

Nitrate Treatment — Effect on Corrosion and Implementation Guidelines

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ABSTRACT

Sulfate-reducing bacteria (SRB) colonization of oil field systems and the associated generation of hydrogen sulfide (H_2S) is a major corrosion concern. Conventional treatment is centered on the use of a blend of biocides to kill all microorganisms. By comparison, nitrate bio-modification technology is a non-biocidal approach for the control of SRB. The effect of the nitrate technology on corrosion, however, remains a concern in the oil industry.

Nitrate bio-modification treatment is based on the principle of selective control of SRB. When nitrate is reduced, its mechanism of action complements the oxidation of a carbon source. Therefore, the reduction of nitrate may result in the intermediate generation of nitrite, ammonia and other lower oxidized forms of nitrogen compounds. Nitrite is both a corrosion inhibitor and an oxidizing agent, and its effect on corrosion depends on its availability in reference to other aggressive anions. The possible generation of detrimental sulfur and other aggressive compounds as a consequence of the bio-modification treatment could also escalate pitting.

A survey of laboratory and field data reveals major discrepancies regarding the effect of the nitrate treatment on corrosion. In seawater injection systems, the treatment marginally reduced corrosion. In contrast, elevated corrosion rates and severe pitting have been reported from production and produced water re-injection (PWRI) systems where the treatment was used.

Nitrate treatment is a maturing technology. This article describes the effect of oil field nitrate treatment on corrosion and specifies the criteria for its successful application.

INTRODUCTION

Bacteria are a major corrosion concern to the oil industry and have been associated with a number of major failures that had devastating safety, environmental and financial consequences¹.

Nitrate has been used for many years in sewage treatment. In the last two decades, a number of oil operators have utilized nitrate treatment to control biogenic souring and sulfate-reducing bacteria (SRB) activity in oil field systems. This oil field treatment is maturing and is now used in approximately 35

fields worldwide², most of which are seawater injection systems. Nitrate bio-modification treatment is promoted as environmentally friendly and relatively inexpensive compared to proprietary biocide dosing. The bio-modification treatment is field specific, however, and in many cases, it has been implemented without sufficient laboratory validation.

Nitrate is not a biocide treatment; it merely promotes the competitive exclusion of SRB and curtails their metabolic activities. The bio-modification treatment requires that nitrate-reducing bacteria (NRB) be present and that nitrate ions be available in sufficient concentrations to stimulate this large group of microorganisms. This requirement is not difficult to meet as NRB has been detected wherever SRB are present in oil field systems.

The effect of nitrate on corrosion remains a matter of contention, with reports varying from nitrate as somewhat beneficial in controlling corrosion to nitrate as significantly increasing localized attacks and corrosion rates. A comprehensive three-year independent study³ revealed that the effect of the treatment on corrosion processes is most noticeable in produced water re-injection (PWRI) applications.

A five-year study⁴ at the University of Calgary further concluded that nitrate dosing might — under certain conditions — increase pitting due to the generation of sulfur/polysulfide and thiosulfate.

NITRATE TREATMENT

A number of reviews covering the various likely control mechanisms of the nitrate bio-modification technology have been published⁵. The principle of nitrate technology treatment is based on the concept of using NRB to out-compete SRB for the limited carbon source in the commingled connate and injection waters, Fig. 1.

- In the case of untreated water (blue bar), the carbon source is utilized by SRB to reduce sulfate to sulfide and associated hydrogen sulfide (H_2S).
- When less than 45 mg/L nitrate is added (blue and burgundy bar), the nitrate concentration is not enough to curtail sulfate reduction and H_2S production.

