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BIOGENIC SULFIDE PRODUCTION IN OFFSHORE PETROLEUM RESERVOIRS UNDERGOING WATERFLOODING

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Abstract

Biogenic sulfide production in oilfield systems occurs due to the metabolic activities of sulfate-reducing prokaryotes. These activities of prokaryotes (bacteria and archaea) in production facilities in oilfields leads to unexpected increase in hydrogen sulfide (H_2S) concentrations over time in produced fluids from petroleum reservoirs. This widespread phenomenon has proven to have dire consequences, affecting production facilities integrity, personnel safety, environment, the quality and market value of fluids produced from oil reservoirs. Several approaches have been employed over the years to control souring, but the effectiveness of each method differs. This paper reviews the occurrence, consequences, and management of biogenic souring in oilfield reservoirs undergoing waterflooding.

Keywords: *Souring; Sulfate-reducing Prokaryotes; Waterflooding; Biogenic sulfide; Oilfield; Reservoir.*

1. Introduction

A considerable amount of hydrocarbons (HCs) are typically not recovered by primary drive mechanisms and secondary recovery methods such as waterflooding is required in order to optimize recovery, thereby improving the sweep efficiency of the reservoir as the injected water makes contact with unswept areas of the reservoir. In most offshore facilities, seawater is usually readily available for injection and in some cases, produced water is re-injected in order to achieve the same purpose. The injection of seawater, a relatively low salinity brine, and high sulfate have been observed to result in sulfide production over a period during the producing reservoir's life cycle (Figure 1). Reservoir souring, which has been described as the most deleterious microbial process during oil production [1], is a phenomenon of increase in hydrogen sulfide (H_2S) concentrations over time in produced fluids from petroleum reservoirs. Once the injection water breaks through, the fraction of produced water (the water cut) increases with time. The previously 'sweet' oilfield begins to produce significant concentrations of H_2S (one of the principal corrosive fluids produced during petroleum recovery) which causes problems with dire consequences for oilfield installations, facilities, HSE, and operational costs, leading to catastrophic damage in susceptible materials. In highly challenging environments, such as deepwater basins, a robust H_2S assessment is necessary during field development design and planning phase, and take relevant decisions on H_2S concentrations in produced fluids. This is important because overestimation of H_2S can result in million-dollar CAPEX while underestimation of the same may result in the emergence of operational expenditures, some of which were stated earlier. This phenomenon is widespread across the petroleum industry, occurring both in onshore and offshore oil production operations, in the reservoir and in surface (topside) processing facilities, and under low and high temperature conditions [2]. This mini review provides a synopsis on the state of current research on reservoir souring by examining evidence presented in previous investigations in oilfields undergoing waterflooding and predict future direction based on the present technologies available in the industry.

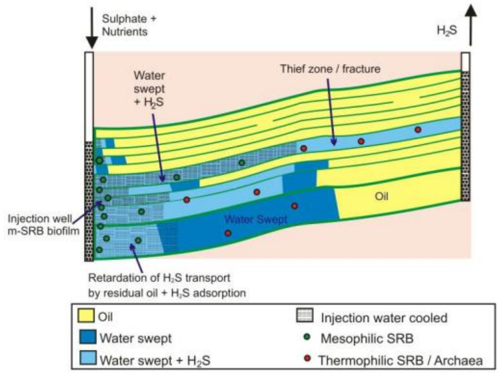

Figure 1. Reservoir souring schematic (*after* [75])

2. Biogenic reservoir souring

In a water-flooded oilfield, sulfate-reducing bacteria (SRB) function as components of a complex microbial community. Biogenic souring in conventional oilfields is due to the reduction of sulfate, thiosulfate or sulphur to sulfide by microorganisms [2-3]. It originates solely from the activities of sulfate-reducing prokaryotes (SRPs) in the water phase and subsequently partitions between water, liquid hydrocarbon, and gas. Souring in oilfield systems is now generally attributed to the activities of this specialized group of microorganisms, *i.e.* SRPs, which is usually present in the injection water but it could as well be indigenous in some reservoirs. They may also be introduced into the reservoir during drilling since it is difficult to maintain a sterile injection system as well as bacteria-free operations during drilling and completion [4]. SRPs are some of the Earth's oldest microorganisms whose initial development and activities date back to the Proterozoic Era [5], and they have probably caused more serious problems in oilfield injection systems than any other bacteria [6]. They are heterotrophic organisms and anaerobes that use sulfates as well as other oxygenated sulphur compounds (sulfites, thiosulfites, trithionate, tetrathionate, and elemental sulphur) as final electron acceptors in respiration processes [7-8]. Reservoir souring which has been reported in about 70% of fields undergoing seawater flooding [9], is due to the combination of abundant electron donors – *selected oil components*, and electron acceptors – *sulfate in the seawater* [10-11].

