THE OCCURRENCE OF CORROSION PROBLEM IN OIL PRODUCTION EQUIPMENT CAUSED BY SULFATE REDUCING BACTERIA AND DISSOLVED OXYGEN

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ABTRACT

One of most problems occur in oil production equipments is corrosion that is caused by some factors, such as the existence of sulfate reducing bacteria and dissolved oxygen in injection water.

Based on the results of laboratory, A–GS and R–GS contain 0.90 ppm and 1.19 ppm dissolved oxygen and have potential to form corrosion problem, except D–GS with 0 ppm dissolved oxygen and no corrosion problem.

After SRB tests, A–GS tube appearance colour is not black, because SRB is not found in the A–GS injection water. Whereas, R–GS and D–GS contain SRB with sulfate reducers > 100,000, therefore   R–GS and D–GS tubes appearance colour are completely black.

Key words: corrosion, sulfate reducing bacteria (SRB), H_2S and O_2 dissolved gas, oil production equipment

I. INTRODUCTION

Water flooding method will be implemented in A, R, D oil fields, South Sumatra. Before implementation of water flooding process into the three oil fields, initial laboratory tests must be carried out to know quality of injection water. The laboratory tests involved a wide scope of research and multi disciplinary knowledge, but in this research is focused on the occurrence of corrosion in oil production equipment caused by H_2S and O_2 dissolved gas. The tests were performed based on standard operational procedure to obtain accurate and reliable laboratory test results.

II. THEORY

This section contains theory sulfate reducing bacteria and dissolved of oxygen (O_2). According to information from Corrosion and Water Technology by Loyd W Jones explains that dissolved gases, such as the dissolved oxygen and hydrogen sulfide as reaction from sulfate reducing bacteria in water are the primary cause of most corrosion problems. Dissolved oxygen is by far the worst of the group. Dissolved oxygen can cause severe corrosion at extremely low concentration.

Oxygen promotes corrosion in two ways. Firstly, it is a powerful cathode depolarization. When an acid substance such as H_2S is present hydrogen gas tends to form on the cathode, viz:

Ionization of H_2S

a. $H_2S \quad \rightarrow \quad H^+ + SH^-$
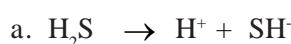
Cathode reduction

b. $2H^+ + 2e \qquad 2H^o \qquad H_2$

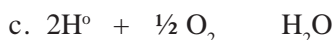$\qquad\qquad\qquad$ Step 1 $\qquad$ Step 2
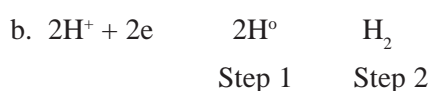
$\qquad$ Step 1 (atomic Hydrogen)

$\qquad$ Step 2 (molecular hydrogen)

Accumulation of gaseous H_2 tends to film over and polarize the cathode. However, if sample O_2 is

present, the second step of equation (b) does not occur and instead.

c. $2H^o + \frac{1}{2} O_2 \quad H_2O$

Thus, the cathode reaction and attendant corrosion is promoted because polarization by H_2 is minimized when oxygen is present.

Secondly, the oxygen removes iron by precipitation of iron oxides at the anode and thus prevents anodic polarization by Fe^{++} ions. Dissolved oxygen can cause severe corrosion at extremely low concentration. If dissolved H_2S and/or CO_2 are present, event trace quantities of dissolved oxygen will drastically increase the corrosive problem. Oxygen is not present in produced water, but often come in contact with it after it is brought to the surface. Information from Applied Water Technology Textbook by CC. Patton that the solubility of oxygen in water is a function of pressure, temperature and the chloride contents. Oxygen corrosion occurs as follows :

Anode reaction

Fe $Fe^{++} + 2 e$

Cathode reaction (in neutral or alkaline waters)

$O_2 + 2 H_2O + 4e \quad 4 OH^-$
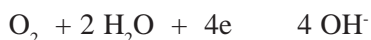
or, combining the two

$4 Fe^{++} + 6 H_2O + 3 O_2 \quad 4 Fe(OH)3$

if, pH is above 4, ferric hydroxide is insoluble and precipitates.

Theory of sulfate reducing bacteria in water, sulfate reducers probably cause more serious problem in oilfield injection system than any other bacteria. They reduce sulfate or sulfite ions in the water to sulfide ions, resulting in H_2S as a by-product. Sulfate reducing bacteria are mostly likely to be found in stagnant or low velocity areas, and beneath scales or sludge. Common places for bacterial activity in injection systems are tanks, filters and water source wells.

Reasons bacteria can cause a lot of problem:

1. Bacteria can conduct splitting of cell is very quick.

2. Several bacteria cells can increase population double in 20 minutes.

3. If, under ideal condition, where from a bacteria can form colonies (containing million of bacteria cells) in several hour.

Biosan laboratory research in USA have investigated about sulfate reducing bacteria (SRB).

