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Corrosion monitoring in Nigerian petroleum industry : A case study of Kaduna petroleum refinery

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Corrosion monitoring in a petroleum refinery was carried out using coupon test method. Five different locations were selected along the pipeline of the cooling water section of the refinery. Analysis revealed that there was corrosion taking place at different rates within the refinery. The lowest rate recorded was 14 mg dm^{-2} day^{-1} and the highest rate was 42 mg dm^{-2} day^{-1}. It is recommended that the chemical dosage of corrosion inhibitors be improved and that a constant monitoring program be adopted.

Monitoring of corrosion refers to the observation and checking of equipment for corrosive spots with the aim of early detection of possible hazards and protection against loss of life, injury, production and property. It also assesses the effectiveness of corrosion control measures via accurate judgments of corrosion rate[1,2].

Corrosion monitoring is an essential part of a well-planned corrosion control program in the refinery. A high corrosion rate over a period of time can give useful information about the technical condition of the plant and consequently instigates possible corrosion control measures to be adopted[3,4].

Intelligent location of monitoring devices comes from the experiences derived from similar plants and knowledge of the processing fluids. Special monitoring attention is given to areas with changes in fluid chemistry where there is condensation of water from gaseous stream, with change in pressure that can cause gases to go out of solution, where free water can settle from crude oil and the heat exchanger surface[5,6].

Electrochemical Phenomenon of Corrosion

Most of the corrosion processes occur by electrochemical mechanism involving the reaction of a metal with electrically conductive solution (electrolytes). They involve two essentially dependent processes namely: anodic process and cathodic process. The anodic process involves the transfer of metal into the solution as ions with an equivalent number of electrons left on the metal while the cathodic process is the assimilation of the electrons in the metals by the atoms, molecules or ions in solution that can be reduced on the cathode. In electrochemical corrosion, metal ions are present in the solution while free electrons occur in the metal. The existing surface heterogeneity on the metal and ionic conductivity of the solution permits local anodic and cathodic reactions on different parts of the metal surface in contact with the solution. For corrosion to progress both the anodic and cathodic reactions must occur simultaneously and at the same rate, otherwise a charge builds-up, stopping corrosion. Thus, the important and basic principle of corrosion is that during metallic corrosion, the rate of oxidation is equal to the rate of reduction in terms of electron production and consumption.

The anode reaction, which results in the corrosion of iron immersed in water or seawater and exposed to the atmosphere, is:

$$Fe \rightarrow Fe^{2+} + 2e \quad \ldots (1)$$

The ferrous hydroxide precipitates from solution and being unstable in oxygenated solutions, it undergoes further oxidation to produce hydrated iron or rust[2,7]:

$$2Fe(OH)_2 + H_2O + \frac{1}{2} O_2 \rightarrow 2Fe(OH)_3 \quad \ldots (2)$$

During corrosion more than one oxidation and one reduction reaction may occur. When an alloy is corroded, its component metal go into solution as their respective ions depending on their relative electrode potentials with more than one oxidation reaction.

There are various methods that can be employed in the monitoring of corrosion in the petroleum industries, this paper focuses on the coupon test method.

Coupon test method

Coupons are pieces of materials placed in the environment to corrode and later analyzed to determine the rate of corrosion. They are useful in monitoring corrosion in pipelines and process vessels. The coupon is generally of the same metallurgical composition as the material whose corrosion is being studied. Coupons are of different shapes and sizes ranging from blade, rod and bottom types. There are also different types of coupons stations holder, which hold the coupon in the fluid streams[8,9].

The process of using the coupons involves careful cleaning, weighing before and after they have been exposed into the corroding environment for sometimes. The coupons are electrically isolated from other metals. The corrosion results from coupons test are affected by their location, handling on installation and removal. It is important that the coupons are protected from corrosion before installation and on retrieval before they are analyzed. The exposure time of the coupon can also affect the result, short exposure time can be misleading as pits (tiny corrosive holes) may not have developed which means the exposure time of the coupon may have to be increased for some more time to ascertain the presence of pits[2,10]. It is a good practice to give proper physical examination of the coupons and measure the maximum pit penetration since this is the most significant number in estimating safe equipment life. Coupons are relatively cheap, readily available and offer a permanent record of the corrosion suffered. The weakness of the method is the assumption that there is a uniform corrosion all through the material.

