 and above 1.54 mole percent, Nitrogen (N_2), 0.50 mole percent, carbon dioxide (CO_2) 0.55 mole percent are preheated to an elevated temperature and pressure to separate each constituent easily and to maintain the minimal inlet temperature and pressure of the feed. (b): Air from the atmosphere containing nitrogen (N_2) 78.09 mole percent, carbon dioxide $(CO_2)0.03$ mole percent, oxygen $(O_2)20.95$ mole percent, argon $(Ar)0.93$ mole percent, Inert 0.003 mole percent are obtained by the liquefied gas processes (as a result of differences in the boiling points and densities) in the air separation unit of the ammonia plant. It involves cooling below critical temperature, compression, condensation, and expansion. Depending on the source of supply of the natural gas, some unknown volume of sulphur compound is contained in it. Sulphur compounds need to be removed from the feed because it is dangerous to the catalyst bed. It can easily form acid (H_2SO_4), which is highly corrosive to the plant.

2.2 Historical Background of the H.P.C.C.

The high-pressure carbamate condenser is a vertical cylindrical tubular heat exchanger (Tom and Boyd, 1987). The shell side is saturated with boiler feed water at low temperature and pressure. The heat of condensation of ammonia and carbon dioxide in the tube side can generate 3.5kg/cm^2 steam in the steam drum. Any pressure difference in the steam drum alter the temperature of the boiler feed water and thus the temperature difference between the shell and tubes sides in the H.P.C.C. The H.P.C.C. is of two types: Type I was manufactured by Kobe steel ltd Japan in 1985. The tube material is made up of: A213M16L: X2CrN M017132 urea grade (BC.01), (Ike et al, 2021). The tube dimensions: OD20, 12163mm. The tube number: 2353 with a minimum overlay thickness of 8mm and 5mm liner material. The equipment was installed for use in September 1987 and finally abandoned due to leakage in the tube in January 1997. It has 779 (33%) plugged tubes at the point of abandonment. Type 2 was manufactured by Foster Wheeler F. John Brown Boilers, Austria in 1972. The tube materials are made up of: X2CrNiMo17132 urea grade (BC.01). The tube dimensions: OD25 X ID20, 12000mm. The tube number: 1870 with 89 tubes plugged as at the time of installation in NAFCON. Over laid thickness of 8mm and nominal thickness of 5mm liner materials. The type 2 H.P.C.C was installed for operation in 1975, abandoned at the IFFCO site in 1993, purchased by NAFCON and installed for use in 1997, and abandoned in NAFCON site in 2001 with a total of 153 plugged tubes. The H.P.C.C. operates in a loop with other high-pressure equipment such as the reactor, stripper, and scrubber. The conversions of ammonia and carbon dioxide into slurries of ammonium carbamate take place in this equipment. The slurry has molecular weight of 78 and a crystallization temperature of 153^{OC}. Both types of H.P.C.C. described above have specified design tube numbers which the corroded parts triggered this study. Hence, the technique of counting process of the tubes, the number of tubes counted and the cumulative effects of the count on the prediction of corrosion rate over the production capacity is examined. However, it is necessary to state that the work of counting at random increment at random moment has been carried out by experts and is in existence.

2.3 Fundamental Corrosion Chemistry

Corrosion processes occur mainly in the wet phase. The wet phase had been all the reaction in aqueous medium. Such reaction is the result of an electrochemical process of REDOX reaction to maintain electrical neutrality. In the process industry corrosion attack is dependent on so many factors such as: condition of thin air formed (oxide films) that exist on the dry metal. Such film induces a modest level of passivity making the surface noble and therefore cathodic to adjacent surface where less protective film may exist. differences in crystal orientation, the presence of contaminants on the surface of the metal and in exceptional case, the effect of stresses above the elastic limit of the metal, which cause rupture of the protective oxide film by plastic deformation. Variation in the dissolved oxygen concentration of a solution in different zones on the metal surface. The variation car give rise to what is called an oxygen concentration cell in which current will flow through from an anodic area in contact with the solution having the low concentration of dissolved oxygen to a cathodic area in contact with the solution having the high concentration. The difference in corrosion potential that can be created by this mechanism can be as high as 100Mega Volt (MV). Certain simplified equations of anodic and cathodic reactions on selected metals are as shown below:

Anodic reaction

$Na \longrightarrow Na+ + e$ ……………………………. 2.23

(Solid) (Ion) (Electron)

