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Reservoir Souring – Latest developments for application and mitigation

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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

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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,

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

where $^{34}S/^{32}S_{standard}$ 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

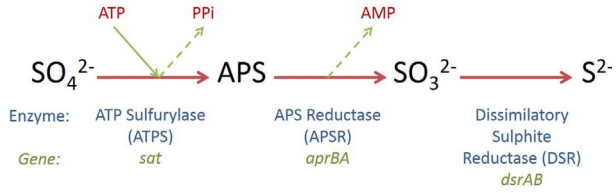


Fig. 1. A diagram showing the central steps in the canonical dissimilatory sulphate reduction pathway. Sulphate is converted to adenosine phosphosulfate (APS) and then to sulphite before the final irreversible conversion to sulphide. Key enzymes and genes involved in the steps of the pathway are shown 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.)

and the low amount of sulphate present (however thiosulfate was not measured in the study). The second mechanism in a separate well, was the utilisation of hydrogen and formate by *Desulfonauticus* to produce sulphide using hydrogen possibly produced by an unclassified *Syntrophorhabdaceae* (Piceno et al., 2014). Interestingly, SRP were detected in all samples despite the level of souring observed and in one case the non-sour samples contained higher relative abundances of many SRP compared to the sour sample. This led the authors to suggest that the SRP may be living fermentatively/syntrophically when sulphate is limited (Piceno et al., 2014). A related study on the same field investigating biogeochemical transformations using metagenomics, revealed that microbial community complexity decreased with increasing temperature as did the number of genes related to hydrocarbon degradation. The authors were able to conclude that *Clostridiales* were the likely hydrocarbon degraders in the low temperature reservoirs and that dissimilatory sulphate-reduction pathways were present in all samples regardless of the souring level observed in the production well. Therefore providing more evidence that in the reservoirs under investigation, sulphate availability, rather than sulphate-reduction potential was limiting for sulphide production (Hu et al., 2016). This is supported by the observations of Evans et al. (2015) in a North Sea field where low sulphate water (< 20 mg/l) was used for water injection. Despite the reservoir temperature (40 °C) souring levels did not increase despite the cessation of a continuous biocide treatment, suggesting that the souring development was sulphate limited (Evans et al., 2015).

While VFAs have been generally accepted as being responsible for driving sulphate reduction in water flooded reservoirs, the contribution of various other oil components as carbon sources is still being investigated. A study by Hasegawa et al. (2014) demonstrated that the aromatics toluene and ethylbenzene, and alkanes were degraded by SRP or fermentative bacteria producing acetate, while other components such as 2–4-xylenol were not degraded (Hasegawa et al., 2014). This is supported by Callbeck et al. (2013), who used bioreactors to generate significant concentrations of acetate from the biodegradation of a heavy oil, consistent with a mechanism in which oil alkanes are metabolised to acetate and hydrogen by fermentative and synthropic bacteria with the hydrogen being used by SRP to reduce sulphate to sulphide (Callbeck et al., 2013). Therefore this mechanism may be responsible for souring in fields where high concentrations of acetate is detected in produced water from water flooded oil fields.

Furthermore Burger et al. (2013a,b) investigated the effect of BTEX compounds, in particular toluene, as a source of dissolved organic carbon for sulphate reduction in spite of their limited solubility (Burger et al., 2013a,b). Agrawal et al. (2012) also identified toluene degradation in fields treated with nitrate for souring control. A further study by Tanji et al. (2014) again highlighted the apparent importance of toluene degradation as an electron donor for sulphate reduction (Tanji et al., 2014).

The archaeon *Archaeoglobus fulgidus* has been isolated from high temperature oil reservoirs and as an SRP, it is suspected to play a role in souring of high temperature fields (Beeder et al., 1994) and were identified in produced water by sequencing of the *dsrAB* gene (Larsen et al., 2008, 2009). Khelifi et al. (2014) determined that an *A. fulgidus* strain was able to oxidise saturated hydrocarbons (C_{10}-C_{21}) using either thiosulphate or sulphate as a terminal electron acceptor at 70 °C. If *A. fulgidus* is capable of thermophilic hydrocarbon degradation under reservoir conditions this may have an impact on souring modelling (Khelifi et al., 2014).

The continued application of metagenomics to oilfield samples is revealing new and unique pathways for hydrocarbon degradation (Sierra-García et al., 2014). However while the impact of such pathways on souring is yet to be elucidated, correctly understanding biodegradation pathways, and therefore potentially available carbon for SRP, will have a significant impact on souring modelling predictions.

There is evidence that the abundance of certain species of SRP have correlations with various environmental factors such as temperature, concentration of acetate propionate and sulphate, and overall salinity in produced water (Guan et al., 2013). If these data can be matched to sulphide generation it may be possible to predict the SRP present and therefore the likely amount of sulphide produced by physicochemical analysis alone. However in the same study, one of the most common genera of SRP observed in oil reservoirs, *Desulfovibrio*, had no correlation to any of the environmental factors involved in the same study (Guan et al., 2013).

DNA recovered from cores taken from an exploratory offshore oil field as part of souring potential assessment study have also been utilised for microbial community analysis. Analysis showed the presence of nitrate-reducing bacteria in all samples and an absence of SRP, despite the high temperature and moderate levels of sulphate (163 mg/l) present in the formation water. The authors therefore suggested that the microorganisms present in the reservoir would respond to nitrate treatment for souring prevention and that souring may occur during water flooding as SRP are introduced from the seawater used (Tsesmetzis et al., 2016).

In summary, metagenomics is revealing the extent to which microorganisms can use various carbon sources to contribute to souring outside of the conventional souring mechanisms. This knowledge will determine the extent to which certain factors influence microbial community structure in reservoirs, and the factors that are most important when modelling or predicting reservoir souring and taking any potential steps for mitigation.

4. Modelling reservoir souring

4.1. Parameters to consider

Effective and accurate prediction of biogenic reservoir souring using computer models is essential when undertaking major technical and economical decisions regarding field development and material selection. Over the last two decades, several mathematical souring models in various dimensions, have been developed to help predict oilfield souring potential.

Currently, there exists a variety of 3D commercial mathematical souring simulation tools for predictive modelling in the industry, but some of the old modelling tools occur as simple 1D, or 2D single well pair simulators, which was before the advent of the full 3D transient multi-well souring simulators, but still useful for assessing potential souring levels in green fields. One of the most challenging scenarios encountered when using these moderately old 1D or 2D tools occur during history matching of field production data (oil and water). In this case, the complete structure and geometry of the reservoir has to be modelled in the souring simulator, which means, all mesh, grid, well and reservoir data are entered manually for each grid block. This increases simulation run times and could potentially affect the accuracy of predictions, as the reservoir heterogeneity is almost impossible to replicate, and therefore makes it difficult to mimic exactly what is happening in a specific reservoir.

With time, reservoir souring simulation tools referencing different souring mechanisms, have been developed for souring predictions. Some of these models adopt a simplistic approach to souring, considering only, but more importantly, the stoichiometric conversion of sulphates and nutrients for worst case souring predictions using spreadsheets and macro based models, with single well pair modelling capabilities. Other simulation tools have full 3D transient capability. Some of the well-known souring simulators available include SourMax, H_2S Model, Dynamic TVS, REVEAL and SourSim®RL.

A good souring model should incorporate the generation and transport of H_2S in an oil reservoir. The generation and transportation of hydrogen sulphide in a porous media constitutes the two key processes of reservoir souring modelling and simulation (Farhadinia

et al., 2008). The ability to recreate the essential environment necessary for generation and transportation of hydrogen sulphide in a souring model, affects the prediction accuracy (Dunsmore et al., 2006). Additionally, comprehensive souring computations to predict the onset and long-term effect of reservoir souring, requires an understanding and knowledge of fluid flow, mineral scavenging, retardation of H_2S as well as phase partitioning of H_2S (water, oil and gas).

Important parameters such as flow rate, porosity, permeability, injector/producer well distance, etc., determine the flow regime and could affect the H_2S generation profile. The setup of a souring model requires an understanding of the mechanism of souring. Several factors such as the distribution of nutrients, sulphates, number of microorganisms as well as observed H_2S concentration at the wellhead could give potential clues to the mechanism of souring. Current literature shows three basic forms of modelling approaches applied in predictive reservoir souring, namely mixing zone, biofilm and thermal viability (Jordan and Walsh, 2004). In all the approaches a nutrient and sulphate source are required for the metabolic activity of SRP, with H_2S generation potentially occurring at the vicinity of the injection well, within the injection-formation water mixing zone or at the production well.

The mixing zone model assumes the growth of SRP in a zone created where the injection water and formation water mix within the reservoir (Ligthelm et al., 1991). The zone of mixing usually lags behind the water front and may expand through the reservoir. The mixing zone approach is applied in models like REVEAL. Two souring models are available in REVEAL (LEGACY and bacterial activity), with both requiring the establishment of an SRP concentration and a convenient temperature range for growth. The mixing zone concept assumes the activity of SRP will only be prolific in areas of the reservoir affected by the injection water source where conditions provided by the reservoir are favourable enough to promote bacterial activity. This approach is supported by established literature and current laboratory work, however, this approach assumes microbes or bacteria are always present at the flood front, and introduced into the reservoir at the rate of the injection during water injection, fluid/chemical introduction during hydraulic fracturing or dormantly resident in the formation.

