

Study of Corrosion Rate in Water Treatment Plant in Oil field

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ABSTRACT

The high cost of corrosion, the corrosion engineers concern and its reduction in oil, gas and petrochemical countries is essential about 10% of the cost of producing a barrel of crude oil cost. Corrosion rates in the world costs 42–80 cents a barrel for crude oil is produced, specific climatic conditions, history of the country's refineries and oil production are the main factors affecting the cost of corrosion in oil country. Corrosion damage is major issues in oil and gas field have become a problem of worldwide significance. It causes plant shutdowns, waste of valuable resources, loss or contamination of product, reduction in efficiency, costly maintenance, and expenses over design can risk safety. The present study focuses on numerous mechanism for controlling corrosion as well as implementation on safety point of view in the process industries. The corrosive causing materials like H_2S which dissolved both in crude and varied in scope and composition. The parameters pH, conductivity, TDS and SRB were analyzed.

Keywords: conductivity, corrosion rate, pH, TDS and WTP

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INTRODUCTION

Corrosion rates in the world costs 42–80 cents a barrel for crude oil is produced, specific climatic conditions, history of the country's refineries and oil production are the main factors affecting the cost of corrosion in oil country. Corrosion damage is a major issue in oil and gas field have become a problem of worldwide significance. Corrosion causes plant shutdowns, waste of valuable resources, loss or contamination of product, reduction in efficiency, costly maintenance, and expenses over design can jeopardize safety [1–3]. Typically, once a plant or any piece of equipment is put into service, maintenance is required to keep it operating safely and efficiently. This is particularly true for aging systems and structures, many of which may operate beyond the original design life. Most crude petroleum contains numerous naturally occurring constituents and impurities

which will cause severe corrosion of the metals from which conventional petroleum refining equipment is constructed. These corrosive or corrosion causing materials are varied in scope and composition. They include materials such as water with brine solution, either naturally admixed or added during production. Another troublesome agent is H_2S , which is dissolved both crude and water which is found within the system. In existing plant, an issue starts to appear which need to be analyzed and find the source and trying to mitigate this issue [4, 5].

In Industrial point of view, especially in steam boiler industry, high purity feed water is required to ensure proper operation of steam generation systems [6, 7]. High purity feed water reduces the use of boiler chemicals due to less frequent blow down requirements (reduction of blow down frequency by as much as a

factor of 10 is possible). Lower blow down frequency also results in lower fuel costs. Scale buildup is reduced due to smaller concentrations of impurities in the boiler feed water that foul heat transfer surfaces. The lower level of impurities also reduces corrosion rate in the boiler. Reverse osmosis is one method of water treatment used to produce boiler quality feed water. So, all reject water will pump into the disposal water tank [8–10]. Due to impurities corrosion issued appear in this tank which cost the plant a lot of money every year. The failure in controlling the corrosion which exist in the DWT means the production of station will stop which should be avoid. Therefore, the corrosion rate will decrease the life of process equipment in industries.

MATERIALS AND METHOD

Equipment

The equipment's used to find the corrosion data are, pH meter, conductivity meter, TDS, DO meter and Sealed SRB vials containing liquid broth.

SRB Testing Procedure

The density of Sulfate Reducing Bacteria (SRB) in water samples can be estimated by injecting known volumes of water samples in broth media contained in sealed vials, in order to produce a series of ten-fold dilutions. Then SRB are computed by noting the dilution in which no growth is visible.

Sampling and testing procedure

To perform SRB test the following steps have to be followed:

- Take a sample of the water under test in a germ-free plastic container, making sure that the container is completely filled and that contamination is avoided.
- Take at least 3 SRB broth vials and number them '1', '2', and '3', and so on, respectively, then take a germ-free disposable 1 ml syringe and insert a

germ-free needle, then slowly withdraw 1 ml from the sample in the plastic container, using the syringe.