$Fe \longrightarrow Fe++ + 2e$ ……………………………... 2.24

(Solid) (Ion) (Electron)

$Al \longrightarrow AL+++ + 3e$ ……………………………… 2.25

(Solid) (Ion) (Electron)

On the other hand:

Cathodic reaction

$2H+ \longrightarrow + \; 2e- \longrightarrow H2$ ……………………………2.26

(Hydrogen ion) (Electron) (Gas)

$2H+ + 1/2\ 02 + 2e- \longrightarrow H_20$ …………………..........2.27

(Air)

$02 + 2H_20 + 4e \longrightarrow 40H$ ………………….……………..2.28

(Hydroxyl ion)

$Fe3+ + e- \longrightarrow Fe2+$ …………………………………. 2.29

(Ferric ion)

The essential requirements for the electron chemical reaction in corrosion therefore is: Thermodynamically unstable metal; and electrolytes (conductor of ions), an electron and an electrical conductor. The combination of these factors an electrical circuit.

2.4 Kinetics of Carbamate and Urea Formation

The high-pressure carbamate condenser (H.P.C.C.) alongside the reactor, stripper and scrubber form a loop, operating at the same pressure and varying temperature. The heat and over all reactions in the loop are determined by the physicochemical equilibrium constituted by ammonia, carbon dioxide, water, and urea thus:

$NH_3 + CO_2 \rightleftharpoons NH_4OCONH_2 \rightleftharpoons NH_2CONH_2 + H_2 0$ Liquid phase …….2.30

Gas phase

The phase behaviour of the components is largely determined by the behaviour of the binary mixture of ammonia and carbon-dioxide, the starting feed stock. According to Tom (1988), the heat of condensation released during ammonia and carbons – dioxide reactions directly affect the strength properties of the H.P.C.C. tubes and hence result in corrosion. The flow regime and the percentage volume of inert at the prevailing conditions of temperature and pressure also affect the yield strength of the tubes which initiated stress corrosion cracking. Hence, the need to established reaction kinetic pathways in the system to determine corrosion rates is necessary.

There is condensation between ammonia and carbon dioxide for carbamate to be formed.

$NH_3 + CO_2 \rightleftharpoons NH_4OCONH_2 \rightleftharpoons \Delta$ H –28.5kcal /mol…………… ..….2.31

The partial condensation reaction serves many useful chemical purposes such as the provision of heat of reaction for the complete reaction as well as maintaining the temperature and pressure of the system. The heat of reaction is provided by the fraction of the gas not condensed in the carbamate as the product leave the condenser into the reactor at a high system temperature and pressure. The semi liquid carbamate then flows from the condenser to the reactor. Each of the phases gives a level of condensation reactions that keep the reaction process to go into completion.

The liquid phase ammonium carbamate is converted into urea and water. The endothermic equilibrium reaction is a fractional conversion. The chemical and technological realization of the process is explained according to Michael (1987).

The carbamate is converted into urea in the reactor. The gas phase from the reactor is absorbed in the high-pressure scrubber in a weak carbamate solution from the recirculation stage. This solution is introduced into the high-pressure carbamate condenser through the high-pressure ejector. inert gases from the scrubber are vented into the atmosphere through the inert vent.

The ejector serves to control the flow volume into the condenser for maximum reaction while the inert vent helps to reduce the accumulation of unwanted gases capable of altering the normal reacting conditions of temperature and pressure to maintain efficiency. The non-converted ammonia and carbon dioxide in the urea solution from the stripper is led to the condenser and the liquid phase via the scrubber to the condenser is carried along the stripper to knock off ammonia, carbon dioxide and water vapour. The fresh ammonia with the carbamate solution from the scrubber and reactor is mixed in the ejector and sent to the condenser to further mix with the carbon dioxide gases from the stripper and are equally distributed through the tubes. The ammonia and carbon dioxide feeds to the synthesis are controlled in such a way that the NH3/C02 ratio in the gas outlet of the reactor ranges from 3.0 to 3.7.