Corrosion rate from the coupon test is calculated as:

$$MDD = [\text{coupon weight (mg)}]/[\{\text{exposed surface area}(\text{dm}^2)\} \times (\text{days of exposure})]$$

where MDD is mg dm^{-2} day^{-1}.

Coupons are installed with spool, which are just short pipe section flanges for easy removal. With this spool bigger sample of the system is studied and another advantage is that it has the same shape location. Spool reflects more accurately the build-up of protective film deposits of corrosion products. The spool is usually removed periodically cleaned and weighed to determine the loss within the period, pit depth and the nature of localised corrosion can be measured directly[11].

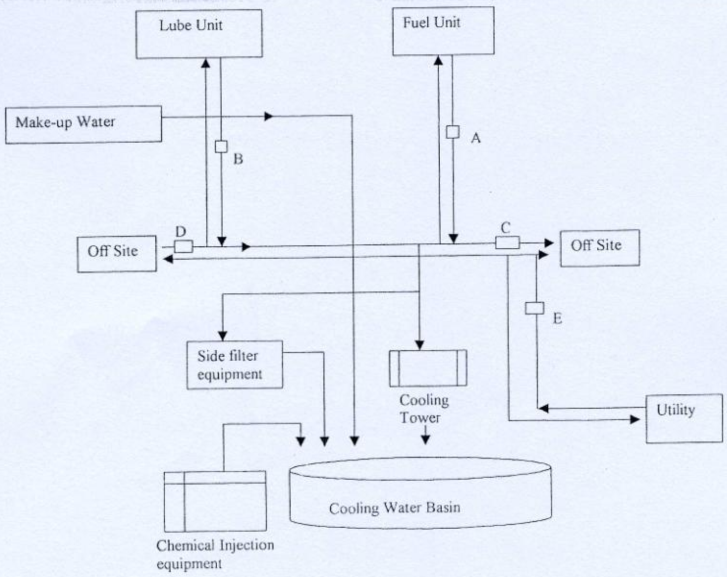

Fig. 1—Schematic diagram showing the points of coupon installation along the cooling water pipeline

Methodology

Five different points were considered along the cooling water pipeline of a petroleum refinery. These five points were named A, B, C, D, and E (Fig. 1). The coupons were cleaned and weighed and the weight recorded. Three coupons were then installed inside the pipeline at the top, middle and bottom at each of the points using coupon station holder to hang them so that there was no contact with the pipeline. After several days the coupons were removed and weighed again. The rate of corrosion was then determined using the formula:

$$MDD=(W_1-W_2) \times 10^3/(A \times D)$$

where, W_1, is the initial weight (g) of coupon, W_2, the final weight (g), A, is the coupon surface area (dm^2) and D, the residence time (days). The following corrosion standards were used to determine the level of corrosion:

0 – 10 mg dm^{-2} day^{-1} {very good}
11-20 mg dm^{-2} day^{-1} {good}
Above 21 mg dm^{-2} day^{-1} {unsatisfactory}

Results and Discussion

The results obtained for the five selected points are presented in Table 1.

Corrosion forms are differentiated on the basis of appearance of the corroded metal. Identification of the form of corrosion is usually by visual observation and sometimes by magnification apparatus. The various corrosion forms include: uniform, crevice, pitting and intergranular[9]. The emphasis here is on the pitting corrosion forms, which is an extremely localized attack resulting in the formation of cavities (holes) due to significant penetration of the metal. At all the five points considered during analysis, pitting was observed indicating that corrosion was taking place at various sites of the pipelines. The corrosion occurring at these points are as a result of electrochemical processes within the pipelines of the cooling water section.

Table 1 presents the coupon results for points A to E. In coupon results for point A, the corrosion rates were 38, 31 and 34 mg dm^{-2} day^{-1} for top, middle and bottom respectively. Going by the recommended standard level the rate of corrosion was on the high level. This is unsatisfactory. Some blackish hard deposits and shallow pitting were observed on the three coupons when withdrawn after cleaning and pickling, this suggests that the cooling water treatment was not good enough which can adversely affect the running of the refinery[2].