- Hold the syringe upright to expel any air and immediately push the needle into the vial numbered '1'. Slowly inject the sample into the vial being careful not to introduce air bubbles.
- Mix the contents of the vial by inverting the vial three times. This will give a (1: 10) dilution of the original sample.
- Take a new sterile 2 ml syringe and needle, hold the vial No. 1 downwards and quickly insert the needle into the rubber cup of the vial. Slowly withdraw 1 ml of the broth into the syringe being careful not to introduce air bubbles.
- Inject this broth into the vial numbered '2', using the same technique as previously described. Transfer 1 ml of broth from vial '2' to vial '3', using a new sterile syringe and needle and the same procedure. Incubate all 3 (or more) broth vials in an upright position in an incubator at 28°C or at the same temperature as the water from which the sample was taken, if this temperature is higher.
- It is important to carry out the procedure exactly as stated, since contamination from vial to vial will result in all vials showing a positive reaction, hence giving a false high result.

Reading

The broth vials will turn black if sulfate reducing bacteria are present. This technique will give a count of SRB as follows (Table 1).

Table 1. SRB counting technique.

| Vial number | 1 | 2 | 3 | 4 |
|------------------------|------|--------|----------|-------------|
| Broth dilution | 1/10 | 1/100 | 1/1.000 | 1/10.000 |
| Probable number of SRB | 1–10 | 10–100 | 100–1000 | 1000–10.000 |

Summary of Method

When sulfate-reducing bacteria (SRB) are in the sample, sulfate is reduced to hydrogen sulfide (H₂S) in the SRB-BART tube during incubation. The H₂S reacts with the ferrous iron in the tube to form black iron sulfides. This sulfide commonly forms in the base as a black slime and/or around the ball as an irregular black ring. Sulfate-reducing bacteria typically grow in anaerobic conditions deep within biofilms (slimes) as a part of a microbial community. Sulfate-reducing bacteria may not be in the free-flowing water over the site of the fouling. Sulfate-reducing bacteria can cause problems such as strong odors, blackening of equipment, slime

formations and the start of corrosive processes [11–14].

Corrosion Coupons and Weight Loss Analysis

The simplest and longest-established method of estimating corrosion losses in plant and equipment is weight loss analysis. A weighed sample (coupon) of the metal or alloy under consideration is introduced into the process, and later removed after a reasonable time interval. The coupon is then cleaned of all corrosion products and is reweighed [15]. The weight loss is converted to a corrosion rate (CR) or a metal loss (ML) as follows (Tables 2, 3):

$$\text{Corrosion Rate (CR)} = \frac{\text{Weight loss (g)} * K}{\text{Alloy Density (g/cm}^3\text{)} * \text{Exposed Area (A)} * \text{Exposure Time (hr)}}$$

The constant can be varied to calculate the corrosion rate in various units:

$$\text{Metal Loss (ML)} = \frac{\text{Weight loss (g)} * K}{\text{Alloy Density (g/cm}^3\text{)} * \text{Exposed Area (A)}}$$

Table 2. Corrosion rate constant calculation.

| Desired corrosion rate unit (CR) | Area unit (A) | K-factor |
|----------------------------------|-----------------|------------------------|
| mils/year (mpy) | in ² | 5.34 x 10 ⁵ |
| mils/year (mpy) | cm ² | 3.45 x 10 ⁶ |
| millimeters/year (mmy) | cm ² | 8.75 x 10 ⁴ |

Table 3. Metal loss constant calculation.

| Desired metal loss (ML) | Area unit (A) | K-Factor |
|-------------------------|-----------------|----------|
| Mils | in ² | 61.02 |
| Mils | cm ² | 393.70 |
| Millimeters | cm ² | 10.00 |

The technique requires no complex equipment or procedures, simply an appropriately shaped coupon, a carrier for the coupon (coupon holder), and a reliable means of removing corrosion product without disruption of the metal substrate. Weight loss measurement is still the most widely used means of determining corrosion loss, despite being the oldest

method currently in use. Weight loss determination has a number of attractive features that account for its continuous acceptance because it is simple and does not require sophisticated instrumentation to obtain the result. Also, a measurement can be directly obtained, with no theoretical assumptions or approximations. This method is applicable to all corrosive environments and gives information on all forms of corrosion. The method is commonly used as a calibration standard for other means of corrosion monitoring, such as Linear Polarization and Electrical Resistance. In instances, where slow response and averaged data are acceptable, weight loss monitoring is the preferred technique [16–20].