This ratio is required for optimum urea formation. For an endothermic urea equilibrium reaction to take place, the heat evolved during the carbamate formation is needed as well as a certain residence time. The latter is obtained by applying sufficiently large reactor volume. To improve the contact between gas and liquid phase and to avoid back mixing, sieve trays are installed. In the first stage of the reactor, about 59% of the carbon dioxide is converted into urea. the reaction mixture formed in the reactor descends through the overflow line to the stripper. A liquid seal is formed in between the stripper and the reactor to ensure stable operation without a reverse flow of the gas mixture into the stripper. The reaction mixture entering the stripper and then to the carbamate condenser is distributed over a large quantity of tubes by means of a liquid divider between the gas tubes and the tube sheet. The temperature of the liquids ranges from 183-195^{o}C$^{\cdot}$ Carbon dioxide gas, passing in counter flow through the tubes causes the partial ammonia pressure to decrease, as a result of which carbamate can start to decompose, provided heat is supplied, (Peter and Hans, 2004).

Depending on the biruet analysis, different condensate levels can be maintained basically for formation of urea solution. During urea formation, biruet is formed as a bye product according to the equation:

$$2NH_2CONH_2 \rightleftharpoons NH_2CONH_2\,CONH_2 + NH_3 + \triangle H \ldots\ldots\ \ldots\ldots\ldots 2.32$$

This is a slow endothermic equilibrium reaction. The equation shows that biuret formation will take place when there is a high urea concentration, a low ammonia concentration and a high temperature. However, biuret is toxic to the plant and can also lead to corrosion. It implies that a combination of the factors above should be avoided as urea solution leaving the reactor contains about 0.3-0.4% biuret in relation to the total urea formed. As a result of the relatively low temperature of carbon dioxide feed, and of slight adiabatic expulsion, the temperature of the descending liquid film in the tubes drops from 195-183^{0}C. The liquid from the stripper, containing ammonia is discharged to the rectification section. The level in the stripper is always maintained low to avoid biuret formation and urea hydrolysis. The gas phase from the reactor containing non-converted ammonia and carbon dioxide as well as inert in discharged to the high-pressure scrubber where condensation of ammonia and carbon dioxide is effected. The heat of condensation is partly removed by circulating conditioned cooling water with a temperature of about 150^{0}C and partly used for heating the weak carbamate solution of about 900C discharged from the low-pressure carbamate condenser (H.P.C.C) by means of the high-pressure carbamate pumps.

The gas /liquid mixture rises through the heat exchanger tubes. In this way circulation is effected which improved the efficiency of the heat transfer. Here the bulk of the gases, with some ammonia and carbon dioxide, may be within the explosion limits. Care must be taken to avoid ignition source being present else the scrubber will rupture. As mentioned earlier, the carbamate solution from the scrubber overflow to the ejector via which it is transported by the liquid ammonia to the carbamate condenser. This also increases the liquid load and thus the efficiency of the condenser to ensure a constant flow to the ejector the suction line connected to the reactor. The pressure of the system is kept at about 163kgf/cm^{2} after the ammonia flow has been discharged. The conditioned cooling water for the scrubber is a closed circuit in which the bottom part of re-circulation heater and circulation water cooler to scrubber is incorporated.

The entire synthesis section is provided with drain circ△t connected with the flush water circuit to ensure proper flushing before, during and after operation.

2 $NH_3 + C0_2 \rightleftharpoons NH_4OCONH_2$----- -- △H= 28.5cal/mol. ……………………..2.33
the molar ration ammonia and carbon dioxide vary from 3.0 to 3.7 in extreme cases. The partial condensation of the feed gases results in the high-level conversion of ammonium carbamate into urea at a high temp. (183-190^{0}C) with the release of water.
$NH_4OCONH_2 \rightleftharpoons NH_2COH_2 + H_2O$ ----------△H= 3-6kcal /mol………… 2.34
For endothermic urea equilibrium:

It is strictly of advantage to note that the chemical reaction that led to urea formation beings in the H.P.C.C. with ammonia and carbon dioxide. Hence, the rate of urea formation and the mechanism can be summarized according to the following equations:

Rate of Urea formation = r1 = NH_40CONH_2 ……………………………………2.35

Rate of urea hydrolysis = r2 = $NH_2COH_2 + H_2O$ …………………………………2.36

Where, r1 and r2 represents the rate of urea formation and urea hydrolysis, respectively.

At equilibrium, r1 and r2 are equal and the net rate of urea formation is zero.

r1 , NH_4OCONH_2 - r2, $NH_2COH_2 + H_2O$ = O……………………………………..2.37
Hence,

$$\frac{NH_2COH_2 + H_2O}{NH_4OCONH_2} = \frac{r_1}{r_2} = r \text{...2.38}$$

The two-reaction rate constants increase with rise in temperature. Every 10^{0}C rise in temperature doubles the reaction rate. Besides, r1 shows a greater increase with temperature than r_2 and 10^{0C} increases the volume by 20%. High temperature means high final conversion and high rate (95%). At this temperature and pressure (up to 168kgf/cm^2 of the reactor, the high percentage volumetric inert constitute a resultant stress on the strength of the tube materials in the H.P.C.C. and the frequent leakage due to corrosion.

