

The Use of Nitrate for the Control of Sulfide Formation in Oklahoma Oil Fields - Final Report

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Title: The Use of Nitrate for the Control of Sulfide Formation in Oklahoma Oil Fields -

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Objectives of the Research Project: In this project we investigated, how relevant is the use of nitrate as a preferred electron acceptor to control the metabolic activity of sulfate reducing bacteria to selected oil fields in Oklahoma.

Summary of Findings: The final stage of the project was devoted to data integration and generalization and preparing a manuscript.

The produced waters at the selected site (Beebe-Konawa oil field) were highly reduced, devoid of nitrate and contained relatively high level of dissolved sulfide (≥ 3.6 mM), while sulfate concentrations were relatively low (0.58 mM) (Table 1). These chemical characteristics were consistent with the prospect of sulfate reduction occurring in the formation. In consistent fashion, we detected sulfate reduction in samples from the Oklahoma field wellheads and from the oil-water separator. The rates of sulfate reduction varied from 0.05 to 0.16 $\mu\text{M S d}^{-1}$ at the wellheads, but were about an order of magnitude higher in the sample from the oil-water separator (Table 2). These data led to the hypothesis that the majority of the sulfide produced at this facility occurred after the oil was pumped aboveground. The potential for nitrate-reducing activity was also higher in samples taken from oil-water separator than from other produced waters (Table 2). For example, in the Beebe-Konawa field, the nitrate-reducing activity in the wellhead samples were 0.016 and 0.012 $\text{mmol L}^{-1} \text{d}^{-1}$, whereas the activity in the sample from the oil-water separator was 0.06 $\text{mmol L}^{-1} \text{d}^{-1}$. We detected both sulfate reducing bacteria (SRB) and nitrate-reducing bacteria (NRB) in the oil field, which indicated a sufficient biodiversity for implementation of nitrate technique.

However in oil-water separator SRB were more numerous and exceeded NRB in two orders of magnitude (Table 2).

We focused our laboratory experiments on the produced waters as possible targets for nitrate amendment to control sulfide production aboveground. Figure 1A shows the sulfide concentrations in laboratory incubations that contained produced water from the oil-water

separator. This water contained a relatively low sulfate concentration (0.35 mM, Table 1), and little sulfide production occurred in the unsupplemented sample. Substantially more sulfide was evident when 5 mM sulfate was added to the incubation mixture, which was further increased when sulfate and oil were added together (Figure 1A). These results suggested that the activity of SRB was limited, in part, by the availability of both a terminal electron acceptor and suitable electron donors.

Produced water from the oil-water separator at the Oklahoma field was used to determine the nitrate-reducing potentials in the presence and absence of the Bebee-Konawa oil. In both cases, the potential was $0.06 \text{ mmol L}^{-1} \text{ d}^{-1}$. Thus, the presence of a separate oil phase did not stimulate the rate of nitrate reduction and dissolved components in the produced water provided an adequate supply of electron donors for the this process.

When produced water samples from the oil-water separator in the Bebee-Konawa field were amended with nitrate (5 mM), approximately half of the amendment was consumed during a 14-wk incubation (Figure 1B). Over the same period, the sulfide concentration was reduced to near undetectable levels in the nonsterile incubations. There was little change in these components in the sterile controls (Figure 1B).

Lower initial nitrate concentrations (1 or 2 mM) in to the produced waters yields only a temporary effect. That is, sulfide was incompletely removed and sulfate reduction resumed after nitrate was depleted.

All of the produced water samples we examined harbored NRB (Table 2). Thus, nitrate treatment in this oil field would be expected to stimulate nitrate-reducing activity and the use of an inoculant would be unnecessary. However, it is not known if our findings will prove generating for other oil field waters.

The amendment of 5 mM nitrate stopped sulfide production in the produced water samples. However, in other oil fields this value could be different. We recommend that each oil field should be assessed to determine whether NRB are present and the nitrate concentration required to suppress sulfide production.