The activities of this bacterial group have been a major concern in oilfield water systems because they are recognized as responsible for the production of H_2S, within reservoirs or topside facilities [12]. Studies by [13-14] revealed that reservoir souring is a normal consequence of injection of sulfate-rich seawater, which cool certain regions of the reservoir and dilute bacterial inhibitory compounds in the formation. Although some of these microorganisms are introduced with injection water – sea and/or produced water, others are indigenous [15-16]. The appearance of significant concentrations of H_2S in produced fluids is a confirmation of several months of SRP activities in the reservoir.

3. Reservoir conditions for souring

The reservoir unit is an essential part of the petroleum system, where the prevailing conditions differ from the typical settings of most living organisms on Earth. It is characterized with low redox potential, generally but not necessarily very high temperature and pressure, presence of sulfate, carbonate and admissible range of electron donors for microbial activities, but lacking electron acceptors, such as oxygen, which is a critical requirement for (aerobic) microbial metabolism. The reservoir condition of the oilfield ecosystem is the main factor that determines the profile of the microbial communities [17], and to a great extent, determines the chances of survival of microorganisms such as SRPs. Although some of these bacteria are indigenous, a reasonable proportion may be introduced into the reservoir from the external environment during oil recovery operations. Low populations of SRP cells are ubiquitous in seawater and many other natural waters that are used for secondary recovery [18]. The growth and propagation of these sulfate-reducers depend on the temperature, pressure, salinity, pH of the aqueous phase, nutrient levels remaining favourable to the bacteria and source of water used in flooding operations, among other factors.

Temperature is the main limiting factor influencing microbial growth in oil reservoirs [20,74]; it has a significant impact on the metabolic rates of microorganisms and strongly influences microbial ecology and biogeochemical cycling in the environment. Souring readily occurs in both low temperature (<45^{0}C) and high temperature (45-80^{0}C) reservoirs. Although it is possible for different kinds of SRP to grow in different environments, most of them are active under restricted conditions: temperatures less than 60-80^{0}C, low salinities, and strictly anoxic conditions. The following SRP types are known based on the order of their growth domain, beginning with the least: **Mesophiles** (mesophilic sulfate-reducing bacteria, ***m-SRB***), which are active at low temperatures (below 45^{0}C), and **Thermophiles** (thermophilic sulfate-reducing bacteria, ***t-SRB*** and **Hyperthermophilic** sulfate-reducing Archaea, ***h-SRA***), which thrive optimally at temperatures >55^{0}C and > 80^{0}C respectively [10,21]. In many offshore oil production operations, souring readily occurs in the vicinity of the water injection well, where cold seawater displaces hot reservoir fluids, thereby resulting in lower temperatures (~50-70^{0}C) that readily support the growth and activity of thermophilic SRP [22-23]. Previous data indicate the presence of microorganisms at maximum temperatures of 80^{0}C to 90^{0}C, above which autochthonous bacteria do not occur [24]. High temperatures (>100^{0}C) can naturally constrain the activity of SRP [2], limit biogenic sulfide production, and as such, the presence of indigenous bacteria in oilfields is limited to threshold temperatures below 100^{0}C. Above this temperature, reservoir fluids are considered too hot to support microbial life. Hyperthermophilic bacteria could not be isolated from water samples whose reservoir temperatures were higher than 82^{0}C [20,25-26], although claims by [26-27] suggest that hyperthermophilic microorganisms were isolated as exogenous bacteria resulting from seawater injections at about 103^{0}C from some reservoirs. Currently, 113^{0}C is the highest temperature a microbe, albeit not a sulfate reducing bacterium, is known to be alive, metabolizing, and reproducing; and this temperature, therefore, represents the upper temperature limit of life [19,28-29].

Although salinity and pH of formation waters can also limit bacterial activities, [30] identified temperature as the controlling factor for sulfide production rather than salinity. They reported that souring rates did not increase when production waters from a highly saline field (8% salinity) was diluted. Salinity ranges from almost fresh water to salt-saturated, and souring has been reported in reservoirs up to about 6% salinity [2]. In addition to temperature, other conditions favourable for SRP activities include total dissolved solids, (TDS) < 100,000 mg/L; redox potential, Eh (under-150mV); pH (between 6 and 9); and pressure (under 45MPa). Depending on the species, SRP activity reduces and they become inactive at very high TDS concentrations. Most SRPs have an optimum pH growth range of 7. Pressure regime within oil reservoirs does not rule out the *in-situ* development of bacteria but may affect the microbial physiology. Although the choice of water source used in a typical secondary recovery operation is largely dependent on availability and cost, it can impact greatly on the extent of souring. Seawater, which is easier and cheaper in offshore flooding operations, typically contains 25-30mM sulfate, providing sufficient electron acceptor for SRPs to thrive.