3.0: MATERIALS AND METHODS.

This project is a stochastic method of corrosion rate determination in the high-pressure carbamate condenser tubes at point of abandonment. It has been carried out in three phases, with each phase having reference to the experimental data contained in the report of STAMICABON. The fundamental principle governing the preliminary study involves a time-response study of an NDT test data generated from failed tubes in the (HPCC) through direct measurement by STAMICABON, has been carried out in three phases of complex analysis. The first phase involves a time-response study of an NDT test data generated on the high-pressure tubes by STAMICABON, and the use of analytical technique to establish the actual corrosion rate at point of abandonment. The principle depends on difference in weight in the tubes over a certain active production time, which by direct conversion can establish the rate of corrosion. An important feature in the NDT method is that the actual production period (year) must be known, which form the basis for the development of the algorithmic models.

3.1: Fundamental Algorithmic Processes on Chemo-statistics of Corrosion Rate:

The algorithms that explain the stepwise approach of the model equations for corrosion rate determination are presented in two stages as follows:

Algorithm for corrosion rate model

```
* *     Given minimum and maximum wall thickness of interest **
* *     Also given the product of the number of tubes measure **
* *      And wall thickness **
* *     To obtain the value of mean difference in weight loss (P) by dividing         the sum of
both ** Note that Number of pipes measured = N and the pipe thickness over time = h. Q is
the product of N and h.
* *     Q by N and subtracting it from maximum wall thickness h **
* *     The final value is divided by the active number of years **
START                   Get (N, h, Q, P); N = 2.8, 2.3, 1.8, 1.5, 1.5
    |                   Q =     N * h
    |                   P =     ΣQ/ΣN
    |                   Put (N * h) ** obtain value of **
    |                   Put (ΣQ/ΣN) ** obtain value of P **
    |           Obtain value of (ty) the number of active year of pipes **
    |                           Count = N
    |                           N ≠ K + 1
    |           While   Count = N
    |               |           Get (ty);
                    |               Do Unit
                    |           Count: = Count + Nmax
                    |               Then
                    |                   Get (CR)
                                Count: = Count = Nmax
                                    Put (All value of N);
```

```
                End
STOP      END   DATA
```

Algorithm For Evaluating Standard Deviation

```
        **Get the average corrosion rate**
        **Also get the deviation from average**
        **Subtract the average from deviation**
        **And square the value obtained**
        **The sum of average and divide by N**
        **The square root of the value obtain is **
        **The standard deviation computed**
START
    Get (CR,Nma,d); N: =5
        $a=(\sum CR)/N$
        $S^2: =(a-d)^2$
            Count = CR.
            Get (($\sum$ CR)/N** obtain value of a
            Get (a-d)2** obtain value of $S^2$
    While count = K + 1
        Do until
        Get $(a-d)^2/N$
            Then
            Get (S.d) **Square root of $S^2$ **
```

```
                        End
                    Data: a,d, $S^2$, S.d.
Stop        End
```

Algorithm for Evaluating One Tail Tests of Hypothesis

```
    ** Given the sum of the selected sample tubes for measurement **
    ** Also given an arbitrary population mean ( $\mu$ )**
    **And the number an arbitrary population ( $\mu$ ) **
    **To obtain the deviation $\sigma^2$ **
    **By taken the square of the difference between**
    **The sample mean and the population mean **
    **And divided through by N, taking square root **
    **The alternative hypothesis $H_0$ obtained by**
    **Subtracting the population mean from the sample mean**
    **And dividing by the half of the deviation**
    **The result is compared with the table data**

START
    Get $(\sigma^2, H_0, Na, \mu) N := 4; a := \overset{\approx}{a} / N.$
                    $\sigma^2 := \frac{1}{N}\sum_{i=1}^{N}(a-\mu)^2$
                H0: $(a^{\approx} - \mu)/(\sigma / \sqrt{\ })$
          Put $\frac{1}{N}\sum_{i=1}^{N}(a-\mu)^2$ **obtain value of $\sigma^2$ **
             Put $(\sqrt{\sigma^2})$** obtain value of $\sigma$ **
             Put (a/N) obtain value of $\tilde{a}$
```

```
        Put $(\tilde{a}-\mu)/\left(\sigma/\sqrt{N}\right)$** obtain value of $H_0$ **

    While count: = N
      |  Do until
      |
      | Count: =      count.
      |               Then
      |               Put (table data)
      |               Put ($H_0$)
      |               Ho > = table data.
      |                   End
    End

Stop
```

Table 1: Comparative Corrosion Rate of Linear Regression Scheme (Lr_{eg})mpy.