Petroleum industry efforts to control sulfide production using either biocides or nitrate injection are largely focused on injecting these control agents into a suitable reservoir. However, our work suggested that reservoirs may not be the only, or even the major, source of sulfide production problems in oil field operations. In our study, the majority of sulfide production and sulfate-reducing activity was evident in aboveground facilities. Enumeration data and activity profiles showed that aboveground facilities could be effective targets for sulfide control measures with nitrate.

The manuscript “The influence of nitrate on microbial processes in oil industry production waters” was submitted to the *Journal of Industrial Microbiology & Biotechnology*.

Table 1 Geochemical characteristics of the samples from the Bebee-Konawa oil field

Oil Field	Sample	pH	Temp (°C)	Chloride (mM)	Sulfide (mM)	Sulfate (mM)
Bebee-Konawa Oklahoma ^a	Well 1	7.8	25	137	3.6	0.38
	Well 2	8.0	27	95	3.6	0.52
	Oil-water separator	7.9	23	100	3.9	0.35

Table 2 Biogeochemical characteristics of the samples from the Bebee-Konawa oil field

Oil field	Sample	Sulfate-reducing activity ($\mu\text{M S d}^{-1}$)	Potential nitrate reducing activity ($\text{mmol L}^{-1} \text{d}^{-1}$)	SRB (MPN mL^{-1})	NRB (MPN mL^{-1})
Bebee-Konawa, Oklahoma	Well 1	0.16 ± 0.04	0.016 ± 0.004	2.5×10^3	2.5×10^2
	Well 2	0.05 ± 0.016	0.012 ± 0.0005	4.5×10^2	2.5×10^5
	Oil-water separator	1.8 ± 0.27	0.06 ± 0.02	2.5×10^3	15

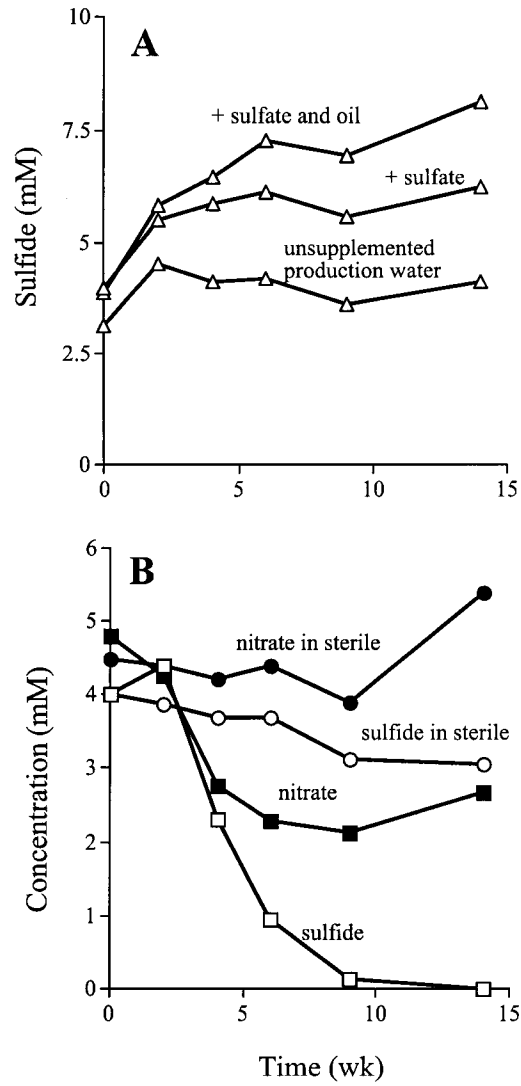


Figure 1. Sulfide and nitrate concentrations in laboratory incubations that contained produced water from the oil-water separator at the Bebee-Konawa field. (A) No nitrate added, (B) amended with 5 mM nitrate.

Progress Summary/Accomplishments:

Publications/Presentations:

Davidova, I.; M.S. Hicks; P.M. Fedorak, and J. M. Suflita, The influence of nitrate on microbial processes occurring in oil industry production waters. *J. Ind. Microbiol. Biotechnol.* 27:80-86.

Supplemental Key Words:

Sulfate reduction, nitrate reducing bacteria, microbial processes, biogeochemical, oil-water separator, oxidation, electron acceptor