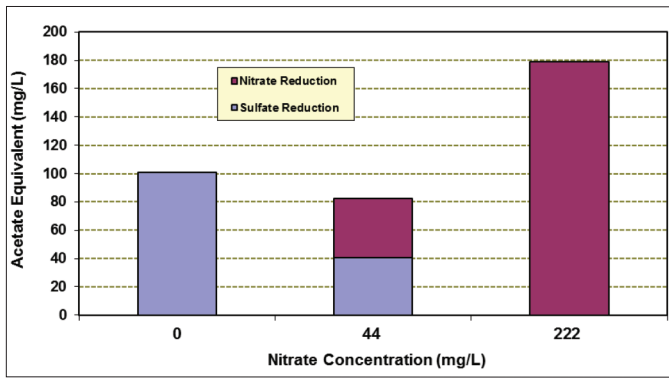


Fig. 1. Principle of nitrate treatment.

Nevertheless, the carbon source is preferentially utilized to reduce nitrate rather than sulfate.

- When sufficient nitrate (+220 mg/L) is injected (burgundy bar), sulfate reduction is curtailed and the carbon source is utilized only to reduce nitrate⁶.

There are two major reasons for the preferential nitrate reduction over sulfate reduction:

1. A significant shift in the redox potential is associated with NRB stimulation. An increase in redox potential by over 330 mV restrains SRB activities, Fig. 2.
2. The oxidation of organic acids and other carbon compounds coupled to denitrification yields over three times more energy than the oxidation of these compounds when coupled to sulfate reduction⁷.

Nitrate bio-modification technology is based on a continual dosing of the reservoir with nitrate as the electron acceptor. Continual dosing in low temperature reservoirs has resulted in the nitrates working to curtail sulfate reduction only in close proximity to the injector, while the SRB was simply pushed deeper into the formation and H₂S generation persisted. A pulse treatment delivering a high concentration of nitrate (1,000 mg/L) that alternated with an otherwise low continual dosage has proven effective in overcoming the zonation problems in low temperature systems⁸.

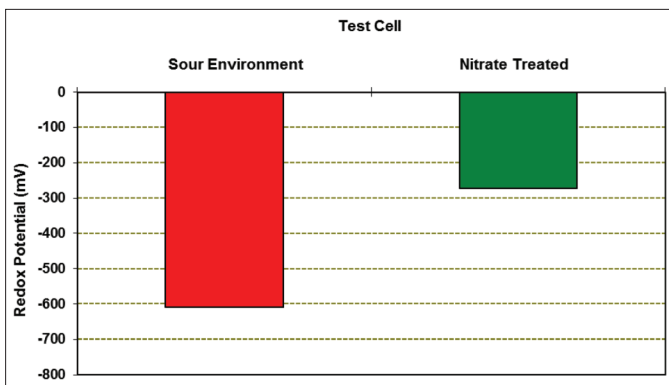


Fig. 2. The effect of nitrate treatment on the redox potential.

CORROSION CONSIDERATIONS

A major concern of nitrate treatment is the possible generation of sulfur/polysulfide, nitrite, ammonium and other products in lower oxidation states between nitrite and nitrogen, leading to corrosion.

Nitrate⁹⁻¹⁴, together with chloride and sulfate, is classified as nonoxidizing. In one study, nitrate electro-reduction was observed in highly concentrated solutions¹⁰ at an elevated temperature; the addition of 150 mg/L of nitrate to de-oxygenated seawater at a flow rate of 4 m/s resulted in a small increase in corrosion. Nevertheless, the corrosion rate after the addition of nitrate was below 0.1 mm/year, which was less than the corrosion rate caused by the addition of 0.5 mg/L chlorine to the same seawater¹⁵.

A number of laboratory studies and field applications have demonstrated that nitrate in seawater only applications has no major impact on the corrosion process of mild steel. In a deaerated system replicating the injection water, the addition of various concentrations of nitrate appeared to marginally lower the rate of linear polarization resistance (LPR) to corrosion of mild steel. The laboratory test involved continually purging the seawater with nitrogen (N₂) and was conducted at 30 °C using mild steel (AISI 1018) coupons, Fig. 3.

In the seawater injection system of the Veslefrikk Statoil oil platform in the North Sea, nitrate dosing showed a reduction of 20,000 in SRB numbers and a 50-fold reduction in SRB activity. In addition, corrosion measurements using metal coupons showed a decrease in weight loss from 0.7 mm/year to 0.2 mm/year¹⁶.