REVEAL and SourSim®RL have in-built thermal modelling capability and can compute the thermal profiles in the reservoir during water injection. Both simulators have been developed with full 3D transient capability and are capable of coupling to a reservoir simulator. This means, the souring solution is solved by coupling with the reservoir simulator to incorporate the full 3D transient, based on the reservoir simulation. Thus, reservoir parameters, fluid flow dynamics and well operating conditions provided by the reservoir simulator are brought into the souring simulator, without any manual inputs, to provide the final souring solution. SourSim®RL has the added capability of being able to couple to more than one type of reservoir simulator. This souring tool can couple to five different common reservoir simulators. Additionally, SourSim®RL applies both mixing zone and biofilm in the same run during modelling, as it is impossible to tell which approach is pragmatically occurring during modelling. Another valid consideration is the ability to include multiple nutrient sources in the model (as VFA may not be the only carbon source) as well as the inclusion of a surface facility design feature.

The biofilm model approach assumes H_2S production occurs as a result of SRP growth in a biofilm formed in the injector near wellbore area (Sunde and Thorstenson, 1993). The extent of biomass in the biofilm and subsequently the rate of H_2S production, is therefore dictated by the availability of nutrients, especially nitrogen (N) and phosphorus (P), in the injection water source. When N or P species are limiting, it leads to a limit on the total biomass, and hence growth ceases to be exponential. This model is adopted by some major operators and applied in various in-house souring simulations. SourSim®RL applies biofilm as an added approach to predict souring as indicated above. The main challenge to the biofilm concept is the assumption that the potential level of souring is exclusively dependent on the available injection water composition (nutrient, and sulphate concentration) and microbial activity around the injector near-wellbore region. The consideration of only this approach in souring could potentially limit the predicted amount of H_2S generation as it is unlikely that biofilm formation could be the only explanation to any souring scenario.

Although the mixing zone and biofilm based models have been established as most appropriate for new waterflood developments, a Thermal Viability Shell (TVS) approach is also widely considered and has been applied in the Dynamic TVS model. The model assumes the souring potential of a water flooded reservoir is dependent upon the establishment of a stable viability shell in either the mesophilic (20–40 °C) or thermophilic (40–80 °C) SRP temperature ranges. The creation of a thermal zone colonised by SRP is restricted to a region close to the injector and may extend to several thousand feet from the injector depending on the volume of water in the viability shell (Eden et al., 1993). The establishment of a thermal envelope where bacterial activity is prolific is an essential attribute to any souring model, however it is unclear whether the current version of this model considers the higher temperature range (80 °C–90 °C) where sulphate-reducing archaea (SRA) can still be active and contribute to reservoir souring.

Key parameters which are relevant and required as part of the essential input data in a reservoir souring simulation, include the following:

1. Conditions to define microbial activity

The activity of microorganisms and subsequent H_2S generation are dependent on sulphate and nutrient availability (such as N and P). Environmental conditions local to the reservoir (temperature, pressure, pH, salinity, etc.) also play a part the rate and extent of H_2S generation.

Carbon source—The presence of a carbon source in the formation is essential during modelling for H_2S generation. The carbon source is the electron donor for respiration and for incorporation into cells as biomass. These carbon sources are usually volatile fatty acids (VFAs), but some SRP can utilise other organic compounds either directly or syntrophically from the oil. Additionally, nitrogen and phosphorous elements occur in trace amounts, and have been discovered as essential nutrient sources in biofilm formation and growth. The effect of such trace elements are only considered in some of the more recent souring models.

Sulphate—Sulphate has a great effect on predicted souring potential, as it acts as the electron acceptor for respiration, where it is reduced to sulphide. It is usually available in low concentrations in formation water, but this varies widely in different reservoirs. It is noted, that the main source of sulphate (SO_4^{2-}) in most souring scenarios is injection water.

Salinity—Most souring simulators incorporate a threshold limit for salinity to define growth. Sulphate-reducing microorganisms, depending on species, have reduced activity and become inactive at very high total dissolved solids (TDS) concentrations. SRP metabolism is known to occur in salinities of fresh water up to approximately 150,000 mg/l TDS. A few instances of growth at 200,000 mg/l have also been observed (unpublished results).

pH—pH is essential in controlling the H_2S partitioning behaviour between oil, water and gas phases at reservoir and surface conditions in the souring model. Sulphate reducing prokaryotes (SRP) are usually active in a pH range from 4.5 to 11.0. This encompasses virtually all pH values found in oil field waters, which are mainly between pH 6 and 8.6. Most SRP have an optimum pH growth range of around pH 7.

Sulphide Concentration–Sulphide itself can be toxic and self-limiting to SRP at high concentrations, and so this upper concentration is usually defined for modelling purposes. Conventionally, an aqueous phase undissociated sulphide concentration in excess of 250 mg/l has been considered the upper limit for SRP growth. However recent data

has shown microbiologically derived H_2S generation producing over 1200 mg/l aqueous sulphide (unpublished results).

Temperature profile *(thermal modelling)*–Most sulphate-reducing bacteria (SRB) are thought to be active from low to moderate temperatures, whilst sulphate-reducing archaea (SRA) are active at high temperatures. The ability of a model to simulate thermal energy flows at the injector near wellbore region and inside the main reservoir during water injection, is therefore essential in establishing the temperature profile to help define zones where microorganisms are most active. This data is also important in controlling the partitioning of H_2S between oil, water and gas phases at reservoir and surface conditions.

Pressure–Pressure varies with depth of formation in oil reserves. Reservoir pressures in excess of 15,000 psi have been found to greatly limit the potential for H_2S generation, as SRP activity is virtually non-existent. Pressure is important in controlling the partitioning of H_2S between oil, water and gas phases at reservoir and surface conditions during modelling.

Other essential parameters–Parameters such as the water flow path and extent of water breakthrough, reservoir data (geometry, geochemical, mineralogy, rock properties and geology), gas lift operations, design of surface facility, etc. also affect H_2S production and so form part of the necessary inputs in souring predictions. All of these parameters must be accounted for in a comprehensive reservoir souring simulation (Evans, 2008). Additionally, effective simulation requires the ability to model souring mitigation options e.g. biocide, H_2S scavenger, nitrate, etc. dosing regimens to investigate effective chemical treatment options.

Generally, a good and essential way to initiate desktop souring simulation is to history match field H_2S data (i.e. historical gas phase well profiles) with the theoretical model. Tuning the model to establish a match with field data results in a base model, which provides confidence in the subsequent forecasts for predictive H_2S modelling.

4.2. Mineral scavenging capacity

The ability of a rock formation to scavenge or retain some or most of the H_2S generated in a sour reservoir is an important factor in the control and prevention of H_2S from reaching producer wells. The presence of iron bearing minerals such as siderite ($FeCO_3$), hematite (Fe_2O_3) and chlorites (e.g. chamosite; $(Fe_5Al)(AlSi_3)O_{10}(OH)_8$) contribute greatly to rock scavenging. These minerals will react to form a sulphide phase product of stoichiometry equivalent to pyrite, (FeS_2) or mackinawite (FeS), with the products contributing towards rock matrix scavenging. Additionally, the abundance of clay minerals such as smectite, dolomite and illite also contribute to scavenging, albeit, lower than the iron-bearing minerals.

Iron is most commonly present as Fe (III)-rich minerals e.g. iron oxides (e.g. haematite, goethite, and limonite) and Fe (III)-rich clays (e.g. beidellite), and when buried and under reduction, it is typically present in sulfides (e.g. greigite, mackinawite, pyrite, chalcopyrite), iron-rich carbonates (e.g. peistomeiste, ankerite, siderite) and iron-rich clays (e.g. glauconite, berthierene, chamosite).

Rock mineralogy could indicate significant scavenging capacity, but unpredictable reservoir scenarios such as significant fracturing, or flow channelization; could lead to short-cutting of flow path through the reservoir between injector/producer wells and so reduce the residence time of the injected fluid in the reservoir, resulting in considerably less H_2S scavenging by the rock material.

The mechanism of scavenging of H_2S by reservoir rocks can be described by reaction of H_2S with iron-minerals and the adsorption of H_2S to mineral surfaces. Laboratory experimental procedures involving static bottle tests and dynamic coreflooding can be carried out using representative plugs from fields, to enable better understanding and quantification of the effective scavenging capacity of reservoir rocks. Published data is available from several dynamic laboratory coreflooding methods for H_2S scavenging on reservoir core material (Ballard and Beare, 1997; McElhiney and Davis 2002). Here, reservoir conditions can be simulated more accurately, by confining core plugs and then flooding with sulphide-bearing brine. Tests are usually carried out on clean core plugs to remove any residual oils. This helps to establish the total scavenging ability of the core samples without the interferences caused by oil partitioning. It is also possible that any oil present may reduce the exposed rock surface area available for contact with the sulphide infused water, due to the relatively small size of the plugs in the laboratory experimental setups. However, it is important to note that the actual reservoir will have fluid phases interacting with the rock surface and so laboratory experiments should ideally include cores with residual oils present for comparison.

As indicated, static test methods involving crushing of rocks for bulk adsorption studies are also possible. Work carried out by Oil Plus and other published research indicates scavenging capacities from static bottle tests are usually higher in magnitude compared to results from conventional core floods, as the crushing of the core presents an expanded surface originating from areas of the formation which are typically inaccessible to a flood front (unpublished results). Dynamic measurements are more acceptable than the bulk crushing or static method because the dynamic method largely addresses the issue of rate kinetics and also minimises the potential of fines migrating within the core – as the position of the mineral within the rock matrix is usually undisturbed/unmoved during flooding (Ballard and Beare,1997).

Pre and post- test SEM/EDX (scanning electron/energy dispersive spectroscopy microscopy) and XRD (X-ray diffraction) analyses on core materials from tests are essential for comparing pre- and post-sulphide scavenging to help establish which mineral constituents are most active during testing. Scavenging capacities for a sandstone formation can be relatively high, depending on the available minerology whereas carbonate formations have generally extremely low or zero scavenging capacities.

