Reservoir souring: sulfur chemistry in offshore oil and gas reservoir fluids

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Abstract

The injection of sulfate-containing seawater into an oil reservoir, for maintaining the reservoir pressure, can promote the growth of sulfate reducing bacteria and archaea near the injection wells, leading to the formation of sulfides such as hydrogen sulfide. However, intermediate sulfur species with different valence states, such as polythionates and polysulfides have been detected in several produced water samples, likely a result of phase partitioning, and chemical and microbial reactions. These sulfur species could affect the microbial communities (e.g., microbially influenced corrosion) and will impact the efficiency of souring mitigation methods. In addition, the presence of these sulfur species can result in operational, environmental, and treatment problems. Therefore, development and implementation of souring control strategies during production cycle of oil and gas reservoirs require identifying the origins, reactivity, and the partitioning behaviour of these compounds. This paper presents an overview of the known mechanisms responsible for reservoir souring and then focuses on the chemical reactions and sulfur species associated with production and consumption of hydrogen sulfide. In this work we highlight complexity of the sulfur chemistry and that the assumption that all the sulfate is reduced to hydrogen sulfide can lead to inappropriate souring management methods. The paper also reviews the detection and analysis methods used for sulfur compounds. The review demonstrates that there is a gap in the current souring models and methods due to the exclusion of key sulfur compounds and challenges in identifying and quantifying these compounds with respect to speed of analysis and sample stability.

Keywords Chemical reactions · Hydrogen sulfide · Sour reservoirs · Sulfur chemistry · Analytical methods

Introduction

The injection of sulfate-containing seawater for maintaining the pressure of oil reservoirs can promote the growth of sulfate reducing bacteria (SRB) and archaea near the injection wells, leading to the reduction of sulfate to sulfide (Holubnyak et al. 2011; Khatib and Salanitro 1997; Stemler 2012; Voordouw et al. 2007; Kaster et al. 2007; Machel 2001; Hubert 2010). Subsequent biologically and chemically mediated reactions result in the formation of elemental sulfur as well as other reduced sulfur compounds. The analysis of produced water samples has shown the presence of other sulfur species such as thiosalts, sulfite, and polysulfides along with sulfide (Witter and Jones 1998; Boulegue et al. 1981). The average oxidation state of these sulfur species is

between that of sulfate-sulfur (+6) and sulfidic-sulfur (−2), and therefore, they are usually referred to as intermediate sulfur species (Fig. 1). These intermediate sulfur species have implications in both chemical and microbial processes and could impact the treatment approaches for soured reservoirs (Hissner et al. 1999; O'Reilly et al. 2001; Tang et al. 2009; Warren et al. 2008; Reid and Warren 2016). The reduced forms of sulfur appear in various oxidation–reduction (redox) reactions and can react with each other in the aqueous solution influencing the souring/scaling process. The level and types of sulfur species (i.e., sulfur speciation) is a function of reservoir temperature, pressure, pH, and composition, therefore, as conditions change within flow-lines and unit operations, these compounds could degrade to corrosion causing and health and safety problematic compounds, and impact effectiveness of the produced water and other treatment systems (Miranda-Trevino et al. 2013; Miranda-Trevino 2013; Witter and Jones 1998). The distribution of sulfur compounds is also important to determine

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Fig. 1 Oxidation reduction reactions in sulfur cycle

souring mitigation measures to either prevent the formation of sulfide or lowering the amount of sulfide already presents.

The role of intermediate sulfur species in biological activity is well documented (e.g. Tang et al. 2009). However, the chemical reactivity, which would affect the sulfur chemistry of the reservoir, topsides, and methods to control reservoir souring (e.g. nitrite injection) is less well understood. There is a gap in knowledge in sulfur chemistry (outside of the formation of hydrogen sulfide and some common sulfur species) in reservoirs where seawater is injected. The objective of this paper is to provide a comprehensive review of research findings in sulfur chemistry in oil reservoirs at low to moderate temperatures to highlight the importance of understanding the sulfur chemistry in determining the full extent of reservoir souring. The first step in studying sulfur speciation in oil reservoirs is to investigate the chemistry of hydrogen sulfide in a multiphase system. There are a number of biogenic and non-biogenic mechanisms that produce H_2S in reservoirs. Once generated within a reservoir, H_2S partitions between different phases present in the reservoir fluid. This partitioning behaviour is a function of temperature, pressure, pH, salinity, and hydrocarbon composition. There are also other reduced sulfur species present in reservoir fluid which could impact H_2S distribution between phases. The reactivity of these compounds is complex and depends upon temperature, pH, as well as the presence of other sulfur species, metals and microorganisms. The occurrence and behaviour of these intermediate sulfur species and their impact on H_2S distribution need to be studied for developing souring control strategies. As most souring management methods are developed based on models (for SRB induced

