Chapter 15
Biocorrosion and Souring in the Crude-Oil Production Process

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15.1 Introduction

To increase the productivity of crude oil from the oil well, the recovery methods have been developed. Waterflooding serves as a main oil recovery method to be applied whenever the geological pressure became inefficient, known as a secondary oil recovery (Plankaert 2005). In the secondary oil recovery process, seawater is commonly injected to enhance oil recovery; however, this method causes biological souring (i.e., sulfide production in oil reservoirs). The crude oil including more than 0.04 mol% of hydrogen sulfide is defined as "sour oil." Seawater contains a high concentration of sulfate (up to 27 mM) that can enhance the growth of sulfate-reducing bacteria (SRB) in the reservoir. Souring causes several problems, including microbiologically influenced corrosion of the tubing material and deterioration of crude oil (Gieg et al. 2011). Microbial sulfate reduction is an important metabolic activity in many petroleum hydrocarbon (PHC)-contaminated aquifers; contamination with mono-aromatic PHCs (e.g., benzene, toluene, ethylbenzene, and xylene) is a regulatory concern due to their solubility and toxicity. Because sulfate reduction can be coupled with the bacterial metabolism of mono-aromatic PHCs, it has received increasing attention as an intrinsic remediation process.

SRBs, which mostly belong to *Deltaproteobacteria* or *Firmicutes*, are among the microorganisms present in oil fields that induce souring. Although corrosion control measures can be used to remove oxygen from the injected water, these create an environment conducive to the growth of SRBs, which are obligate anaerobes. SRBs derive energy by coupling the oxidation of electron donors to the reduction of sulfate to sulfide. Previous studies have revealed that SRBs use volatile fatty acids (VFAs)

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and crude-oil components (e.g., toluene) as electron donors. The most common method to prevent souring is the injection of biocide, metabolic inhibitors such as nitrite or molybdate into reservoirs to inhibit SRB growth (Jayaraman et al. 1999; Nemati et al. 2001; Tang et al. 2009), and/or air injection to prevent anaerobic condition (Ochi et al. 1998), but these methods have yielded limited success. An alternative approach is nitrate injection, which seeks to promote the growth of nitrate-reducing bacteria (NRB) as competitors of SRB for the electron donors in the reservoir, such as volatile fatty acids (VFAs) (Agrawal et al. 2012). Thus, nitrate injection might be used to prevent and treat souring. Nitrate injection is an attractive solution to souring because nitrate is cost-effective and relatively nontoxic and can distribute evenly in the reservoir (Dunsmore et al. 2006; Gieg et al. 2011). However, so far, the effect of nitrate injection on the biocorrosion of carbon steel has not been well known.

In this chapter, the biological souring mechanisms and the prevention methods for souring are introduced. Moreover, the biocorrosion of carbon steel in the environment where the souring occurs and/or the prevention of souring is applied to the souring.

15.2 Identification of Crude-Oil Components and Microorganisms that Cause Souring Under Anaerobic Conditions

For biological souring, three factors are strongly related. They are sulfate as an electron acceptor, organic compounds as electron donors, and sulfate-reducing bacteria as biocatalyst. In the oil production process, the sulfate plentifully exists in the injection seawater. Therefore, to understand the mechanism of souring, the other two factors should be clarified. Various kinds of organic compounds, such as aromatics, hydrocarbons, and so on, are included in the crude oil, and a small amount of them is dissolved in the injection seawater.

To identify the preferential substrate for souring, the mixtures of the several crude-oil components (alkanes [AL], aromatics [AR], 2,4-dimethylxylenol [XY], naphthenic acids [NA]) and crude oil [CR] diluted 1:100 with biologically inert branched alkane 2,2,4,4,6,8,8-heptamethylnonane (HMN) were overlaid on the seawater supplemented with microorganisms from oil field water (OFW) taken from oil field (Akita, Japan) (Hasegawa et al. 2014). XY and NA were investigated as the organic compounds with the intramolecular oxygen, while ALs and ARs were investigated as dominant compounds in the crude oil. All of them were incubated in high-pressure vessels under 1 MPa at 28 °C for about 3 months. The components of crude oil that decomposed under anaerobic conditions were identified. Toluene, ethylbenzene, and alkanes (C_7–C_{17}) were selectively degraded. On the other hand, no change was observed for XY and NA. It is concluded that decomposition of aromatics [AR] and alkanes [AL] was accompanied by the production of acetate as an intermediate, followed by its oxidation. In XY and NA, no biological activity was

observed. It shows they are toxic to microorganisms, and the degradation of these compounds has not been well studied.

