J. Appl. Environ. Biol. Sci., 5(10S)185-188, 2015

ISSN: 2090-4274
Journal of Applied Environmental and Biological Sciences
www.textroad.com

A New Method to Control Hydrogen Sulfide in Tertiary Oil Recovery Process

Farshad Dargahi[1*], Davood Bargahi[2], Khashayar Zendebodi [3], Farshad Samsami[3]

[1]. Young researchers and elite club, Bushehr branch, Islamic Azad University, Bushehr; Iran
[2]. M.sc, petroleum engineering, Bushehr branch, Islamic Azad University, Bushehr; Iran
[3]. B.sc student, petroleum engineering, Bushehr branch, Islamic Azad University, Bushehr; Iran

Received: April 20, 2015
Accepted: June 15, 2015

ABSTRACT

Hydrogen sulfide formation with biogenic origin is one of the most important sources of hydrogen sulfide production in most of gas and oil reservoir all over the world. This process is often observed in reservoir which have undergone flooding from sea water in tertiary oil recovery programs. Traditionally, treatment is utilized in order to overcome the problems of hydrogen sulfide presence. Recent studies show that utilizing these components is often expensive and ineffective. In recent years, in most important oil companies, the use of nitrate-based components to control, prevent, and eliminate biogenic sulfate in produced water re-injection systems from tank or sea water reinjection have excellent use of biocide components. This method is based on the selective replacement of sulfate reduced harmful bacteria (SRB), which are main factors in sulfide production with a set useful micro-organisms that are naturally found in the reservoir and their growth is improved by nitrate-based components. This technology is called Bio- Competitive Exclusion (BCX). This technology not only controls hydrogen sulfide, but also has impressive use in tertiary oil recovery plans, with its mechanism being examined in this article.

KEYWORDS: Hydrogen sulfide, tertiary oil recovery, nitrate-based component, NRB, SRB, BCX

1. INTRODUCTION

Various mechanisms are suggested in relation to hydrogen sulfide production in geologic time scale or in a short period of time (in time period of a reservoir production), which are in close relation to temperature and tank properties (1). The most important mechanisms consist of:

A- Bacterial revival of sulfate solution in temperatures of less than 80 degrees centigrade.
B- Thermo chemical sulfate revival in temperatures above 140 degrees centigrade.
C- Cracking of sulfate containing organic components in temperatures over 175 degrees centigrade.
D- Revival of sulfide minerals such as mono pyrite or pyrite
E- Oxidation reactions- recovery of components without sulfite.
F- Hydrogen sulfide migration from dry areas in deep and adjacent formations.

One of the hydrogen sulfide production sources is bacterial revival of sulfate (SRB). This mechanism is often common in surface tanks and in low temperatures (less than 80 degrees centigrade) and can be the major factor of creation of less than 5 percent value of hydrogen sulfide in new sediments. In this mechanism, sulfate can be provided from the dual water, dissolution of anhydrite, injection of sea water in tertiary oil recovery methods or revival of pyrite by injected water. The cracking of sulfate containing organic components which is found little in kerogen and oil, is involved in hydrogen sulfide creation in temperatures over 175 degrees centigrade. This process also because of the limitation of sulfate containing organic minerals cannot produce more than 5 percent of hydrogen sulfide in hydrocarbon reservoir. As a result of sulfide mineral revival such as mono pyrite and pyrite and also oxidation reactions- revival of sulfite less components some hydrogen sulfide is also produced. The dominant mechanism of hydrogen sulfide production in deep reservoirs is the process of thermo chemical revival of sulfate which is produced as a result of direct reaction of anhydrite and hydro carbonic light gas in depth (more than 4 kilometers depth) and temperatures of more than 120-140 degrees centigrade. In this article, the effective mechanisms in hydrogen sulfide production in tertiary oil recovery process and its controlling procedures have been examined.

*** Corresponding Author:** Farshad Dargahi, Young researchers and elite club, Bushehr branch, Islamic azad university, Bushehr; Iran. farshaddargahi22@gmail.com

2. RESULTS AND DISCUSSION

Sulfate micro biological reclamation (SRB).