Coupon Preparation and Cleaning

The select of technique for the preparation of the coupon surface before inserting it inside the pipeline, and for cleaning the

coupon after use, is critical in finding useful data. Both the consequence and reproducibility of weight loss data are highly sensitive to the inherent suitability of these techniques, and to the care with which they are executed. Surface finishing methods vary across a broad range for specific applications. Blasting with glass bead, sand, or other aggregate can provide an acceptable finish for some applications. Sanding with abrasive belts, or surface or double disc grinding with abrasive stones also provides an excellent surface for evaluation. Cleaning of specimens before weighing and exposure is critical to remove any contaminants that could affect test results. Reference should be made to NACE Recommended Practice RP-0775 and ASTM G-1 and G-4 for further detail on surface finishing and cleaning of weight-loss coupons [21–25].

Coupon Position and Orientation

Irrespective of the degree of care exercised in the surface preparation of coupons, many uncontrollable factors (*e.g.* microstructural defects) can reduce the accuracy of weight loss determinations. Therefore, using duplicate or multi-replicate coupon samples is considered good practice. Coupon orientation must be consistent in order to make different data sets comparable. Generally, an orientation parallel to the process flow is preferable since this more nearly reflects the true condition experienced by the vessel wall. Metal samples corrosion monitoring systems coupon holders have an automatic flow alignment feature [26]. All other holders are marked on the top side with flow direction for manual alignment. Positioning is another critical factor in obtaining relevant information. For example, a multi-phase product may produce layered flow, giving rise to corrosion rates that vary with depth in the process stream. Such situations can be monitored with a ladder-strip coupon holder [27].

Possibly the most common issue in coupon positioning arises from the fact that a true representation of the corrosion experienced by the pipe/vessel can only be established when the weight loss coupon is in the plane of the vessel/pipe wall. Only in this position can the coupon experience the same flow regime as the pipe surface being monitored. In response to this situation, the use of flush-disc coupons has become widespread [28]. The general issue of coupon orientation and positioning in relation to flow regime, plant geometry, and process fluid is complex and tends to be specific to each application. However, the most common coupon configurations have been discussed above.

Coupon Holders

Specific design of coupon holders incorporates basic factors such as number, style, and configuration of coupons as well as system entry method.

Fixed (Pipe Plug) Coupon Holders

The simplest system entry design for coupon holders is the fixed or pipe plug coupon holder. These normally offered on a 3/4", 1", or 2" NPT pipe-plug. The size of the plug to be used is the limiting factor as to the coupon configuration that can be used. These coupon holders are usually constructed in AISI 316L stainless steel have a pressure rating of 3000 psi, and a temperature rating of 450°F/232°C [29, 30]. This design of coupon holder is recommended for use in a by-pass loop which can be isolated, or in systems having frequent and regular shut-down, since system depressurization is required during insertion and removal.

Retractable Coupon Holders

A design that is commonly used in the refining and petrochemical industry is the retractable type coupon holder design. It employs a packing gland that allows insertion and removal, through a ball-valve, without system depressurization. A safety cable and safety nut is also provided

to prevent blowout. Retractable coupon holders can be used up to 1500 psi and 500°F (260°C), and are constructed of AISI 316L stainless steel. Normally, a 1" FNPT packing gland is used in conjunction with either a 1", or a 1½" full port ball valve, depending on the type of coupon configuration chosen.

Retrievable Coupon Holders

The oil and gas production industry generally employs retrievable coupon holders that operate with high pressure access systems. This will allow insertion/removal under pressures up to 3600 psi. Metal samples corrosion monitoring systems supplies both generic (HP) and proprietary (MH) coupon holders. The retrievable coupon holder is installed on to the solid plug. The assembly can then be inserted or removed from the system using a special service valve and retrieval tool.