souring) where the primary assumption is usually the production of only hydrogen sulfide from sulfate reduction. This can potentially result in ineffective souring management approaches. Therefore, in this work, we review the possible sulfur species that can be formed. We also detail the challenges in detection and analysis of sulfur compounds in oil and gas fluids.

Reservoir souring and hydrogen sulfide formation

At temperatures above 250 °C, aqueous sulfate, derived from seawater, pore water, or from dissolution of solid calcium sulfate (mainly gypsum and anhydrite), can be reduced by a variety of organic compounds such as alcohols, polar aromatic hydrocarbons, and saturated hydrocarbons (Toland 1960; Kiyosu and Krouse 1990; Krouse et al. 1988; Machel 1987; Orr 1977; Belkin et al. 1985). This thermal redox reaction or thermochemical sulfate reduction (TSR) can result in high concentrations of H_2S in the reservoir fluid (more than 10%). TSR is well documented in the field and experiments have been conducted to investigate the reactions involved, possible products, and the effect of temperature, type of oxidants, presence of sulfur species and metal cations, and the pH on the TSR rate (e.g. Orr 1977; Sassen 1988; Anderson and Machel 1988; Krouse et al. 1988; Heydari and Moore 1989; Ligthelm et al. 2000; Goldstein and Aizenshtat 1994; Worden et al. 1995, 1996, 2000; Chen et al. 2009; Hutcheon et al. 2009; Zhang et al. 2007, 2008; Amrani et al. 2008; Yuan et al. 2013).

Thermolysis and/or aquathermolysis of aromatic thiophene-type organosulfur compounds such as thiophene and aliphatic organic sulfides such as tetrahydrothiophene in heavy oil also produces H_2S (Hoffmann and David 2018; Marcano et al. 2013; Clark et al. 1983, 1984b). Aquathermolysis reactions between oil and steam are dominant at temperatures below 240 °C, while thermolysis (i.e., in the absence of water) dominates at higher temperatures. The amount of H_2S production by thermal decomposition of oil is proportional to the sulfur content of the oil and is typically less than 5%. Thiols, sulfide, disulfides, polysulfides, thiophenes, benzothiophenes, and dibenzothiophenes are typical sulfur species in bitumen with disulfides and thiols the most reactive and benzothiophenic compounds the most stable sulfur species (Clark et al. 1983, 1984b).

Oxidative and reductive dissolution of metal sulfides under acidic conditions may also produce sulfate ions (a source for SRB growth) and H_2S during water flooding or steam injection (Marsland et al. 1989; Hutcheon 1998).

MS represents sulfide mineral, M is the metal base, and O and R are oxidized and reduced compounds in the redox reaction, respectively. The acidic components come from the injection water or the degradation of injected biocides and corrosion and scale inhibitors (Khatib and Salanitro 1997; Xu and Schoonen 1995). Iron sulfides, such as pyrite and pyrrhotite are common metal sulfide minerals associated with reservoirs forming under reducing conditions (Rickard et al. 1995). Pyrite is oxidized to sulfate and hydrogen reducing the pH of the environment (Hutcheon 1998; Rimstidt and Vaughan 2003). At pH values lower than 7, pyrite oxidation by dissolved oxygen produces tetrathionate and sulfate, while, at higher pH values, thiosulfate and sulfite are the major reaction products (Xu and Schoonen 1995). An increase in temperature is accompanied with an increase in the rate of pyrite oxidation and sulfate concentration. The rate of pyrite oxidation at 25 °C is rapid enough to be observed in a few years (Hutcheon 1998). The most favorable decomposition reactions for pyrite at low pH values ($\text{pH} < 7$) and under reducing conditions, generating H_2S are (Peters 1976):

