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To cite this article: C. C Okoro & O. Amund (2015) Souring and Corrosion Potentials of Onshore and Offshore Oil-producing Facilities in the Nigerian Oil-rich Niger Delta, Petroleum Science and Technology, 33:17-18, 1563-1570, DOI: 10.1080/10916466.2015.1072559

To link to this article: http://dx.doi.org/10.1080/10916466.2015.1072559

Published online: 24 Nov 2015.

Petroleum Science and Technology, 33:1563–1570, 2015

ISSN: 1091-6466 print / 1532-2459 online
DOI: 10.1080/10916466.2015.1072559

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Souring and Corrosion Potentials of Onshore and Offshore Oil-producing Facilities in the Nigerian Oil-rich Niger Delta

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Souring and corrosion potentials of two oil producing facilities were determined by monitoring microbial activities in CSB-K medium and MPN counts of SRB and APB in API RP-38 and ZPRA-5 broth medium, respectively. Corrosion rate measurements were carried out by weight loss method. Our investigation revealed that microbiological activities at the onshore facility were dominated by methanogenesis with zero potential for souring and high potential for corrosion while that of offshore facility were dominated by sulfate reduction with high potential for both souring and corrosion. Biocide treatments were effective against the sulfate-reducing bacteria but not effective against the methanogens associated with corrosion.

Keywords:: souring, corrosion, sulfate reduction, methanogenesis, SRB, APB

INTRODUCTION

Oil field reservoir souring is the undesirable production of hydrogen sulfide (H_2S) in oil reservoirs by sulfate-reducing bacteria (SRB). This is a common problem during secondary oil recovery when sea water is injected to produce the remaining oil in the reservoir. SRB reduce sulfate in the injection water to sulfide, while oxidizing degradable organic electron donors present in the oil reservoir. The production of sulfide by SRB in the oil and gas fields causes other problems such as corrosion, reservoir plugging, deterioration of product quality, and decrease in the permeability of fine pores of underground petroleum reservoirs, which impedes the secondary recovery of petroleum by water injection (Voordouw et al., 1996; Birkeland, 2005).

The overall economic impact of microbial reservoir souring can be very significant, yet there are few technologies aimed at preventing the initiation of reservoir souring. Treating the symptoms of souring by shutting in the wells most affected or by sweetening the soured gas has been the standard industry response in the past. Attempts to prevent the initiation of souring have relied mainly on treating injection water with biocides. Recently, technologies based on principles of microbial ecology have been applied with apparent success (Vance and Trasher, 2005; Hubert and Voordouw, 2007; Voordouw et al., 2007).

Microbial-induced corrosion (MIC) can be defined as an electrochemical process where the participation of microorganisms is able to initiate, facilitate or accelerate corrosion by changing the electrochemical conditions at the metal solution interface (Videla and Herera, 2005). Microorganisms

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are ubiquitous in oil and gas environment and may influence both the initiation and propagation of all known types of metallic corrosion. As a consequence, MIC poses a serious risk for the integrity, performance, and reliability of nearly all metals used in oil and gas operations such as iron, steel, aluminum, titanium, and their alloys.

The main objective of the present investigation therefore was to establish the souring and corrosion potentials of a Nigerian deep water offshore oil producing facility that uses high-sulfate and high-saline sea water for injection and an onshore oil producing facility that uses low-sulfate and low-saline underground water for injection.

MATERIALS AND METHODS

Sample Collection

Liquid oilfield samples from Obigbo, Bonny, and Bonga were collected in sterile nalgene sample bottles, filled to the brim, and capped to minimize exposure to air. The solid samples were collected in sterile ziplock bags.

Chemical Analysis of Samples

The pH of the samples was measured using an Orion pH meter. Aqueous sulfide was analyzed using the diamine method (Trüper and Schlegel, 1964) and NH_4^+ with the indophenol method (AHPA, 1992). Sulfate, NO_3^-, NO_2^-, and the volatile fatty acids (VFA) acetate, propionate, and butyrate were analyzed by high-pressure liquid chromatography (HPLC), as described elsewhere (Grigoryan et al., 2008). For analysis of inorganic anions, a 100 μL of sample was combined with a 400 μL HPLC anion buffer, while for analysis of VFA, a 300 μL of the sample were combined with a 20 μL 1 M phosphoric acid.