Biological conversion of crude-oil components to produce sulfide can be divided into two steps: oxidation of oil components to produce VFA (Step 1) and reduction of sulfate to sulfide coupled with oxidation of VFAs (Step 2). There are two possible degradation mechanisms of crude-oil components. One is the complete oxidation of crude-oil components to CO_2 by SRB. This mechanism is supported by the detection of *bssA* genes that were most likely the *bssA* gene of *Desulfobacula toluolica*. In this mechanism, toluene-degrading SRB is involved in both Step 1 and Step 2. The other is syntrophic oxidation. Detection of acetate indicated that the oil field microorganisms excreted acetate as a by-product, and the subsequent decreases indicated that other microorganisms such as SRB consume acetate and produce sulfide. Production of sulfide in AL was much less than in AR, although acetate was produced in both vessels. Moreover, toluene and ethylbenzene were completely degraded, and *bssA* affiliated with SRB was detected in AR. The metagenomic analysis of 16S rRNA gene sequencing revealed that *Desulfotignum* spp. detected in AR were affiliated with the toluene-degrading SRB, *D. toluenicum*. Although it remains unclear whether alkanes were degraded by SRB, it seems that degradation of aromatic hydrocarbons mainly toluene contributes significantly to souring.

Community analysis revealed that abundant classes in day 49 were distributed among *Deltaproteobacteria*, *Gammaproteobacteria*, and *Clostridia*. Specifically, the proportions of *Deltaproteobacteria* and *Clostridia* were increased in AL, AR, and CR after 49 days. Many SRBs, including *Desulfotignum* spp., belong to *Deltaproteobacteria*. The dominant *Clostridia* were *Fusibacter* spp., a genus of anaerobic fermenting bacteria. Although the proportion of *Fusibacter* was lower than in AL and CR, *Fusibacter* spp. were also detected in AR. *Fusibacter paucivorans*, isolated in an oil-producing well, can transform glucose to acetate by fermentation (Ravot et al. 1999). Therefore, *Fusibacter* spp. detected in this experiment might be involved in acetate production by fermentation. Minor phylotypes were distributed within the *Bacteroidetes*. The involvement of *Bacteroidetes* in hydrocarbon degradation has been investigated (Zrafi-Nouira et al. 2009; Popp et al. 2006). *Acinetobacter* spp., which belong to *Gammaproteobacteria*, were also detected in AL, AR, and CR. Abboud et al. (2007) reported that some strains of *Acinetobacter* spp. are involved in biodegradation of crude-oil components.

15.3 The Effect of Nitrate Injection on the Biological Souring Under the Presence of Sulfate-Reducing Bacteria (SRB) and Nitrate-Reducing Bacteria (NRB)

As described in the introduction, to prevent souring, the nitrate addition is applied to the oil-producing process. Kamarisima et al. (2018) revealed that the nitrate addition at the beginning could suppress the biological souring by chemical analysis and by