5. Mitigating reservoir souring

5.1. Nitrate and nitrite

Nitrate treatments have been shown to be effective as a selective inhibitor of SRP activity with a number of advantages over conventional biocide treatments. These include a reduction in costs and toxicity and compatibility with other process chemicals.

There are several mechanisms by which nitrate treatment is thought to control reservoir souring. The first proposed mechanism is the stimulation of nitrate-reducing bacteria (NRB), which out-compete SRP for electron donors. Similarly, some SRP may switch metabolism from sulphate-reduction to nitrate-reduction (Eckford and Fedorak 2002a,b). The second mechanism is the stimulation of nitrate-reducing, sulphide-oxidizing bacteria (NRSOB), that can use nitrate or nitrite to re-oxidise sulphide to elemental sulphur and sulphate (Hubert et al., 2003). The final mechanism is the inhibition of SRP and the removal of sulphide through the production of nitrite, nitrous oxides and other nitrate reduction products (Nemati et al., 2001; Greene et al., 2003). Nitrite, in particular, inhibits dissimilatory (bi)sulphite reductase, the enzyme which catalyzes the reduction of sulphite to sulphide in SRP, thus blocking sulphate respiration.

The dose required for inhibition depends on the concentration of available electron donors, the biomass concentration and on the presence of nitrite reductase enzymes, which would act to negate the inhibitory effect of nitrite by reducing it further. In addition core variables such as temperature, pH, pressure and total dissolved solids (TDS) have all been shown to influence the effectiveness of nitrate treatments. Furthermore, under dosing nitrate can lead to zonation, whereby a nitrate dose is consumed but excess VFAs remain available to SRP deeper in the reservoir.

For over 20 years operators have been using nitrate treatment technology as a means of controlling SRP activity. As such, significant

experience and performance history is available of the benefits and risks associated with use of nitrate treatment. This has been discussed in detail elsewhere (Energy Institute, 2016; Gieg et al., 2011; Eroini et al., 2015). However the potential negative effects of nitrate treatments are sometimes overlooked and are summarised here.

Reports regarding the effect of nitrate treatment on corrosion processes are contradictory, as both increased corrosion rate and the inhibition of corrosion have been reported, with the differences thought to be dependent on operating conditions. Corrosion issues associated with nitrate treatment have never been associated with seawater injection alone (either in the laboratory or in the field) but only in certain instances of produced water re-injection (PWRI) or mixed seawater and PWRI (Energy Institute 2016).

In the absence of H_2S, it seems that traces of nitrite, which is a by-product of NRB activity, is the likely agent of enhanced general and/or localised corrosion in nitrate-treated PWRI systems. Rizk, (2006) confirmed a strong correlation between the presence of nitrite (at concentrations of less than 10 mg/l) and enhanced corrosion and Vik et al. (2007) suggested that prolonged biological generation of low levels of nitrite may induce pitting corrosion. A problem is that the microbial generation of nitrite from nitrate reduction is unpredictable and can vary depending on factors such as temperature, water chemistry and the overall microbiological population. It must also be considered that nitrite itself promotes corrosion at concentrations below 161 mg/l but serves as a corrosion inhibitor at concentrations of 460–920 mg/l. Corrosion and souring control by nitrite therefore requires a dose that is sufficiently high to both inhibit sulphate-reduction and prevent chemically catalyzed nitrite corrosion (Hubert et al., 2005).

In the presence of H_2S (i.e. re-injection of sour water) the situation is more complicated because nitrite can react directly with H_2S (Sturman and Goeres, 1999). A variety of sulphur compounds may be produced by these reactions and some new corrosion phenomena can occur. These will vary depending on the products (elemental sulphur, thiosulphate or polythionic acids) as well as the temperature and pH. For example there is evidence that nitrate-reduction can occur at higher temperatures (50–70 °C) than nitrite-reduction (unlikely above 50 °C) therefore in the mixing zone of the reservoir, nitrite can be produced and passed deeper into the reservoir to efficiently inhibit SRP activity (Fida et al., 2016). However the generation of large amounts of nitrite in the reservoir, may have adverse effects as the nitrite reacts with sulphide and residual nitrite reaches the production metal work.

Another important factor that has to be considered in nitrate treatment is the possible formation of elemental sulphur by NRSOB. NRSOB can make up a large proportion of the microbial community during nitrate injection and some strains of NRSOB in oil field brines are believed to carry out sulphide oxidation to elemental sulphur in the presence of nitrate and organic carbon (Rizk, 2006). Evidence for this was provided by Wright et al., (1997) wherein sulphur formation was observed in laboratory tests of remediating treatments of sour West Texas oil field waters when nitrate and organic carbon were used to stimulate NRSOB (Wright et al., 1997). If elemental sulphur were to be generated, elevated localised corrosion rates are a potential consequence (Vik et al., 2007; Schaschl, 1980).

The effect of nitrate treatment on reservoir souring and corrosion processes is still not fully understood despite years of laboratory and field experience. It appears to be greatly influenced by the specific microbial activity and the physico-chemical conditions of the system under treatment. The specific nature of the nitrate treatment mechanism is also not straightforward, with under dosing, microbial zonation and nitrate-reducing sulphate-reducing bacteria (NRSRB) all having a role in the effectiveness (or not) of nitrate treatment. Thus, it is important to evaluate the benefits of nitrate treatment and potential consequences on a case by case basis.

5.2. Biocides

Biocides are routinely used during waterflooding to control microbial populations and mitigate against MIC and biofouling in injection wells and process equipment. Despite this, biocides have not been extensively studied for their effectiveness in preventing reservoir souring specifically, particularly under representative reservoir conditions of temperature, pressure and water characteristics (salinity, carbon source and abundance, sulphate concentration, etc.). In addition, the results of only a few field trials on the effectiveness of biocides to control or remediate souring have ever been published. The main types of biocides used and their known interactions with SRP have been reviewed in detail elsewhere (Gieg et al., 2011 and references within). Biocide testing for control and MIC mitigation is well understood (Skovhus, 2014) while information on conducting biocide testing for souring prevention or remediation is limited. Here studies focusing directly on the effect of biocides on souring and behaviour of biocides under reservoir conditions are presented.

Of the few laboratory studies conducted investigating the effect of biocide dosing on H_2S generation, (specifically remediation of H_2S generation), the majority have used sand pack columns. The first of these studies was conducted by Reinsel et al. (1996) where up-flowed sand packs filled with crushed sandstone were used to investigate the effect of glutaraldehyde treatments on H_2S generation by sessile bacteria from North Sea produced water. Upon cessation of biocide dosing H_2S production immediately resumed in the top part of the column and took two weeks to resume in the entire column (Reinsel et al., 1996).

Two studies on the effect of Tetrakis(hydroxymethyl)phosphonium sulphate (THPS) on H_2S generation in sand pack bioreactors have been conducted. In batch dosing experiments, THPS with added penetrant was more effective than the unformulated THPS and once weekly doses of THPS demonstrated an ability to control reservoir souring under fracture/flow conditions (Jones et al., 2010). In a related study the continuous injection of 30 mg/l THPS reduced H_2S to below detection limits within a few days (Jones et al., 2011).

A study by Xue and Voordouw (2015), used up-flowed sand packs to investigate reductions in sulphide generation by SRP using pulse dosing low concentrations of biocide for 5 days and dosing high concentrations for 1 h. This study was unique in that it clearly defined its recovery level to facilitate accurate comparisons between treatments. The biocides investigated included glutaraldehyde, cocodiamine, benzalkonium chloride (BAC) and THPS. Cocodiamine performed the best in the five day pulse experiments, with a recovery time of 300 h at 50 ppm dosing. In the high concentration experiments, glutaraldehyde performed the best, producing a recovery time of 135 h after dosing 2000 ppm for 1 h (Xue and Voordouw, 2015).

Gardner and Stewart (2002) used CDC bioreactors to investigate the effect of glutaraldehyde on H_2S generation by SRB biofilms. Biocide was dosed at 500 ppm and then the bioreactor was shut-in for a period of 7 h before restoring flow. The dose at 500 ppm for 7 h slowed the recovery time significantly compared to controls. Control experiments recovered to 90% of the steady state level after 7.3 h, while the biocide treatment delayed recovery for 73 h (Gardner and Stewart, 2002).

A number of field studies have been conducted where the effect of various biocide treatments on souring have been observed. Littman and McLean (1987) investigated the injection of metronidazole, and its effectiveness in controlling H_2S in four waterfloods in the USA. In all cases, continuously applying biocide to the injection water led to a decrease in the H_2S measured in the production system (Littman and McLean, 1987). Larsen et al. (2002) documented 6 trials using THPS in the Skjold/Gorm oil production systems for the control of H_2S production. All trials were batch treatments, except for one. These studies demonstrated varied effects on H_2S production.

