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Nitrate for Corrosion Control, Souring Control and Improved Oil Production

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استخدام النيترات للتحكم في التآكل والحمضية وتحسين إنتاج النفط

برادن دنسمور وجاليس ديفس

تعتبر أملاح النيترات رخيصة الثمن نسبيا وسهلة المناولة وصديقة للبيئة ، لذلك فقد استخدمت منذ زمن للتحكم في البكتيريا المختزلة للكبريتات (SRB) وفي معالجة مياه الصرف الصحي وتستخدم الآن على نطاق واسع في منظومات حقول النفط.

لقد تم في هذه الورقة مناقشة الآليات المختلفة التي تعمل النيترات بواسطتها للتخفيض من كثافة تجمعات البكتيريا المختزلة للكبريتات والمسببة للتآكل ورفع حموضة المكامن الناتجة عن الكبريتيد المفرز كإنتاج جانبي. ولقد تم التدليل على أن النيترات تستطيع تخفيض التآكل والحموضة الناتجة عن تكون البكتيريا المختزلة للكبريتات في المختبر وفي الحقل، وإضافة إلى ذلك فان النيترات لها قدرة تحفيز تكون البكتيريا الحميدة المانعة لتكون البكتيريا المختزلة للكبريتات، ومن ثم تحسين استرداد النفط المتبقي بالمكامن.

Abstract: *Nitrate salts are relatively cheap, easy to handle and environmentally friendly. They have historically been used to control sulphate-reducing bacteria (SRB) problems in the municipal waste-water industry and are now becoming widely used in oil field systems. Nitrate acts via numerous mechanisms, which are discussed, to reduce the population of SRB in a system. SRB are responsible for microbiologically influenced corrosion (MIC) and souring of reservoirs by the sulphide by-product, which they excrete. Evidence is presented to show that nitrate can reduce corrosion and souring by SRB in the laboratory and also in the field. In addition, nitrate can also stimulate useful bacteria, which can prevent the return of SRB and also improve residual oil recovery from reservoirs.*

INTRODUCTION

Oilfield microorganisms have been shown to originate in the subsurface and to enter wells, along with substrates that may enhance their growth, upon water injection for secondary oil recovery. Sulphate in the injected water, e.g. seawater, provides the electron acceptor to allow growth on the organic nutrients present in formation water (Bass and Lappin-Scott [1]). In many oilfields this gives rise to a dominant population of sulphate-reducing bacteria (SRB). SRB are responsible for problems such as souring (contamination) of crude oil with sulphide, a respiratory by-product (Ligthelm *et al.* [2]; Sunde *et al.* [3]). In addition, SRB can enhance corrosion of pipelines and process equipment while biofilm growth can block porous rock near to injection well bores (Jack and Westlake [4]).

The oil industry has traditionally responded to microbial problems with chemical biocide treatments. However, biocides may persist in marine environments (Martinez *et al.* [5]), are often

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ineffective (Boivin, [6]), and SRB have been shown to develop resistance to some biocides (Lui *et al.*[7]). The use of nitrate to alter the ecology of a sour oil field system was proposed by Jenneman *et al.* [8]. In the laboratory 22 mg/l nitrate ion addition was insufficient to reduce sulphide production but was able to maintain sulphide inhibition after previous treatment with 44 mg/l (Reinsel *et al.* [9]).

Nitrate and nitrite have been shown to reduce sulphide levels and SRB numbers in field trials at concentrations of less than 300 mg/l (Sturman and Winters [10]) and recent field experience in the North Sea has shown that nitrate at much lower concentrations is also successful. The various potential mechanisms, by which nitrate can act, are presented here. The advantages and disadvantages of using nitrate when compared to dosing conventional biocides are discussed, and some case histories from recent field use are also presented. Finally, advice on using nitrate in oil field situations is given.

HOW NITRATE WORKS

There are several mechanisms by which nitrate or nitrite may remediate souring and these are discussed below. However, it is first necessary to briefly discuss the relevant bacterial metabolic reactions in order to understand the principle of nitrate treatment. Essentially, anaerobic bacteria reduce compounds such as nitrate, nitrite or sulphate in the same way that animals respire oxygen. In combination with this, bacteria must also oxidise a suitable carbon source as food.

Sulphate reduction: Carbon source + $SO_4^{2-} \rightarrow CO_2$ + H_2S + Energy
Carried out by sulphate-reducing bacteria (SRB)

Nitrate reduction: Carbon source + $NO_3^- \rightarrow CO_2$ + NO_2^- + Energy
Carried out by nitrate-reducing bacteria (NRB)

Denitrification: Carbon source + $NO_3^- \rightarrow CO_2$ + N_2 + Energy
Carried out by denitrifying bacteria (DNB)

(NB: Importantly, nitrate reduction and denitrification produce more energy than sulphate reduction).