(t_p)years	**C_R (*Exp*) mpy**	**C_R (L_{reg}) mpy**
8.2	**0.033**	**0.034**
5.1	**0.040**	**0.050**
6.9	**0.052**	**0.064**
8.6	**0.054**	**0.070**
10.1	**0.058**	**0.080**

Where t_p is the active production period of pipes and x_1….x5 are corrosion rates corresponding to specify number of years (Table 1 and 2).

Table 2: Simulated Values of 20% Pica Experimental Data (Lr$_{eg}$)mpy.

(t_p)years	C_R (*Exp*) mpy	C_R (L_{reg}) mpy
9	2.50	22.5
48	2.45	117.6
105	2.40	252.0
45	2.35	105.8
207		497.9

Where t_p is the active production period of pipes and x_1….x5 are corrosion rates corresponding to specify number of years and Pica is the Percentage increase counting approach.

Table 3: Simulated Racop Values of Number of Tubes and Wall Thickness Measurement (Lr$_{eg}$)mpy.

(t_p)years	C_R (*Exp*) mpy	C_R (L_{reg}) mpy
7	2.50	17.50
40	2.45	98.00
87	2.40	208.80
37	2.35	86.95
171		411.25

Where t_p is the active production period of pipes and x_1….x5 are corrosion rates corresponding to specify number of years and Racop is the Random counting process.

4.0: RESULTS AND DISCUSSIONS.

Table.1 is the test data from STAMICARBON and Table.2 is the simulated data using the percentage counting approach on the test data for the same period (2.8yrs). Table.3 represent the simulated data using the random counting process with reference to the experimental data.

Table.1 and.3 maintained the same number of sampled tubes while Table.2 is 20% increase on the total number of tubes in table.1. It should be noted that 171 tubes represent about 7.3% of the total number of tubes (2353) in the H.P.C.C. tube bundle. The reason for allowing tables.1 and.3 to have the same sample size is to follow the pattern of the NDT data set. However, table.2 follow a gradual increase in the number of tubes with the least value at the maximum thickness (2.50mm), and a total sample size of 205 representing 8.7% of the number of tubes in the H.P.C.C. bundle. Increasing the pipeline inspections, adopting the right maintenance and operation control including temperature, pressure, gas flow rate and concentrations reduced the rate of corrosion and failure as shown in the application of Percentage counting approach (Pica), Random counting process (Racop) and linear regression methods to validate results in figure 1 also indicate steady rise in corrosion rates. These steps are further compared with the simple approach in corrosion rate determination using the weight loss method in appendix 1. This sample calculation presents determined corrosion rate values above tolerant limit using the weight loss method.

