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When nitrate treatment wins the battle against microbial reservoir souring but loses the war

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A B S T R A C T

The injection of seawater into a hydrocarbon reservoir (seawater flooding), as an oil recovery method, triggers microbial reservoir souring, through which microorganisms consume sulfate ions and produce hydrogen sulfide, which is hazardous, corrosive, and detrimental to the environment if enters production wells. A strategy to mitigate this problem is to add nitrate or nitrite to the injection seawater, also known as nitrate or nitrite treatment. This study investigates nitrate treatment in a simulated real-world sector scale hydrocarbon reservoir in the Danish North Sea through a non-isothermal multi-phase multi-component bio-chemical model and field observations. The common expectation is that the higher the concentration of nitrate or nitrite in the injection seawater the less hydrogen sulfide production. However, the results of this study show that slowing down the microorganisms (or mitigation through nitrate treatment) may cause higher hydrogen sulfide production from production wells. Put differently, not only the total amount of hydrogen sulfide generated inside the reservoir matters, but also the location of the generation zone and its distance from production wells. Therefore, it is possible that insufficient amounts of nitrate cause the generation zone to move toward the production wells. Hence, more hydrogen sulfide is produced during the lifetime of the reservoir. Moreover, considering laboratory and field scale measurements, in the presence of coupled multi-physics processes, the growth rates at the field scale are significantly lower than those observed in the laboratory experiments, under in-situ conditions, utilizing actual reservoir fluid samples.

1. Introduction

A challenge associated with water flooding subsurface hydrocarbon reservoirs is microbial reservoir souring. Mainly due to the lower temperature of the injection water compared to that of a deep reservoir and the high concentrations of sulfate ion (SO$_4^{2-}$) in the injection water, a suitable situation is created for Sulfate Reducing Bacteria (SRBs) to reduce sulfate and produce hydrogen sulfide (H$_2$S) (reaction 1 in Table S1), which is a corrosive and hazardous gas with detrimental environmental effects (Al-Janabi, 2020; Mahmoodi et al., 2022; Mitchell et al., 2021). Microbial sulfate reduction has been reported to take place in various environments (Liu et al., 2015; Parthipan et al., 2023).

One mitigation strategy for microbial reservoir souring is the addition of nitrate ions (NO$_3^-$) to the injection water. There are various mechanisms through which the presence of nitrate can mitigate souring. First, the heterotrophic reduction of nitrate through Nitrate Reducing Bacteria (NRBs) consumes Dissolved Organic Carbon (DOC), which is required for sulfate reduction through SRBs (reaction 2 in Table S1). In this way, the amount of DOC could be limited for souring (also known as bio-competition) (Xue and Voordouw, 2015; Agrawal et al., 2012). Second, the reduction of nitrate produces nitrite (NO$_2^-$), which has a direct inhibitory effect on the activity of SRBs (Veshareh et al., 2021). It is also worth noting that there are NRBs that can reduce nitrite to nitrogen (reaction 3 in Table S1), consuming even more of the DOC, and thus contribute to bio-competition on DOC consumption. Third, Nitrate/Nitrite Reducing Sulfide Oxidizing Bacteria (NRSOBs) are able to reduce nitrate or nitrite and oxidize sulfide back to sulfate (reactions 4 and 5 in Table S1) and potentially elemental sulfur (Jahanbani Veshareh and Nick, 2019; Qi et al., 2022; Veshareh et al., 2021). Finally, some SRBs are able to use alternative terminal electron acceptors to sulfate such as sulfonates, nitrate, nitrite, iron and manganese (Marietou, 2016). This suggests that with the presence of nitrate or nitrite in the environment, some SRBs may switch to the more energy-efficient nitrate or nitrite reduction instead of sulfate reduction (Eckford and Fedorak, 2002; Eckford and Fedorak, 2002).

In the real world, however, dosages of 70 and 120 ppm of a 45%
calcium nitrate solution have been used in different fields, often without a good technical reason, whilst levels of souring have continued to rise (Mitchell et al., 2021). These amounts of nitrate may be efficient in laboratory setups, but the full-scale reservoir may show a different behavior especially because of the higher duration of the time that sulfate and nitrate and/or nitrite are present in the reservoir before they reach the production wells. Moreover, it is a common expectation that the higher the concentration of nitrate or nitrite in the injection seawater, the better the treatment. However, considering the distance between hydrogen sulfide generation zone inside the reservoir and the location of the production wells, this expectation could be wrong. This calls for the study of souring in field-scale reservoir models with the purpose of more reliable predictions and re-visiting the common understanding of the impact of nitrate treatment on H$_2$S production.

