EI Research report

The use of nitrate treatment in oilfield systems to control reservoir souring: A review of current status

RESEARCH REPORT

THE USE OF NITRATE TREATMENT IN OILFIELD SYSTEMS TO CONTROL RESERVOIR SOURING: A REVIEW OF CURRENT STATUS

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FOREWORD

Over the past 15 years, a method that has emerged to considerably reduce the level of biogenic hydrogen sulfide (H_2S) production in oilfield systems is the treatment of injection water with nitrate (NO_3^-). Nitrate treatment technology is increasingly used for the control of sulfate (SO_4^{2-})-reducing microorganisms, and hence the prevention and mitigation of biogenic H_2S by oil production and oilfield service companies. However, its success and the effect of NO_3^- on corrosion processes vary considerably and appear to be specific to operating conditions. For instance, the use of nitrate treatment in seawater injection has not been observed to increase corrosion rates and there is indication that it may even reduce corrosion. However, there is evidence that the application of NO_3^- in a produced water reinjection (PWRI) system can lead to an increase in both general and localised corrosion.

With that in mind, this review supersedes the first edition, *The stimulation of nitrate-reducing bacteria (NRB) in oilfield systems to control sulfate-reducing bacteria (SRB), microbiologically influenced corrosion (MIC) and reservoir souring: An introductory review,* 2003, Energy Institute (EI). Currently, nitrate treatment is used on a number of installations in a variety of environmental conditions. Based on the current literature, reports and presentations, as well as the experimental and trial data, this review aims to enhance this publication with information now available, relating to experimental investigation and industry experience.

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1 INTRODUCTION

1.1 INTRODUCTION

Water injection is a recognised and frequently used procedure for pressure maintenance and the improvement of oil recovery in many oilfields around the world. However, an unwanted side effect of water injection can be reservoir souring, which refers to the increase in concentration of hydrogen sulfide (H_2S) in production fluids. This is typically due to the introduction of sulfate (SO_4^{2-}) from the injected seawater into the formation water, leading to the proliferation of SO_4^{2-} reducing microorganisms and the formation of sulfide (S^{2-}). Whilst several biotic and abiotic mechanisms have been proposed as contributors towards reservoir souring (Khatib and Salanitro, 1997), the reduction of SO_4^{2-} by sulfate-reducing bacteria (SRB) and sulfate-reducing archaea (SRA) is thought to be a significant source of souring in water-injected reservoirs. These two groups of microorganisms, SRB and SRA, are collectively referred to as sulfate-reducing prokaryotes (SRP) and it is thought that their growth is promoted due to the combination of abundant electron donors such as selected oil components and carboxylic acids in the formation water and electron acceptors (SO_4^{2-}) in the seawater, river, lake or aquifer water.

Reservoir souring is of major concern to the oil industry, as H_2S is toxic and corrosive, increases the safety risk to personnel, affects crude oil sales value and requires substantial capital expenditure/operating expenditure for remedial operations. Therefore, considerable attention has been focused on reducing H_2S concentration in produced fluids. To prevent H_2S production, biocides are often added to the injection water. However, the treatment can be expensive and is often ineffective due to inhibition of the biocide by high temperatures or reaction with biofilm and minerals. Recalcitrant biocides also lead to environmental problems and moreover, certain biocides decompose during the process, potentially serving as additional growth substrates for SRB (Myhr et al, 2002). However, an alternative method known to reduce the level of produced H_2S is nitrate treatment. This is achieved by controlling the microbiological production of H_2S as well as reducing H_2S already present in a petroleum reservoir by adding nitrate (NO_3^-) to the injection water and pumping it to the oil-bearing formation. As such, many oil production and oilfield service companies recognise the addition of NO_3^- as a method for decreasing the net production of H_2S.

1.2 MICROBIOLOGICAL METABOLISM

In order to better understand the role and impact of microorganisms involved in the processes of reservoir souring and nitrate treatment, it is first helpful to have a basic knowledge of microbiological metabolism and the terms used to describe such processes.

Metabolic reactions characteristically proceed in a systematic and highly regulated manner that maximises the use of the available nutrients and energy. In order to carry out metabolic processes, microorganisms require a constant input and expenditure of usable energy. Microorganisms often obtain their energy by mediating chemical reactions which typically involve the use of an electron donor (a reducing agent that donates electrons to another compound) and an electron acceptor (an oxidising agent that accepts electrons transferred to it from another compound), referred to as reduction-oxidation (redox) reactions. There are a number of different electron donors and acceptors, both organic and inorganic that can be utilised by microorganisms; however, it should be noted that organic molecules are the most common electron donors in an oilfield environment.

Microorganisms can either be:

- organotrophs – organisms that, during electron transfer, can use organic molecules (i.e. petroleum hydrocarbons) as an electron donor, or
- lithotrophs – organisms that are capable of obtaining their energy from inorganic compounds (i.e. sulfide).

In a simple example, consider bacteria growing on an organic carbon source in the presence of oxygen (O_2):

$$\text{Carbon source} + O_2 \rightarrow \text{carbon dioxide } (CO_2) + \text{water } (H_2O) + \text{Energy}$$

In this example the carbon source has been oxidised, donating electrons in the presence of O_2, or aerobically, resulting in the reduction of O_2. This is because organic carbon tends to be oxidised preferentially by the electron acceptor that supplies most energy to the microorganisms, namely O_2. Consider also, a bacterium growing on a carbon source in the absence of O_2 with only a carbon source available to act as both the electron donor and acceptor, resulting in fermentation:

$$\text{Carbon source} \rightarrow \text{Alcohol} + CO_2 + \text{Energy}$$

However, this process is not energy efficient and so bacteria often utilise alternative electron acceptors such as NO_3^- and SO_4^{2-} in the absence of O_2. Therefore, when conditions become anoxic, reduction of other electron acceptors becomes energetically favourable. For instance, once O_2 is depleted, certain facultative anaerobes – bacteria that are capable of proliferating with or without O_2 – can use NO_3^- as an electron acceptor. As O_2 levels decrease even further, obligate anaerobes – bacteria that survive and grow only in the absence of O_2 begin to use the remainder of the available electron acceptors. Consequently, redox conditions begin to rapidly change, usually from oxidising to reducing conditions.

1.3 THE BIOLOGICAL NITROGEN CYCLE

The global biogeochemical nitrogen cycle (N-cycle) consists of varied processes that interconvert the different nitrogenous compounds in the biosphere, in which prokaryotic microorganisms (organisms that lack a membrane bound nucleus, i.e. bacteria and archaea) play a principal role. Inorganic nitrogen is found in several oxidation states, ranging from ammonium (NH_4^+) (−3), its most reduced form, to its most oxidised, NO_3^- (+5). The N-cycle includes both oxidative and reductive reactions catalysed by enzymes with different redox cofactors (Schmidt and Schaechter, 2011), for assimilatory, dissimilatory or respiratory purposes. These processes perform key roles in a given ecosystem and will be discussed in further detail in section 2.