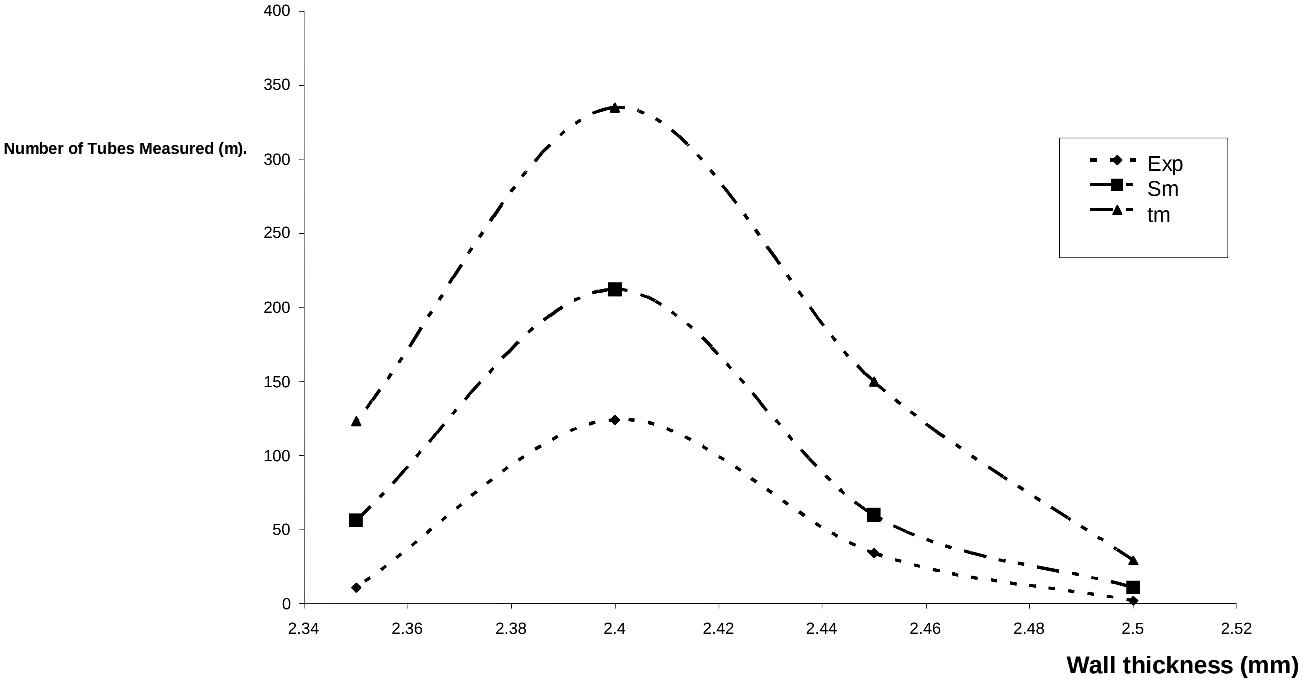

Fig 1. Comparative corrosion Vs. Time in controlled maintenance (mm) (1997).