In addition to the efficacy of biocides in mitigating reservoir souring, information on the stability of biocides under reservoir conditions of temperature, pressure and pH is limited. As temperatures

and pressures increase in the reservoir, any chemical equilibrium will shift (Kahrilas et al., 2015). This may lead to unexpected chemical reactions or degradation of biocides. For example, the conventionally used biocide glutaraldehyde is known to be ineffective at high temperatures (above 75 °C) so the use of non-traditional oil and gas biocides such as 4,4-dimethyloxazolidine and tris (hydroxymethyl) nitromethane (THNM) are being explored for use in souring control in reservoirs with high temperatures (Yin et al., 2016). Furthermore, McGinley et al. (2011) observed that glutaraldehyde stability in both field and synthetic water samples is effected by temperature and the presence of ammonium chloride. They observed that 90% of 1000 ppm glutaraldehyde incubated at 60 °C degraded within 24 h (McGinley et al., 2011). The stability of THPS is strongly dependant on temperature and pH, as well as the presence of steel (Zhao et al., 2009). Barman and Preston (1992) have also demonstrated that isothiazolinone biocides have very short half-lives at alkaline pH (9.5 or higher) (Barman and Preston, 1992). Furthermore Williams and Schultz (2015) highlighted the importance of investigating the impact of several common oil and gas process additives and organic matter have on biocide efficiency. Biocides were mixed with biological organics such as trypticase soy, xanthan gum, guar and polyacrylamide cross-linker. Glutaraldehyde dosed with each process additive separately showed good stability, as did DBNPA, however approximately 30% of the DBNPA degraded in the presence of 500 ppm polyacrylamide (Williams and Schultz, 2015). DBNPA is well known to react with bisulphite/sulphite and other reducing agents, as is isothiazolinone (McIlwaine, 2006) and many other commonly used biocides. Other production chemicals may also increase the availability of carbon, nitrogen and phosphorus in injected seawater systems, significantly restricting or enhancing the growth rate of SRP (Sunde et al., 1990). Finally the stability of biocides can also influenced by geology and biogeochemistry, therefore it is important to have an understanding of the subsurface as it may influence the fate of the biocide when it is injected (Kahrilas et al., 2015).

The main challenge associated with biocide dosing for reservoir souring is ensuring that the concentration of biocide required to inhibit sulphide generation or kill SRP present in the reservoir itself is maintained for the required contact time. This challenge can be exacerbated by of the presence of biocide resistant populations (either biochemical or lack of biofilm penetration), sorption of biocide to the reservoir matrix, the biocide passing through fractures (bypassing regions of microbial growth) or biomass plugging protecting areas of microbial growth (Gieg et al., 2011). These factors, combined with the relatively uncharacterised behaviour of biocides under representative reservoir conditions, greatly reduces the confidence in the ability of biocides to control or remediate souring and data is very limited on the efficacy of biocides to prevent souring. For example, Vance and Thrasher (2005) concluded that if mass of SRP close to an injector is in the order of tonnes, a large dose of biocide will be required to kill only the SRP as microorganisms other than SRP are also present in the biofilm. In addition, the demand for biocide will be even greater because the biocide will react indiscriminately with all types of biomass. Therefore to be effective and maintain control, batch doses must be repeated at a rate or frequency related to the regrowth or recolonisation of SRP (Vance and Thrasher 2005). However the required biocide concentration is likely to be far higher than the concentration dosed to protect the water injection system. As dosing will need to be more frequent or even continuous, operating costs will inevitably increase potentially making other souring mitigation options more viable.

5.3. Sulphate removal

Sulphate removal using nanofiltration membrane technology has been utilised offshore since 1988 (on the Brae Alpha platform) to mitigate against issues caused by inorganic scaling (Heatherly et al., 1994). It was immediately apparent that removal of sulphate from injected seawater could potentially mitigate against reservoir souring, however at the time, there was some discussion as to the importance of sulphate in microbial reservoir souring.

An early study by Rizk et al. (1998) carried out laboratory tests in bioreactors under sulphate limiting conditions. The authors found that H_2S generation decreased in relation to the decrease in concentration of available sulphate. The concentration of hydrogen sulphide generated correlated with complete stoichiometric conversion of available sulphate to hydrogen sulphide. However, at no point did the bioreactors ever completely cease generation of hydrogen sulphide. The authors contributed this to residual sulphate remaining from earlier incubations with sulphate-rich water (Rizk et al., 1998). However, reservoir mineral scavenging of biologically produced hydrogen sulphide could be significant enough to mean that hydrogen sulphide is not encountered in produced fluids (McElhiney and Davis, 2002).

Despite the early laboratory studies, the cost of sulphate-removal technologies (predominantly nano-filtration membranes) precluded early adoption and it wasn't until much later that it was considered for field use, even then only for more technically-demanding offshore installations. After a thorough technical evaluation, sulphate-removal technology was chosen for the Ursa and Princess deep water reservoirs in the Gulf of Mexico as part of a new water flood project (Alkindi et al., 2007). The need for this mitigation was driven by the higher HSE risks associated with operating in a deep water environment. The existing well-casing metallurgy was unable to cope with any amounts of H_2S above 20 ppm at bubble point pressure, therefore for any water flood, mitigation measures needed to be put in place. The authors therefore carried out experiments to measure the scavenging capacity of the reservoir minerals. They found that the scavenging capacity was sufficiently high enough to mitigate against production of H_2S in the producing wells as long as sulphate-removal was incorporated into the system design. The authors therefore proposed sulphate-removal as a souring mitigation option.

In a related study, Walsh et al. (2008) reviewed the data available for the 12 sulphate-removal plants operating in the world at that time. These were all built primarily for scale control but the authors found that no H_2S was generated from any of these fields, despite the conditions for reservoir souring to occur without sulphate removal. The authors concluded that reservoir minerals were responsible for scavenging the small amounts of H_2S that could be generated from the 20–40 mg/l sulphate that was being injected (based on best available performance nanofiltration membranes at the time) (Walsh et al., 2008).

Since then however, one of the fields reviewed in the Walsh et al. (2008) study, started generating 15 ppm of H_2S in the bulk gas (Robinson et al., 2010). An in-depth study demonstrated that this was due to biological generation of H_2S in the reservoir by SRP. Quantitative polymerase chain reaction (qPCR) based analysis of fluids from the production system showed high concentrations of SRB and SRA despite no SRB being detectable by MPN (Robinson et al., 2010; Jensen et al., 2013). Calculations also showed that between 32 and 76% of the < 50 mg/l sulphate remaining after sulphate removal was being converted to H_2S by SRP within the reservoir. The reservoir temperature (115 °C) at the South Arne field seemed to be providing some protection from more significant souring (i.e. complete stoichiometric conversion), however there was also significant cooling due to water injection, with the two wells producing the largest amounts of H_2S being cooled significantly due to short-circuiting of injection water (Robinson et al., 2010). The chalk minerology (pure calcite) for this reservoir would mean that there is minimal reservoir scavenging of microbially generated H_2S. It is important therefore to understand that although sulphate-removal reduces the concentration of sulphate in the injection water, it does not eliminate it completely and materials selection should be carried out with a worst case scenario in mind (NACE MR0175/ISO 15156).

5.4. Novel souring mitigation options

As discussed herein, the dominant forms of microbial mitigation for souring control are the use of nitrate/nitrite and biocides. There has been some recent work carried out using (per)chlorate discussed below and this shows some promise. However, despite the commercial and environmental issues surrounding reservoir souring, the number of solutions still remains relatively low. We will therefore discuss below some of the alternative options currently being researched.

5.4.1. Perchlorate

Due to the limitations with regards to souring control through nitrate treatment as discussed above, researchers have been investigating the potential of other metabolic homologues in mitigating sulphide production by SRP. Initially hypothesised by Postgate (1952), perchlorate (ClO_4^-) and chlorate (ClO_3^-) (referred to herein collectively as (per)chlorate) have been gaining attention recently as inhibitors of sulphidogenesis, with a patent on its use in controlling biogenic sulphide production being granted recently (Coates, 2014).

Despite its early identification as a potential inhibitor of sulphidogenesis, work into understanding (per)chlorate reduction has only really gained momentum since it was discovered as a significant groundwater contaminant in the late 1990s (Coates and Achenbach, 2004). Early work therefore focused on (per)chlorate reduction with a view to bioremediation of this toxic anion in aquifers (Coates and Achenbach, 2004). It has only been more recently that (per)chlorate has been unequivocally demonstrated as an inhibitor of microbial sulphate reduction (Gregoire et al., 2014; Engelbrektson et al., 2014; Leibensteiner et al., 2014; Carlson et al., 2015a Carlson et al., 2015a).

Engelbrektson et al. (2014) found that 10 mM (1224 mg/l) of sodium perchlorate or 10 mM (1064 mg/l) of sodium chlorate inhibited sulphide generation for 51 days in a flow-through packed column, whereas with 10 mM (840 mg/l) sodium nitrate, sulphidogenesis was initially inhibited but sulphide breakthrough was observed after 23 days. Gregoire et al. (2014) also found that a number of different isolates, including *Arcobacter* sp. strain CAB and *Azospira suilum* strain PS were able to oxidise H_2S to elemental sulphur coupled to (per)chlorate reduction. The strains tested oxidised H_2S in preference to organic carbon sources present in the growth media, leading to the potential of microbial H_2S oxidation as a means of removing H_2S from waste streams containing this contaminant. However, the production of elemental sulphur presents a significant corrosion risk. Despite this, a recent patent pending has been filed on this *modus operandi* (Coates, 2016).

Mesophilic anaerobic (per)chlorate reduction is known to proceed through the reduction of the anion by a reductase enzyme, producing chlorite (Coates and Achenbach, 2004). Many of the reductase enzymes identified are non-specific and reduce a wide range of substrates, including nitrate, chlorate, iodate and bromate (Kengen et al., 1999; Marangon et al., 2012). This however results in the production of a particularly reactive intermediate, chlorite, which may cause cellular damage if left to accumulate in the cell (de Geus et al., 2009). Classically, it has been proposed that (per)chlorate reducing bacteria degrade chlorite to chlorine and molecular oxygen using a chlorite dismutase enzyme, encoded by the *cld* gene (de Geus et al., 2009; Liebensteiner et al., 2014). This gene has been identified in a number of mesophilic to moderately thermophilic (per)chlorate reducing microorganisms, encompassing nine bacterial and two archaeal phyla (Maixner et al., 2008). Recently however (per)chlorate reduction has also been identified in hyperthermophilic microorganisms that are commonly found in oil reservoirs (Liebensteiner et al., 2013; Liebensteiner et al., 2014; Liebensteiner et al., 2015), however these microorganisms do not have a *cld* homologue. In this case, the authors hypothesise that chlorite reacts abiotically with reduced sulphur species (such as H_2S) to oxidise the sulphide to sulphate, thereby reducing (per)chlorate in a mixed biotic/abiotic reaction (Liebensteiner et al., 2013).

