Journal of Biotechnology 256 (2017) 57–67

Contents lists available at ScienceDirect

Journal of Biotechnology

journal homepage: www.elsevier.com/locate/jbiotec

Reservoir Souring – Latest developments for application and mitigation

Richard J. Johnson[a,*], Benjamin D. Folwell[a], Alexander Wirekoh[a], Max Frenzel[a], Torben Lund Skovhus[b]

[a] Oil Plus Ltd., Dominion House, Kennet Side, Newbury, Berkshire, RG14 5PX, United Kingdom
[b] VIA University College, Centre for Applied Research and Development in Building, Energy & Environment, Chr. M. Østergaards Vej 4, DK-8700 Horsens, Denmark

ARTICLE INFO

Keywords:
Reservoir souring
Hydrogen sulphide
Sulphate-reducing prokaryotes (SRP)
Oil and gas
Microbiologically influenced corrosion (MIC)
Water flooded oil fields

ABSTRACT

Sulphate-reducing prokaryotes (SRP) have been identified in oil field fluids since the 1920s. SRP reduce sulphate to sulphide, a toxic and corrosive species that impacts on operational safety, metallurgy and both capital and operational cost. Differences in water cut, temperature, pressure and fluid chemistry can impact on the observed H_2S concentration, meaning that an increase in H_2S concentration does not always correlate with activity of SRP. However it wasn't until the 1990s that SRP activity was accepted as the leading cause of reservoir souring (i.e. an increase in H_2S concentrations) in water flooded oil fields.

The process of sulphate-reduction has been well documented at the genetic, enzymatic and physiological level in pure cultures under laboratory conditions. DNA sequencing has also identified new groups of microorganisms, such as archaea which are capable of contributing to reservoir souring. This has led to some recent advances in microbial control and detection, however, despite this, many of the methods used routinely for microbial control and detection are over a century old. We therefore look towards emerging and novel mitigation technologies that may be used in mitigating against reservoir souring, along with tried and tested methods. Modelling and prediction is another important but often under-used tool in managing microbial reservoir souring. To be truly predictive, models need to take into account not only microbial H_2S generation but also partitioning and mineral scavenging. The increase in 'big data' available through increased integration of sensors in the digital oil field and the increase in the DNA sequencing capabilities through next-generation sequencing (NGS) therefore offer a unique opportunity to develop and refine microbial reservoir souring models. We therefore review a number of different reservoir souring models and identify how these can be used in the future.

With this comprehensive overview of the current and emerging technologies we will highlight areas where significant development effort could generate rewards that can improve detection, prediction and control of microbial reservoir souring.

1. Introduction

Reservoir souring is the process whereby a previously sweet reservoir (i.e. one containing no H_2S) starts to produce sour fluids (i.e. those containing some level of H_2S). Changes in the relative masses of gas, oil and water produced during an oil field's lifetime can give the impression of souring, as can production from new zones and this may not be microbiological in nature. Changes in the relative mass of produced water and production gas may also give the effect of an increased H_2S concentration, despite no microbial activity (Vance and Thrasher, 2005). However, whilst reservoirs can be naturally sour, a large proportion of reservoirs become sour due to the actions of sulphate-reducing prokaryotes (SRP) after secondary recovery by water flooding. It is important to understand that the effects of microbial reservoir souring (i.e. an increase in H_2S in the produced fluids) are only the last in a long line of processes including microbial generation of H_2S, H_2S partitioning, transport and scavenging by reservoir minerals. By the time H_2S is first observed in the produced fluids, a number of years have likely passed since SRP started generating H_2S in the reservoir.

The economic costs of reservoir souring can be substantial, with an estimated 2% cost-increase for sour service materials on any given project at the design stage (Al-Rasheedi et al., 1999). However, this can increase by up to an order of magnitude if sour service materials need to be retro-fitted (Vance and Thrasher, 2005). With many oil and gas megaprojects exceeding USD 1 billion, these costs can be significant. Corrosion as a whole is estimated to cost the upstream oil and gas industry around USD 1.4 billion annually in the US alone, so the effects

---

[*] Corresponding author.
E-mail addresses: richard.johnson@oilplusltd.com (R.J. Johnson), tols@via.dk (T.L. Skovhus).

http://dx.doi.org/10.1016/j.jbiotec.2017.04.003
Received 21 December 2016; Received in revised form 31 March 2017; Accepted 3 April 2017

Table 1
Common side effects of hydrogen sulphide exposure and the gaseous concentrations at which they occur. Adapted from Williamson (2010).

Concentration (ppm)	Effect
0.0047	Smell detectable
20	Eye and respiratory irritation
150–200	Olefactory nerve is paralysed
320–530	Pulmonary odema
530–1000	Loss of consciousness and coma
> 1000	Permanent brain damage and death after only one breath

of reservoir souring contribute to a high overall cost of corrosion in the industry (Federal Highways; Koch et al., 2016).

In addition to the economic impact of reservoir souring, there are also significant health and safety impacts for workers who come into contact with sour fluid and gas streams. Hydrogen sulphide is the second most common cause of inhalation death behind carbon monoxide poisoning (Jiang et al., 2016). It is a colourless gas that is heavier than air and has a typical 'rotten eggs' smell at low concentrations (Williamson, 2010). The physiological effects of hydrogen sulphide are shown in Table 1 and it should be noted that symptoms may not be apparent straight away. Hydrogen sulphide is also sensitising so repeated exposure can cause worsening of symptoms at lower concentrations.