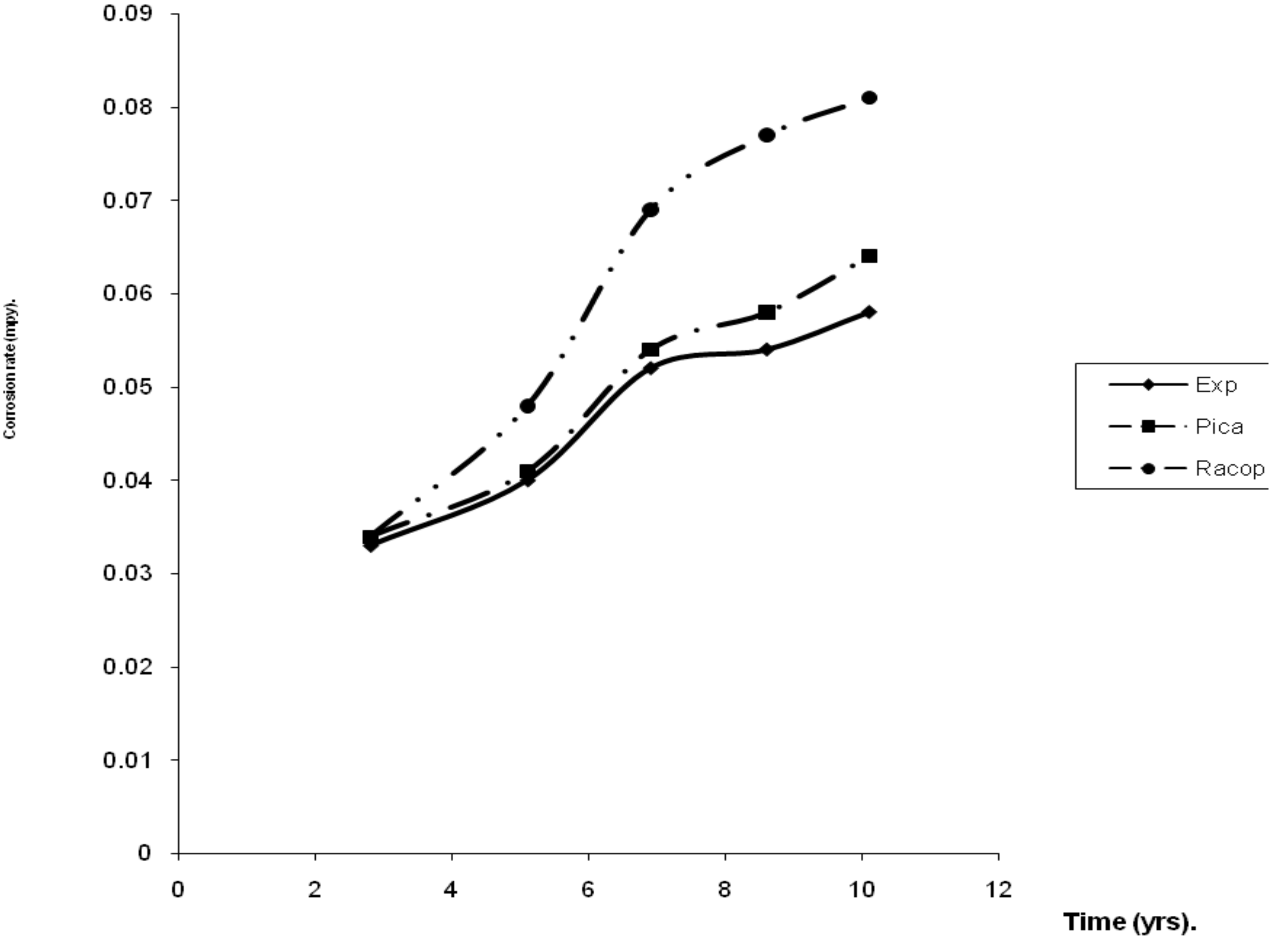

Fig 2: Comparative Corrosion Vs time graph showing Exp, Pica and Racop of LReg .

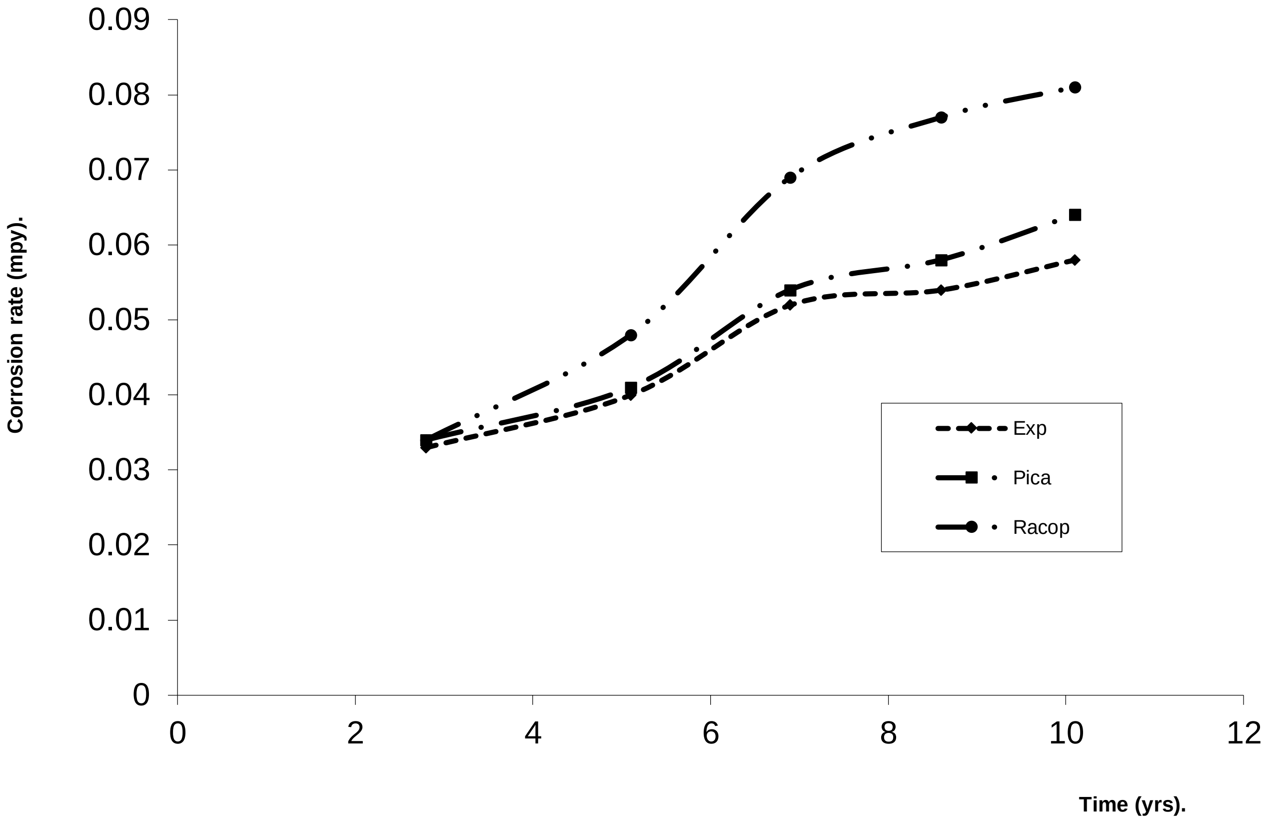

Fig 3:Comparative Corrosion VS time graph showing Exp, Pica and Racop.