(Per)chlorate is therefore thought to inhibit sulphide generation by direct oxidation of extracellular sulphide by (per)chlorate reducing microorganisms (Gregoire et al., 2014) or through intracellular oxidation in sulphide reducing microorganisms (Liebensteiner et al., 2013). Additionally, reduction of perchlorate ($E^{0\prime} = +797$ mV) and chlorate ($E^{0\prime} = +794$ mV) is more thermodynamically favourable than both sulphate reduction ($E^{0\prime} = -217$ mV) and nitrate reduction ($E^{0\prime} = +750$ mV), potentially leading to a community shift and competitive inhibition mechanism similar to that found in nitrate treatment (Gregoire et al., 2014). This is in addition to the findings that (per)chlorate is toxic to SRP (Engelbrektson et al., 2014), leading to a number of potential mechanisms for (per)hlorate inhibition of sulphidogenesis.

5.4.2. Anthraquinone

Some early work focused on anthraquinone as an inhibitor of sulphide production in SRP (Cooling et al., 1996; Burger and Crews, 2001). This showed some significant promise, with sulphide levels reduced by 95% in waste water systems (Dickinson et al., 2005) and 97.8% in a sandpack column within 24 h (Burger and Crews, 2001). However, anthraquinone is soluble at high pH but at neutral or low pH (as would generally be encountered in oil reservoirs), anthraquinone forms colloidal particles (Harless et al., 2000). These particles are insoluble in water and would therefore adsorb to reservoir rock. This could cause significant problems with injectivity and would limit the chemical's reach into the reservoir and suggests why it hasn't seen more widespread use, particularly for souring control.

5.4.3. Adjuvants

One new idea being considered is the use of adjuvants to traditional biocides to increase their effectiveness (Wen et al., 2010; Xu et al., 2012). Wen et al. (2010) discussed the use of chelating agents to enhance the effects of antibiotics due to their ability to increase the permeability of the outer cell membrane of Gram-negative bacteria. The commonly used chelating ethylenediaminetetraacetic acid (EDTA) is however non-biodegradable and there are concerns that it may accumulate in the environment after discharge. Therefore, Wen et al. (2010) tested the effectiveness of two chelating agents, ethylenediaminedisuccinate (EDDS) and *n*-(2-hydroxyethyl)iminodiacetic acid (HEIDA) at improving the biocidal efficacy of both glutaraldehyde and THPS against two strains of *Desulfovibrio*. The authors found that both HEIDA and EDDS improved growth inhibition of THPS and glutaraldehyde under laboratory conditions, with more chelating agent needed under higher nutrient conditions. The water chemistry could therefore have a great effect on the effectiveness of the chelating agent, particularly as high cation concentrations (i.e. Ca^{2+} and Na^+) will consume the chelating agents, reducing their ability to enhance the biocidal effects under planktonic conditions (Wen et al., 2010).

Xu et al. (2012) have taken this idea further by including an alcohol (methanol) into the biocidal cocktail. They use EDDS (1000 ppm) in combination with methanol (10%) and glutaraldehyde (30 ppm) to treat *Desulfovibrio vulgaris* biofilms and found that the combination of these three ingredients was more effective than glutaraldehyde alone (30 ppm). The authors also investigated the microorganism's ability to reduce sulphate (through measuring sulphate consumption) to determine the effect that this cocktail would have on mitigating H_2S generation. In the lab tests, sulphate consumption was reduced by nearly half over 7 days (Xu et al., 2012). These results are encouraging, however no mention was made of the temperature or pressure conditions under which this work was carried out. The elevated temperatures and pressures in a reservoir scenario and short time scale over which these tests were conducted suggests that further work should be carried out to assess the suitability of this cocktail under reservoir conditions. Particularly as glutaraldehyde polymerises at elevated temperatures and methanol has a boiling point of 65 °C at ambient pressure (Rasmussen and Albrechtsen, 1974). Many reservoirs can easily be in excess of these temperatures.

5.4.4. Molybdate

Other authors have investigated new active ingredients and specific inhibitors of sulphate-reduction (Carlson et al., 2015b; de Jesus et al., 2015). Molybdate is a known inhibitor of sulphate-reduction and has been so for a number of years (Newport and Nedwell, 1988). It is thought to be metabolised from molybdate to adenosine 5′-phosphomolybdate (APMo) by ATP sulfurylase/sulphate adenosyltransferase, the enzyme involved in the first step of the dissimilatory sulphate-reduction pathway. This enzyme usually converts sulphate to adenosine 5′ phosphosulphate (APS) (Carlson et al., 2015b). AMPo is unstable and rapidly degrades as compared to APS which is converted to sulphite and onto sulphide by the APS reductase and dissimilatory sulphite reductase enzymes. This primarily drives an ineffective cycle which uses intracellular ATP and competes for substrate with sulphate. Newport and Nedwell (1988) also reported that molybdate had more than one site of action and postulated that there was also an effect on sulphate transport.

de Jesus et al. (2015) therefore tested the effectiveness of molybdate as an inhibitor of SRB activity on a mixed consortium of SRB pre-enriched from an oil field produced water. Their results showed that 12.8 mg/l of molybdate was able to inhibit sulphide generation in the presence of 2000 mg/l sulphate and sulphide generation could be inhibited for up to 360 h (de Jesus et al., 2015). Carlson et al. (2015b) also found that molybdate was a specific inhibitor of sulphide production, along with the other transition metals vanadate and tungstate. However, higher concentrations (i.e. over above 1 mM) were toxic to all microorganisms in a mixed marine enrichment culture, demonstrating non-toxic inhibitive effects (Carlson et al., 2015b). However the authors found that monofluorophosphate (MFP) was a strong selective inhibitor of sulphate-reducing microorganisms. MFP was also tolerated by nitrate and (per) chlorate reducing metabolisms so the authors speculated that it could be used as a synergistic SRP inhibitor with nitrite or chlorite as a strong synergistic effect was observed. Work with the tn5:*rex* mutant of *Desulfovibrio aleskensis* (a mutant that overexpresses the central pathway of sulphate reduction (Kuehl et al., 2014)) demonstrated that MFP's mechanism of action was through non-competitive inhibition of the sulphate reduction pathway at high concentrations, with the release of cytoplasmic fluoride ions also being implicated in MFP toxicity (Carlson et al., 2015b).

5.4.5. Bacteriophage

More novel mitigation options for sulphate-reducing microorganisms have also been proposed in the form of bacteriophage (Summer et al., 2011). Phage are bacteriolytic, however they tend to be highly specific in their target host (i.e. will only kill a single species or even strain of bacteria). Summer et al. (2011) found two bacteriophage present in black mud from an efflux brine pond at a concentration of 1.5×10^5 plaque forming units (pfu) per ml. These phage were active against co-cultures of *Haloanaerobium* and *Desulfovibrio*. However, even the authors noted that it was unlikely that the phage attacked both species and that the phage could have attacked one member of the co-culture, meaning that the other species was unable to survive without its counterpart (Summer et al., 2011). Removing one SRP from an oilfield microbial consortium may only generate a niche that will be filled by another SRP, meaning that sulphidogenesis will still occur and to completely inhibit sulphidogenesis as many bacteriophage may be needed as there are SRP. However, there are many complex and little understood community interactions at the microbial level. Therefore, through greater understanding of microbial community dynamics, it may be possible to target one or more microorganisms that are essential to the functioning of sulphate-reducing communities. However, until that position is reached, targeted molecular mitigation strategies may be more focused on the functional genes involved in sulphate-reduction. New gene editing and silencing tools such as CRISPR-Cas and antisense RNA may be used to manipulate functional gene expression (Robinson and Dunsmore, 2009).

5.4.6. Diphenyliodonium salts

Perhaps the most promising novel souring mitigation technology has recently been developed by Geissler and Keasler (2016), with a patent for this recently granted. The authors found that diphenyliodonium salts (chloride and nitrate salts) were effective at inhibiting sulphidogenensis and specifically SRP. Concentrations over 1 ppm diphenyliodonium chloride were effective at stopping hydrogen sulphide generation for up to 305 days and microbial community analysis demonstrated that there were no SRP detectable. However, in controls (untreated), over 97% of the microbial population consisted of microorganisms capable of reducing sulphate (Geissler and Keasler, 2016). There was some reduction in the number of active microorganisms in treated samples over longer time periods, however there was still microbial activity over shorter incubation times, suggesting that the diphenyliodonium salts are not universally biocidal and are specific to SRP.

6. The future of reservoir souring and its mitigation

It is always difficult and maybe futile to predict the future but despite the decades of research and development into reservoir souring and its mitigation, new tools and technologies are still being used to discover different, previously unknown aspects of this global phenomenon. This demonstrates that there are still many areas for development. Reservoir souring modelling is advancing at a rapid pace and the authors postulate that it will soon become standard practice in new field developments, as it already is in some of the major oil companies at the minute. The authors hope this will bring along with it more detailed appraisal of reservoir souring challenges at the exploratory drilling and development stage of oil and gas projects, with parameters such as water chemistry, rock mineral scavenging capacity and microbial community analysis becoming standard analysis at the exploration stage. This approach will reduce the number of 'surprises' and ensure that fields are correctly developed according to their risk of reservoir souring.