In the United Kingdom, workplace exposure limits are set by the Health and Safety Executive (HSE, 2005). The short term exposure limit set by this document is 10 ppm of H_2S over 15 min and the long-term exposure limit is 5 ppm over 8 h. Repeated or prolonged exposure can also cause headache, nausea, irritability, insomnia, eye inflammation and a chronic cough (Williamson, 2010). The cellular mechanism for toxicity is believed to be through inhibition of mitochondrial respiration (Jiang et al., 2016) and treatment traditionally has been through exposure to fresh air, with administration of oxygen if available. However, recent papers have discovered that cobinamide is effective at alleviating hydrogen sulphide toxicity in mammalian cell cultures (Jiang et al., 2016) and a lethal rabbit model (Brenner et al., 2014).

2. Identifying microbial souring

Increasing H_2S concentration in the produced gas is not necessarily an indicator that microbial reservoir souring is occurring. The amount of H_2S in the gas phase depends on the pH, pressure, temperature, and ionic strength, as well as the ratio of the produced phases (Burger et al., 2013a,b). Increasing water cut over time will cause an increase in gas H_2S concentration as the gas makes up a reduced proportion of the production.

In order to determine whether H_2S production is increasing, the total mass of H_2S (kg/day) must be determined by summing the amount in each of the phases. This can be complicated if gas lift is being used to enhance recovery. In some cases the lift gas may be sour, and this additional source of H_2S must be accounted for in any calculations. If the mass of produced H_2S is increasing, then the source of the H_2S needs to be identified.

A common approach to determine whether reservoir souring is biogenic or non-biogenic in origin is to compare the sulphur isotope distribution (^{34}S to ^{32}S) in the source sulphate to that in the produced sulphide. Microbial sulphate-reduction preferentially utilises sulphate containing the lighter ^{32}S, rather than the heavier ^{34}S. This isotope fractionation results in H_2S containing less ^{34}S than the source sulphate. Enrichment or depletion of ^{34}S is reported as a δ value relative to a standard,

$$\delta^{34}S = \left[\left(\frac{(^{34}S/^{32}S)_{\text{sample}}}{(^{34}S/^{32}S)_{\text{standard}}}\right) - 1 \times 1000\right]$$

where $^{34}S/^{32}S_{\text{standard}}$ is $(45{,}004.5 \pm 9.3) \times 10^{-6}$, as found in troilite from the Canyon Diablo meteorite (CDT). Values are reported per mille (‰). Seawater is most commonly used for injection during secondary oil recovery, the natural $\delta^{34}S$ of sulphate in seawater is ~ +21‰ (Rees et al., 1978). A more negative sulphur isotope ratio with respect to that of the source sulphur suggests microbial sulphate-reduction. Typically the sulphide generated by microorganisms will have $\delta^{34}S$ values of −40 to −10‰ (Martins and Marques, 2006). Conversely, values for ‰ $\delta^{34}S$ vs CDT of between +5 and +20 suggests the sulphide is a result of the reservoir being naturally sour as a result of geochemical processes. Interpretation, however, must be treated with caution as much depends on the isotopic ratio of the source sulphur and isotopic overlap of microbial, petroleum organic and thermochemical sources.

Ideally, multiple samples from across the field and within a production system should be analysed to give a comprehensive overview of sulphide sources across the field. It is important that both sulphate and sulphide are collected at the same point to pinpoint the source of the souring (i.e. reservoir vs SRP growth in the topsides). Modelling by Hubbard et al. (2014) suggested that the clearest increase in $\delta^{34}S$ of the residual sulphate would be observed during initial waterflood breakthrough.

The presence of isotopically light sulphide therefore, in combination with labile carbon and energy sources and appropriate salinity and temperature, indicate that microbial souring is occurring in-reservoir. This should be corroborated where possible with the use of molecular microbiological techniques to confirm the presence of sulphide generating (sulphate- or thiosulphate-reducing prokaryotes) in the reservoir (Skovhus et al., 2007; Juhler et al., 2012; Skovhus et al., 2014).

3. Microbial reservoir souring mechanisms

While both biotic and abiotic mechanisms have been proposed as responsible for reservoir souring, sulphate reduction by microorganisms is the most significant for H_2S production in oil reservoirs as a result of water flooding (Vance and Thrasher 2005). This process is influenced by the water source, concentrations of sulphate, carbon sources, other nutrients and trace metals; in addition to factors such as temperature, pressure, salinity and the viable SRP community. The mechanisms by which microbial generation of H_2S are generally thought to occur have been reviewed in detail elsewhere (Gieg et al., 2011; Vance and Thrasher 2005) and are shown at a molecular level in Fig. 1. Recent work has shown that rather than a direct conversion as per the canonical sulphate-reduction pathway, sulphide may also be generated via a series of trithionite intermediaries (Bradley et al., 2011). The limits under which microbial reservoir souring can occur and information on the factors influencing souring are expanding as more reservoirs are water flooded for secondary oil recovery and next generation molecular based analysis methods are increasingly employed.

Data from two high temperature sour wells (130–200 mg/l sulphide) in Alaska suggested two possible souring mechanisms were taking place. The first was the potential for thiosulfate-reduction by *Thermoanaerobacter* due to the absence of SRP in the produced water

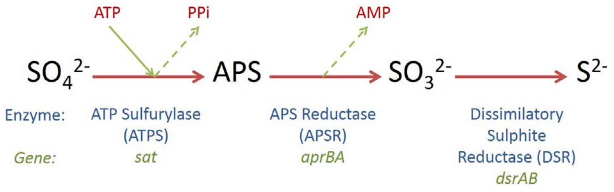

Fig. 1. A diagram showing the central steps in the canonical dissimilatory sulphate reduction pathway. Sulphate is converted to adenosine phosphosulfate (APS) and then to sulphite before the final irreversible conversion to sulphide. Key enzymes and genes involved in the steps of the pathway are shown in blue and green respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)