Understanding the role of coupled processes in real systems is key to design safe and effective mitigation solutions. We approach this issue through combining the observed field data with a novel workflow coupled with multi-physics simulation to study the underlying mechanisms that drive a nitrate treatment ineffective or detrimental. We utilize reactive transport modeling to investigate souring and nitrate mitigation in a large sector of a hydrocarbon field in the Danish North Sea. In this study, the results of the simulation cases are compared to the field observations. Then, the intensity of reservoir souring is compared to the amount of produced H$_2$S from the production wells and the propagation of H$_2$S plume inside the porous media of the reservoir. This study allows re-assessing the current mitigation solutions applied.

2. Methods

A non-isothermal multi-component bio-chemical model has been developed to couple with a reservoir simulator and simulate microbial reservoir souring in subsurface reservoirs. The microbial reactions and the governing laws and input values to compute their kinetics are taken from Cheng et al. (2016), whose model has been validated against the experimental data of Engelbrektson et al. (2014) (Table S1). Furthermore, the effect of temperature on the growth rate of bacteria has been added based on the work of Rosso et al. (1995) (Table S2). Moreover, the composition of formation brine and seawater were set to resemble the case of this study based on Cheng et al. (2016) and Vigneron et al. (2017) (Table S3). Notably, although a microbial guild can comprise various strains of microorganisms with various specifications, only one microbial strain for each of the functions (sulfate reduction, nitrate/nitrite reduction, and nitrate/nitrite reduction sulfide oxidation) has been considered in this study (Cheng et al., 2018). Moreover, biofilm generation inside the porous media has been neglected in this work, but it can have an effect in the flow and bioavailability. (D’Acunto et al., 2019; Sanderlin et al., 2013)

In this work, we introduce a correction factor to the Monod equation ($\gamma$ in equation 5 in the supplementary material), which includes the combined effect of bioavailability, bacterial mobility, mixing, nutrients and temperature front, and heterogeneity from pore to grid block scale (micrometers to tens of meters). These effects decrease the effective growth rates ($r_{ef}$) used for field-scale modeling through the availability of nutrients or the variations in the environment within a large grid block (Hesse et al., 2010; GHARASOO et al., 2012; Hesse et al., 2009; Carrera et al., 2022; Tartakovsky et al., 2009). In reality, the $\gamma$ factor is a function of time and space. However, in this work, for the sake of simplicity, a constant $\gamma$ has been assumed to be used to match the history of the field with the model.

A sector of a hydrocarbon field in the Danish North Sea has been selected to investigate microbial reservoir souring and the effectiveness of nitrate treatment. The sector comprises 3 horizontal production wells and 2 horizontal injection wells in between them (Figure S1). The middle production well is the target of this study. The black oil reservoir model had already been created in the commercial reservoir simulator Eclipse 100 and history matched against field production data. Then, the souring model was run reading the output of the reservoir simulation (the flowchart of the coupling method is depicted in Figure S2).

Two cases of no treatment and a continuous addition of 50 mg/l of nitrate to the injection seawater as the souring treatment strategy are investigated for four different values of $\gamma$. Very low, low, medium, and high $r_{ef}$ correspond to $\gamma$ values of $10^{-5}$, $10^{-4.5}$, $10^{-4}$, and 1, respectively, for all microbial pathways. A detailed description of possible pathways can be found in our previous publications (Jahanbani Veshareh and Nick, 2019; Veshareh and Nick, 2021). For the sake of simplicity, we consider fixed $\mu_{max}$ values for all microbes. Our workflow however can capture multiple $\mu_{max}$ for microorganisms with different functions that have various trophic conditions and thus their maximum specific growth rates may also vary (Veshareh and Nick, 2021).

The mathematical model and kinetic and thermodynamic parameters have been introduced in the supplementary material.

3. Results and discussions

The results of this study are presented in two sections. First, the effect of the intensity of microbial activities (effective growth rate of microorganisms) is studied and then the effect of a continuous addition of 50 mg/l of nitrate to the injection water on each of the cases is discussed.

3.1. Effective growth rate ($r_{ef}$)

Expectedly, the total amount of H$_2$S generated inside the reservoir decreases as effective growth rate decreases (Fig. 1A). In case of high effective growth rate, the microorganisms consume all the sulfate injected with the seawater before any of it reaches the production well, which does not fit the sulfate production data at all (Fig. 1C). Therefore, the complete conversion of seawater sulfate is not the case for the studied field. In such case, the maximum total amount of H$_2$S would be generated inside the reservoir, meaning sulfate would be the limiting factor. It goes without saying that the total amount of generated hydrogen sulfide inside the reservoir is not measurable in practice.