Souring mitigation has changed little over the past few decades, with the exception of nitrate treatment. However, despite promising results, even nitrate treatment has not been shown to be an effective option in all scenarios. New competitive inhibitors such as (per)chlorate may fill this gap or even sulphate-reduction specific inhibitors such as molybdate and monofluorophosphate. At the same time sulphate-removal nanofiltration membranes are decreasing in cost and at the point they become cost-effective in a wider range of cases, they may eventually be used routinely for souring prevention. At that point, significant reservoir souring may become a thing of the past. However, if there's one thing that microorganisms are capable of time and time again, it is to surprise, and the battle against control of sulphide generating microorganisms is far from won.

Conflicts of interest

RJ, BF, AW and MF are employed by Oil Plus, which provides souring simulations using SourSim®RL as a commercial service.

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References

Agrawal, A., Park, H.S., Nathoo, S., Gieg, L.M., Jack, T.R., Miner, K., Voordouw, G., 2012. Toluene depletion in produced oil contributes to souring control in a field subjected to nitrate injection. Environ. Sci. Technol. 46, 1285–1292.

Al-Rasheedi, S., Kalli, C., Thrasher, D., Al-Qabandi, S., 1999. Prediction and evaluation of the impact of reservoir souring in North Kuwait, a case study. In: Paper SPE 53164. SPE Middle East Oil Show & Conference. Society for Petroleum Engineers, Houston,

USA.
Alkindi, A., Wright, R.P., Moore, W., Walsh, J., Morgenthaler, L., Kuijvenhoven, C., 2007. Challenges for waterflooding in a deepwater environment. In: Paper OTC 18523. Offshore Technology Conference. Society for Petroleum Engineers, Houston, USA.
Ballard, T.J., Beare, S.P., 1997. Examining the natural abstraction of hydrogen sulphide in reservoir environments, chemicals in the oil industry. R. Soc. Chem. 211, 157–169.
Barman, B., Preston, H., 1992. The effects of pH on the degradation of isothiazolone biocides. Tribiol. Int. 25, 281–287.
Beeder, J., Nilsen, R.K., Rosnes, J.T., Torsvik, T., Lien, T., 1994. *Archaeoglobus fulgidus* isolated from hot North Sea oil field waters. Appl. Environ. Microbiol. 60, 1227–1231.
Bradley, A.S., Leavitt, W.D., Johnston, D.T., 2011. Revisiting the dissimilatory sulfate reduction pathway. Geobiology 9, 446–457.
Brenner, M., Benavides, S., Mahon, S.B., Lee, J., Yoon, D., Mukai, D., Azer, S.M., 2014. The vitamin B12 analog cobinamide is an effective hydrogen sulfide antidote in a lethal rabbit model. Clin. Toxicol. 52, 490–497.
Burger, E.D., Crews, A.B., 2001. Inhibition of sulfate-reducing bacteria by anthraquinone in a laboratory biofilm column under dynamic conditions. In: CORROSION. Paper 01274. NACE International Houston, USA.
Burger, E.D., Jenneman, G.E., Carroll, J.J., 2013a. On the partitioning of hydrogen sulfide in oilfield systems. In: Paper SPE-164067. SPE International Symposium on Oilfield Chemistry. Society of Petroleum Engineers, Houston, USA.
Burger, E.D., Jenneman, G.E., Gao, X., 2013b. The impact of dissolved organic-carbon type on the extent of reservoir souring. In: Paper SPE-164068. SPE International Symposium on Oilfield Chemistry. Society of Petroleum Engineers, Houston, USA.
Callbeck, C.C., Agrawal, A., Voordouw, G., 2013. Acetate production from oil under sulfate-reducing conditions in bioreactors injected with sulfate and nitrate. Appl. Environ. Microbiol. 79, 5059–5068. http://dx.doi.org/10.1128/AEM.01251-13.
Carlson, H.K., Kuehl, J.V., Hazra, A.B., Justice, N.B., Stoeva, M.K., Sczesnak, A., Deutschbauer, A.M., 2015a. Mechanisms of direct inhibition of the respiratory sulfate-reduction pathway by (per) chlorate and nitrate. ISME J. 9, 1295–1305.
Carlson, H.K., Stoeva, M.K., Justice, N.B., Sczesnak, A., Mullan, M.R., Mosqueda, L.A., Coates, J.D., 2015b. Monofluorophosphate is a selective inhibitor of respiratory sulfate-reducing microorganisms. Environ. Sci. Technol. 49, 3727–3736.
Coates, J.D., Achenbach, L.A., 2004. Microbial perchlorate reduction: rocket-fuelled metabolism. Nat. Rev. Microbiol. 2, 569–580.
Coates, John D., 2014. Microbial metabolism of chlorine oxyanions as a control of biogenic hydrogen sulfide production. U.S. Patent No. 2014/0134736.
Coates, John D., 2016. Methods for immediate souring control in gases or fluids produced from sulfidogenic reservoir systems. U.S. Patent No. 2016/0017206.
Cooling, F.I., Maloney, C.L., Nagel, E., Tabinowski, J., Odom, J.M., 1996. Inhibition of sulfate respiration by 1,8-dihydroxyanthraquinone and other anthraquinone derivatives. Appl. Environ. Microbiol. 62, 2999–3004.
Dickinson, A., Peck, G.E., Arnold, B.D., 2005. Effective chemistries to control SRB, H_2S, and FeS problems. In: SPE Western Regional Meeting. Society of Petroleum Engineers. Paper SPE-93007. Society of Petroleum Engineers, Houston, USA.
Eckford, R.E., Fedorak, P.M., 2002a. Planktonic nitrate-reducing bacteria and sulfate-reducing bacteria in some western Canadian oil field waters. J. Ind. Microbiol. Biotechnol. 29, 83–92.
Eckford, R.E., Fedorak, P.M., 2002b. Chemical and microbiological changes in laboratory incubations of nitrate amendment sour produced waters from three western Canadian oil fields. J. Ind. Microbiol. Biotechnol. 29, 243–254.
Eden, B., Laycock, P.J., Fielder, M., 1993. Oilfield Reservoir Souring, Health and Safety Report – Offshore Report, vol. 92. OTHpp. 385.
Energy Institute (Folwell, B.D and Palmer-Brown, W.), 2016. The Use of Nitrate Treatment in Oilfield Systems to Control Reservoir Souring: a Review of Current Status. EI publications.
Engelbrektson, A., Hubbard, C.G., Tom, L.M., Boussina, A., Jin, Y.T., Wong, H., Piceno, Y.M., Carlson, H.K., Conrad, M.E., Anderson, G., Coates, J.D., 2014. Inhibition of microbial sulfate reduction in a flow-through column system by (per) chlorate treatment. Front. Microbiol. 5, 315.
Eroini, V., Anfindsen, H., Mitchell, A.F., 2015. Investigation, classification and remediation of amorphous deposits in oilfield systems. In: Paper SPE-173719. SPE International Symposium on Oilfield Chemistry. Society of Petroleum Engineers, Houston, USA.
Evans, P., Nederlof, E., Richmond, W., 2015. Souring development associated with PWRI in a North Sea field. In: Paper SPE-174529. SPE Produced Water Handling & Management Symposium. Society of Petroleum Engineers, May, Houston, USA.
Evans, P., 2008. Reservoir souring modelling, prediction and mitigation. In: Paper No. OMAE2008-57085, ASME 2008, 27th International Conference on Offshore Mechanics and Arctic Engineering. ASME New York, USA.
Farhadinia, M.A., Bryant, S.L., Sepehrnoori, K., Delshad, M., 2008. Development and Implementation of a Multi-Dimensional Reservoir Souring Module in a Chemical Flooding Simulator. UTCHEMpp. 1–14.
Federal Highway Administration Report, 2002. Corrosion Costs and Preventative Strategies in the United States. FHWA-RD-01-156.
Fida, T.T., Chen, C., Okpala, G., Voordouw, G., 2016. Implications of limited thermophilicity of nitrite reduction for control of sulfide production in oil reservoirs. Appl. Environ. Microbiol. 00599. http://dx.doi.org/10.1128/aem.00599-16.
Gardner, P., Stewart, L., 2002. Action of glutaraldehyde and nitrite against sulphate-reducing bacterial biofilms. J. Ind. Microbiol. Biotechnol. 29, 354–360.
Geissler, B., Keasler, V.V., 2016. Diphenyliodonium salts as sulfidogenesis inhibitors and antimicrobials. U.S. Patent No. 2016/0222762.
Gieg, L.M., Jack, T.R., Foght, J.M., 2011. Biological souring and mitigation in oil reservoirs. Appl. Microbiol. Biotechnol. 92, 263–282.
Greene, E.A., Hubert, C., Nemati, M., Jenneman, G.E., Voordouw, G., 2003. Nitrite reductase activity of sulphate-reducing bacteria prevents their inhibition by nitrate-reducing, sulphide-oxidizing bacteria. Environ. Microbiol. 5, 607–617.
Gregoire, P., Engelbrektson, A., Hubbard, C.G., Metlagel, Z., Csencsits, R., Auer, M., Conrad, M.E., Thieme, J., Northrup, P., Coates, J.D., 2014. Control of sulfidogenesis through bio-oxidation of H2S coupled to (per) chlorate reduction. Environ. Microbiol. Rep. 6, 558–564.
Guan, J., Xia, L.P., Wang, L.Y., Liu, J.F., Gu, J.D., Mu, B.Z., 2013. Diversity and distribution of sulfate-reducing bacteria in four petroleum reservoirs detected by using 16S rRNA and dsrAB genes. Int. Biodeterior. Biodegr. 76, 58–66.
Health and Safety Executive, 2005. EH40/2005 Workplace Exposure Limits. HSE Books, Sudbury, UK.
Harless, M., Yuan, M., Cowan, J.K., 2000. 10-Anthraquinone applications to control biogenic production of hydrogen sulfide in the near wellbore formation in gas storage fields. In: CORROSION. Paper 00121. NACE International Houston, USA.
Hasegawa, R., Toyama, K., Miyanaga, K., Tanji, Y., 2014. Identification of crude-oil components and microorganisms that cause souring under anaerobic conditions. Appl. Microbiol. Biotechnol. 98, 1853–1861.
Heatherly, M.W., Howell, M.E., McElhiney, J.E., 1994. Sulfate removal technology for seawater waterflood injection. In: Paper OTC 7593. Offshore Technology Conference. Houston, USA.
Hu, P., Tom, L., Singh, A., Thomas, B.C., Baker, B.J., Piceno, Y.M., Andersen, G.L., Banfield, J.F., 2016. Genome-resolved metagenomic analysis reveals roles for candidate phyla and other microbial community members in biogeochemical transformations in oil reservoirs. mBio 7 e01669-15.
Hubbard, C.G., Cheng, Y., Engelbrekston, A., Druhan, J.L., Li, L., Ajo-Franklin, J.B., Coates, J.D., Conrad, M.E., 2014. Isotopic insights into microbial sulfur cycling in oil reservoirs. Front. Microbiol. 5. http://dx.doi.org/10.3389/fmicb.2014.00480.
Hubert, C., Nemati, M., Jenneman, G., Voordouw, G., 2003. Containment of Biogenic Sulfide Production in Continuous Up-Flow Packed-Bed Bioreactors with Nitrate or Nitrite. Biotechnol. Prog. 19, 338–345.
Hubert, C., Nemati, M., Jenneman, G., Voordouw, G., 2005. Corrosion risk associated with microbial souring control using nitrate or nitrite. Appl. Microbiol. Biotechnol. 68, 272–282.
Jensen, M.L., Lundgaard, T., Jensen, J., Skovhus, T.L., 2013. Improving risk based inspection with molecular microbiological methods. In: Paper 2247. CORROSION. NACE International Houston, USA.
Jiang, J., Chan, A., Ali, S., Saha, A., Haushalter, K.J., Lam, W.-L.M., Glasheen, M., Parker, J., Brenner, M., Mahon, S.B., Patel, H.H., Ambasudhan, R., Lipton, S.A., Pilz, R.B., Boss, G.R., 2016. Hydrogen Sulfide–Mechanisms of Toxicity and Development of an Antidote. Sci. Rep. 6, 20831.
Jones, C., Hernandez, K., Curtis, T., 2010. Extending performance boundaries with third generation THPS formulations. In: Paper 10257. CORROSION. NACE International Houston, USA.
Jones, C., Downward, B., Edmunds, S., Hernandez, K., Curtis Smith, T.F., 2011. A novel approach to using THPS for controlling reservoir souring. In: Paper 11219. CORROSION. NACE International Houston, USA.
Jordan, L.C., Walsh, J.M., 2004. Selection of an active souring management solution for a Gulf of Mexico waterflood. In: Paper 04759. CORROSION. NACE International Houston, USA.
Juhler, S., Skovhus, T.L., Vance, I., 2012. A Practical Evaluation of 21st Century Microbiological Techniques for the Oil and Gas Industry. Energy Institute (ISBN 978-0-85293-638-2).
Kahrilas, G., Blotevogel, J., Stewart, P., Borch, T., 2015. Biocides in hydraulic fracturing fluids: a critical review if their usage, mobility, degradation and toxicity. Environ. Sci. Technol. 49, 16–32.
Kengen, S.W., Rikken, G.B., Hagen, W.R., Van Ginkel, C.G., Stams, A.J., 1999. Purification and characterization of (per) chlorate reductase from the chlorate-respiring strain GR-1. J. Bacteriol. 181, 6706–6711.
Khelifi, N., Amin Ali, O., Roche, P., Grossi, V., Brochier-Armanet, C., Valette, O., Ollivier, B., Dolla, A., Hirschler-Réa, A., 2014. Anaerobic oxidation of long-chain n-alkanes by the hyperthermophilic sulfate-reducing archaeon, Archaeoglobus fulgidus. ISME J. 8, 3057–3060.
Koch, G., Varney, J., Thompson, N., Moghissi, O., Gould, M., Payer, J., 2016. International Measures of Prevention, Application and Economics of Corrosion Technologies Survey. NACE International, Houston, Texas.
Larsen, J., Sanders, P., Talbot, R., 2000. Experience with the use of THPS for the control of downhole hydrogen sulphide. In: CORROSION. Paper 00123. NACE International Houston, USA.
Larsen, J., Skovhus, T.L., Saunders, A.M., Højris, B., Agerbæk, M., 2008. Molecular Identification of MIC Bacteria from Scale and Produced Water: Similarities and Differences. In: CORROSION. Paper 8652. NACE International Houston, USA.
Larsen, J., Sørensen, K., Højris, B., Skovhus, T.L., 2009. Significance of troublesome sulfate-reducing prokaryotes (SRP) in oil field systems. In: CORROSION. Paper 9389. NACE International Houston, USA.
Liebensteiner, M.G., Pinkse, M.W., Schaap, P.J., Stams, A.J., Lomans, B.P., 2013. Archaeal (per) chlorate reduction at high temperature: an interplay of biotic and abiotic reactions. Science 340, 85–87.
Liebensteiner, M.G., Tsesmetzis, N., Stams, A.J., Lomans, B.P., 2014. Microbial redox processes in deep subsurface environments and the potential application of (per) chlorate in oil reservoirs. Front. Microbiol. 5, 428. http://dx.doi.org/10.3389/fmicb.2014.00428.
Liebensteiner, M.G., Pinkse, M.W., Nijsse, B., Verhaert, P.D., Tsesmetzis, N., Stams, A.J., Lomans, B.P., 2015. Perchlorate and chlorate reduction by the Crenarchaeon *Aeropyrum pernix* and two thermophilic Firmicutes. Environ. Microbiol. Rep. 7, 936–945.