Nitrate was used to treat the injection systems of a Saudi Aramco oil field in central Saudi Arabia¹⁷. The system was transporting commingled produced water and aquifer water. The produced water had a marginal carbon dioxide (CO₂) content, and the concentration of known fatty acids was below the detection limit. The highest H₂S concentration detected in the untreated system was less than 20 mg/L. The use of nitrate continued for over three years until the system was moth-balled. Prior to nitrate treatment, the system had been treated

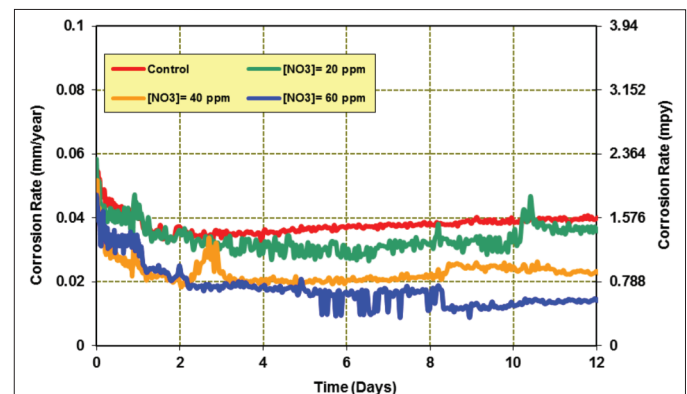


Fig. 3. Corrosion effect on steel (AISI 1018) of nitrate (NO₃) seawater at 30 °C, purged with nitrogen (N₂) gas.

with continual dosing of biocide. During the biocide treatment, the system experienced a number of corrosion failures. No corrosion failures were detected over the three years that nitrate was used in the top surface facilities.

In contrast, reports on the effect of nitrate dosing in PWRI systems from other fields have showed a negative impact. A field trial by Norsk Hydro (Statoil) showed that the addition of nitrate to a mix of produced water and aquifer water with a high CO₂ content resulted in a steep increase in the corrosion rate: from less than 0.1 mm/year to over 1 mm/year. The increase in corrosion rate was also accompanied by severe pitting¹⁸.

Nitrate dosed into the PWRI system of the Norske Shell Draugen field was successful in controlling SRB activity, but again the nitrate treatment led to an alarming increase in the LPR corrosion rate, from 0.1 mm/year to 1 to 2 mm/year¹⁹.

A particular type of NRB (the nitrate-reducing, sulfide-oxidizing bacteria labeled NR-SOB) is capable of utilizing sulfide as an electron donor, which prevents sulfide accumulation. It has been demonstrated that the byproduct of NR-SOB denitrification depends on the initial nitrate to sulfide (N/S) ratio. In the case of an N/S ratio of 2.2 or above, sulfate would be expected to form. At N/S < 2.2, sulfur would be expected to form; this formation of sulfur could result in devastating corrosion problems²⁰.

Concerns have been raised that nitrate dosing could result in the generation of ammonia, which is particularly corrosive to copper. An Energy Institute study in London, however, did not detect any changes in the ammonia concentration after dosing with nitrate. A Natural Sciences and Engineering Research Council of Canada (NSERC) study concluded that only around 4% of the added nitrate is reduced to ammonium. Since ammonium is needed for the synthesis of biomass, and also reacts with the nitrite that is generated along with it through a reaction catalyzed by anamox bacteria, Eqn. 1, ammonium concentrations may actually decrease following nitrate injection. This study noted that the lowest ammonium concentrations in the Enermark Medicine Hat Glauconitic field were observed during the period of nitrate injection, indicating that increased amounts of a NRB biomass formed downhole under these conditions⁴.