Produced water re-injection (PWRI) which was rarely used in offshore secondary recovery operations due to the abundance of seawater, is now being considered in order to reduce pollution resulting from produced water discharge [31-32]. Although surface and groundwater sources are usually considered in onshore operations, the volume of such may be limited due to water demand, which may encourage PWRI. Produced water may contain sulfate as an electron acceptor, and/or carbon and energy sources favourable for sulfate-reducing activity in the reservoir, thereby resulting in tenfold increase in sulfide when compared with normal seawater injection [32]. Studies have shown that oil organics present in oilfield fluids drive sulfate reduction in water flooded reservoirs and surface facilities. They are usually considered to comprise volatile fatty acids (VFAs), such as propionate, butyrate and acetate, and hydrocarbons like alkanes and toluene [33-35]. These metabolizable carbon sources are potential electron donors, which are utilized by SRP within the reservoirs to generate sulfide [2,36-37].

4. Consequences of reservoir souring

H_2S is a highly toxic and flammable gas and is one of the most corrosive fluids produced during production operations. The production of H_2S raises major health and safety concerns in field operations because of its propensity to poison different systems in the human body when exposed to about 800ppm of the gas for 5 minutes and may lead to loss of lives arising from its inhalation. Pitting corrosion directly beneath a growing bacterial colony can occur in metallic materials and pipelines used in the production, processing and export facilities. Biogenic H_2S generation can increase the corrosivity of oilfield water, especially in originally sweet systems, resulting in substantial increase in corrosion rates and pitting attack [6]. This is because bacteria find it much easier to colonize on the pipe wall than in moving stream of fluid. In the presence of moisture, H_2S can act as a catalyst in the absorption of atomic hydrogen in steel, thereby promoting sulfide stress cracking (SSC) and blistering in high strength steels. SSC is a form of hydrogen embrittlement, which affects corrosion resistant alloys (CRAs), and carbon steels causing catastrophic damage. Hydrogen-induced cracking (HIC) is another damaging mechanism, which affects carbon and low alloy steels but not CRAs. H_2S corrosion may occur during drilling and in production wells and surface facilities. New, unexpected equipment may be introduced, while in some cases, substitution of existing equipment, an option which may not always be feasible from technical and economic standpoints [38]. At the onset of reservoir souring, deployment of chemical scavengers or corrosion inhibitors becomes necessary in order to protect the production facilities. Hence, reservoir souring increases the operational costs of oil production, when it is not predicted in the field development plan. The installation of chemical sweetening systems to ensure the quality of crude produced meets export or refinery specifications is another complexity caused by reservoir souring. Other problems associated with sulfide production include clogging of filters and other equipment by the black insoluble iron sulfide powder formed and production of poor quality oil and gas, which is not in conformance with export criteria thus reducing the market value of products.

5. Reservoir souring mechanisms

There are several ways in which H_2S can be generated on both geologic and/or human timescales, the relevance of which will depend on reservoir temperature and production practice [39-40]. The two main mechanisms proposed for reservoir souring assessment are **biogenic** (microbial) and **abiotic** (geochemical) souring mechanisms. The abiotic souring mechanisms include (i) *Thermochemical Sulfate Reduction (TSR)*, where H_2S and sulfate react to produce elemental sulphur and polysulfides, which subsequently react to oxidize and dehydrogenate organic compounds, redistributing the sulphur between H_2S and hydrocarbons. This ultimately results in H_2S increase in the reservoir [4,41-44]. (ii) *Thermal Decomposition of Organic Sulfur compounds* (denaturation), primarily above 175^{0}C [4,44-46]. (iii) *Hydrolysis of Metal Sulfides* – [Dissolution or Reductive Dissolution of mineral phases such as iron monosulfide (FeS) or Pyrite (FeS_2)] [4,10,45-46]. (iv) *Desorption of H_2S from formation sediments*, where soluble H_2S fractions in petroleum, according to geochemical investigations, are sorbed to formation sediments similar to gaseous hydrocarbons [4,47]. (v) *Conversion of injected sulfite*, which is used as an oxygen scavenger [10].