On the other hand, the concentration of H$_2$S in the produced gas from the production well shows an unexpected trend. Expectedly, in the early stages of production (e.g., before 2014 when comparing very low and high effective growth rates in Fig. 1B), the H$_2$S concentration in the production fluids is lower in case of lower effective growth rates (i.e., slower microbial activities). The main reason here is that it takes more time for the microbial community to grow large enough to be able to reduce a considerable amount of sulfate to hydrogen sulfide before reaching the production well when the effective growth rates are lower. However, with decreasing the effective growth rate from high to medium and from medium to low, higher hydrogen sulfide content is predicted to be present in the produced gas from the production well after a long time. Nevertheless, with a further decrease of effective growth rate from low to very low, less hydrogen sulfide will be produced from the production well (Fig. 1B).

Looking at the visualized reservoir (Fig. 2), one can readily notice the size of H$_2$S plume inside the reservoir. In the high effective growth rate case, despite higher concentrations of H$_2$S, a smaller plume of H$_2$S is formed. Hence, most of the generated H$_2$S inside the reservoir is yet far away from the production well. Nevertheless, as the effective growth rate decreases, despite lower average concentrations of H$_2$S in the medium, a bigger plume has been created, which has already reached the production well (Fig. 2C). Consequently, as the effective growth rate decreases, the H$_2$S concentration around the production well first increases because the H$_2$S plume reaches the production well earlier (i.e., H$_2$S generation zone in the reservoir is closer to the production well), and then decreases because the concentration in the plume of H$_2$S decreases enough to reverse the trend (Fig. 1B).

This observation gives rise to the concern that a good match between
the simulation results and the field data with H$_2$S concentration in the produced gas may result in very misleading interpretations about the real effective growth rates of microbial activity (e.g., the high and low effective growth rate cases have somewhat similar results in this sense in Fig. 1B). That is the first reason why it is necessary to confirm simulation results in a way other than fitting on hydrogen sulfide concentration in the produced gas.

Furthermore, the concentration of produced hydrogen sulfide was measured in the gas phase at separator conditions. However, the measured field data (the blue circles in Fig. 1B) is probably heavily affected by gas lift, which is the injected gas into the production well with the purpose of lowering pressure drop along the wellbore. Unfortunately, no reliable data on the injection rate and H$_2$S concentration in the injected lift gas is available for the case of this study. Based on the non-reliable data, the lift gas in this case contains quite high concentrations of hydrogen sulfide (above 100 ppmv). Since, based on simulation results, the H$_2$S content in the gas coming from microbial activities inside the reservoir is expected to be considerably lower than that until 2018, the uncertainty in the lift gas data could fade out the H$_2$S concentrations coming from the reservoir, and thus it is not reliable to match the history of measured field data with the simulation results. That is the second reason why it is necessary to match the history with other measurements. It is worth noting that there could be some possible methods of validation, such as drilling monitoring wells to measure H$_2$S concentrations in a location closer to the injection well or installing downhole permanent sensors, which have not been done for the case of this study.

In this work, sulfate concentration in the produced water is chosen for matching the history since microbial reservoir souring may heavily affect the sulfate concentration response in the production well. It is

![Fig. 1. A: Total amount of hydrogen sulfide inside the porous medium of the reservoir (in kilograms). B: The concentration of hydrogen sulfide in the produced gas (from the middle production well) in separator conditions. C: The concentration of sulfate ion in the produced water from the target production well. In all figures, $r_{eff}$ is the effective microbial reaction rates and the arrows represent the effect of a continuous addition of 50 mg/l nitrate to the injected water.](image-url)
assumed that the sulfate concentration in the produced water has a one-to-one relationship with the intensity of souring, which omits the complexity of $H_2S$ data in produced fluids. Put differently, the slower the microbial activities, the higher sulfate from the injection seawater reaches the production well, thus higher concentrations of sulfate are produced (Fig. 1C). Indeed, other mechanisms that could possibly affect the concentration of sulfate ion in the reservoir (e.g., barite scale formation) are assumed to have a negligible effect compared to microbial souring. The simulation results of the high effective growth rate case (with a correction factor of $\gamma = 1$) shows no proper agreement with the field data (Fig. 1C). Compared to the field data, the simulation results of this case predict much lower concentrations of sulfate ions in the produced water, implying a total consumption of injected sulfate with the seawater. However, the simulation cases with lower effective growth rates start to behave more like the field data. Indeed, in this specific sector model, it is still uncertain what value for the correction factor of the effective growth rate would match best with the field data (note the few cases in Fig. 1C that match the history). However, it is safe to say that the case of low effective growth rate with nitrate treatment and the cases of very low effective growth rate with or without nitrate treatment better match the field data compared to the other cases.

It is worth noting that there are other production wells in the same field that show a more characteristic behavior in their sulfate concentration in the produced water (more like the behavior of the low effective growth rate case in Fig. 1C). How early the sulfate concentration curve in the produced water of a well would show such a characteristic behavior is probably dependent on how long it takes for how much of the injection seawater to reach the production well.