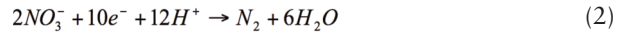


The NSERC study revealed that the addition of nitrate to sour waters under conditions of sulfide excess can yield corrosive sulfur and polysulfide, and reduce nitrate to nitrite. The study also showed that the types of byproducts resulting from the addition of nitrite to autoclaved produced water media containing sulfide were significantly affected by temperature. Most of the sulfide was converted to thiosulfate at 80 °C, while the sulfide was mostly converted to sulfur at 23 °C; polysulfide was equally generated under the different temperatures. On the other hand, nitrite was reduced to N₂ at 80 °C, with the highest concentration of ammonium being detected at 40 °C. The study concluded that the reaction products of nitrite and

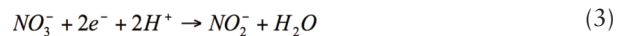
sulfide are threefold to sevenfold more corrosive than the reactants themselves, depending on temperature⁴.

THE ROLE OF NITRITE

A few bacteria species (principally *Pseudomonas* and *Bacillus*) have the ability to reduce nitrate to molecular N₂.



A commonly encountered reaction is the intermediate generation of nitrite.



The generated nitrite can be further reduced to N₂ through a number of lower oxidation state species.

The intermediate biological generation of nitrite within the surface biofilm is a corrosion concern. Nitrite is a well-known oxidizing and passivation-type corrosion inhibitor for carbon steel and cast iron. Nitrite is widely used in cooling waters where it promotes the formation of an extremely thin, protective ferric oxide film (the passive film), without providing the necessary solubility of a ferrous iron salt to sustain localized corrosion, such as pitting. Nitrite can passivate steel even in the absence of dissolved oxygen¹⁰, but nitrite has a double-edged effect; it can either inhibit or promote corrosion, depending on its concentration and the presence of other chemical species.

For nitrite to be a corrosion inhibitor, it has to be added in excess of other aggressive ions that may be present, such as chloride, sulfate and nitrate. When nitrite is present in an insufficient concentration to counterbalance the coexisting aggressive ions, it can promote corrosion; the type and severity of that corrosion depends on the concentration of nitrite relative to the other aggressive ions:

- General corrosion is expected to occur when significantly less nitrite is present.
- Pitting corrosion is expected to occur when only a slight insufficiency of nitrite precludes complete passivation.

Seawater contains about 18,000 mg/L of chloride and around 3,000 mg/L of sulfate. The concentration of chloride in produced water usually well exceeds its concentration in seawater. Since the nitrate treatment is based on a significantly low dosage rate, the nitrite generation is expected to be comparatively very low; both the beneficial promotion of conventional nitrite passivation and the adverse occurrence of pitting are improbable scenarios, based on the effect of the biologically generated nitrite in the bulk solution. Yet no precise measurements have been conducted to assess the chemical changes induced by nitrite generation within the biofilm and the possibility of localized pockets that may prompt pitting.

SULFIDE CORROSION VS. CORROSION WITH NITRATE TREATMENT

The purpose of nitrate treatment is to control SRB and associated biogenic sulfide corrosion. The effect of sulfide films on corrosion is highly unpredictable and depends on a number of factors, including O₂ residual, CO₂, chloride content, water cut and temperature. Some sulfide films are non-stoichiometric and therefore unstable. In a study conducted by the Energy Institute³, continuous monitoring — using the LPR technique — demonstrated the hugely unpredictable effect of sulfide on the corrosion of mild steel, Fig. 4. While the LPR corrosion rate in one controlled (sour environment) cell was below 0.5 mm/year (blue line) for the total duration of the 75-day test, an alarming corrosion rate of around 4.5 mm/year (red line) was recorded in a duplicate cell. The LPR results were confirmed by electrochemical impedance, noise and weight loss analyses. X-ray diffraction examination carried out on coupons from the duplicate test cells indicated the likelihood of a different iron sulfide formation occurring in the otherwise duplicate cells²¹. The sudden drop in the corrosion rate on day 51 is believed to be due to the repair of the surface film of the electrode.

