

An Evaluation of Cessation of Nitrate Treatment of High-Volume Seawater Injection Systems.

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ABSTRACT

Treatment of seawater injection systems with nitrate, as a potential method of mitigation against reservoir souring, was first started in the North Sea almost twenty years ago. It was initially indicated that field experience mirrored the positive effect seen in the laboratory. However, it has become more apparent with time that the treatment has had limited effect against souring in a number of fields and, in addition, several potentially negative side effects.

There has, since the introduction of nitrate injection, been uncertainty around the effect of cessation of the treatment whether, for example, an established population of nitrate reducing microorganisms might be able to switch metabolism to sulphate reduction and thereby exacerbate levels of souring.

This paper will present data from bioreactor studies designed to test the effect of cessation of sub-optimal nitrate treatment in the laboratory. In addition, well data from a field where nitrate treatment was stopped will be used to support the conclusion that there appears to be no negative effect on reservoir souring development.

Key words: Nitrate; Cessation; Reservoir Souring; Mitigation

INTRODUCTION

Subsurface microbial generation of hydrogen sulphide (H_2S), commonly known as reservoir souring, is a clearly identified, but still not fully understood phenomenon associated with injection of sulphate containing waters for secondary oil recovery. In offshore fields in the North Sea regions the primary source of injection water is seawater, containing approximately 2700 mg/l sulphate. Cooling of the reservoir by high volume injection permits initiation of microbial growth and subsequent development of souring.

Treatment of injection water with nitrate as a mitigation method for reservoir souring has become increasingly widespread over the last fifteen years and has been reported to be an effective field method.^{1, 2, 3} Nitrate injection is understood to change some or all of the reservoir microbiome from mainly sulphate reducing prokaryotes (SRP) to one enriched in heterotrophic nitrate reducing prokaryotes which compete with the SRP for degradable organic electron donors, for example, volatile fatty acids (short chain organic acids) or other components of hydrocarbon degradation, thereby preventing biogenic sulphide production.

The Gullfaks field in the Norwegian sector of the North Sea has been widely cited^{4,5,6,7,8} in connection with and, in some instances, to justify the introduction of nitrate treatment as a mitigation method for reservoir souring. On the basis of improved understanding of souring development in the field and data availability, a review⁹ of the effectiveness of mitigation techniques was undertaken. This indicated that the previously reported effect attributed to the use of nitrate could also be explained by the natural souring development in the field.

Given that souring was also seen to be continuing to develop in other fields in the portfolio it was decided to address the potential impact of cessation of nitrate treatment. There has been a long held, but untested disquiet in the industry surrounding the potential effect of stopping nitrate treatment. It has been suggested that nitrate reducing populations might convert from the more energetically favourable nitrate reduction to sulphate reduction should nitrate be unavailable, leading to a significant increase in H_2S production.

It is probable that the lateral extent of souring in many mature fields is sufficiently large that it is not possible from a logistics point of view to inject sufficient nitrate to fully mitigate sulphate reduction. Dosages of between 70 and 120 ppm/v 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.

The paper describes the laboratory work carried out to assess the impact of cessation of sub-optimal nitrate treatment and reviews the subsequent monitoring data for a full field stop.

EXPERIMENTAL PROCEDURE

Experimental assessment of effects of nitrate treatment in bioreactors

To assess the effect of cessation of nitrate treatment in the laboratory a range of pressurized bioreactors using an oil filled sand matrix were established. A light (approximately 1.2 cp viscosity, 37 API gravity) dead oil was used from a field with a clearly defined history of reservoir souring. The sand matrix was pre-inoculated with an oil degrading, sulphate reducing consortium, taken from other souring studies. The bioreactors were held at approximately 69 bar (1000 psi) pressure, to minimize metabolic gases coming out of solution, and at a temperature of 30°C (+/- 1°C). The bioreactors were continuously injected with a deaerated mix of reconstituted (aquarium type) and natural seawater, taken from a North Sea beach area, in a ratio of 9:1, at a rate of 0.1 cm³ per minute. The pore (swept)

volume of each bioreactor was approximately 400 cm³ giving a residence time of approximately 67 hours.

Effluent sulphide (as soluble sulphide ion) concentration from the bioreactors was measured daily using zinc acetate capture followed by methylene blue colourimetric quantification. As the bioreactors were pressurized, the assumption was made that there was no free H₂S gas.

A series of eight replicate bioreactors were established and sulphide generation stabilized for 83 days prior to start of nitrate addition. A commercially available 45% w/v calcium nitrate solution was used throughout the study.

The bioreactors were randomly divided into three groups of replicates. The first group was the untreated control, the second would be the control group continuously treated with nitrate, although not to completely eliminate souring and the third group initially treated at the same nitrate concentration, with the treatment subsequently stopped. An initial concentration of 20 mg/l nitrate was optimised to 15 mg/l to ensure full nitrate utilisation whilst at the same time permitting sulphide generation in the bioreactor. It is well demonstrated¹⁰ that nitrate can fully control sulphide generation within this type of system, providing an excess is injected, however, a sub-optimal treatment has not been previously reported. Following 78 days of nitrate injection, the treatment was stopped in three of the bioreactors, giving the final experimental matrix shown in Table 1.

