



Biogenic sulfide control by nitrate and (per)chlorate – A monitoring and modeling investigation

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ABSTRACT

Biosouring is commonly encountered during secondary oil recovery when seawater or another high sulfate water source is utilized for flooding; as a result, effective souring control is of great interest to the oil industry. Here we describe a laboratory study to evaluate the relative effectiveness of souring interventions through the injection of nitrate, chlorate and perchlorate, collectively (per)chlorate, solutions and whether in-situ galvanic potential measurements can be used for convenient and quantitative tracking of sulfide dynamics. Nitrate has typically been the chemical of choice for souring treatments, while the efficacy of (per)chlorate as a new candidate inhibitor has only been explored recently. (Per)chlorate is known to inhibit oil reservoir souring via mechanisms such as toxicity, bio-competitive exclusion and sulfur redox cycling. Two sets of experiments under different matrix and inoculation conditions were conducted to evaluate treatment efficiency under variable baseline physical and biogeochemical conditions. Our data demonstrated the sensitivity of the galvanic potential signals to sulfide concentrations where the sulfide-galvanic potential correlation is similar to the theoretical predictions based on the Nernst equation, demonstrating the feasibility of using galvanic potential as a quick and economical method for quantifying in situ sulfide concentrations for tracking reservoir souring processes and subsequent intervention effectiveness. Our results show that all three chemicals were effective at suppressing sulfidogenesis. A reactive transport model for perchlorate treatment was developed to simulate the reaction processes and explore the interactions between the underlying competing mechanisms of this inhibitor. A baseline simulation captured the temporal patterns of the effluent chemical species. Subsequent simulations in which individual inhibition mechanisms were systematically removed elucidated the relative role that each inhibition mechanism played at the different phases of the experiment. The simulation results complement the experimental findings. Our study supports the potential advantages of souring control with (per)chlorate treatments, and the application of galvanic signal as an economic, in-situ monitoring approach for tracking souring dynamics and treatment efficacy.

1. Introduction

Microbial souring in oil reservoirs, i.e. the production of hydrogen sulfide (H₂S) (via sulfidogenesis) due to the metabolism of sulfate reducing microbes (SRMs), is commonly encountered during the secondary recovery phase when sea water flooding is applied (Gieg et al., 2011). Hydrogen sulfide is a corrosive and highly toxic gas that poses serious threats to oilfield infrastructure, pipelines, and environmental and human health (Beauchamp et al., 1984; Reiffenstein et al., 1992). Measures and interventions associated with these threats cost the oil industry billions of dollars every year (Gregoire et al., 2014).

Currently, the main strategies for reservoir souring control include sulfate removal from the injection water, H₂S scavenging, reservoir biocide treatment and thermodynamic controls (Gieg et al., 2011). Amongst these different approaches, thermodynamic control methods are gaining popularity (Engelbrekton et al., 2014; Gregoire et al., 2014; Hubert and Voordouw, 2007). Such methods work with the principles of reaction thermodynamics by injecting energetically more favorable electron acceptors, such as nitrate, into soured reservoirs (Voordouw et al., 2009; Hubert, 2010; Hubert and Voordouw, 2007). Since nitrate reduction is energetically more favorable than sulfate reduction, it tends to occur first, outcompeting sulfate reduction for

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limited electron donors (also known as bio-competitive exclusion). In addition, studies have found direct inhibitory/toxicity effects of nitrite (an intermediate during nitrate reduction) on microbial sulfate reduction (Callbeck et al., 2013). Nitrate addition can also stimulate nitrate reducing, sulfide oxidizing bacteria (NR-SOB) that can remove sulfide by coupling nitrate reduction to sulfide oxidation (De Gussemé et al., 2009; Hubert and Voordouw, 2007). While nitrate treatment is the prevailing souring control option, chlorate and perchlorate, collectively (per)chlorate, have recently been investigated as new candidate inhibitors.

Similar to nitrate, (per)chlorate reduction is also energetically more favorable than sulfate reduction. Earlier studies have also pointed to specific inhibitory/toxicity effects of (per)chlorate on sulfate reduction (Bauerle and Huttner, 1986; Carlson et al., 2014; He et al., 2010; Postgate, 1952; Sunde and Torsvik, 2005). In addition, dissimilatory (per)chlorate reducing microbes (DPRM) innately oxidize H₂S to non-soluble elemental sulfur (Coates and Achenbach, 2004; Coates et al., 1999; Mehta-Kolte et al., 2017), thus removing the source of souring from the fluid phase irreversibly. As such, (per)chlorate has been suggested and tested as an alternative, and potentially more effective sulfide inhibitor (Engelbrekton et al., 2014; Gregoire et al., 2014). However, because the microbes that can readily metabolize (per)chlorate are not naturally abundant due to the scarcity of (per)chlorate in nature, how (per)chlorate addition stimulates DPRMs growth and functionality toward sulfate inhibition is still under investigation. In addition, how the (per)chlorate toxicity effect, bio-competitive exclusion effect, and its direct sulfide oxidation effect work in concert to achieve the overall suppression of sulfate reduction requires further investigation.