SANICHECK SRB (presented in Table 2.1) was used as test system counting sulfate reducing bacteria and explained two points;

1. Relationship between sulfate reducers with tube appearance in days of incubation.

2. Interpretation of quantitative results.

Table 2.1 is interpretation based on results of sulfate reducing bacteria tests data (sulfate reducer / ml). The colour of tube appearance after SRB test was completely black when the sample contained SRB (presented in Table 2.1). Apart from that, Lemigas ever carried out SRB tests, and found a sample containing SRB with the colour of tube appearance was black (see in Figure 2.1) below.

Reaction of H_2S occurrence:

$SO_4^= + 4H_2 + 2H^+ \quad H_2S \quad + 4 H_2O$

Figure 2.1
A sample contains sulfate reducing bacteria with black colour tube appearance

Table 2.1
Interpretation of quantitative results

SANI/CHECK° SRB

Test System for Counting Sulfate Reducing Bacteria

DESCRIPTION OF TEST

Anaerobic sulfate reducing bacteria are ubiquitous in the environment. They are found in secondary oil recovery effluents, estuarine waters, deep wells, cooling waters, metalworking fluids, water-based hydraulic fluids, and petroleum based products that in some way become contaminated with water. During their growth they are responsible for fouling, objectionable hydrogen sulfide odors, corrosion of metals, and pitting of concrete. It is essential that these organisms be monitored and controlled to prevent damage caused by their metabolic activities.

SANI—CHECK SRB are tubes of culture media that is specifically formulated to promote the growth of anaerobic sulfate reducing bacteria. The medium contains reducing agents that maintain a low oxidation reduction potential and thus allows for maximal growth. When the organisms grow in this medium, sulfate is reduced to sulfide and a black precipitate of iron sulfide is formed. The degree of blackening through the medium is directly proportional to the amount of sulfate reducer growth.

SANI-CHECK SRB is designed to be used in areas where little or no formal laboratory facilities are available. Everything needed to perform 25 tests is enclosed including: 25 SANI-CHECK SRB tubes, 25 CO_2 tablets, 25 identification labels, 25 applicators, one bottle mineral oil [15ml], one sample vial with cap, one 1ml dropper, one alligator clip, and one instruction sheet.

Collection of Sample

Oily Sample
Microorganisms are unable to grow in the absence of water. In contaminated oil/water systems, the organisms will be found at the interface and in the water layer. Therefore, it is important that sampling be done from these locations. A sample vial is included with SANI-CHECK SRB. The vial should be filled with a freshly collected sample that has only a minimal oil layer on its surface. Excess oil can be skimmed from the surface of the sample with the enclosed dropper.

Water and Other Sample
No special sampling precautions are necessary. The sample may be tested using the provided vial or any other suitable container.

DIRECTIONS FOR USE

1. Open a SANI-CHECK SRB tube by peeling off the protective seal and removing the cap. Grip an applicator with the alligator clip and insert applicator into liquid sample. Immerse for approximately 5 seconds, withdraw, and drain excess fluid by running applicator along the inner lip of vial or other sample container. [Dry surfaces may be sampled by pre-wetting the applicator with tap water and swabbing a representative portion of the test area.]

2. Holding applicator with clip, insert into tube of agar, taking care to center it as much as possible. Push the applicator into the tube until it is about even with the surface of the agar.

3. Add 2-3 drops of mineral oil to the tube.

4. Place a CO_2 tablet into the tube. Replace cap loosely. Wait 30 seconds and tighten cap.

5. For best results, place tube in any location where the temperature will be close [within 5 degrees] to that of the environment from which it was taken.

6. Observe the tube regularly for results and compare to the chart below.

	Sulfate Reducers/ml*				
Days of Incubation:	1	2	3	4	5
TUBE APPEARANCE					
completely black	$\geq 10^5$	$\geq 10^5$	$\geq 10^4$	$\geq 10^1$	$\geq 10^0$
narrow zone of black around applicator center .	$\geq 10^3$	$\geq 10^4$	$\geq 10^3$	$\geq 10^2$	$\geq 10^1$
no reaction	$< 10^3$	$< 10^4$	$< 10^3$	$< 10^2$	$< 10^1$

*Figures shown have been calculated by Biosan Laboratories using anaerobic plate counts and a pure culture of Desulfovibrio desulfuricans [ATCC #7757]

$\geq$ greater than or equal to
$<$ less than

Interpretation of Quantitative Results

Sulfate Reducers/ml	Interpretation
10^5 [100,000] or more/ml	Heavy
10^3-10^4 [1,000-10,000]/ml	Moderate
10^2-10^3 [100-1,000]/ml	Low
10^1-10^2 [10-100]/ml	Very Low
10^1 [10] or less/ml	Generally Insignificant

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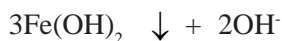
Black colour