Under basic conditions, pyrite is decomposed to sulfate and sulfide, while, in the presence of an oxidant, it is converted to elemental sulfur (Peters 1976):

Reservoir pores contain both water and hydrocarbons and as the hydrocarbon is produced, capillary forces result in water retention in the small pores of the reservoir rock. This initial water saturation may vary from 5 to 50% (Katz 1959; Standing 1977). This formation water has the capacity to absorb (from soured reservoir fluids) and potentially store H_2S . As reservoir pressure decreases during production, the solubility of H_2S in water decreases, liberating formation water H_2S to the produced reservoir fluid. This is a potential mechanism for souring the fluids, even if souring mitigation measures have been put in place upstream. Seto and Beliveau observed this phenomena, in the Caroline field, where souring was attributed in part to the migration of H_2S from the aqueous phase in the reservoir (Seto and Beliveau 2000). This is an important phenomena, as it could in part explain the observation of H_2S in produced fluids even after a reservoir has been treated to prevent souring (e.g. nitrate injection).

Bacterial sulfate reduction (BSR), is a common and widespread process in shallow burial diagenetic settings, and considered “instantaneous” on a geological time scale leading to the generation of H_2S . Biogenic sulfide production results in soured oil and gas in the reservoir and topside processing facilities including oil–water separation units, water storage tanks for produced water, and flowlines. There are various comprehensive reviews on the types of sulfate reducers (Barton and Fauque 2009; Muyzer and Stams 2008; Grigoryan et al. 2008; Bodtker et al. 2008; Wei et al. 2010; Agrawal et al. 2010; Orphan et al. 2000; Kumaraswamy et al. 2011), bioreaction mechanisms, products, and geochemical characteristics of BSR (Machel 1987, 1992; Machel et al. 1995; Noth 1997; Morse et al. 1987; Goldhaber and Orr 1995).

Anaerobic microorganisms that reduce sulfate are either indigenous in deep subsurface reservoirs or can be introduced into a reservoir during drilling operations or water flooding (Gieg et al. 2011). The latter has been found to be a source of multiple components including sulfate, carbon sources, and sulfate reducing communities that influence oilfield souring. The extent of microbial souring depends on the water-flooding operations (i.e. seawater injection or produced water re-injection) (Voordouw et al. 2009; Lysnes et al. 2009), salinity (Wilhelms et al. 2001; Stetter et al. 1993), temperature (Voordouw et al. 2009; Kaster et al. 2007), and sources of carbon and other nutrients (Grigoryan et al. 2008).

Oilfield souring control: chemical treatments

Microbial activity offshore is managed by a number of different methods. Injection of biocides at the topside and/or to the injection water is the most common method. Biocides suppress microbial growth and activity, particularly in reservoirs where souring is confined to the zone around injection well (Gieg et al. 2011). Common biocides for controlling microbial activity include glutaraldehyde, tetrakis (hydroxymethyl) phosphonium sulfate (THPS), benzalkonium chloride, formaldehyde, and sodium hypochlorite (Videla and Herrera 2005; Kaur et al. 2009). Biocides are relatively simple to administer, however, continued use of them can lead to increase in biocide-resistant microbial communities. Biocides are potentially hazardous to oilfield personnel and the environment and difficult to inject deep into reservoir making treatment of SRB distant from injection well challenging.