Retrievable coupon holders are generally constructed in AISI 316L stainless steel to meet the requirements of NACE standard MR-0175 for sour service use. These are

available for all standard coupon configurations. Retrievable, retractable, and pipe plug style coupon holders cover the needs of most industries and applications. However, the requirement for special coupon holder designs is significant and metal samples corrosion monitoring systems has the facility to design and build coupon holders to any customer-supplied specification.

RESULTS AND DISCUSSION

Corrosion Rate

The corrosion rate of outlet pipeline of Waste Water Tank in the water treatment is very high. The coupon results showed the outlet flow from the DWT was highly corrosive. It is fluctuating between 21 and 230 mpy during the experiment period. This range is very high and also higher than the acceptable rate which is 5 mpy as per NACE standard, so the water analysis experiment was conducted to find out the reasons of this issue. Four parameters were measured to find the reasons of this high corrosion rate. Table 4 shows the corrosion rate surveys results which calculated by given Formula:

$$\text{Corrosion Rate (CR in mpy)} = \frac{\text{Weight loss (g)} * 5.34 * 10^5}{\text{Alloy Density (g/cm}^3\text{)} * \text{Exposed Area (A)} * \text{Exposure Time (hr)}}$$

Table 4. CRAT WTP disposal tank.

| Corrosion surveys results | | | | Acceptable corrosion limit (mpy) |
|---------------------------|-----------|----------------------|----------------------|----------------------------------|
| Start date | End date | Exposing time (days) | Corrosion rate (mpy) | |
| 25-Jun-15 | 24-Jul-15 | 29 | 74 | 5 |
| 24-Jul-15 | 25-Aug-15 | 32 | 21 | 5 |
| 25-Aug-15 | 28-Sep-15 | 34 | 85 | 5 |
| 28-Sep-15 | 16-Nov-15 | 49 | 62 | 5 |
| 16-Nov-15 | 17-Dec-15 | 31 | 174 | 5 |
| 17-Dec-15 | 20-Jan-16 | 34 | 115 | 5 |
| 20-Jan-16 | 13-Feb-16 | 24 | 225 | 5 |
| 13-Feb-16 | 13-Mar-16 | 29 | 151 | 5 |
| 13-Mar-16 | 1-Apr-16 | 19 | 230 | 5 |
| 1-Apr-16 | 3-May-16 | 32 | 84 | 5 |

The fluctuations on average corrosion rate were shown in Figure 1. The highest reading found at 230 mpy and lowest reading at 21 mpy in (13-Mar-2016 to 1-Apr-2016) and (24-Jul-2015 to 25-Aug-2015) respectively and average corrosion rate was 122.1 mpy. All coupons samples were found covered by with thick layer of black stuff. Also, the type of the corrosion detected was pitting corrosion as well as general corrosion in some surveys (under deposit corrosion).

Pitting is the most common cause of corrosion failures occurring in oil and gas industry production equipment [19]. It occurs when the metal undergoing

corrosion suffers metal loss at localized areas rather than over a large area or the entire surface area. The entire driving force of the corrosion reaction is concentrated at these localized areas. The corrosion rate at these areas will be many times greater than the average corrosion rate over the entire surface.

Pitting is much more dangerous than uniform corrosion because the pitted area can become penetrated in a short time. Corrosion rate of the coupon was plotted in the below figure, the red line indicating the acceptable corrosion rate. Refer appendix B to see the pictures of the coupon samples.