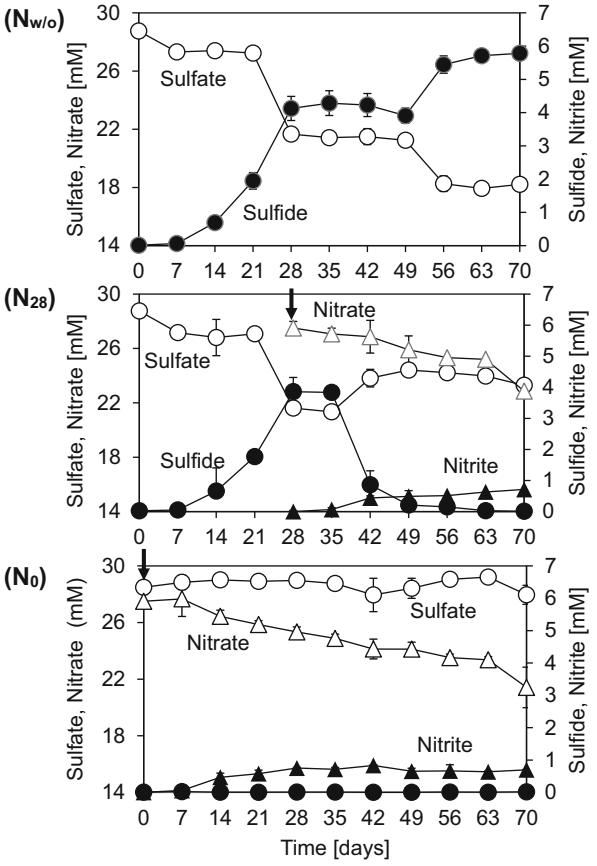

Fig. 15.1 Effect of nitrate addition on sulfide production and sulfate reduction. Arrows indicate the nitrate addition (Kamarisima et al. 2018)

biological analysis. By chemical analysis, it was revealed that without the addition of nitrate ($N_{w/o}$) to the artificial souring environment using the 2% of crude oil in the 2,2,4,4,6,8,8-heptamethylnonane (HMN) as a substrate, the sulfide production and sulfate consumption were simultaneously observed in the seawater medium (Fig. 15.1). Moreover, after souring occurred by SRB derived from the oil field water, the nitrate addition at day 28 (N_{28}) was also effective for the decrease of sulfide production and suppression of sulfate reduction. On the other hand, when 27 mM of nitrate at the same level of sulfate (27 mM) in the seawater was added from day 0 (N_0), no sulfide production occurred for 70 days. According to the results of biological analysis based on 16S rRNA gene sequences shown in Fig. 15.2, in the conditions of $N_{w/o}$ and N_{28}, the relative abundance of *Desulfotignum* sp., one of the representative SRBs suspected to be the primary degrader of toluene, became dominant after 28-day incubation. It was thought that this SRB caused souring for the initial stage of incubation. Moreover, in the condition of N_{28}, the dominant *Desulfotignum* sp. did not disappear till the end of incubation, even though the sulfide production was suppressed after nitrate addition at day 28. In the case of N_0

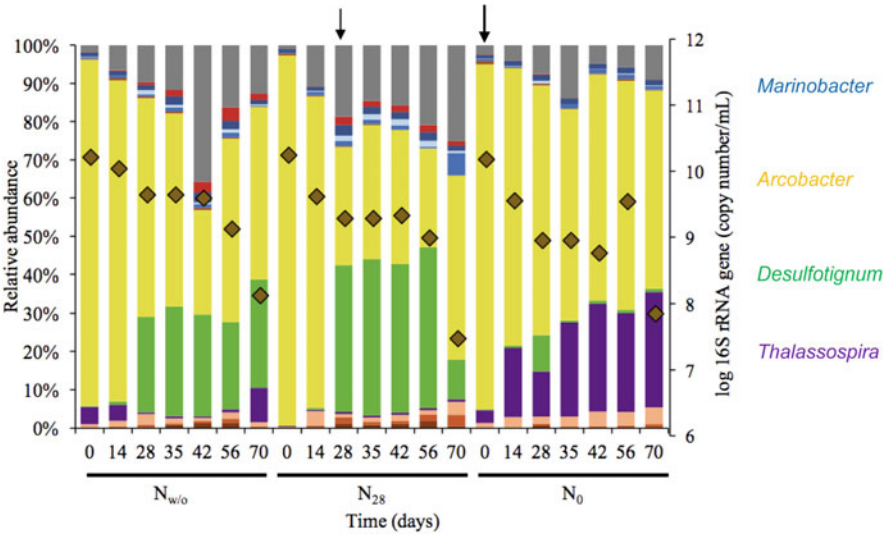

Fig. 15.2 Bacterial community profile in 70 days of incubation. The symbols of diamond and arrows indicate 16S rRNA gene copy number and time of nitrate addition, respectively (Kamarisima et al. 2018)

condition, instead of *Desulfotignum* sp., *Thalassospira* sp. became dominant as the incubation period. *Thalassospira* is known as the heterotrophic nitrate-reducing bacteria (hNRB). Therefore, it is reasonable that the NRB abundance increased instead of SRB after nitrate addition to the microbial mixture. SRB and hNRB might share similar sources of electron donors, such as the hydrocarbon fraction (especially toluene) in crude oil.