Nitrate injection at the injection well or at the production well in the produced water treatment is an alternative to biocide treatment (Sunde et al. 2004; Sturman and Goeres 1999; Dolfing and Hubert 2017; Myhr et al. 2002). Unlike biocides, nitrate flows readily into an oil-bearing formation and shifts the microbial activity from SRB to nitrate reducing bacteria (NRB). The addition of nitrate into an injection well stimulates nitrate reducing bacteria (NRB), which are responsible for the reduction of nitrate to nitrite. The produced nitrite acts as an SRB inhibition agent. It is also an effective H_2S scavenger as it reacts with sulfide resulting in the generation of elemental sulfur and nitrogen (Sturman and Goeres 1999). Microbial competition between NRB and SRB for electron donors (oil-derived organics or H_2) and nitrate-driven sulfide oxidation are the two mechanisms proposed for the NRB-facilitated souring control (Sunde et al. 2004; Dolfing and Hubert 2017). There are concerns that nitrate treatment shifts the corrosion risk from production to injection wells due to the oxidizing potentials of nitrate and nitrite (Martin 2008; Hubert et al. 2005). Depending on the ratio of nitrate to sulfide, fully oxidized sulfate or partially oxidized sulfur-polysulfides may be generated; sulfide is oxidized to sulfate at high nitrate to sulfide ratios with the reduction of nitrate to nitrite, while, at low ratios, sulfur-polysulfide formation is favored (Sturman and Goeres 1999). The latter conditions can be encountered at oilfield topside at low temperatures (4–85 °C) (Dolfing and Hubert 2017). These intermediate sulfur species could also be formed rapidly by chemical reactions, when soured produced water containing substantial sulfide concentrations is exposed to air (Johnston et al. 2010). The oxidation of sulfide to sulfate is a kinetically slow reaction that requires a biological catalyst to occur at a significant rate. Therefore, partially oxidation of sulfide to elemental sulfur and other intermediate sulfur species is a more probable reaction

pathway. The formed intermediate sulfur compounds may cause corrosion. The corrosive nature of these compounds has been well documented (Dowling 1992; Alekseev et al. 1990; Fang et al. 2011). Polysulfide, for example, acts as an oxidizer that receives electrons from steel surfaces to form sulfide (Ramo and Sillanpaa 2003). Sulfur can react rapidly with metallic iron to form iron sulfide and other iron sulfur compounds such as greigite (Fe_3S_4) and pyrite (FeS_2) (Johnston et al. 2010; Dronen et al. 2014). The formed iron sulfide is essentially insoluble in aqueous solution leading to high local corrosion rates. Partially oxidized sulfur species can acidify natural waters (O'Reilly et al. 2001). These reduced forms of sulfur entering the environment can also influence the bioavailability of heavy metals due to complexation and precipitation (Witter and Jones 1998).

These findings have implications for reservoir souring management strategies (Nemati et al. 2001). For example, under conditions encountered in oilfields, where there is an abundance of electron donors, sulfate reduction to sulfide is more favorable than sulfide oxidation to elemental sulfur. Sulfide oxidation to intermediate sulfur species is, on the other hand, most problematic in oil/water topside separation tanks where nitrate levels are low. The occurrence and behaviour of these intermediate sulfur species and their impact on souring/scaling process need to be investigated for developing souring control strategies. This could be achieved through identifying the possible compounds involved and studying the thermodynamic and reaction rate data with respect to these species present.

Sulfur chemistry and reservoir souring

Intermediate sulfur species in produced fluids indicate that there are microbial and chemical reactions occurring as the reservoir fluids flow from injection to production wells. The reactivity of these compounds is complex and depends upon temperature, pH, as well as the presence of other sulfur species, metals, and microorganisms. The possible origins of these compounds have been studied under different temperature and pH conditions (Takano et al. 1994; Zhang and Millero 1993; Chen and Morris 1972; Xu et al. 2000; Gieg et al. 2011; Orphan et al. 2000; Tang et al. 2009; Muyzer and Stams 2008; Barrett and Clark 1987; Moura et al. 1997; Dalsgaard and Bak 1994). The incomplete redox reactions involving H_2S , sulfur dioxide, or sulfate are likely causes of the generation of sulfur oxyanions. Partial reoxidation of H_2S to sulfur may occur in low-temperature aerobic environments, where molecular oxygen presents, and in high-temperature anaerobic environments, excess sulfate acts as the oxidant. Intermediate sulfur species can also be reduced to sulfide due to the SRB activity. Some sulfate reducers can reduce sulfur compounds such as thiosalts, sulfite, and

sulfur (Muyzer and Stams 2008; Barrett and Clark 1987; Moura et al. 1997; Dalsgaard and Bak 1994). Thermophilic sulfur reducers and thiosulfate reducers have been isolated from produced water at temperatures ranging from 60 to 90 °C (Gieg et al. 2011; Orphan et al. 2000). A mesophilic SRB has been detected in oil fields at temperature of 30 °C and pH 7, and reduced sulfate, sulfite, and thiosulfate in the presence of lactate (Gieg et al. 2011).