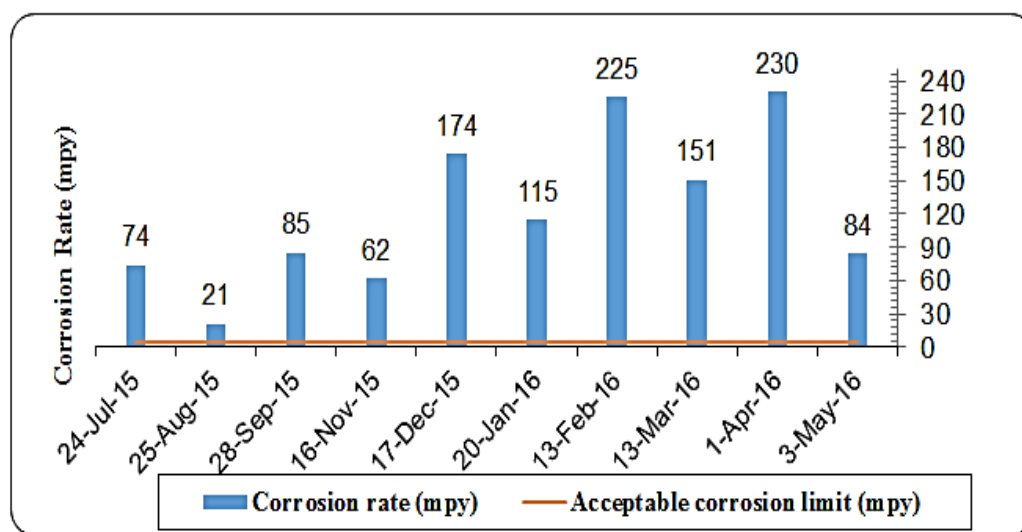


Fig. 1. Corrosion surveys-waste water tank.

The coupon results showed the all collecting coupons were covered by iron sulfide FeS because the H_2S reacts with iron to form iron sulfide and hydrogen. The corrosion rate was investigated by measuring the pH, conductivity, TDS and SRB survey. Also in some surveys SO_2 , DO were measured.

The Effect of pH on Corrosion Rate

The relation between the corrosion rates of the coupons and the pH of the water samples in the same period is illustrated in Figure 2. It was observed that corrosion rate of the coupons is fluctuating even the

pH changing very narrow range 6.20–6.66. The average pH of the water sample is 6.46. The pH does not fall below 5 it maintains at 6. The highest value of corrosion was 230 mpy when the pH is 6.26 which was not the lowest pH value recorded in this experiment and the lowest value of corrosion rate recorded was 21 mpy at 6.4.

The effects of pH in the corrosion rate is shown in Figure 2 it was observed that corrosion is minimum between pH 7 to 12 and it will increase rapidly below 5.

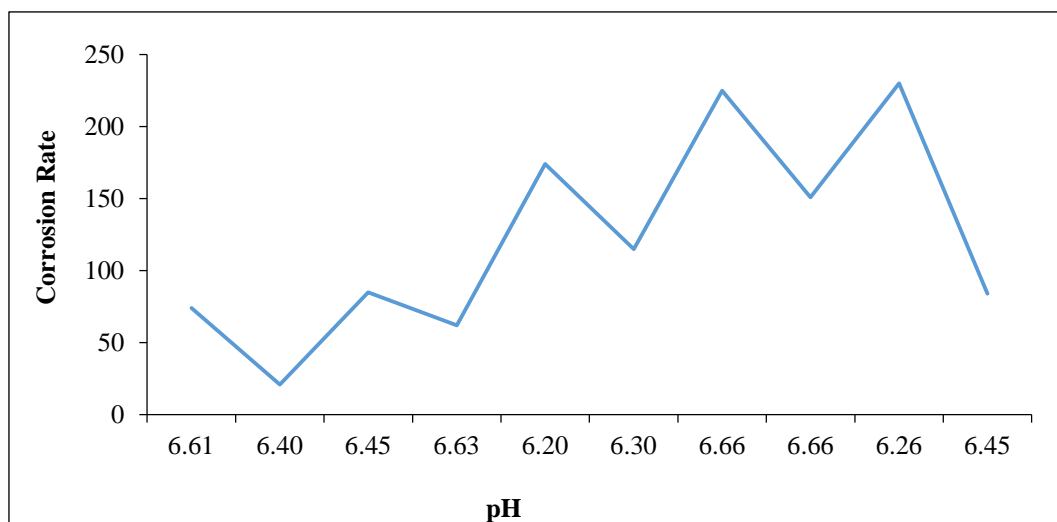


Fig. 2. Variation of corrosion rate with pH.