The possible mechanisms by which nitrate may control souring are:

Bacterial Competition:

Sulphide formation by SRB is prevented by NRB/DNB out-competing the SRB for the available carbon nutrients. They can out-compete the SRB because more energy is produced by respiring nitrate and so NRB/DNB will grow and reproduce faster than the SRB. This is often the major mechanism behind souring control with nitrate, hence use of nitrate may be described as a bio-competitive exclusion process.

Biological Oxidation:

Perhaps a secondary mechanism in most cases, the activity of nitrate-reducing, sulphide-oxidising bacteria (NRSOB) causes sulphide removal and sulphate production. The exact mechanism is unknown but potentially:

$$H_2S + NO_3^- \rightarrow NO_2^- \text{ (or } N_2\text{)} + SO_4^{2-} \text{ (or elemental S)}$$

Inhibition of SRB:

NRB inhibit SRB activity by production of nitrite, which is biocidal and increases the redox potential of the system away from the optimum redox for SRB activity. It has also been suggested that nitrite may scavenge sulphide to a degree.

NRB + $NO_3^- \rightarrow$(possibly via NO / N_2O) $\rightarrow NO_2^-$ (or NH_4^+)

Change of Electron Acceptor:

Some SRB are able to switch electron acceptor and may use nitrate in preference to sulphate if it is readily available. Hence they act as NRB, generating by-products such as nitrite and ammonium instead of sulphide.

It is likely that in the environment a combination of all the above factors leads to effective treatment of souring by nitrate application.

Hence, given the variety of possible mechanisms it is important to define the optimum NO_3^- concentration for any given situation.

WHY USE NITRATE ?

Advantages

The advantages of nitrate treatment over conventional biocides are numerous. Firstly, and most importantly, nitrate offers a realistic option to treat a reservoir (biocides are more successful when used on topside equipment). Nitrate does prevent sulphide generation by bacteria but does not depend on killing SRB to be effective. This can be considered an advantage as biocide strategies rarely give a 100% kill of nuisance bacteria. Therefore, some bacteria will always be available to grow and divide to be a source of contamination to other areas of a system.

Nitrate is a cheaper chemical per litre than most biocides. Table 1 gives approximate comparative costs to some popular types of biocide. However, dosing may be roughly equivalent when overall costs are considered (see disadvantages below).

Table 1. Approximate costs of anti-microbial chemicals. Price per year based on dosing a 200,000 BWPD water injection system.

	Pric/litre (US$)	Dose regime (hypothetical)	Price/ year (US$)
Nitrate (50% Ca $(NO_3)_2$	0.25	60 continuous	575,000
THPS (50% solution)	4	500 for 1h 2xLweek	500,000
Glutaraldehyde (50% solution)	2.5	500 for 1h 2x/week	345,000

(* does not include transport/manpower).
(Dose regimes in mg/l nitrate ion or mg/l biocide product).

Nitrate is considerably less toxic than any biocides or H_2S scavengers in use. It is therefore, by definition, safer to handle and more environmentally friendly. It is classified as posing little or no risk to the environment (PLONOR) although there are some environmental effects, discussed below. By comparison glutaraldehyde and THPS are in HOCNS category C which means discharges in excess of 15 tonnes/ platform/year have to be notified to the authorities (in the UK).

Disadvantages

Despite the cheaper cost per litre, dosing nitrate is often carried out continuously. It is therefore more expensive overall because large volumes are needed to maintain the desired bacterial population. Higher transport costs also result, which can be a major factor when considering an offshore application. Further additional costs are related to increased manpower for dosing and monitoring.

Nitrate does not kill bacteria, and while this can be an advantage as discussed above it can also be considered a disadvantage depending on the situation. In some cases biomass of any kind is undesirable. A beneficial population of NRB may prevent sulphide generation but this biomass may risk formation damage in some cases. Nitrate is also a nutrient source for all types of bacteria and in a situation where it was previously limiting to growth its addition may stimulate damaging growth by bacterial types other than NRB.

Due to the complexities of nitrate dosing, to subtly alter the bacterial population, specialist advice is often required and more intensive monitoring needed. The results from such monitoring again may require interpretation by specialists.

Finally, proper control trials in operating oilfields are usually not possible and so results, which may take some time to show, can be difficult to prove. Yet such proof is often demanded at an early stage in order to continue trials and field dosing.

CASE HISTORIES FROM THE LABORATORY AND THE FIELD

Corrosion Control

Statoil has successfully used nitrate on the Veselfrikk field in the North Sea. From the onset of seawater injection in 1994 through to 1997, an increase in SRB and corrosion rates was measured. Nitrate was then applied, resulting in corrosion rates one third as great as pre-treatment rates. This was accompanied by the overall quantity of sessile bacterial biomass remaining constant. The theory behind the successful corrosion control by nitrate centres around disruption of the iron sulphide : mild steel galvanic corrosion cell which commonly forms when SRB biofilm creates and entrains iron sulphide.