Bacterial Activity and Viable Cell Counts for SRB and APB

The activities of SRB, as well as of heterotrophic and of sulfide-oxidizing nitrate-reducing bacteria (hNRB and soNRB) were measured in Coleville synthetic brine (CSB-K) medium as described elsewhere (Okoro et al., 2014). Counts for SRB and acid producing bacteria (APB) were also taken as described elsewhere (Okoro et al., 2014).

Methane Production Tests and Corrosion Rate Measurements

CSB-K medium inoculated with 5% sample or 1 g of solid sample were used to determine the ability of viable organisms in the samples to produce methane. The 30 mL medium was poured into an 80 mL bottle and inoculated with 2.5 mL sample. Each sample was incubated with and without two carbon steel coupons (5 $\times$ 0.5 $\times$ 0.1 cm). The head space of each bottle was filled with 10% N_2 and 90% CO_2 gas. A serum bottle with medium only served as a control. Each sample was incubated at 32°C and 100 rpm shaking. Methane production was detected by injection of 0.2 mL of culture headspace into an HP 5890 gas chromatograph equipped with a stainless steel column (0.049 cm $\times$ 5.49 m) Porapak R 80/100. Injector and temperatures were 150 and 200°C, respectively. After

TABLE 1
Sample Descriptions and Their Water Chemistry (mM)

Sample Code	*Sample Description*	*pH*	*NaCl*	*Conduc, mS/c*	*Sulfate*	*Sulfide*	*Ferrous Ion*	*Ammonium*	*Ace.*	*Pro.*	*But.*
T_PW	*Treated produced water from Obigbo	8.1	174	17.94	0.09	0.02	0	0	0	0	0
UT_PW	**Untreated produced water from Obigbo	8	157	16.23	0	0.03	0	0.01	0.45	0	0
IW	Underground injection water from Obigbo	7.6	1	0.15	0.036	0.02	0	0.08	0	0	0
PIG_WON	Water from Pig runs onshore from Bonny	7.8	220	22.67	0	0.01	0	0	1.65	0	0
ELC	Export line crude from Bonny	8.3	199	20.59	0.005	0.02	0	0.03	0	0	0
PIG1_SOFF	Solid sample from pig runs_1 offshore from Bonga	6.9	28	2.86	8.87	3.14	0.16	0	0.03	0.12	0
PIG2_SOFF	Solid sample from pig runs-2 from Bonga offshore	6.9	32	3.38	11.57	2.71	0.69	0	0.04	0.20	0
PW_HC INLET	Produced water from hydrocyclone inlet from Bonga	7.8	400	41.28	19.09	BD	BD	6.34	4.77	0.68	0.25
PW_LPSP	Produced water from LP seperator from Bonga	8.2	360	37.14	17.08	BD	BD	6.30	4.87	0.74	0.34
PW_BOT	Produced water from bulk oil treater from Bonga	8.2	387	39.90	19.98	BD	BD	5.93	5.09	0.17	0.25
IW_FILTER	Injection water after filtration from Bonga	7.9	510	52.58	27.66	BD	BD	0.07	0	0	0.2

*Hydrocarbon content <50 ppm. **Hydrocarbon content >50 ppm. BD = below detection limit; Ace = acetate; Pro. = propionate; But. = butyrate.

culturing, corrosion rates were determined by the weight loss method as described previously (Okoro et al., 2014). LPR probe was also used to measure corrosion rates in samples.