Effect of Conductivity on Corrosion Rate

The electrical resistance of typical electrolytes is usually much higher than that of metal, therefore the resistance of the electrolyte is normally predominate in the corrosion cell reaction. The more conductive the electrolyte, the easier current can flow and the faster corrosion will occur. The amount of metal that dissolves is directly proportional to the amount of current flow between anode and

cathode. From Figure 3 it was observed that the fluctuating of the conductivity affecting the corrosion rate of Coupon during the experiment. The water analysis showed the conductivity of the sample was very high. It was ranging between 55000 and 6900 $\mu\text{s cm}$. When the corrosion rate was 230 mpy the conductivity was 35636 $\mu\text{s cm}$ these high readings should be normal since the water analyzed was rejected water.

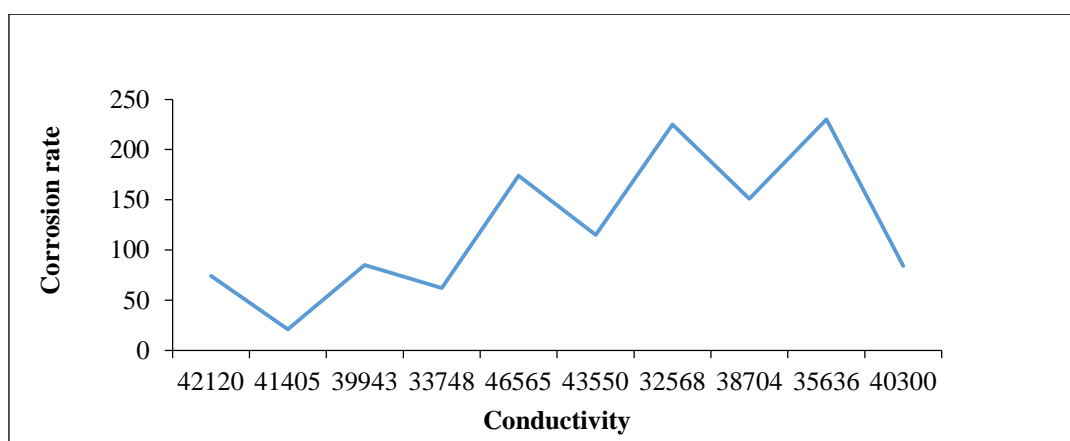


Fig. 3. Variation of corrosion rate with conductivity.

Effect of TDS on Corrosion Rate

TDS is determined from the conductivity of the water sample, since the ionic composition for most streams is similar. The conductivity reading is converted to milligrams of total dissolved solids/liter.

($\text{TDS} = 0.67 * \text{conductivity}$). Figure 3 shows the relation between the TDS and Corrosion rate which is almost constant and very high. It is cleared from Figures 4 and 5, the shapes of both figures are same.

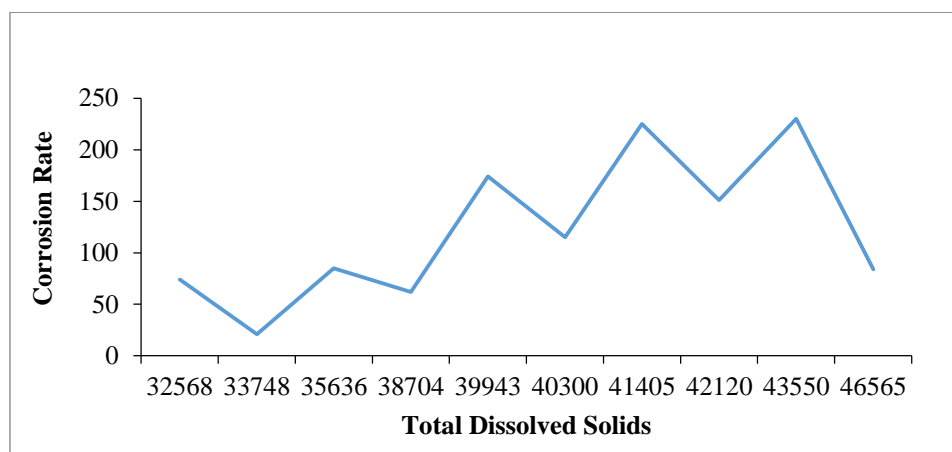
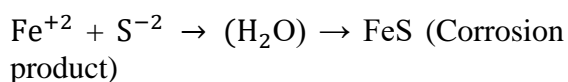
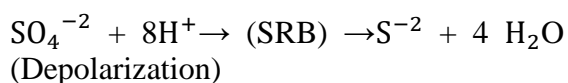


Fig. 4. Variation of corrosion rate with TDS.