Table 1: Experimental matrix for the bioreactors

Designation and number of replicate bioreactors	Treatment
Untreated control x 3	None
Nitrate treated x 2	15 mg/l nitrate continuously
Nitrate outage x 3	15 mg/l nitrate for 78 days followed by stop of treatment

Field test of nitrate treatment cessation

The field selected for a controlled test of the effect of stop of nitrate treatment produces oil from moderate temperature (94 - 96°C) Triassic and Lower Jurassic sandstone formations. The field has injected approximately 30 – 40000 m³ per day of deaerated seawater for pressure maintenance since 1993. Injection water was, until 2007, routinely treated with biocide (typically 400 ppm/volume of product for two hours, twice a week) after which nitrate was used at a continuous dosage of 70 ppm/volume of a 45% w/v calcium nitrate solution. At both a well and field level there was no demonstrable effect of nitrate treatment on the reduction or prevention of reservoir souring and a decision was taken in 2014 to test the effect of cessation of treatment.

Seven wells with clearly defined injection water breakthrough patterns were selected for close monitoring, through measurement of H₂S in the separated gas phase, during well testing. Using test data, the total H₂S production from each well was calculated and interpolated with allocated production rates to show the H₂S production. Using water analyses from the routine well tests the proportion of injected water in the produced water was used to calculate a souring index,⁹ (the concentration of H₂S in the injection water fraction of produced water) in order to give a standardized description of souring development. The main objective of the test was to identify if there was a negative effect on the souring trend, reflected at well and field level.

RESULTS

Laboratory test of nitrate treatment cessation

Figure 1 shows the effluent sulphide concentration for the untreated control bioreactors. Whilst there is a degree of variation between the replicate systems, the outlet sulphide shows a steady upward trend.

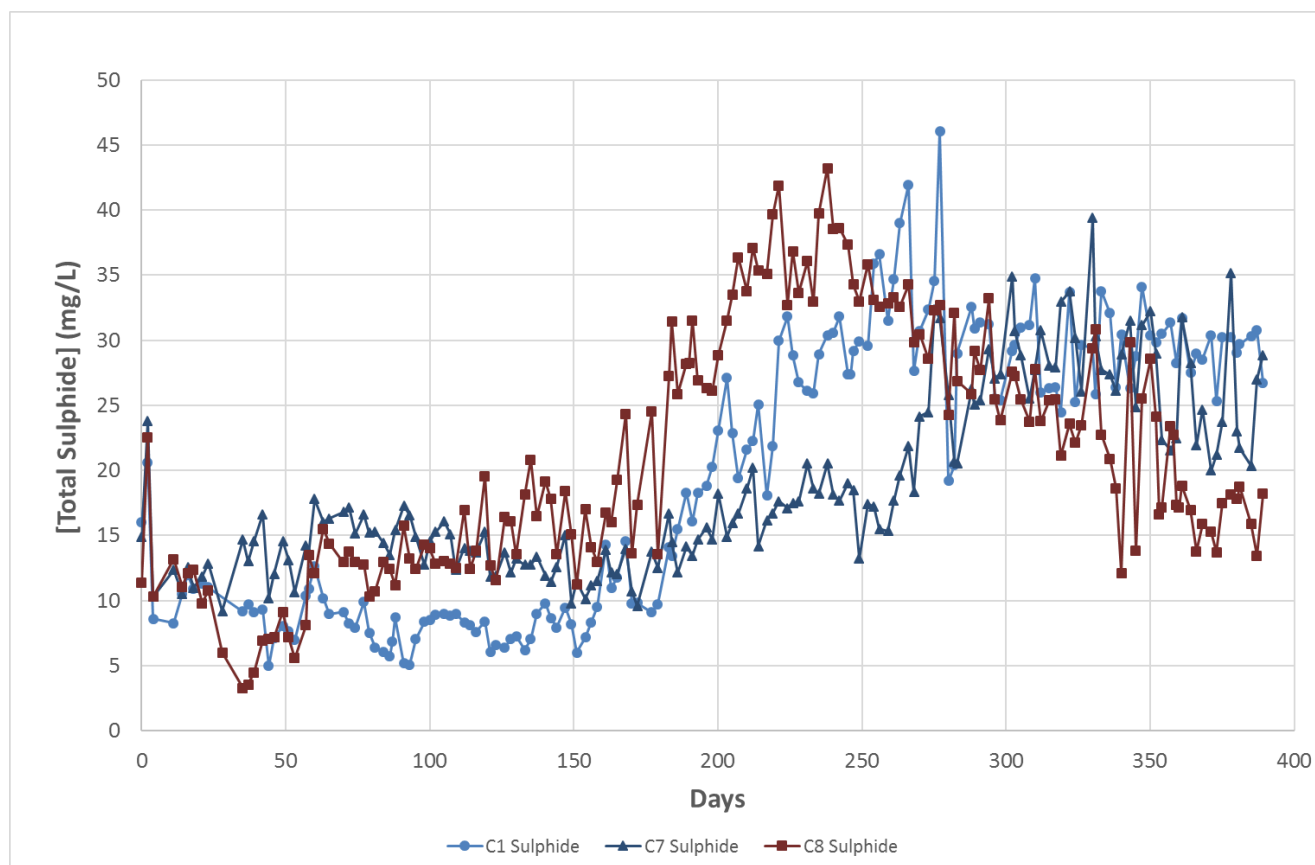


Figure 1: Measured sulphide production in untreated control bioreactors

Figure 2 shows the effluent sulphide concentration of the bioreactors treated continuously with nitrate. The injected nitrate concentration is also shown in the figure. After an initial fall in sulphide production at start of nitrate injection, the effluent concentrations rose steadily to reach a maximum of approximately 40 - 60 mg/l before eventually falling, probably as a result of nutrient limitation in the bioreactor.