Thiosalts

Thiosalts are important intermediate sulfur species which are undesirable in the environment as they can acidify natural waters (Witter and Jones 1998; Druschel et al. 2003; O'Reilly et al. 2001; Wang et al. 2013; Miranda-Trevino et al. 2013; Millero 1986; Kuyucak and Yaschyshyn 2007). Their reactivity is dependent upon temperature, pH, and the presence of oxygen and other thiosalts, metals, and microorganisms (Miranda-Trevino et al. 2013). Strong oxidants and biological and/or chemical catalysts such as iron catalyze the chemical breakdown of polythionates to thiosulfate and sulfite (Schippers and Sand 1999). Thiosalts formed in the reservoir could rapidly react to form H₂S or other sulfur species on the top-sides (i.e., in produced water systems). Thiosalts can also be produced from the oxidation of pyrite. The two common oxidants are ferric ion and oxygen. The former is the main oxidant at low pH values, and the latter is more important at neutral pH (Schippers et al. 1996; Schippers and Sand 1999):

In acidic aqueous solutions at temperatures between 4 and 30 °C, thiosulfate is further oxidized to tetrathionate as follows (Miranda-Trevino et al. 2013; Takano et al. 1994; Zhang and Millero 1993; Chen and Morris 1972; Xu et al. 2000):

Pyrite has been shown to act as a catalyst in the tetrathionate formation reaction in both acidic and basic conditions (Xu and Schoonen 1995):

Tetrathionate is stable in acid solutions, and degrades to thiosulfate and sulfite at neutral pH. At low pH values, however, tetrathionate is decomposed to sulfate if the ferric ion presents:

In the presence of a strong alkaline media, trithionate is a probable intermediate of tetrathionate reduction (Xu and Schoonen 1995):

At pH 3.5–4 and temperatures between 20 and 70 °C, trithionate and pentathionate are formed from tetrathionate decomposition through a second-order reaction (Miranda-Trevino 2013; Zhang and Jeffrey 2010):

Trithionate is stable in neutral and acidic conditions and its reactivity increases with pH (Miranda-Trevino et al. 2013):

At high temperatures, between 70 and 150 °C, the proposed reaction for degradation of trithionate is as follows:

The presence of ferric ion promotes the oxidation of trithionate at pH near to neutral (Wang et al. 2013; Zhang et al. 2011).

The oxidation of trithionate at pH below 7 and in highly basic solutions (pH around 12) follows the same reaction. However, in acidic conditions, the produced thiosulfate is further oxidized to tetrathionate and sulfite. At pH between 3.5 and 4 and temperatures between 20 and 70 °C, trithionate is first decomposed to tetrathionate and sulfate and then to sulfur dioxide and sulfur:

Hydrogen sulfide and polysulfide ions

Hydrogen sulfide is a weak acid in water and depending on the pH of the environment, it may exist as bisulfide or sulfide ions. In low-temperature diagenetic settings ($T < 100^\circ\text{C}$), where oxygen is available and pH conditions are favorable, sulfide can be oxidized to elemental sulfur. Several models have been developed to predict the partitioning behaviour of H₂S in reservoir fluids and to investigate the effects of temperature, pressure, fluids composition, ionic strength,

and water pH on the H_2S mass production rate (Eden et al. 1993; Burger et al. 2005; Schofield and Stott 2012; Ligthelm et al. 2000; King and Al-Najjar 1977; Sunde et al. 1993; Tyrie and Ljosland 1993). The dissolution of H_2S in water involves a series of chemical reactions: the dissociation of the molecular H_2S to bisulfide and sulfide ions and the self-ionization of water (Burger et al. 2013):

The equilibrium constants for the above reactions are obtained over a wide range of temperature (Burger et al. 2013). The solubility of H_2S in a salt solution decreases as the ionic salt concentrations increase. This phenomenon, called the salting-out effect, may be characterized by Setschenow and formulated in terms of the ratio of solubilities in pure water and in an aqueous salt solution at a constant temperature (Burger et al. 2013).