However, in the condition of N_{28}, *Thalassospira* sp. did not become dominant, although a small relative abundance of *Marinobacter* sp., also one of the NRB, appeared at the final stage. In all conditions, *Arcobacter*, considered as nitrate-reducing and sulfide-oxidizing bacteria (NR-SOB) (De Gusseme et al. 2009), were the most dominant species. NR-SOB are chemoautotrophic bacteria that can oxidize sulfide coupled to reduction of nitrate. Oxidation of sulfide under denitrifying condition could lead to the formation of sulfur or sulfate. This is the reason why under the N_{28} condition the sulfide was not observed at the later culture period even though hNRB was not dominated after nitrate addition. The bacterial community could be divided into four groups (Fig. 15.3): (1) fermentative bacteria, (2) hNRB, (3) NR-SOB, and (4) SRB. Each group was thought to play a unique role in biological souring under each condition. Considering these relationships, at the limiting nitrate concentration to suppress SRB activity, 1 mM, SRB could coexist with NRB and promote a more diverse bacterial community (Kamarisima et al. 2019).

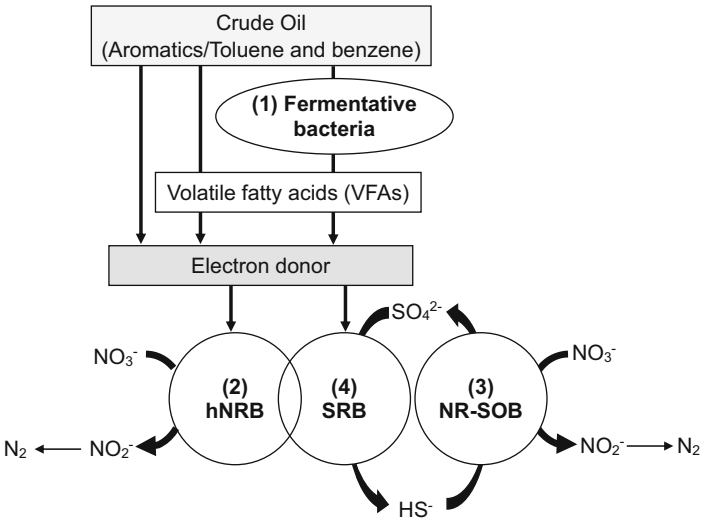

Fig. 15.3 Possible microbial interactions based on possibility of their preference electron donor and electron acceptor under microbial souring following nitrate injection (Kamarisima et al. 2018)

15.4 The Effect of Nitrate Addition on Microbiologically Influenced Corrosion (MIC)

In oil and gas industrial appliances, corrosion contributes to an increase in the cost due to corrosion control and mitigation. Microbiologically influenced corrosion (MIC) has been reported to accelerate the corrosion process more than 50-fold compared to sterile conditions as reported elsewhere (Koch et al. 2001; Kruger 2011). Several groups of bacteria have been reported and proved to play a role in MIC, such as SRB (Enning and Garrelfs 2014), NRB (Iino et al. 2015), acid-producing bacteria (Gu 2012), methanogen (Uchiyama et al. 2010), and iron-oxidizing bacteria (Emerson 2018). Among them, SRB was proposed as the primary player not only of microbial souring in the crude oil but also of MIC in oil and gas industry appliances.

MIC in the oil and gas industry often occurs during or after water injection to increase the yield of oil production. The treatment for MIC is varied among the places, which includes chemical and physical treatment. The most known chemical treatment for MIC control is the application of biocide, which then turns up that it has a high cost and toxic to the environment (Skovhus et al. 2017). Since one of the leading groups of bacteria in MIC is SRB, then a similar approach for SRB control was applied to MIC as well, which is nitrate treatment. Hydrogen sulfide was known as a corrosive agent which is produced by SRB. Various studies of nitrate treatment show successful results of controlling the production of hydrogen sulfide (Gieg et al. 2011; Hubert et al. 2005; Kamarisima et al. 2018; Voordouw et al. 2009). To date, however, the application of nitrate treatment for MIC control was limited. Only

several studies are available in the monitoring of nitrate treatment for MIC in the past 10 years. In this section, one example of nitrate-treatment effect on MIC is introduced.