SRB Surveys

Microbiologically influenced corrosion is pitting type corrosion [19]. Microorganisms can exert considerable influence on the corrosion rate. The type of bacteria most commonly associated with corrosion in oil field operations is the sulfate reducing bacteria (SRB). The metabolic process of the SRB reduces sulfates to sulfides and consume large quantities of hydrogen in the process to produce H_2S . The polarization film in cathode area provide the hydrogen. Therefore, SRB act as strong depolarizes which causes accelerated corrosion rate.



The survey result shows that contamination of all samples with SRB. The column of bottles changed represent the average of four reading every 7 days. The total number of bottles was taken as 6 shown in Table 5.

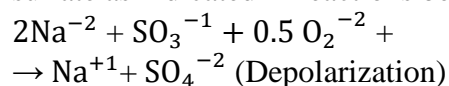
SRB are capable of causing severe corrosion of iron material in a water system because they produce enzymes which have the power to accelerate the reduction of sulfate compounds to the corrosive hydrogen sulfide, thus SRB act

as a catalyst in the reduction reaction. However, in order for this reduction to occur, four components must be present. That is, SRB must be present; Table 5 shows the SRB are existing, also sulfates must be present; which was in this experiment 1500 ppm, in addition and external energy source in the form of free electrons must be present; the reading of conductivity was very high in this experiment and the temperature of the water must be less than approximately $65^\circ C$; in this experiment the temperature was less than $45^\circ C$.

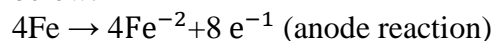
Furthermore the average reading of pH was 6.4 and it does not fall below 5 because the H_2S is weak acidic [19] which another evidence of existing of bacteria, SRB can survive in a wide range of pH conditions but commonly have a pH optimum for growth between pH 5–9. SRB populations have been obtained at temperatures ranging from the psychrophilic to the hyper thermophilic range. The effect of pH on growth rate of SRB was determined in pH range 5.8–7. The highest growth rate was observed at pH 6.7 and in this experiment the average pH was 6.46 which close to 6.7.

A water system naturally contains sulfate based compounds, but when sulfite was added to a closed water system as an oxygen scavenger and corrosion inhibitor,

the sodium sulfite was oxidized to sodium sulfate as indicated in reactions below:



Excess electrons occur in a water system as a result of iron corrosion at the anode and cathode cells as indicated in reactions below.



The resultant accelerated corrosion mechanism of iron by the sulfate reducing bacteria is illustrated in equations below.

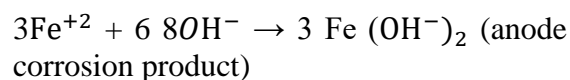
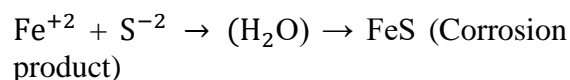
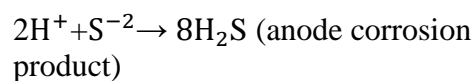
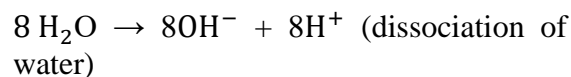
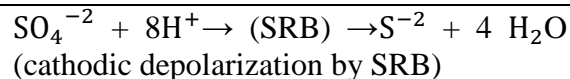


Table 5. Disposal tank sampling point.