4.1: **Discussions**

Figures 6.1-6.3 represent the distribution of the number of tubes sampled for analysis. Figure 6.1 shows normal tube distribution with sample size of 171 and the Peak of the curve correspond with TSP (2.40mm) at 96. The distribution curve skewed toward MaTT (2.50mm), 3 and shifted away from MiTT (2.35mm), 29 with a distribution of LSS to MaTT. Figure 6.2 is an improvement on 6.1 (40%) increased. Although the TSP tubes accounted for less than 30%, CR at the same tp was at MTLV (0.054mpy) when MaTT (5) and MiTT(41) are compared. The significance of the distribution pattern is that premium is given to TSP tubes, so that such tubes must have high sample size (hss) in the analysis to establish the actual corrosion rate. Note also that MaTT values need to be increases so that the service life of the equipment when Td is $\leq$ 30% could be determined. Figure 6.3 is the tube distribution with sample size of 465, representing approximately 20% of the population. The total Td accounted for 15% of the population predicting CR at tp =1.8years above MTLV (O.064mpy). These results quite contradict field report of the technical partner which indicated that corrosion rate was within the maximum tolerable limit. The results of the curves therefore graded as Racop > Pica > Exp. The fact that the peak of the Racop analysis is well spread indicated that it represents the actual tube distribution. This in turn represents the stress–strain relationship of the tubes when subjected to maximum load at on-stream time. At that point the effect of process variables such as temperature and chloride ion concentration directly increase stress distribution which helped to accelerate tube's leakages. These are responsible for the rapid drop in tensile properties of the tubes and hence increase CR along Td$\leq 2.40mm$. Also, increased CR directly increased the heavy metal and chloride ion concentrations in process waters which enhanced pressure drop in the tubes due to severe leakages. It could be seen that RACOP distribution present high frequency and good symmetrical pattern that depicts good normal distribution of the tubes. It is also an indication that even at 20% sample size, the corrosion rate forecast could be assumed unacceptably high. The corrosion values of the experimental data could be considered slightly high (0.058mpy) at this point, while that of Pica is high enough to signal danger (0.064mpy). The trend shows peak corrosion rate at the MTLV (0.59mpy) at point of abandonment. Rapid urea production further enhances stressed tubes within $\leq$ 2.45mm and the already Td to collapse with ease. Operators and Management must learn to respect design specification of equipment so as to limit damage, even if the equipment is new, to prolong its service life. Alteration of design specification gradually alters the process variables which in turn could introduce high concentration of chloride ions as tube leakages increased.

5.0: CONCLUSION AND RECOMMENDATIONS.

Developing algorithms for corrosion rate failure analysis and digitalization of chemical process plant activities are fundamental to stochastic modeling of corrosion trend under high temperature, high pressure operating systems in the industry. Adequate data samples reflective of the time and condition of operation must be harnessed to simulate the ideal operating condition of the plant and the environmental factors that might influence corrosion activities. The type and nature of carbon steel must be considered in the modeling process, with proper understanding of the algorithmic process and computational skills to reflect plant conditions. For corrosion monitoring and control to be effective, there should be routine surveillance, strategic inspection, and scheduled maintenance in time while strict regulations and adherence to standard operating conditions for startup and shut down operation should be encouraged. The use of statistical tools in operational optimizations helps in early warning signals and precision forecast before the actual damage is done when fatigues and failures occur. Real time surveillance using automated scientific tools like automated control panels and simulators could help in safeguarding the employees from undue exposure to corrosion induced equipment failure, environmental danger such as gas fume attacks, gas fume entrapment, product spills entrapment and death. Adequate personal protective equipment and regular safety training is advocated for plant operators in the field and regular equipment inspections should be carried out at intervals. The use of algorithms in developing computer programming languages should be made mandatory and such skills incorporated into the curriculum for engineers and scientists - critical mass needed for the operation of chemical and manufacturing plants for economic sustainability.

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