By comparison, the green line shows the average LPR corrosion rate of duplicate cells treated continuously with nitrate. While nitrate corrosion was on average higher than the lowest sulfide corrosion, and both crept up to 0.5 mm/year on day 75, nitrate corrosion rate was more consistent than that of sulfide corrosion.

DIFFERENT APPLICATIONS OF NITRATE TREATMENT

Nitrate treatment is field specific, and laboratory work is needed to establish the effective nitrate concentration for a field and predict its effect on corrosion. Many field deployments have been based on criteria that simply mimic those of other applications without allowing for specific conditions.

Methods to predict the effective dosage rate are still far from agreed upon. While the added nitrate concentration should balance the total oxidation of the carbon source, Eqn. 4, a number of successful cases have used nitrate dosing concentrations lower than the stoichiometric requirement. There are also reports of impractically high nitrate concentrations

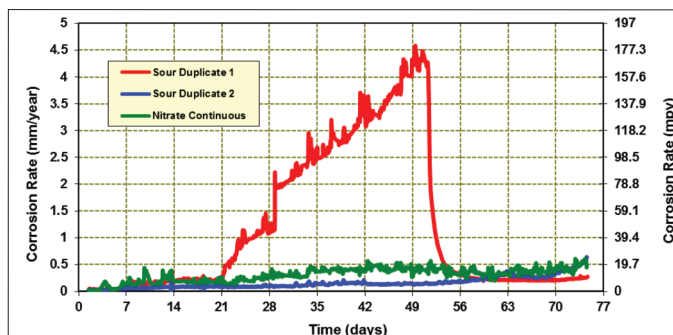
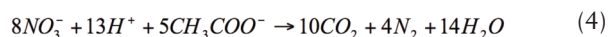


Fig. 4. Comparison of nitrate corrosion to more unpredictable sulfide corrosion.

needed to control souring in a high carbon media. For example, in a sulfidic oily waste, a nitrate concentration of 3,000 mg/L was needed to inhibit sulfate reduction, and 1,000 mg/L of nitrate was required to prevent sulfide accumulation²².



In a number of cases, nitrate was injected in addition to a biocide. This practice is mainly to control bacteria in the tubular; to enable nitrate to travel deeper into the reservoir; and to minimize the risk of microbial zonation. Nevertheless, such an approach carries the risk of also killing the NRB population.

The use of nitrate treatment in production systems for controlling the detrimental effect of SRB continues to be a major challenge. In addition to the amounts required to treat the carbon-rich produced water with its elevated microbial population, nitrate dosing in the production system is also subject to losses in the hydrocarbon phase. This may further increase the cost burden of the treatment, particularly in the case of continuous dosing.

Tests of nitrate's partitioning tendency using different ratios of crude oil (superlight API = 49.1°) to sterile seawater and different nitrate concentrations — in the form of calcium nitrate — have confirmed that nitrate predominantly partitions in the water phase. Therefore, one approach to nitrate treatment of production systems would be to design the treatment based solely on the specific requirement of the water cut in the system.

Figure 5 shows the partitioning tendency of nitrate in a two-phase system.

GUIDELINES FOR IMPLEMENTING NITRATE TREATMENT

Although nitrate treatment is maturing, it still has not been fully evaluated to establish clear criteria for implementation covering a wide range of different oil field conditions. Available data confirms that nitrate treatment has mostly been beneficial as it has succeeded in controlling souring and even shown marginal corrosion control improvement in seawater injection systems; as discussed, reports on its effect on corrosion in PWRI systems conflict significantly.