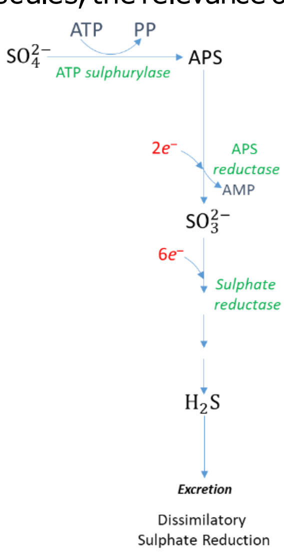

Figure 2. Biochemical pathway showing the steps involved in the dissimilatory sulphate reduction (*modified after* [76])

According to [10], the direct thermochemical reduction of sulfate from seawater is the only one of these abiotic mechanisms that could explain why flooding with seawater particularly seems to cause souring, while the other mechanisms are responsible for the low indigenous H_2S levels in reservoir fluids. The metabolic activities of sulfate-reducing prokaryotes (SRPs) that are resident in oil reservoirs result in biogenic souring, a mechanism which involves biological reduction of sulfate.

6. Souring prediction and conceptual models

There is an obvious technical, safety and commercial requirement in being able to predict the likelihood of souring in a reservoir prior its development or the probability of its occurrence and timing of it, consequent upon changes in reservoir management of the producing field [48]. Prediction of the onset, timing and severity of souring is considered very important in making decisions about material selections and treatment strategies. A souring management plan should be part of the field development and should be implemented throughout the reservoir lifecycle. Information about the souring potential and forecast profile of H_2S production versus time during the field production lifetime are vital in the development of souring management plan. These predictions are performed using the dynamic reservoir models built on simulators, which were adapted to account for souring. The following parameters are necessary in souring predictions because they affect H_2S production: water flow path, reservoir geology, mineralogy and geochemistry, *etc.*, and should be accounted for in reservoir souring simulation [49].

There are several mathematical models, built upon existing concepts in literature, which allow prediction of biogenic souring in waterflooded reservoirs. The two main conceptual models recognized in the industry are the **mixing zone** and **biofilm** souring simulation models.

The mixing zone model describes the generation of H_2S by bacteria in the moving area where the reservoir water and injected seawater are mixed [50]. According to this model (Figure 3), souring occurs at the injection flood front, where it mixes with formation water and both carbon sources and sulfate are present [10].

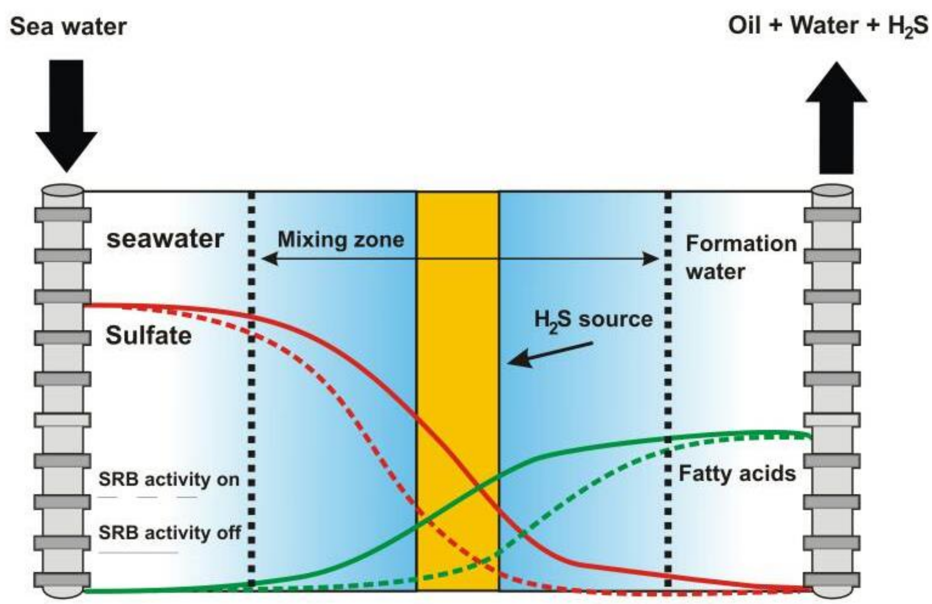

Figure 3. Schematic of the mixing model. Solid lines are the concentrations with no bacterial reaction and dashed lines are concentrations with bacterial reactions (*after* [77])

This mixing zone, which is driven by diffusion and dispersion processes, is considered to move through the reservoir in the direction of the waterflood. This implies that in a mature waterflood the mixing zone, and hence the zone of SRB activity, will be deep in the reservoir, remote from the injection well [48]. The SRBs use the available VFA contained in the formation water together with the sulfate from the seawater to produce H_2S. The biotic generation of

H_2S in this model is independent of the physical and chemical constraints of the reservoir [51] and the model does not account for the effects of nutrient concentrations and temperature upon SRB activity. The presence of siderite, haematite or other iron-rich minerals in the reservoir coupled with partitioning between the residual oil and water phases, delays produced H_2S breakthrough at surface facilities despite SRP growth.