RESULTS

Chemical Analysis of Samples

Chemical analysis data are all shown in Table 1. For Obigbo and Bonny terminal samples, the pH ranged from 6.8 to 8.3. Sulfate concentration was negligible in all the samples except the pig solids samples that had high sulfate concentration (8.8 and 11.5 mM). Nitrate and nitrite concentrations were below the detection limit of HPLC. The ammonium concentration in the samples ranged from 0 to 0.08 mM. Ferrous iron was found mainly in the pig solids samples at a concentration of

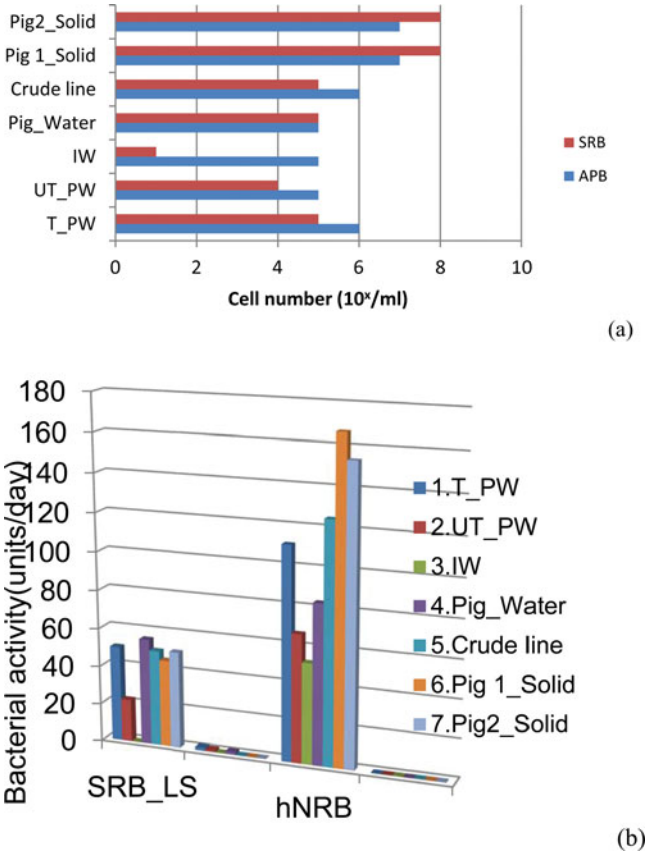

FIGURE 1 Bacterial activities and MPN results of Obigbo and Bonny terminal samples. (a) MPN for SRB and APB; (b) bacterial activity.

0.16–0.69 mM. Acetate was present only in the untreated produced water and water sample from pig runs (TNP). The highest concentration of VFA was found in the water samples from pig runs (1.65 mM).

For Bonga samples, the pH of all samples was near neutral, from 7.86 to 8.26. The sulfate concentration was 19 mM and 27 mM in the produced and injection waters respectively, because the site uses seawater for injection (Table 1). The sulfide, nitrate, nitrite and ferrous iron levels were below the detection limit of the HPLC. The ammonium concentration in the produced water was around 6 mM, but a very low concentration (0.07mM) was found in the injection water. Acetate concentration ranged between 4.77 to 5.09 in all the samples except the injection water and solid pig run samples. Detailed results are shown in Table 1.

Bacterial Activity and Viable Cell Counts for SRB and APB

For Obigbo and Bonny terminal samples, the MPN counts for SRB were higher for the pigging solid samples (10^8/mL) than for the water samples (10^{1-5}/mL). All samples had APB numbers that ranged from 10^5/mL to 10^7/mL (Figure 1a). For bacterial activity tests, all samples showed nitrate

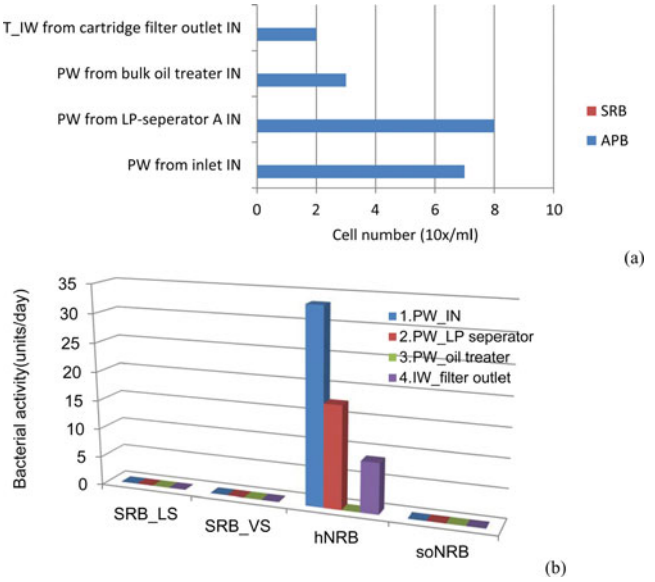

FIGURE 2 Bacterial activities and MPN results of Bonga samples. (a) MPN for SRB and APB; (b) bacterial activity.