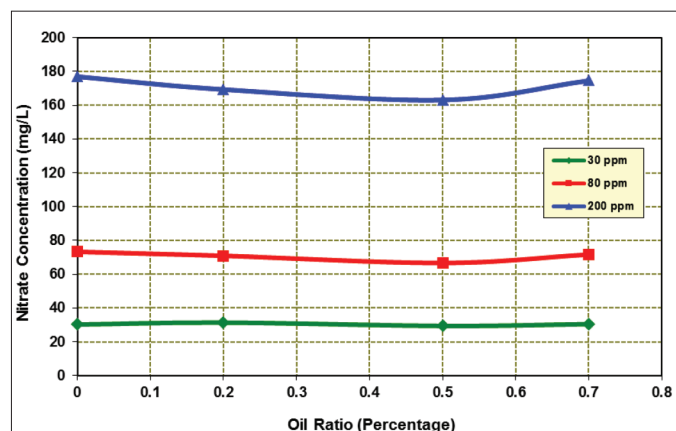


Fig. 5. Partitioning tendency of nitrate in a two-phase system.

For nitrate treatment to be entirely beneficial, a number of criteria have to be considered to ensure effective biological control without compromising the corrosion aspect. This is even more important in systems with moderate to high carbon concentrations available for use by bacteria. Guidelines such as the following will help ensure an effective and safe nitrate treatment:

- Nitrate treatment is field specific. The treatment cannot be replicated based on its performance in other fields. Laboratory evaluation should be conducted prior to any field implementation to establish the effective nitrate concentration and its likely effect on corrosion.
- Assessing the efficiency of a nitrate bio-modification treatment should be based on changes in the concentration of sulfide in the system. SRB monitoring is useful only with molecular microbiology analysis to avoid media selectivity and the possibility of stimulating an inactive bacteria population.
- After laboratory evaluation, the treatment should be closely monitored in the field to ensure optimization. The monitoring process involves collecting enough chemical, biological and corrosion data to enable prompt and effective corrective action and avoid undesirable side effects.
- Nitrate treatment should be considered from the start of water injection for secondary recovery to ensure a robust NRB population.
- Different dosing procedures, such as pulse or batch treatment, should be evaluated to enhance the treatment efficacy, prevent zonation and cut costs.
- Close corrosion monitoring should be conducted using coupons and other available means to assess ongoing corrosion.
- Monitoring nitrite is critical, even though it is impractical in the field, as it may not be detected in the bulk solution. Any detection of nitrite must be considered alarming and will require evaluating the ecological system to ensure that nitrite-reducing bacteria are not being inhibited.
- A corrosion inhibitor should be considered for nitrate treatment in PWRI systems.

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BIOGRAPHY



Dr. Tony Y. Rizk joined Saudi Aramco's Research and Development Center (R&DC) in July 2006 and is currently a Science Specialist. Throughout his career of more than two decades in the oil and gas industry, he has initiated and managed a number of research and deployment projects related to microbial corrosion, bacteria control through nutritional limitation, oil field microbiology and chemicals, nitrate corrosion, encapsulation for slow downhole release and enhanced oil recovery. Tony has pioneered the development of new technologies that have been successfully implemented worldwide. His research activities have been featured on BBC-1 television as part of a program covering innovative science in the northwest area of the United Kingdom.

Tony assumed a number of roles while at the R&DC and is now focusing on technical activities to better serve the field. His work has involved microbially induced corrosion, water treatment, nitrate anti-SRB treatment, biocide selection and treated sewage effluent (TSE) for secondary recovery injection.

Tony has chaired a number of international, regional and local conferences and forums including:

- The Energy Institute, Reservoir Microbiology Forum, London (2007 and 2008).
- Saudi Aramco Technical Exchange Forum, Dhahran (2010 and 2011).
- Technical Chairman of the 14th and 15th Middle East Corrosion Conference and Exhibition, Bahrain (2012 and 2014).
- Session Chairman of the Society of Petroleum Engineers (SPE) conference on MIC at Calgary, Canada (2009).

He is an active member of the National Association of Corrosion Engineers (NACE) and has assumed different voluntary roles, including Chairman of the NACE Dhahran Saudi Arabia Section for the 2014-2015 term.

Tony received his M.S. degree in Quality and Reliability Engineering/Management from Birmingham University, Birmingham, U.K., and in 1992, he received his Ph.D. degree in Corrosion Science from Manchester University, Manchester, U.K.