The second conceptual model is the biofilm model described by [11]. This model is perceived as a more detailed modelling approach to H_2S generation by SRPs and it considers that H_2S generation occurs in a region close to the injection well (Figure 4), as the lower temperature and water salinity provides better conditions to the SRB activity. In this model, H_2S is generated only in the near injector area, and bacteria growth needs to be supported by elements contained in the seawater (VFA and other food, sulfate) to generate H_2S. The biofilm model results in a slow increase of H_2S concentration to values significantly smaller than that obtained with the mixing zone model. Scavenging of H_2S in the reservoir is treated as a two-step process: the first step involves dissolved components and the second phase involves solid-phase components [11,48]. This model is sensitive to the nutrient phase of the injected water, since this is assumed to provide the limiting nutrient for SRB growth [48].

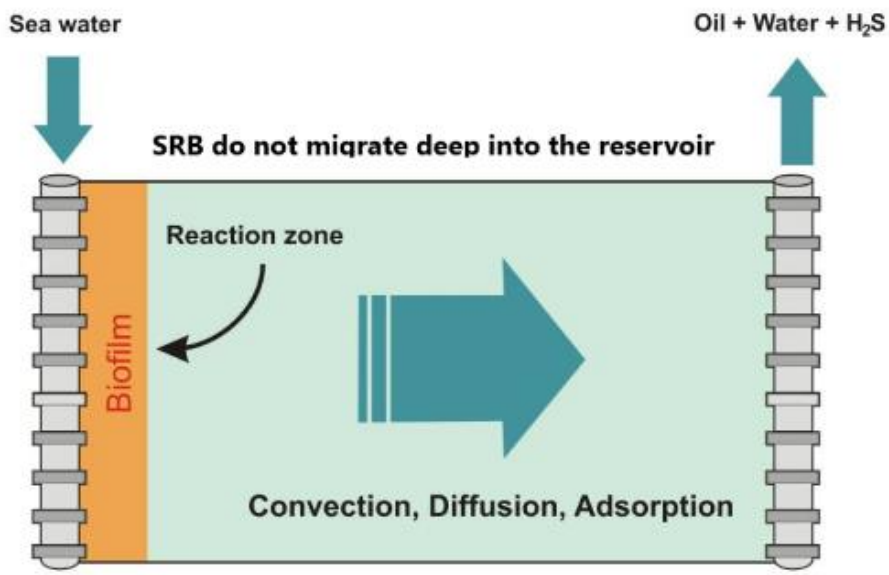

Figure 4. Schematic of the biofilm model. H_2S is generated in an area around the wellbore (*after* [77])

Remediation process design benefits from modelling tools, which have proven to be effective and accurate in predicting the physicochemical changes that develop with the water front advances. A reservoir souring simulator is expected to be able to model fluid flow within the reservoir environment, which usually has a complex geometry.

There is a great level of physical difficulty and data uncertainties involved in modelling reservoir souring. Apart from the detailed geological description and knowledge of reservoir flow paths, which are related to quantification of bacterial activity under reservoir conditions, identification of limiting factors to SRB metabolism (availability of carbon sources, sulfate content, trace nutrients like nitrogen, phosphorous), H_2S mineral scavenging capacity of the reservoir rock and outstanding souring conceptual models.

7. Strategies for souring prevention and mitigation

This paragraph pertains to the methods applied with the aim to control the biogenic reservoir souring. These can be categorized into three groups: those that attempt to prevent H_2S from being formed, those that attempt to deal with the H_2S after it has been generated and produced from the reservoir, and those that reduce the mass of H_2S that is generated [48]. Souring prevention strategies typically intervene on the injection side of the water cycle (Figure 5):

injection water quality control (limiting nutrient and bacteria introduction in the reservoir), biocide injection [52-53], and nitrate injection [54]. Otherwise, usually referred to the production side of the water cycle (Figure 5), souring mitigation strategies comprise practices like application of effective hydrogen sulfide scavengers and/or nitrite squeezes in production wells [55]. These strategies are not mutually exclusive, therefore two or more are simultaneously applied in the same oilfield.