Souring Control

A successful trial performed by Maersk Oil in the Skjold Field varied the concentration of nitrate, when applied as $NaNO_3$ from 87 – 270 mg/1 nitrate ion (Larsen[10]). However, these treatments required continuous addition of chemical and so for offshore applications logistics and related costs tend to limit the maximum applicable dose concentration. However, recently nitrate injection has been performed from day one on a new field development, which has so far resulted in delaying the onset of predicted souring. In this case dosing was performed at a considerably lower rate, some 60 mg/l nitrate ion (Larsen[11]).

By contrast to these successful treatments Shell performed an unsuccessful field trial on North Cormorant where dosing at a maximum of 34 mg/l nitrate ion did not result in any detectable decrease in H_2S. The trial was not ideal however and the dose rate was as low as 17 mg/l nitrate ion during some periods (Frigo[12]).

Microbially Enhanced Oil Recovery (MEOR)

Non-deaerated seawater, nitrate and phosphate are currently being injected to Statoil's Norne field, which has apparently resulted in around 6% additional oil reserves (30 million barrels) being produced over the last year. This process also involves the injection of a special consortium of bacteria known to produce surfactants. These surfactants are produced *in situ* at the oil : water interface and are said to be many times more efficient than injection of chemical surfactant. Oil Plus and the UK DTI are planning joint industry research projects to investigate this potentially lucrative process.

HOW TO USE NITRATE SUCCESSFULLY

Pre-Trial Assessment

Before any decision to use nitrate in the field, a pre-trial assessment must be completed. Nitrate is not suitable for every situation and the applicability of any particular strategy must be assessed. Nitrate can be applied from day one of water injection (refer to the above section) and in many cases this may be the best time to begin treatment if the souring potential for a new development is high. In addition, the appropriate dose concentration should be determined to add maximum value at minimum cost. There is no recommended dose for all situations, it varies depending on carbon source availability in the reservoir among other things. Some simple field-testing can often help give an accurate assessment and provide a baseline from which to begin treatment. Recommended dose rates should be determined using a combination of field experience and laboratory studies. A simple example laboratory study shows how there is a distinct cut-off in efficiency of nitrate under certain conditions; in this case 62 mg/l is effective. (Fig. 1) - Please note that the carbon source for these tests was specific to a given situation and these

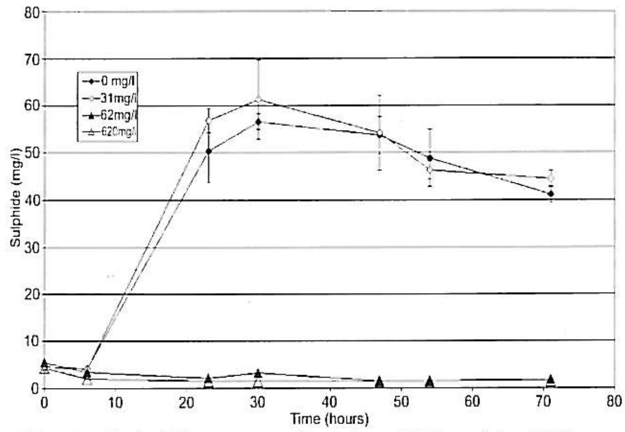

Fig. 1. Sulphide generation by SRB with different concentrations of nitrate (mg/l nitrate ion). Note: required nitrate concentrations vary widely depending on situation/ water/ carbon sources etc.

concentrations can vary dramatically for different fields.) Depending on the prevalent mechanisms in a particular field, a different concentration of nitrate may be needed. In addition, any nitrate treatment should be designed to complement existing anti-microbial measures, and the appropriate dosing point should be selected.

Field Trial

Comprehensive monitoring must be carried out, prior to and during a field trial. This is essential to evaluate the nitrate treatment in the field. Specialist advice will be needed and should be sought in order to ensure that the potential benefits of nitrate injection are realised. Monitoring should include tests for nitrate, nitrite and sulphide, as well as nitrate-reducing bacteria and nitrate-reducing, sulphide-oxidizing bacteria. In addition, molecular tools can be used to detect successful nitrate treatment: certain species of nitrate-utilizing bacteria have been associated with successful nitrate treatment. At this stage it is also crucial to optimize the nitrate dose rate.

Full Field Use

A monitoring system needs to be established to assess the long-term efficacy of any treatment. This routine testing should be set-up by a specialist consulting team, during the field trial, so that any necessary training and equipment can be handed over for correct continued monitoring by on-site staff. Periodic assessment of the data should then be made, perhaps with expert advice, to ensure that nitrate dosing is optimized, saving on unnecessary expenditure, and that the nitrate treatment continues to have the desired effect. Comparison of nitrate use, versus biocide and H_2S scavenger expenditure can also be made to determine the benefit of using nitrate.

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