and sulfate reduction activity when lactate and nitrate were added except the injection water sample (Figure 1b). Sulfate reduction with VFA showed very low activity in the produced water and pig run water samples but the reverse was the case with lactate. No so-NRB activity was seen in all the samples. In Bonga samples, the highest number of APB (10^8/mL) was found in produced water from LP separator. Injection water from the cartridge filter outlet had 10^2/mL of APB. However, no SRB was found in the samples because the samples had already been treated with THPS based biocides and nitrate, which seem to selectively inhibit SRB growth and not APB (Figure 2a). Consequently, there were no SRB and so-NRB activities but hNRB activities were observed in the produced and injection water samples as shown in Figure 2b.

Corrosion Rate Measurements Under Methanogenic Conditions

The two pig run samples with coupons had the highest methane formation after four weeks of incubation (1.28–1.41 mM; Figure 3a). The crude line (1.33 mM) and pig water (1.21 mM) samples with coupons had higher methane production rate than the untreated produced water (UT-PW; 0.091mM) and treated produced water (T-PW, 0.78mM; Figure 3a). Treated produced water and injection water (IW-C) with coupons showed a longer lag phase than other samples with coupons. Pig run solid samples produced less than 0.3 mM methane and other samples without coupons showed less than 10 μM of methane over the incubation period. No methane was produced in the control bottles. The highest corrosion rates were recorded in the pig solid sample (0.0154 ± 0.0009 mm/year; Figure 3b). The pig water (0.0114 ± 0.0013) and crude line (0.0121 ± 0.0018) samples showed the second highest set of corrosion rates (Figure 3b). Treated PW and untreated PW had similar corrosion rates. Injection water and the control bottle had corrosion rates of 0.0037 mm/year and 0.0039 mm/year, respectively. It appears that methane production is closely related to corrosion rate in the Obigbo samples and weight loss measurement is also related to microbial activity.

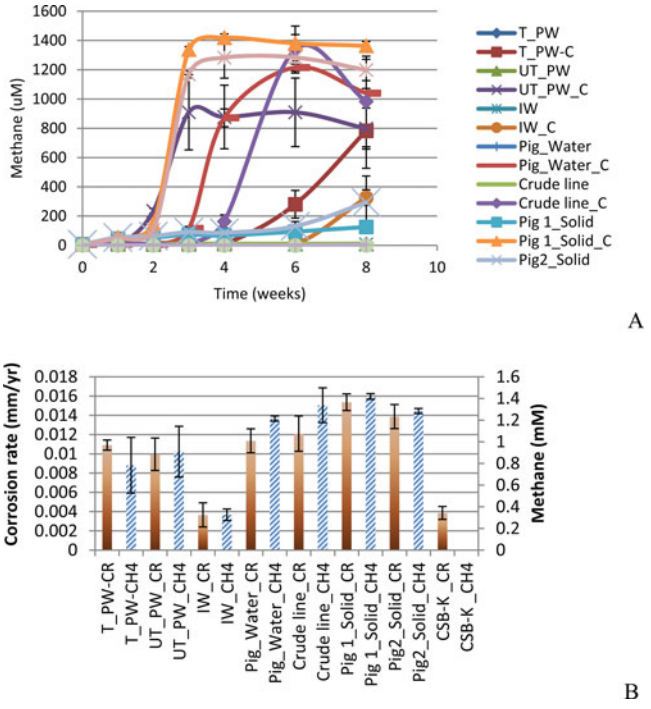

FIGURE 3 Methane production and corrosion rate measurements of Obigbo and Bonny samples and solid pig run samples from Bonga: (a) methane production with or without coupon; (b) corrosion rate and maximum produced methane.