3.2. Nitrate treatment

For the case of high effective growth rate, the addition of 50 mg/l of nitrate to the injection seawater has a small effect on the total amount of $H_2S$ inside the reservoir whereas the same treatment results in a considerably lower total amount of $H_2S$ inside the reservoir for medium, low, and very low effective growth rates (Fig. 1A).

In case of high effective growth rates, the nitrate is mostly consumed in the vicinity of the injection well and there is still time for the sulfate reducers (fast in this case) to almost fully consume the sulfate and produce hydrogen sulfide. For the medium effective growth rate case, it takes more time for the NRBs and NRSOBs to consume all the nitrate. Therefore, by the time nitrate is fully consumed, the SRBs (slower than the previous case) do not have enough time to consume as much sulfate as they would have without the treatment. In case of low and very low effective growth rates, nitrate is never fully consumed (i.e., some nitrate reach the production well) and thus the slow SRBs have no time to consume a considerable amount of sulfate (Fig. 1A).

Looking back at the $H_2S$ concentrations in the produced gas from the production well (Fig. 1B), in case of high and medium effective growth rates, a complex behavior is observed. Before 2018, the nitrate treatment shows a positive effect while after 2018, more $H_2S$ is produced from the production well due to an insufficiently effective nitrate treatment compared to the cases with no nitrate treatment. This is a consequence of a shift in the $H_2S$ generation zone inside the reservoir.
toward the production well. Therefore, it is possible that a non-sufficient amount of nitrate in the injection seawater even increases the concentration of H$_2$S in the produced fluids. In such a case, the planned cessation of production time is of importance, meaning if the plan was to stop production from the well before 2018, the effect of such treatment would be positive. Otherwise, such nitrate treatment causes more H$_2$S produced from production wells. This is in accordance with the findings of a recent experimental work (Mitchell et al., 2021) who observed that sub-optimal dosed nitrate treated bioreactors produced sulfide more rapidly than untreated controls. Although they attributed this observation to the stimulation of sulfide generation in the bioreactors in case of a sub-optimal nitrate treatment in some way, the current study suggests that a shift in the sulfide generation zone may also be a contributing factor. They also presented field data that questions the effectiveness of nitrate treatment. Moreover, the simulation results of Mahmoodi and Nick (2022) also show a shift in the location of hydrogen sulfide plume inside the reservoir, which implies a sub-optimal nitrate treatment may result in an earlier increase in the concentration of hydrogen sulfide in the production well.

4. Environmental implications

A sub-optimal nitrate treatment strategy to mitigate reservoir souring may have significant negative environmental impacts in various ways. First, insufficient concentration of nitrate in the injection seawater may increase the amount of hydrogen sulfide produced from the production wells during the lifetime of the project. Aside from the hazards directly associated with hydrogen sulfide, it also leads to increased corrosion in the tubulars, higher use of chemicals for H$_2$S scavenging and corrosion inhibition, and thus higher consumption of materials (Rathnayake et al., 2019; Wang et al., 2022). More importantly, the addition of excessive amounts of nitrate to injection water results in the presence of un consumed nitrite and nitrate in the produced water. Added chemicals and an increased nitrate or nitrite concentration requires costly treatment of the produced water before it is discharged into the sea, as they may impact marine and terrestrial ecosystems (Carreyn et al., 2021; Zhao et al., 2022; Zou et al., 2021; Lee et al., 2009).

5. Conclusions

The effectiveness of nitrate treatment to prevent souring is studied in a sector model in the Danish North Sea, which shows:

1. The effective growth rate of bacteria in a large-scale reservoir may be considerably lower than small scale studies, which is due to the combined effects of bioavailability and thermal, mixing, and chemical processes.

2. A sub-optimal nitrate treatment strategy to mitigate souring may result in higher hydrogen sulfide production from production wells despite a lower total amount of generated hydrogen sulfide inside the reservoir.

3. Unconsumed nitrate in case of excessive nitrate injection could increase the need for post-production water treatment.

The findings highlight the need for a careful study of each specific reservoir in large scale simulations with the purpose of finding the optimum nitrate concentration. Considering the coupled effects of thermal, mixing, chemical and biochemical reactions, we show that not only the current understanding of the mechanisms is defective, but also our proposed approach has reliable predictive capabilities. The presented approach is new and can be used by scientists and engineers for estimating the effective field scale reaction rates, which are required for designing operational strategies.

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CRediT authorship contribution statement

Ali Mahmoodi: Conceptualization, Methodology, Formal analysis, Writing – original draft, Visualization. Mohammad Reza Alizadeh Kiapli: Formal analysis. Hamidreza M. Nick: Conceptualization, Writing – review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Supplementary materials


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