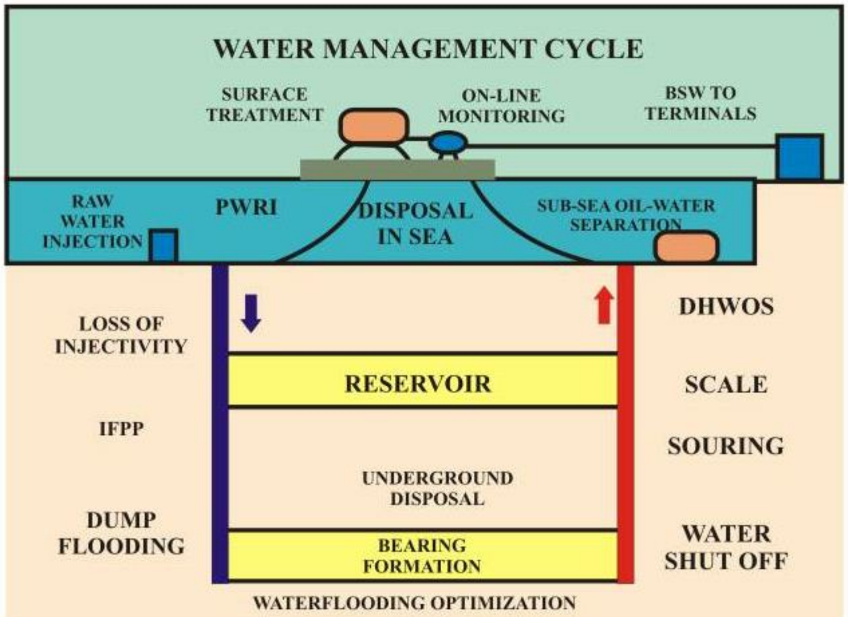

Figure 5. Water management cycle (*after* [78])

8. Biocide injection

Biocides are chemical compounds that kill bacteria or inhibit their growth. Formaldehyde, bronopol, chlorine, glutaraldehyde, benzalkonium chloride, cocodiamine and tetrakis hydromethyl phosphonium sulfate (THPS) are examples of commonly used biocides in injection waters and production facilities to reduce or eliminate H_2S-producing bacteria. They are widely used in treatment of seawater intended for injection to control bacteria growth in surface facilities, and in the prevention and mitigation of microbially influenced corrosion (MIC). Although the ability of biocides to produce intended results appear very controversial with limited success recorded in field application [56-58], however the injection of THPS has been reportedly proven successful in souring prevention in a North Sea field due to the high reservoir temperature [59]. THPS is one of the most promising biocides in use in oilfields today [60], due to its broad spectrum of activity, its capacity to dissolve FeS and can be effective in eradicating biofilms when used with surfactant [61]. Biocide testing for microbial population control and MIC mitigation is well understood [62] while information on conducting biocide testing for souring prevention or remediation is limited [63]. Details of laboratory trials and field application of biocide has been discussed in details elsewhere [2, 63]. Strictly speaking, the efficacy of biocides depends on reservoir temperature, permeability and water chemistry [64] and a prior knowledge of the target organisms (type of organism, microbial population, and mode of existence–planktonic, sessile or in biofilms) is crucial for selection of an effective biocide and dosage of application. Therefore, to be effective and maintain control, batch doses must be repeated at a rate or frequency related to regrowth or recolonization of SRP [48].

9. Nitrate injection

For more than 20 years, nitrate treatment technology has proved effective in souring prevention. In fields with resident temperatures above 60^0C [65], nitrate injection serves as a selective inhibitor of SRP activities and has been widely considered a mature technology which induces growth of heterotrophic nitrate-reducing bacteria (hNRB) and sulfide-oxidizing NRB (soNRB). The hNRB compete for the same oil organics as the SRB, while the soNRB oxidize sulfide directly. Most soNRB are chemolithotrophs using CO_2 as the sole source of carbon. The second way by which nitrate is believed to control reservoir souring is the stimulation of nitrate-reducing bacteria (NRB), which outcompete SRP for electron donors. Finally, the nitrite produced by NRB also strongly inhibit SRP. A great success was recorded within the first one year of application of nitrate in Bonga field, Nigeria [9]. The Enermark field (Alberta, Canada), which has a low resident temperature (30^0C) and is injected with water with a low sulfate concentration, decreased produced sulfide by 70% in the first 5–7 weeks, but this was followed by recovery to pre-nitrate injection levels [66]. Establishment of discrete zones of hNRB activity in the near-injection wellbore region (NIWR) and of SRB activity deeper in the reservoir (Figure 1) was hypothesized to cause the recovery. Injected nitrate is unable to inhibit sulfide production by SRB under these conditions. This problem may not occur in high temperature reservoirs, because deeper regions are too hot for significant microbial activity. Hence, only the NIWR needs to be nitrate-treated. As a result, nitrate and nitrite break-through in producing wells is commonly observed in high but not in low temperature reservoirs. There are contradictory reports of localized corrosion and increased corrosion rates as an effect of nitrate treatment, but it is advisable to address every field experience as specifics, and not generalize. This has been discussed in details elsewhere [2,63]. However, we can overlook the negative effects by concentrating on the successes recorded, while dedicating more resources to laboratory and field studies, in order to fully understand the likelihood and severity of post-nitrate injection corrosion reports.