Rate constants for the oxidation of sulfide in seawater and formation of sulfite, sulfate, and thiosulfate were determined as a function of pH, temperature, and salinity. The reactions are overall second-order reactions, first-order with respect to both sulfide and oxygen (Zhang and Millero 1993):

It is believed that the dissolution of elemental sulfur in aqueous sulfide solutions is the precursor for the formation of polysulfide anions (Petre and Larachi 2006):

The distribution of the resulting anions reaches equilibrium rapidly which leads to the formation of different chain lengths:

In aqueous solutions, the autooxidation of the polysulfide anions also occurs rapidly which results in thiosulfate formation:

If the formation of thiosulfate is not suppressed, it can be oxidized to polythionates. Under alkaline conditions, hydrogen sulfide reacts with polythionates and forms polysulfides (Steudel 1996). Polysulfides are relatively unstable and are easily decomposed to elemental sulfur when exposed to water. The solubility of sulfur in the solution is mainly controlled by temperature and pressure and it has been shown that high bottom hole temperatures and low wellhead pressures provide favorable conditions for sulfur deposition which blocks the pores in the formation (Shedid and Zekri 2002; Adesina et al. 2012). The influences of operational and reservoir parameters on elemental sulfur plugging in oil and gas reservoirs have been studied by several investigators (Shedid and Zekri 2002; Abou-Kassem 2000; Chernik and Williams 1993; Roberts 1997). A decrease in temperature and pressure also leads to the decomposition of polysulfides (Bojes et al. 2010). Polysulfides are also known to play a key role in the formation of volatile sulfur compounds in natural aquatic systems (Petre and Larachi 2006). Polysulfide ions can react with H^+ to form hydrogen polysulfides which, near or below pH 7, lead to the formation of homocyclic molecule S_8 . The formed elemental sulfur can precipitate as a solid and cause plugging in the reservoir, well-bore, or surface facilities (Millero 1986):

Hydrogen polysulfides have relatively strong acidities in the gas phase which correlate with the chain length. Hydrogen polysulfides can react with basic species such as bicarbonate ions in the formation water and produce water-soluble ionic polysulfides as follows:

Sulfur can also be oxidized to other sulfur oxyanions such as sulfate, sulfite, polysulfides, and thiosulfate. As pH of the solution increases through neutral conditions, the rate of oxidation of sulfide increases, whereas it decreases in more alkaline solutions (Wang et al. 2013; Machel 1992):

In the presence of a transition metal, like ferric ion, the overall process of sulfide oxidation may be represented as follows:

Table 1 summarizes the published reaction rates reported for different sulfur species under acidic and basic conditions.

As indicated above, thiosalts are active intermediates in bacterial reactions but not discussed in detail here. However,

it is clear from the discussion above that the type of sulfur compound can vary significantly within the reservoir and topsides processing facilities depending on the temperature, pressure, and pH. These same compounds can act as growth promoters or inhibitors of bacterial growth and corrosion. Therefore, a more complete understanding of how sulfur partitions and chemically reacts is required to better manage reservoir souring and topsides damage/safety concerns.

Detection and quantification of reduced sulfur compounds

Sulfur and sulfur-oxygen species are highly reactive, and speciation, decomposition, and oxidation of these compounds will occur. This makes the chemistry of such solutions quite complex and, therefore, difficult to accurately analyze (Moses et al. 1984; Takano and Watanuki 1998;

Safizadeh and Larachi 2014). Chemical techniques such as titration, gravimetric analysis, and colorimetric techniques have been used for the analysis of thiosalts including, thio-sulfate, trithionate, tetrathionate, and pentathionate either individually or in a mixture (Miranda-Trevino et al. 2013; O'Reilly et al. 2001). Thiosulfate can be determined by titrimetric methods where iodine or iodate is usually used as the titrant (Ciesielski et al. 2001) and in mixtures with other sulfur species such as sulfide and sulfite using formaldehyde to mask sulfite (Harris 2010). Total thiosalts have been determined by acidimetric titration carried out at the methyl orange or at the phenolphthalein end-point (Makhija and Hitchen 1978). The method has been described to distinguish between non-oxidizable sulfate and the oxidizable thiosalts. Samples containing as low as 0.1 mg of thiosalts can be analyzed easily and accurately.