Sulfate revival bacteria (SRB) are one kind of anaerobic bacteria which are biologically various and have the capacity of sulfate ion reduction ($SO^{2-}{}_4$) to H_2S while growing on oxygen components such as the existing volatile fatty acids (VFA) in the tank manufacturing water. These fatty acids are found in most of the oil producing reservoir waters and may be a dominant factor in sulfate reviving bacteria growth in oil reservoir during flooding in tertiary oil recovery projects. These fatty acids include formic acid, acetic acid, propyunic acid, lactic acid, phenols, and benzoates (3).

The mechanism of hydrogen sulfide production by sulfate revival bacteria (SRB) is shown by the following equation:

(2) SRB+VFA+$SO^{2-}{}_4$*+ Favorable Growing Conditions→* H_2S*…………..*

As it is obvious in the above equation, the reviving bacteria need favorable growth condition for metabolism and sulfate ion reduction to hydrogen sulfide. The laboratory experiments show that these bacteria can't tolerate in fluid salinity (NaCl) more than 150000ppm and their activity is ceased. Three groups of reviving bacteria are known: Mesophilic, Thermophilic, and Hyperthermophilic, each of which grows in a unique temperatures range (<80ºC). Normally, each of these bacterial groups gathers in different parts of the reservoir. However, most of the time reservoir conditions do not allow microbiological activities, unless some variations in dominant condition of reservoir such as injection of sea water which reduces the reservoir temperature and also contains high percentage of sulfate and reviving bacteria happen. In fact, reservoir fluid cooling and reduction of water salt due to mixture of sea water and the formation water, existence of fatty acids with low molecular weight and the existent anaerobic condition in reservoir are among the factors which create an opportunity to bacterial activities like sulfate reducing bacteria and hydrogen sulfide protection and reservoir dryness. Studies manifest that tank dryness because of the microbiological activities are controlled and achieved due to combination of the following factors (4):

- Sulfate density in injected sea water
- Temperature reduction of reservoir as a result of water injection
- Organic acid presence with low molecular weight
- Reduction in salinity degree of formation water as a result of mixture with injected sea water

Hydrogen sulfide (H_2S) of the above activities can cause serious problems in production and also dangers in terms of staff safety. In addition, hydrogen sulfide in low density when dealt with unexpectedly, can lead to death. Hydrogen sulfide can react to metal components such as iron and pyrite appears as a black cover on exploitation tools and transmission lines.

The damaging effect from sulfate reducing bacteria (SRB) can be summarized as follows:

- Tank and oil and gas well dryness
- Corrosion of wellhead facilities
- Reduction in reservoir permeability because of metal sediments and as a result of production reduction
- Serious dangers for staff and the environment
- Enormous expenses of facility replacement

3. Sulfide elimination and control

Traditionally in oil industry, biocide materials which are dangerous and toxic are used during water injection to reservoir to face problems due to bacterial reduction of sulfate, tank dryness, and corrosion because of hydrogen sulfide. Experiences have revealed that utilizing these components are so expensive and most importantly use of biocides have not always been successful as some of the micro organisms are adaptable and can remain alive and become resistant against these components and as a result make utilization of these components, ineffective. In addition, the more active and stronger the biocide, the higher possibility of becoming inactive because of other components than target bacteria like the existing components in tank water, reservoir, and surface facilities. This concept is especially true about biocides such as aldehydes or the components which are a bit soluble in oil or also it is possible that they become inactive by the specific amount of existing salt in production water. This makes it necessary for biocides to be tested exactly in real conditions before use (5).

The procedure to use nitrate-containing components (Nitrate Based Technology)

The Nitrate compounds technology, which is discussed here, is about the reservoir and systems which are involved in flooding operations for tertiary oil recovery projects. In contrast to the method of using biocides which is

based on killing all the bacterial, the nitrate compound technology is based on selective growth of useful nitrate reducing bacteria (NRB) population, which replaces the harmful sulfate reducing bacteria.
This completely different approach that is based on an understanding of ecology and microbiology of reservoir are briefly compared in Table 1 using the biocides.