The results of the methane formation in Bonga samples were totally different from Obigbo and Bonny samples (Figure 4a). Methane production was seen in samples without coupon and produced trace value of less than 15 uM. No methane was produced in the bottles with coupon present, possibly due to the absence methanogenic activities in Bonga samples. The highest corrosion rate was seen in the produced water of oil treater (PW_oil treater) sample (0.0060 ± 0.0011 mm/year) and the other samples had less than 0.005 mm/year, including the control bottle (Figure 4b).

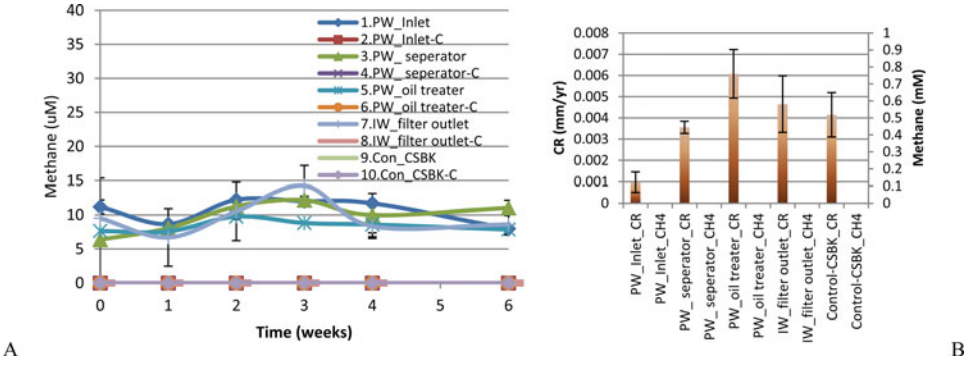

FIGURE 4 Methane production and corrosion rate of Bonga samples: (a) methane production with or without coupons; (b) corrosion rate and produced methane.

DISCUSSION

The main objective of the present investigation is to demonstrate the souring and corrosion potential of two geologically different oil-producing facilities. One is an onshore oil-producing facility that uses zero sulfate and zero saline underground water for injection and whose microbiological activities are dominated by methanogenesis while the other is a deep water offshore oil-producing facility that uses high-sulfate and high-saline seawater for injection and whose microbiological activities are dominated by sulfate reduction by SRB.

For the onshore oil-producing facility (Obigbo), methane production were observed in all samples when they were incubated with CSB-K medium and carbon steel. Corrosion rates determined from these incubations were related to methane production. This is an indication that in the absence of sulfate, methanogenic archaea using alternative electron acceptors can contribute to corrosion (Grabowski et al., 2005; Magot, 2005; Okoro et al., 2014).

In Bonga samples, both the injection and produced water had high sulfate (20–27 mM) and acetate (4.7–5.0 mM) concentration which is expected of a deep water offshore field (Oduola et al., 2009; Pharm et al., 2009; Okoro et al., 2014). Expectedly, the activities of SRB and sulfide oxidizing, nitrate reducing bacteria (so-NRB) were extremely low due to continuous nitrate injection and biocide dosage, which directly inhibit the activities of the SRB and the so-NRB, thereby preventing souring (Oduola et al., 2009). However the activities of hNRB were found to be high due to continuous nitrate injection that seems to stimulate the activities of the hNRB (Oduola et al., 2009). Despite low microbial activity due to biocide usage and nitrate injection, corrosion rate measurement of the injection and produced water using LPR method was high (0.356 ± 0.019 mm/year and 0.505 ± 0.072 mm/year). This indicates that corrosion was not mediated by methanogens but rather SRBs.

CONCLUSION

The onshore oil production facility at Obigbo with low saline and zero sulfate concentration have potential for corrosion due to the activities of the methanogenic archaea but souring is not possible because of nonavailability of sulfate and SRB. The deep water offshore oil production facility at Bonga have high potential for both souring and corrosion because of the availability of sulfate, acetate and SRB but souring and corrosion is being controlled by the combined action of nitrate injection and biocides.

ACKNOWLEDGMENTS

The authors thank Jaspreet Mand, Dongshan An, Hyung Soo Park, and Johana Voordouw for analytical assistance.

FUNDING

This work was supported through grants from Petroleum Technology Development Fund (PTDF), Nigeria, and a Natural Sciences and Engineering Research Council (NSERC) Industrial Research Chair Award to Gerrit Voordouw.

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