Nitrate addition was proved to inhibit souring caused by SRB. However, the addition of nitrate can have contributed to cause severe corrosion. Based on bacterial community analysis, the bacterial community was different in the condition without and with nitrate addition as well as in the planktonic and biofilm sample of both conditions. In general, nitrate addition has increased the diversity of bacterial community in both planktonic and biofilm zone. There was no domination of specific bacteria in the planktonic zone of condition with nitrate addition until 90 days, and then *Arcobacter* became dominant for the later time. The common bacteria found in planktonic and biofilm site on condition with nitrate addition were identified as *Arcobacter*, *Marinobacterium*, *Acetobacterium*, *Marinobacter*, *Rhodospirillaceae* (f), *Tindallia*, *Halomonas*, *Fusibacter*, and *Bacteriodales*. Most of these bacteria were classified as NRB. Thus, it proved the enhancement of NRB in the condition of nitrate addition. In the biofilm attached to the surface of carbon steel coupon, these bacteria may produce various kinds of metabolites, especially volatile fatty acids, and provoke the pitting corrosion. The corrosion behavior of condition amended with nitrate was characterized by the formation of pitting corrosion as the localization of acid-bacteria and extracellular polymeric substance (EPS)-forming bacteria. Moreover, surface roughness was also contributed for more extensive pitting corrosion. The rougher the surface, the more pit was formed.

15.5 The Effect of Alkaline Addition on Souring and Microbiologically Influenced Corrosion (MIC)

Seawater injection into oil reservoirs for secondary oil recovery is frequently accompanied by souring (increased sulfide concentrations) in crude oil. The hydrogen sulfide produced by microbiological sulfate reduction in the seawater causes various problems, including corrosion of tubing materials and deterioration of crude oil. Sulfate-reducing bacteria (SRBs) play major roles in souring. However, under high pH (>9), most microbes (including SRBs) cannot grow. Moreover, it is known that iron corrosion is theoretically negligible under the alkaline condition. To investigate new approaches to simultaneously control souring and metal corrosion, Miyanaga et al. (2017) analyzed souring and metal corrosion under high-pH conditions (Fig. 15.4). NaOH was added to adjust the pH clean seawater (ca. pH 8) to 11 or 13. Then, a carbon steel test coupon was incubated for 123 days and supplemented with microbes separated from oil field water (OFW) and crude oil. At pH 11 and pH 13, the corrosion rate of the test coupon was decreased. Additionally, souring did not occur at pH 11 and 13, although it took place at pH 8 with microbes. Next-generation sequencing analysis of the 16S rRNA gene revealed drastic changes in the microbial consortia for pH 8 after incubating for 111 days.

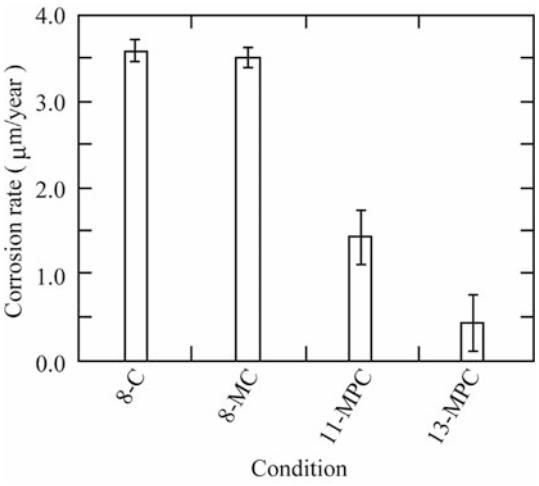

Fig. 15.4 Corrosion rate of the carbon steel coupons. Each number indicates pH value. M and P indicate with microbes and precipitate, respectively (Miyanaga et al. 2017)

Desulfotignum, which shows a high identity compared to that of toluene-utilizing SRB, became dominant. It is thought to contribute a biological souring by utilizing toluene in the crude oil at pH 8. On the other hand, at pH 11, the microbial consortia did not change significantly after 111 days of incubation. At pH 13, the microbial consortia drastically changed compared with that of initial condition (OFW) due to cell lysis. That is, even under strict conditions (e.g., pH 13), some bacteria are not lysed, increasing their relative ratio without growth. Alkaline addition could inhibit not only metal corrosion but also biological souring.

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