Mechanism of corrosion occurence

$$4 Fe + SO_4^= + 4H_2O \rightarrow FeS +$$

Ferro sulfide

The cause of plugging

$$3Fe(OH)_2 \downarrow + 2OH^-$$

Ferro hydroxide

The cause of corrosion

III. RESULTS AND DISCUSSIONS

Dissolved oxygen factor contributes significantly to corrosive water. Also, if dissolved iron is present in water, the entry of oxygen into the system can result in the precipitation of insoluble iron oxides which may result in plugging. The analyzed samples for dissolved oxygen tests were A–GS, R - GS and D–GS. The results of dissolved oxygen concentration determination in laboratory for three samples mentioned above were presented in Table 3.1 and Figure 3.1 below. The concentrations of dissolved oxygen in the A–GS, R–GS and D–GS were 0.9 ppm, 1.0 ppm and 0.0 ppm. The low concentration of dissolved oxygen in A-GS and R–GS water samples can cause low corrosion problem in production facilities. D–GS water sample doesn't indicate corrosion problem, because dissolved oxygen concentration in the water is zero. According to "Corrosion and Water Technology for Petroleum Producers" by Loyd W. Jones: 1

ppm of O_2 is as corrosive as 100 ppm of H_2S or 50 ppm of CO_2 under the test conditions. At 8 ppm, O_2 is roughly 5 times more corrosive than 800 ppm of H_2S. Corrosion rate are directly proportional to O_2 concentration, viz., corrosion rate increases or decreases in proportion to O_2 content of the water when O_2 is the only corrosive agent present.

Sulfate reducing bacteria (SRB) laboratory tests

Sulfate reducers probably cause more serious problem in oilfield injection system than any other bacteria. They reduce sulfate or sulfite ions in the water to sulfide ions, resulting in H_2S as a by-product. Sulfate reducing bacteria (SRB) are mostly likely to be found in stagnant or low velocity areas, and beneath scales or sludge. Common places for bacterial activity in injection systems are tanks, filters and water
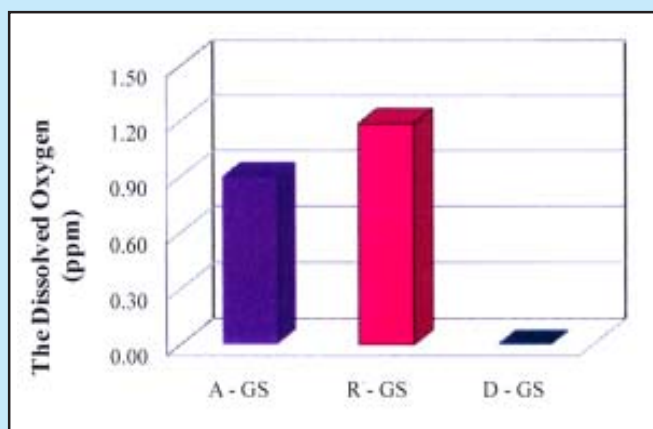

Figure 3.1
Results of dissolved oxygen concentration determination

No.	Injection water sample	Text book (ppm)	Conc. Dissolved oxygen
1	A - GS	1.00	0.90
2	R - GS	1.00	1.19
3	D - GS	1.00	0.00

Tabel 3.1
Results of determination of dissolved oxygen concentration

Figure 3.2
A - GS tube appearance
colour after SRB test

Figure 3.3
R - GS tube appearance
colour after SRB test

Figure 3.4
R - GS tube appearance
colour after SRB test

source wells. SRB test was conducted on A–GS, R–GS and D–GS injection water samples in laboratory and the results can be seen in Table 3.2 and in Figures 3.2. 3.3 and 3.4. Based on the SRB tests results, A–GS contained sulfate reducing bacteria with amount > 1000 reducer/ml (low interpretation of quantitative results) and its tube appearance colour can be seen in Figure 3.2

No.	Injection water sample	Sulfate reducing bacteria (reducers/ml)
1	A - GS	1.00
2	R - GS	1.00
3	D - GS	1.00

Table 3.2
Results of total bacteria counts determination

SRB existed in R–GS injection water sample with amount > 100,000 reducer/ml (heavy interpretation of quantitative results) and its tube appearance colour (completely black) were described in Figure 3.3.

After SRB laboratory test, D – GS tube appearance colour showed completely black (see in Figure 3.4) with heavy interpretation of quantitative results, because amount of SRB in D–GS injection water sample > 100,000 reducers/ml.

IV. CONCLUSIONS

Based on the results of laboratory tests, SOP and literature can be concluded as follows:

1. A–GS and R–GS injection water have potential to form corrosion problem, because the both water contain 0.90 ppm and 1.19 ppm dissolved oxygen, whereas D– GS injection water can not cause corrosion problem caused by zero ppm dissolved oxygen.

2. Sulfate reducers in A–GS injection water is 1000 reducers/ml, therefore A–GS tube appearance colour is not black after SRB test (see in Figure 3.2).

3. R–GS and D–GS contain sulfate reducing bacteria with high sulfate reducers / ml more than 100,000, therefore R–GS and D–GS tubes appearance colour are completely black after SRB test (see in Figure 3.3 and Figure 3.4).

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