10. Sulfate removal

Removal of sulfate ions from seawater by membrane filtration, such as reverse osmosis and/or nano-filtration are physical approaches widely employed in souring control and prevention of scale formation ahead of waterflooding operations in reservoirs containing barium and strontium in the formation water [59]. Sulfate removal by nano-filtration can be regarded as a souring prevention method [67], but in practice, reasonably high costs are involved. Scale control is the main reason whenever this technique is adopted, souring control being considered only as an indirect benefit of sulfate removal in cases where water sulfate content is the limiting factor to SRB metabolism. Reverse osmosis in the opinion of [21], is not far from achieving sulfate concentrations below 20mg/L at high sustainable flow rates. Nanofiltration is used in injection water facilities to reduce salinity and sulfate concentration, and has been reported to significantly reduce the concentration of sulfate below 40mg/L [60]. The effects of sulfate removal in both laboratory and field trials has been discussed elsewhere [63]. Others [59], believe this is more feasible for greenfields than for brownfields, which have been under waterflooding continuously, however in the opinion of [68], the effect of mixing waters on the final sulfate concentration in the injection water should also be carefully assessed. The effectiveness of these techniques should be tied to its continuous operation and adequate maintenance. Although the chance of success of these techniques is high, their major setback is the high capital expenditure (CapEx) involved. However, with further improvements in technology, it may become more realistic in field-scale application.

11. Sulfide scavengers

To control H_2S after it has been generated in the reservoir requires the use of chemical additives that can react with one or more sulfide species. As noted by [69], the application of chemical techniques to oilfield waterflooding operations involve the use of neutralizers, oxidizers, and scavengers. They include sodium hydroxide, ammonia, amines, triazines, aldehydes and metal oxides.

12. Molecular methods

Our understanding of the phylogenetic diversity, metabolic capabilities, ecological roles, and community dynamics of oil reservoir microbial communities is far from complete despite several years of study, partly due to the heterogeneous nature of reservoirs and the monitoring techniques adopted [60]. The use of molecular methods has allowed a broader characterization of microbial assemblages in the oilfield ecosystems [70]. Culture-dependent approach in microbial community analyses gives molecular descriptions of microbial communities present in oilfield reservoirs. This technology is fast, accurate and gives true analyses of complex microbial community structure. Its results (or outcomes) are not affected by whether the microorganisms are lively in the laboratory or not and not limited to those that can be isolated or cultured [71]. Current molecular techniques include 16S rRNA sequencing and analysis, Denaturant gradient gel electrophoresis (DGGE), Terminal restriction fragment length polymorphism (T-RFLP), Fluorescent *in situ* hybridization (FISH), and Quantitative polymerase chain reaction (qPCR), among several others. Details of the principles and uses has been discussed in details elsewhere [71].

It is important to note that each of these methods used to study the composition of microbial community has its limitations. We present a summary of the uses and limitation of each of these in Table 1 [72]. Due to the limitations of each of the molecular techniques, a more comprehensive assessment of microbial diversity in oilfield reservoir environments is required. A combination of culture-and molecular-based techniques is suggested by [70]. The use of both molecular and cultivation techniques, would provide more insights into the microorganisms that might be involved in the biogeochemical transformations that take place in these environments.

Table 1. A summary of techniques currently used to study complex microbial ecosystems [72]

Methods	Uses	Limitations
Cultivation	Isolation; "the ideal"	Not representative, slow and laborious
16S rRNA Sequencing	Phylogenetic Identification	Laborious and subject to PCR biases
DGGE/TGGE/TTGE	Monitoring of community/population shifts, rapid comparative analysis	Subject to PCR biases, semi-quantitative, identification requires clone library
T-RFLP	Monitoring of community shifts, rapid comparative analysis, very sensitive, potential for high throughput	Subject to PCR biases, semi-quantitative, identification requires clone library
SSCP	Monitoring of community/population shifts, rapid comparative analysis	Subject to PCR biases, semi-quantitative, identification requires clone library
FISH	Detection, enumeration, comparative analysis possible with automation	Requires sequence information, laborious at species level
Dot-blot hybridization	Detection, estimates relative abundance	Requires sequence information, laborious at species level
Quantitative PCR	Detection, estimates relative abundance	Laborious
Diversity microassays	Detection, estimates relative abundance	In early stages of development, expensive

Non-16S rRNA profiling	Monitoring of community shifts, rapid comparative analysis	Identification requires additional 16S rRNA–based approaches