Traditionally, total sulfide species or hydrogen sulfide in natural waters has been measured by colorimetric methods

Table 1 Summary of sulfur reactions from the literature under both acidic and basic conditions

Reaction	pH	T (°C)	References
Polysulfides			
$\text{H}_2\text{S} \leftrightarrow \text{H}^+ + \text{HS}^-$	5–8	–	Morse et al. (1987)
$\text{HS}^- \leftrightarrow \text{H}^+ + \text{S}^{2-}$	> 7	–	Morse et al. (1987)
$\text{H}_2\text{S} + \text{SO}_3^{2-} + 0.5\text{O}_2 \rightarrow \text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O}$	4–10	–	Zhang and Millero (1991)
$\text{HS}^- + 2\text{Fe}^{3+} \rightarrow 1/8\text{S}_8 + \text{H}^+ + 2\text{Fe}^{2+}$	5–8	–	Wilkin and Barnes (1996)
$n\text{S}^{2-} + 2(n-1)\text{H}_2\text{O} \rightarrow \text{S}_n^{2-} + 2(n-1)\text{OH}^- + (n-1)\text{H}_2$	> 7	> 70	Schippers and Sand (1999)
$n\text{HS}^- + (n-1)/2\text{O}_2 \rightarrow \text{S}_n^{2-} + \text{H}_2\text{O} + (n-2)\text{OH}^-$	–	–	Zopfi et al. (2004)
$\text{S}_n^{2-} + 3/2\text{O}_2 \rightarrow \text{S}_2\text{O}_3^{2-} + [(n-2)/8]\text{S}_8$	–	–	Petre and Larachi (2006)
$\text{HS}^- + \text{SO}_3^{2-} + 0.5\text{O}_2 \rightarrow \text{S}_2\text{O}_3^{2-} + \text{OH}^-$	5–8	–	Zopfi et al. (2004)
$\text{H}_2\text{S} + 1.5\text{O}_2 \rightarrow \text{SO}_3^{2-} + 2\text{H}^+$	4–10	–	Zhang and Millero (1993)
$\text{SO}_3^{2-} + 0.5\text{O}_2 + \text{H}_2 \rightarrow \text{SO}_4^{2-} + 2\text{H}^+$	4–10	–	Zhang and Millero (1993)
Thiosalts			
$\text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{S} + \text{SO}_4^{2-}$	12	> 70	Moses et al. (1987)
$\text{S}_2\text{O}_3^{2-} + 2\text{O}_2 + \text{H}_2\text{O} \rightarrow 2\text{SO}_4^{2-} + 2\text{H}^+$	> 7	25	Miranda-Trevino (2013)
$\text{S}_3\text{O}_6^{2-} + \text{Fe}^{3+} + 1/2\text{O}_2 \rightarrow \text{S}_2\text{O}_3^{2-} + \text{SO}_4^{2-} + \text{Fe}^{2+}$	7–9	30	Miranda-Trevino et al. (2013)
$2\text{S}_4\text{O}_6^{2-} \rightarrow \text{S}_5\text{O}_6^{2-} + \text{S}_3\text{O}_6^{2-}$	9	4–30	Miranda-Trevino et al. (2013)
$\text{S}_3\text{O}_6^{2-} + 2\text{OH}^- \rightarrow \text{S}_2\text{O}_3^{2-} + \text{SO}_4^{2-} + 2\text{H}_2\text{O}$	> 7	–	Druschel et al. (2003)
$4\text{S}_4\text{O}_6^{2-} + 6\text{OH}^- \rightarrow 5\text{S}_2\text{O}_3^{2-} + 2\text{S}_3\text{O}_6^{2-} + 3\text{H}_2\text{O}$	> 7	–	Druschel et al. (2003a)
$2\text{S}_4\text{O}_6^{2-} + 6\text{OH}^- \rightarrow 3\text{S}_2\text{O}_3^{2-} + 2\text{SO}_3^{2-} + 3\text{H}_2\text{O}$	> 7	–	Druschel et al. (2003a)
$4\text{S}_4\text{O}_6^{2-} + 4\text{H}_2\text{O} \rightarrow 6\text{S}_2\text{O}_3^{2-} + \text{S}_3\text{O}_6^{2-} + \text{SO}_4^{2-} + 8\text{H}^+$	< 7	25–70	Zhang and Jeffrey (2010)
$\text{S}_2\text{O}_3^{2-} + \text{O}_2 \rightarrow \text{S}_4\text{O}_6^{2-} + \text{SO}_3^{2-}$	< 7	25	Druschel et al. (2003)
$3\text{S}_3\text{O}_6^{2-} \rightarrow \text{S}_4\text{O}_6^{2-} + 1/8\text{S}_8 + 2\text{SO}_4^{2-} + 2\text{SO}_2$	4	35	Zhang and Jeffrey (2010)
$2\text{S}_2\text{O}_3^{2-} + 2\text{Fe}^{3+} \rightarrow \text{S}_4\text{O}_6^{2-} + 2\text{Fe}^{2+}$	2.9–6.6	25–70	Xu and Schoonen (1995)
$\text{S}_3\text{O}_6^{2-} + \text{H}_2\text{O} \rightarrow \text{S}_2\text{O}_3^{2-} + \text{SO}_4^{2-} + 2\text{H}^+$	2–4	70–150	Miranda-Trevino et al. (2013)
$2\text{S}_2\text{O}_3^{2-} + 2\text{H}^+ + 0.5\text{O}_2 \rightarrow \text{S}_4\text{O}_6^{2-} + \text{H}_2\text{O}$	2.9	25–70	Miranda-Trevino et al. (2013)
$4\text{S}_4\text{O}_6^{2-} + 3\text{Fe}^{3+} + 2.75\text{O}_2 + 4.5\text{H}_2\text{O} \rightarrow 4\text{SO}_4^{2-} + 3\text{Fe}^{2+} + 9\text{H}^+$	4	70	Druschel et al. (2003)
$2\text{S}_4\text{O}_6^{2-} \rightarrow \text{S}_5\text{O}_6^{2-} + \text{S}_3\text{O}_6^{2-}$	9	4–30	Miranda-Trevino et al. (2013)
$2\text{S}_2\text{O}_3^{2-} + \text{H}^+ \rightarrow \text{HSO}_3^- + \text{SO}_3^{2-} + 2\text{S}^0$	2.9	25	Zopfi et al. (2004)
$5\text{S}_2\text{O}_3^{2-} + 6\text{H}^+ \rightarrow 2\text{S}_4\text{O}_6^{2-} + 2\text{S}^0 + 3\text{H}_2\text{O}$	< 7	70–150	Barrett and Clark (1987)
$\text{S}_3\text{O}_6^{2-} + \text{H}_2\text{O} \rightarrow \text{S}_2\text{O}_3^{2-} + \text{SO}_4^{2-} + 2\text{H}^+$	2–4	70–110	Xu et al. (2000)