In addition to understanding the mechanisms controlling the effectiveness of each inhibitor in suppressing sulfide production in oil reservoirs, effective and economic methods to monitor H₂S concentration are also critical for tracking the progression of biosouring and the evaluation of the efficacy of any interventions. Currently, such evaluations are carried out based on the measurements of H₂S concentrations in the production fluids (often the gas phase) at the ground level, e.g. using the Draeger tube method. These methods provide only discrete measurements that often lack accuracy due to sulfide loss from pressure change or volatilization during sample handling. In addition, such methods often require handling of fluids with extreme precaution due to the toxicity of the sulfide gas even at very low concentrations (Reiffenstein et al., 1992). The importance of monitoring sulfide evolution during souring and its intervention calls for safe and economic downhole monitoring strategies capable of measuring sulfide concentrations in the reservoir under the in situ pressure and temperature conditions, without human exposure, in real time, continuously, and at low cost. Downhole in situ measurements also allow sulfide monitoring in injection or production wells during the idle periods when no fluid samples are available for direct measurements.

Electrochemical methods offer the potential to meet these challenging monitoring objectives. It is well recognized that redox active ions, sulfide in this case, can be detected using electrochemical methods based on redox (i.e. galvanic) reactions occurring between a measurement electrode situated in the sulfide monitoring zone and a reference electrode outside of the monitoring zone due to the presence of a redox gradient between these two electrodes that drives half cell reactions. Metals including platinum, silver, copper and gold amalgam alloy are amongst the materials that have been studied for sulfide detection and the sensitivity of these electrodes has been tested in the laboratory and some field studies (Brendel and Luther, 1995; Kapusta et al., 1983; Personna et al., 2008; Williams et al., 2007; Williams et al., 2010; Zhang et al., 2010). For example, Williams et al. (2007, 2010), Personna et al. (2008) and Zhang et al. (2010) conducted experiments on microbial sulfate reduction and found a correlation between sulfide occurrence and a decrease of the electrodic potential of Ag/AgCl and Cu/CuSO₄ electrodes. Kapusta et al. (1983) studied the effect of sulfide

oxidation on platinum electrode surface and associated electrochemical signals. Brendel and Luther (1995) demonstrated the sensitivity of gold amalgam alloy electrodes to dissolved sulfide (along with several other redox sensitive species) in aqueous solutions using voltammetric methods. While the sensitivity of galvanic signal to the presence of sulfide has been demonstrated, studies on the accuracy of galvanic measurements in providing quantitative estimation of sulfide concentration have been limited, particularly for systems undergoing complex biogeochemical treatments in complex aqueous geochemical conditions commonly encountered in the oilfield reservoirs.

The objectives of this study were to (1) evaluate the relative efficacy of souring interventions through the injection of nitrate, chlorate and perchlorate solutions and explore the different mechanisms (i.e. toxicity, bio-competitive exclusion, direct sulfide oxidation) contributing to their inhibition effects on sulfidogenesis, (2) investigate the specific mechanisms underlying the effectiveness of the perchlorate treatment via reactive transport modeling of the system, and (3) explore the feasibility of galvanic potential measurements for rapid and quantitative monitoring of souring and desouring processes. Microbes from the San Francisco bay water were incubated and used to induce the souring conditions in the laboratory experiments, similar to the microbial community introduced into offshore oil reservoirs during the secondary recovery with seawater injection.

2. Materials and methods

2.1. Column experiments

Two sets of column experiments with different mineral matrices and inoculation strategies were conducted in order to assess the impacts of solid matrix and treatment procedures on souring development, souring treatments efficiency and the associated galvanic potential signals. Four columns were set up in each set of experiments (sandstone and bay mud); eight columns were set up in total. Each column received one type of treatment that included nitrate, chlorate, perchlorate and control (no treatment) (Fig. 1). The bay mud and sandstone columns were ran for ~20, and 50 days, respectively. All experiments were conducted under room temperature (20 ± 2 °C), and ambient pressure conditions with additional 1–2 PSI nitrogen (N₂) head space pressure at the influent bottles.

Both unconsolidated and consolidated matrices were evaluated. The unconsolidated column experiments were conducted using pre-soured Ottawa sand and San Francisco bay mud mixture packed in transparent PVC columns (3" ID × 7" length, hereafter referred to as bay mud columns). While not measured, due to the unconsolidated nature of the material, the expected permeability of the packed column was in the range of a few Darcies. The bay mud/bay water matrix served as the source of the microbial community, including sulfate reducers, indigenous to the marine environment (bay water/mud and microbial inoculum obtained from Engelbrekton and Coates lab at UC Berkeley). The bay mud and bay water mixture was incubated and pre-soured with 2 g/L yeast extract under anaerobic and ambient temperature conditions for several days to enrich the microbes before packed into the columns.

A second set of column experiments was conducted with Berea sandstone cores (Cleveland Quarries, 1.5" ID × 4" length, hereafter referred to as sandstone columns) cast with epoxy resin in PVC columns. Berea is a well-characterized quarried sandstone used for reservoir petrophysics studies. The purpose of the epoxy casting was to eliminate wall effects on laminar flow in the columns (Cohen and Metzner, 1981). The sandstone cores were sterilized at 120 °C for 2 h before the experiment. The permeability of the sandstone cores is ~100 milliDarcy as measured by gas permeametry, at least an order of magnitude smaller than that of the bay mud columns. Four columns were also setup for this experiment: one as the control column that was soured but received no desouring treatments and three other columns

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