Ligthelm, D.J., de Boer, R.B., Brint, J.F., 1991. Reservoir souring: an analytical model for H2S generation and transportation in an oil reservoir owing to bacterial activity. In: SPE, Offshore Europe Conference. Paper 23141. NACE International Houston, USA.

Littman, E.S., McLean, T.L., 1987. Chemical control of biogenic H_2S in producing formations. In: SPE Production Operations Symposium. Paper SPE-16218. Society of Petroleum Engineers, Houston, USA.

Maixner, F., Wagner, M., Lücker, S., Pelletier, E., Schmitz-Esser, S., Hace, K., Spieck, E., Konrat, R., Le Paslier, D., Daims, H., 2008. Environmental genomics reveals a functional chlorite dismutase in the nitrite-oxidizing bacterium '*Candidatus Nitrospira defluvii*'. Environ. Microbiol. 10, 3043–3056.

Marangon, J., de Sousa, P.M.P., Moura, I., Brondino, C.D., Moura, J.J., González, P.J., 2012. Substrate-dependent modulation of the enzymatic catalytic activity: reduction of nitrate, chlorate and perchlorate by respiratory nitrate reductase from *Marinobacter hydrocarbonoclasticus*. Biochim. Biophys. Acta (BBA)-Bioenerg. 1817, 1072–1082.

Martins, M.D.O., Marques, L.C.D.C., 2006. Assessment of oilfield souring mechanisms by mass spectrometry analysis of the sulfur isotopes ratio. In: Paper SPE-104016. International Oil Conference and Exhibition in Mexico. Society of Petroleum Engineers, Houston, USA, January.

McElhiney, J.E., Davis, R.A., 2002. Desulphated seawater and its impact on t-SRB activity: an alternative souring control methodology. In: CORROSION. Paper 02028. NACE International Houston, USA.

McGinley, H., Enzien, M.V., Jenneman, G.E., Harris, J.B., 2011. Studies on the Chemical Stability of Glutaraldehyde in Produced Water. In: Paper SPE -141449-MS. SPE International Symposium on Oilfield Chemistry. Society of Petroleum Engineers, The Woodlands, Texas, USA.

McIlwaine, D., 2006. Oilfield application for biocides. In: Paulus, W. (Ed.), Directory of Microbicides for the Protection of Materials: A Handbook. Springer, Berlin.

NACE MR0175/ISO 15156, 2015. Petroleum and Natural Gas Industries—Materials for Use in H_2S-containing Environments in Oil and Gas Production. NACE International, Houston, Texas, USA.

Nemati, M., Mazutinec, T.J., Jenneman, G.E., Voordouw, G., 2001. Control of biogenic H_2S production with nitrite and molybdate. J. Ind. Microbiol. Biotechnol. 26, 350–355.

Newport, P.J., Nedwell, D.B., 1988. The mechanisms of inhibition of Desulfovibrio and Desulfotomaculum species by selenate and molybdate. J. Appl. Bacteriol. 65, 419–423.

Piceno, Y.M., Reid, F.C., Tom, L.M., Conrad, M.E., Bill, M., Hubbard, C.G., Fouke, B.W., Graff, C.J., Han, J.B., Stringfellow, W.T., Hanlon, J.S., Hu, P., Hazen, T.C., Andersen, G.L., 2014. Temperature and injection water source influence microbial community structure in four Alaskan North Slope hydrocarbon reservoirs. Front. Microbiol. 5, 13.