Table 1. Comparison between the technology of basic nitrogen compounds and the Biocide Treatment method

Nitrate Based Treatment	Biocide Treatment
Growth of Nitrate-reducing bacteria (NRB) along with the stopping of the growth of sulfate-reducing bacteria (SRB)	The method is based on killing all microorganisms
Soluble in water, does not dissolve in oil, are insensitive to the amount of salt, cheap, non-toxic and safe	May be dissolved in the oil, sensitivity to salt, expensive, highly toxic and dangerous
Completely consumed, Their activity increase with time, insensitive to temperature Accessible and easy Injection, adapt to other chemical control methods	Loss and deactivation of the compound because of absorption and growth resistance, Microbiology, sensitivity to temperature, Its difficulty in controlling and its injection in some times, may be not adaptive with other chemical methods

Preliminary studies carried out in the laboratories of LATA P(10) show that the volatile fatty acids dissolved in water (VFA) that exist naturally in the water reservoir and include acetic acid, butyric, and propionic, are the main key of the growth of sulfate-reducing bacteria in the reservoirs. Formerly sulfate ions dissolved in water for injection were considered as the main factor in the growth of sulfate-reducing bacteria and forming hydrogen sulfide. Surly sulfate is necessary but the existence of volatile fatty acids (VFA) dissolved in water provides a sufficient and necessary source for the growth and activity of sulfate-reducing bacteria and as a result formation of the hydrogen sulfide. These compounds are in formation waters and may also be present in the injected water.

Studies show that by replacing nitrate instead of sulfate, the production of hydrogen sulfide in the reservoirs that are under the process of enhance recovery, can be greatly reduced. Nitrate as an electron acceptor causes microbiological restoration of nitrate. Energy generated by nitrate reducing is three times more than the energy generated by sulfate reducing. Sulfate reducing required to 8 electrons per mole while only nitrate reducing needs two electrons per mole. This causes that when the sulfate and nitrate are simultaneously, nitrate is preferred selected to accept electrons. Population of nitrate -reducing bacteria (NRB) is increased by direct competition for consuming energy produced by VFA and also limiting it. This leads to an exponential increase in the population of the nitrate-reducing bacteria (NRB) that for consuming limited amount of VFA compete with sulfate-reducing bacteria. The competition among the community of the bacteria is known as the technology of (Bio-Competitive Exclusion) BCX. (7).

In the technology of using basic nitrogen compounds, there is no need for the injection of laboratory bacteria or cultured ones in the reservoir because the storage medium includes natural nitrate-reducing bacteria and can consume nitrate through its metabolism and increases their numbers. The importance of the natural bacterial populations appears when fixing the use of base nitrates compounds for the enhance oil recovery projects.

BCX Technology offers two ways to solve the problem of sulfides: the reaction and Proactive methods.

In the reaction method, BCX Technology is injected to the system that is already infected and producing sulfide, this causes the reduction and elimination of the present sulfate-reducing bacteria and a decrease in the concentration of Hydrogen sulfide. In Proactive method, operations start before the contamination of the reservoir and therefore never let the sulfate-reducing bacteria to grow and prevent the problem of the production of hydrogen sulfide. It is clear that Proactive method has priority, but unfortunately, most of the world's major reservoirs have already been sour and hence the emphasis is on reaction operations (treatment).