Table 1—Coupon test results for points A to E
Flow rate = 1 ms^{-1}; Area (A) = 0.31 dm^2

Coupon location	W_1 (g)	W_2 (g)	W_1-W_2 (g)	MDD (mg dm^{-2} day^{-1})
For point A				**D = 38 days**
Top	11.1420	10.6999	0.4423	38
Middle	11.3683	11.0061	0.3622	31
Bottom	11.3758	10.9764	0.3994	34
For point B				**D = 35 days**
Top	10.5105	10.24498	0.2656	25
Middle	11.3436	11.1485	0.1951	18
Bottom	10.7109	10.2806	0.4303	40
For point C				**D = 65 days**
Top	11.4549	10.9209	0.5340	27
Middle	11.3630	10.6809	0.6821	34
Bottom	11.3397	10.4960	0.8437	42
For point D				**D = 57 days**
Top	11.1917	10.8860	0.3057	17
Middle	10.9742	10.6710	0.3032	17
Bottom	10.9262	10.6716	0.2546	14
For point E				**D = 50 days**
Top	11.5788	11.1636	0.4152	26
Middle	11.5119	11.2324	0.2795	18
Bottom	11.5893	11.3273	0.2620	16

The coupon results for point B show that the corrosion rates were 25, 18 and 40 mg dm^{-2} day^{-1} for top, middle and bottom respectively. The corrosion rate for the bottom was significantly higher than the top and middle. This is attributed to the facts that the coupon used at the bottom position has been used before to test the suitability of recycling coupons for determining corrosion rate. The corrosion rate at the top position was unsatisfactory as it was above 21 mg $dm^{-2}day^{-1}$ while at the middle position the corrosion rate was satisfactory indicating that there was higher rate of corrosion at the top than middle. Brownish soft deposits embedding blackish substances sparsely distributed over the coupon surfaces were seen for the top and middle positions while they were more evenly distributed on the coupon at the bottom position. The cleaning and pickling of all the coupons reveal shallow pitting directly under the location of the deposited substances[2].

In the coupon results for point C, the corrosion rates were 27, 34 and 42 mg dm^{-2} day^{-1} for top, middle and bottom respectively. Compared to the corrosion standard, the corrosion rate at this point is also high. Shallow even pittings were observed on the coupons, suggesting that the corrosion rate may not be that alarming, with the residence time of sixty-five days a deeper pitting could have been expected.

The coupon results for point D show that the corrosion rates were 17, 17 and 14 mg dm^{-2} day^{-1} for top, middle and bottom respectively. From the corrosion rate standards, the rate of corrosion at this point is low suggesting that corrosion is not yet a serious problem at this point. Brownish sludge deposits were observed on the coupon surfaces when inspected and shallow pittings were seen directly under where the sludge substances were deposited when the coupons were cleaned and pickled. The coupon test results showed slow rate of corrosion is in agreement with the observation of shallow pitting on the coupons for a residence time of 57 days. From this it could be said that the cooling water treatment is alright, which seems economical for the refinery plant[2,5].

In the coupon results for point E, the corrosion rates were 26, 18 and 16 mg dm^{-2} day^{-1} for top, middle and bottom respectively. The corrosion rates at the top of the pipeline were not satisfactory but that for the middle and bottom were allright. These suggest that there is a higher rate of corrosion at the top. On all the coupon surfaces, brownish sludge deposits were observed, cleaning and pickling of the coupons reveal shallow pitting directly under the location of the brownish sludge.

Conclusions

From the various results obtained the rate of corrosion exceeded the standard level, which indicated that corrosion was going on at various part of the refinery. Brownish sludge deposits were observed on the coupon surfaces when inspected, which showed even pitting on the coupons under which the sludge substances were deposited when the coupons were cleaned and pickled. These indicate that there was corrosion despite the low coupon test results from some points and with time it might become a serious problem for the refinery if the water treatment is not improved.

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