Postgate, J.R., 1952. Competitive and non-competitive inhibitors of bacterial sulphate reduction. Microbiology 6, 128–142.

Rasmussen, K.E., Albrechtsen, J., 1974. Glutaraldehyde. The influence of pH temperature, and buffering on the polymerization rate. Histochemistry 38, 19–26.

Rees, C.E., Jenkins, W.J., Monster, J., 1978. The sulphur isotopic composition of ocean water sulphate. Geochim. Cosmochim. Acta 42, 377–381.

Reinsel, M., Sears, J., Stewart, P., McInerney, M., 1996. Control of microbial souring by nitrate, nitrite or glutaraldehyde injection in a sandstone column. J. Ind. Microbiol. 17, 128–136.

Rizk, T., Stott, J.F., Eden, R., McElhiney, J.E., Hardy, J.A., Davis, R.A., Di Iorio, C., 1998. The effect of desulphuated seawater injection on microbiological hydrogen sulphide generation and implication for corrosion control. In: CORROSION. Paper 287. NACE International Houston, USA.

Rizk, T., 2006. The Effect of Nitrate Anti-souring Treatment on Corrosion of Mild Steel. Energy Institute, London UK.

Robinson, K., Dunsmore, B., 2009. Method for reducing bacterial sulphide content in hydrocarbons using an antisense nucleic acid sequence to a nucleic acid sequence encoding sulphite reductase. UK Patent No. GB2433261. London: Patent Office.

Robinson, K., Ginty, W.R., Samuelsen, E.H., Lundgaard, T., Skovhus, T.L., 2010. Reservoir souring in a field with sulphate removal: A case study. In: SPE Annual Technical Conference and Exhibition. Paper SPE 132697. Society of Petroleum Engineers, Houston, USA.

Schaschl, E., 1980. Elemental sulfur as a corrodant in dearated neutral aqueous environments. Mater. Perform. 19, 9–11.

Sierra-García, I.N., Alvarez, J.C., De Vasconcellos, S.P., De Souza, A.P., Dos Santos Neto, E.V., De Oliveira, V.M., 2014. New hydrocarbon degradation pathways in the microbial metagenome from brazilian petroleum reservoirs. PLoS One 9. http://dx.doi.org/10.1371/journal.pone.0090087.

Skovhus, T.L., 2014. Biocide testing against microbes. In: Dobretsov, S., Thomason, J.C., Williams, D.N. (Eds.), Biofouling Methods. Wiley-Blackwell, New Jersey, pp. 76–86.

Skovhus, T.L., Caffrey, S., Hubert, C., 2014. Applications of Molecular Microbiological Methods. Caister Academic Press (ISBN 978-1-908230-31-7). www.horizonpress.com/ammm.

Skovhus, T.L., Højris, B., Saunders, A.M., Thomsen, T.R., Agerbæk, M., Larsen, J. "Practical Use of New Microbiology Tools in Oil Production", SPE 109104, SPE Offshore Europe Conference 2007, Aberdeen, U.K., 4–7 September 2007.

Sturman, P.J., Goeres, D.M., 1999. Control of hydrogen sulfide in oil and gas wells with nitrate injection. In: SPE Annual Technical Conference and Exhibition. Paper SPE-56772. Society for Petroleum Engineers, Houston, USA.

Summer, E.J., Liu, M., Summer, N.S., Gill, J.J., Janes, C., Young, R., 2011. Phage of sulfate reducing bacteria isolated from high saline environment. In: CORROSION. Paper 11222. NACE International Houston, USA.

Sunde, E., Thorstenson, T., 1993. Field-related mathematical model to predict and reduce reservoir souring. In: SPE International Symposium on Oilfield Chemistry. Paper SPE 25197. Society for Petroleum Engineers, Houston, USA.

Sunde, E., Thorstenston, T., Torsvik, T., 1990. Growth of bacteria on water injection additives. In: SPE Annual Technical Conference and Exhibition. Paper SPE-20690-MS. Society for Petroleum Engineers, Houston, USA.

Tanji, Y., Toyama, K., Miyanaga, K., 2014. Identification of crude oil component which facilitate biological souring. In: CORROSION. Paper 3853. NACE International Houston, USA.

Tsesmetzis, N., Alsop, E.B., Vigneron, A., Marcelis, F., Head, I.M., Lomans, B.P., 2016. Microbial community analysis of three hydrocarbon reservoir cores provides valuable insights for the assessment of reservoir souring potential. Int. Biodeterior. Biodegr. http://dx.doi.org/10.1016/j.ibiod.2016.09.002.

Vance, I., Thrasher, D.R., 2005. Reservoir souring: mechanisms and prevention. In: Olliver, B., Magot, M. (Eds.), Petroleum Microbiology. American Society of Microbiology, Washington, USA, pp. 123–142.

Vik, E.A., Janbu, A.O., Garshol, F.K., Henninge, L.B., Engebretsen, S., Kuijvenhoven, C., Oilphant, D., Hendriks, W.P., 2007. Nitrate based souring mitigation of produced water-side effects and challenges from the draugen produced water re-injection pilot. In: International Symposium on Oilfield Chemistry. Paper SPE-106178. Society of Petroleum Engineers, Houston, USA.

Walsh, J., McElhiney, J., Maxwell, S., Burger, E., Davis, R., 2008. Adoption of a process to prevent souring associated with seawater waterflooding in the Ursa-Princess fields, deepwater Gulf of Mexico. In: SPE International Oilfield Corrosion Conference. Paper SPE 113317. Society of Petroleum Engineers, Houston, USA.

Wen, J., Zhao, K., Gu, T., Raad, I., 2010. Chelators enhanced biocide inhibition of planktonic sulfate-reducing bacterial growth. World J. Microbiol. Biotechnol. 26, 1053–1057.

Williams, T., Schultz, C., 2015. Effect of environmental parameters on the stability and performance of oil and gas biocides. In: SPE International Symposium on Oilfield Chemistry. Paper SPE-173782-MS. Society of Petroleum Engineers, Houston, USA.

Williamson, N., 2010. Problems caused by microbes and treatment strategies health and safety issues from the production of hydrogen sulphide. In: Whitby, C., Skovhus, T.L. (Eds.), Applied Microbiology and Molecular Biology in Oilfield Systems. Springer, Netherlands, pp. 151–157.

Wright, M., Jenneman, G.E., Gevertz, D., 1997. Effect of nitrate on sulfide-bio-scavenging by indigenous bacteria in produced brines from West Texas oil fields. In: Proc. 4th Int. Petroleum Environ. Conf. September. pp. 731–745.

Xu, D., Wen, J., Gu, T., Raad, I., 2012. Biocide cocktail consisting of glutaraldehyde, ethylene diamine disuccinate (EDDS), and methanol for the mitigation of souring and biocorrosion. Corrosion 68, 994–1002.

Xue, Y., Voordouw, G., 2015. Control of microbial sulphide production with biocides and nitrate in oil simulating bioreactors. Front. Microbiol. 6, 1387. http://dx.doi.org/10.3389/fmicb.2015.01387.

Yin, B., Williams, T., Koehler, T., Morris, B., Manna, K., 2016. Targeted microbial control for hydrocarbon reservoir: Identify new biocide offerings for souring control using thermophile testing capabilities. Int. Biodeter. Biodeg (in press).

Zhao, K., Wen, J., Gu, T., Kopliku, A., Cruz, I., 2009. Mechanistic modelling of anaerobic THPS biocide degradation under alkaline conditions. Mater. Perform. 48, 62–66.

de Geus, D.C., Thomassen, E.A., Hagedoorn, P.L., Pannu, N.S., van Duijn, E., Abrahams, J.P., 2009. Crystal structure of chlorite dismutase: a detoxifying enzyme producing molecular oxygen. J. Mol. Biol. 387, 192–206.

de Jesus, E.B., de Andrade Lima, L.R.P., Bernardez, L.A., Almeida, P.F., 2015. Inhibition of microbial sulfate reduction by molybdate. Braz. J. Petrol. Gas 9, 95–106.

Glossary

Antisense RNA: An RNA molecule antisense to the gene of interest, commonly used for gene silencing.

BTEX: Benzene, toluene, ethylbenzene and xylene; water soluble aromatic hydrocarbons.

CRISPR-Cas: An RNA guided nuclease which allows customised gene editing.

EOR: Enhanced oil recovery. A combination of methods (i.e. microbial, polymers or surfactants) used in combination or after secondary oil recovery to improve oil recovery.

Injectivity: The ability to inject water into a reservoir for secondary oil recovery. Injectivity is dependent on the permeability of the rock and can be affected by high levels of solids in injection waters, microbial biofilm growth in the rock matrix or swelling of clays in the reservoir, amongst other things.

Lift gas: A method of lifting oil out of wells by injecting gas at the bottom of the well, which lifts produced fluids to the top of the well.

Matrix: The matrix of rock in the reservoir.

Produced water: Water produced alongside oil and gas production.

PWRI: Produced water re-injection. A method of re-injecting produced water into the reservoir to sweep oil from the reservoir to the producing wells and maintain pressure in the producing wells.

Sand Pack Column: A laboratory column packed with sand through which fluid is passed in a single direction. Used to simulate a waterflood on a laboratory scale.

Scale Control: Control of inorganic scale, often formed from the change of fluid temperature or by mixing two incompatible waters. Commonly controlled using scale inhibitors.

Secondary Oil Recovery: A method of improving oil recovery by water injection into the reservoir. Water injection improves recovery by sweeping the water from the injector to the producer wells and by maintaining reservoir pressure.

Water cut: The percentage of produced water produced from oil wells along with oil and gas.

Water Flooded Oilfield: An oil field that has undergone secondary recovery.