| Location | Date cultivated | Date last read | Days incubated | Bottles changed |
|------------------------------|-----------------|----------------|----------------|-----------------|
| Disposal tank sampling point | 30-Jun-15 | 28-Jul-15 | 28 | 4 |
| | 25-Jul-15 | 22-Aug-15 | 28 | 4 |
| | 23-Aug-15 | 20-Sep-15 | 28 | 6 |
| | 17-Nov-15 | 15-Dec-15 | 28 | 4 |
| | 25-Dec-15 | 22-Jan-16 | 28 | 4 |
| | 22-Jan-16 | 19-Feb-16 | 28 | 4 |
| | 14-Feb-16 | 13-Mar-16 | 28 | 5 |
| | 12-Mar-16 | 9-Apr-16 | 28 | 4 |
| | 14-Apr-16 | 12-May-16 | 28 | 3 |
| | 2-May-16 | 30-May-16 | 28 | 4 |

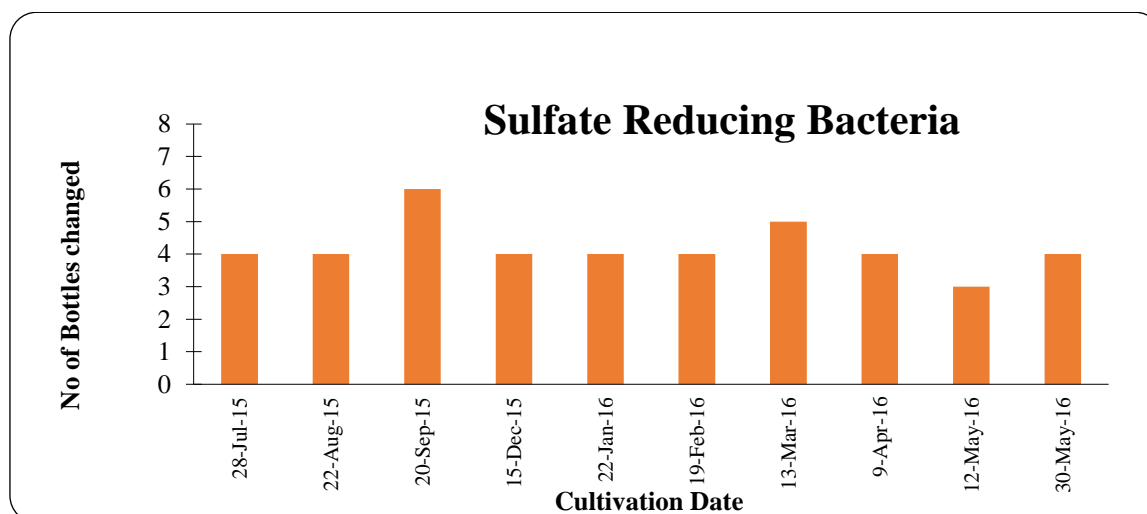


Fig. 5. Sulfate reducing bacteria – WTP disposal tank sampling point.

CONCLUSION

The following conclusions were made from the experimental investigation.

- Corrosion problems occur in oil field production operations are due to the presence of water. In order to corrode

the metal surface must be in contact with a water phase was investigated.

- H₂S has generated by sulfate reducing bacteria (SRB) and also these bacteria contribute to corrosion by their ability to flourish in the absence of oxygen and their ability to change sulfate ions into hydrogen sulfide.
- The anaerobic conditions under a colony constitute a differential aeration cell. The study of parameters support the high fluctuating of corrosion rate occur in Water Disposal Tank, but the main reason was found to be the existing of SRB.
- In order to reduce the possibility of sulfate reducing bacteria proliferation in a water system, the following activities are recommended.
- Maintain a water temperature greater than 65°C for hot water heating systems and domestic hot water systems.
- Reducing corrosion of iron material in hot water heating and chilled water systems by eliminating air ingress into the system and by maintaining the prescribed inhibitor concentration in the system.
- If sulfate reducing bacteria are detected in a chilled water or hot water heating system must be added to the circulating system at a typical concentration of approximately 10 ppm. Subsequent biological analysis will determine when additional biocide treatment is required.
- Diverse type of biocide need to be used to eliminate the Bacteria clusters and fixed agitator inside the DT Tank Analyzing the feed and output of DT frequently.

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