13. Rock mineralogy and scavenging capacity

Mineral scavenging capacity of a rock formation is its ability to retain little or most of the H_2S generated in a sour reservoir. Once generated in the subsurface, H_2S can be scavenged, and whatever remains will partition on the topsides between the fluid phases as dictated by pressure, temperature, pH, salinity, chemistry and GoR of the system [21]. The mineral scavenging capacity of a reservoir rock can be measured under laboratory conditions or inferred from history matching. In irreversible scavenging, reservoir rock minerals react with H_2S generated and the waterflooded zone reacts with the produced H_2S until it reaches the saturation point. The presence of iron-rich minerals such as siderite ($FeCO_3$), haematite (Fe_2O_3), magnetite (Fe_3O_4) and chlorites (such as, chamosite – $(Fe_5Al)(AlSi_3)O_{10}(OH)_8$), is of utmost importance in evaluating the H_2S scavenging capacity of reservoir rocks [10-11,21,63]. These minerals react to form a sulfide phase product of stoichiometry equivalent to pyrite, (FeS_2) or mackinawite (FeS), with the products contributing towards rock matrix scavenging [63]. H_2S generated by SRPs react with these iron-rich minerals from the fluid phase as follows:

$FeCO_3 + H_2S \rightarrow H_2O + CO_2 + FeS$ .... (i)

$Fe_2O_3 + 3H_2S \rightarrow 3H_2O + FeS_2 + FeS$ .... (ii)

$Fe_3O_4 + 4H_2S \rightarrow 4H_2O + FeS_2 + 2FeS$ .... (iii)

The solubility of these minerals in the aqueous (water) phase determines their involvement in the scavenging reactions to precipitate iron sulfide either as a range of monosulfides (FeS) or disulfide (FeS_2) pyrite [48]. The presence of framboidal pyrite in core samples from behind the waterfront can be interpreted as evidence of scavenging of H_2S generated during the waterflood [10]. When present in abundance, clay minerals such as smectite, dolomite and illite also contribute to scavenging, although, lower than the iron minerals [63]. *Sensu stricto*, the H_2S produced by SRP in the water phase is partitioned to other phases, and is mobilized in all phases present towards the production wells. The residual oil and free gas in the reservoir retains part of the H_2S, which can be consumed by reacting with iron minerals, such as siderite within the reservoir. Although the relative abundance of these minerals in reservoir rocks may be determined by petrographic analysis of core samples, the rate of scavenging is rather difficult to predict [48]. Reservoir rock mineralogy gives indications of the significance of its scavenging capacity, which is expressed by the reaction of H_2S with iron minerals and the adsorption of H_2S to mineral surface. A comparison of the 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 to help establish which mineral constituents are most active during testing [63]. Laboratory studies, involving static bottle testing and dynamic corefiooding experiments with core plugs from the reservoir units of interest, give significant insights and effectively quantify the scavenging capacity of reservoir rocks. Results obtained from experiments conducted to measure H_2S adsorption on crushed reservoir rocks [11] and uncrushed core [73] give between 5 and 19,600μg of H_2S per g of rock under laboratory conditions. Scavenging capacities for a sandstone formation can be relatively high, depending on its mineralogic composition whereas carbonate formations have generally extremely low or zero scavenging capacities.

Generally, results obtained from dynamic measurements are more acceptable than the bulk crushing or static method. That's because dynamic methods address, to a large extent, 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 [73]. Inasmuch as it is important to have significant quantities of iron minerals in the bulk rock composition, the surface area available for interaction with H_2S in the water traveling through the pores determines the scavenging capacity, with reasonable contributions from the water-rock interactions, ion exchange, oxidation and reduction, and other physical adsorption processes [48].

14. Concluding remarks

As production of crude oil continues, especially in frontier basins, we expect industry players to invest in the most appropriate technology for managing souring.

Sulfate removal from injection water, biocide application and nitrate injection are the most viable options for controlling biogenic souring in most waterflood operations. These approaches have proven to be successful in most field applications, but expensive. As cheaper options are being sought, there is need for more focused investment in research and development (R&D) in order to gain better insight into the complex interaction among the microbial communities and their activities within the reservoir, improve understanding of nitrate injection and biocide dosing strategies and invent cost effective sulfate removal technologies.

The use of molecular biology technology would reveal the diversity and species composition of the oilfield microbial community thereby ensuring better understanding and control of biogenic souring. We recommend a combination of molecular and culture-based techniques for a comprehensive assessment of microbial diversity in oilfield reservoir environments. In addition, results from such investigations should be integrated with the formation water chemistry, isotope analysis of sulphur in the sulfate from formation water and knowledge of the natural H_2S mineral scavenging from petrographic studies.

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