Improved formula of base nitrates Compounds

While the start of stopping mechanisms of sulfate-reducing bacteria can only occurs with nitrate injection, studies show that the addition of nitrite (NO_2) with nitrate increases the effect of this technology. Nitrate is one of the intermediate products of the metabolism of bacterial Nitrate-reducing that has the ability of inhibiting some activities of sulfate-reducing bacteria and also acts as the chemical scavenger of hydrogen sulfide. Studies show that activities of sulfate reducing thermophilic bacteria in the high concentrations of 2 ppm nitrite reaches zero, while the concentration of nitrate to 100 ppm cannot seriously hamper the activities of the mentioned bacteria. Results of the research group of LATA (8) have shown that Nitrates / nitrites are more effective and less costly than the use of each of the compounds alone. In addition, group of LATA, for increasing the effect of nitrate / nitrite compound, has used a compound named Molybdenum (Mo) that is a type of enzyme inhibitor of the activity of sulfate reducing bacteria. Entering even a small concentrations of Mo targets directly the process of SRB and can be considered as a tracer of injection waters. Nitrates / nitrites / Mo compound could be provided in the form of different ratio of the three components, to comply with the requirements of the different systems of production, making greater flexibility, and increasing effectiveness of the compound and economical aspects. Comparison of the differences and operation of these triple compounds in comparison with the use of nitrate alone for sulfide removal is shown in Table 2.

Table 2. Comparison of the technology of using nitrates alone and compound of nitrate / nitrite / Mo

Nitrate alone	Nitrate / nitrite / Mo compound
In many cases, the concentration can only change	If necessary NO3 / NO2 / Mo ratio and their concentration can change
Selectively effective only on nitrate reducing bacteria (NRB)	Diverse Microbiological samples are more effected
Produced secondary nitrogen compounds are transient and not controllable	Mo and NO2 can act directly for the fast control of SRB

While research indicates the efficiency of nitrates / nitrites/ Mo to the compound of nitrate alone, it should be noted that the specific conditions prevailing in each reservoir is different from the other reservoir. The differences that include components such as water and microbiological Consortium including populations of NRB and SRB, can be specifically different. As a result, the reservoir may respond differently to the basic nitrate compound because of the variety of environmental conditions. These conditions consist of:

• Various components of the water formation of the reservoir including VFA and their concentration
• Different concentrations of salt
• The matrix of the reservoir

All the factors mentioned above are important about the proper application of nitrates / nitrites / Mo compound in a special reservoir. In all studies, the use of nitrates / nitrites/ Mo compound provides more chance and flexibility to control hydrogen sulfide compared to the method of nitrite alone. (9)

4. CONCLUSION

1- Using basic nitrates compound for controlling the production of biogenic hydrogen sulfide is superior compared to the biocide method.
2- Using the formula of the nitrate / nitrite/ Mo would be more effective over the control of the Hydrogen sulfide production problems compared to the use of nitrate compounds only.
3- One of the main effects of using nitrate compounds and activities of nitrate reducing bacteria, is their indirect role In the process of enhancing oil recovery and it's flowing into the reservoir. During the reaction, the amount of gas such as H2, N2, CO2, CH4, solvents like butanol, isopropanol, ethanol and acetone, and also several types of surfactant are produced, which increases the reservoir's oil mobility.

REFERENCES

1. Rabbani A R. Geochemistry of non-hydrocarbon gases from natural gas reservoirs. Amir Kabir University Press. 2007
2. Cavallaro A N, Alberdi M I. Overview of H2S Souring Cases in Argentina Reservoirs: Origin and Mitigation Sceneries. SPE 2007;107376
3. Khatib Z I, Salanitro J P. Reservoir Souring: Analysis of Surveys and Experience in Sour Waterfloods. SPE 1997;38795
4. Martins O, Marques L C C. Assessment of Oilfield Souring Mechanisms by Mass Spectrometry Analysis of the Stable Sulfur Isotopes Ratio. SPE 2006;104016
5. Dennis D M, Hitzman D O. Advance Nitrate-Based Technology for Sulfide Control and Improved Oil Recovery. SPE 2007;106154
6. Sprel G T. A New Microbial Technology for Enhance Oil Recovery and Sulfide Prevention and Reduction. SPE 1994;27752
7. Dennis M. Worldoil magazine 2004;225(11)
8. Hitzman D, Dennis M. MEOR Using Synergistic H2SPrevention and Increased Oil recovery. SPE 89453
9. Giangiacomo. Field Testing of the Biocompetitive Exclusion Process for Control of Iron & Hydrogen Sulfides. SPE 1997;38351