with methylene blue (Sakamoto-Arnold et al. 1986; Lawrence et al. 2000). Various electrochemical methods based on different pulse voltammetry of silver or mercury electrodes, amperometric detectors, as well as potentiometry have been widely used to measure dissolved sulfide in aqueous media (Sakamoto-Arnold et al. 1986; Green and Blough 1994; Jeroschewski et al. 1996; Jorgensen 1990; Ciglenečki et al. 2014). Cyclic voltammetry or linear sweep voltammetry was used for separating free polysulfides, elemental sulfur, and bisulfide with fast scan rates (Rozan et al. 2000).

These chemical methods are time-consuming. Electrochemical methods such as polarography and voltammetry can determine two or three species in a single scan faster than wet chemistry methods. To directly determine total ionic polysulfides in the presence of other sulfur species (e.g., polythionates and sulfide), differential pulse polarography in combination with a dropping mercury electrode was used (Kariuki et al. 2001). Due to the specificity of the technique and the lack of interferences, the method is attractive for the measurements of samples with polysulfide concentrations between 10^{-5} and 10^{-3} M.

Spectrophotometry methods have been applied to determine total polythionates, thiosulfate, and sulfite mixed in various ratios (Koh 1990). The method has also been used for polythionates and sulfide mixtures (Miura et al. 1998). Tetrathionate has also been measured by mixing with iodate to form sulfate and iodide and the formed iodide was measured as triiodide via spectrophotometry (Miura et al. 1991). The spectrophotometric methods cannot simultaneously measure all the thiosalt species due to requirement of masking and conversion of one form of the compound to another (Miura et al. 1998).

Thiosalt species have also been analyzed using spectroscopic analyses such as infra-red (IR) and ultraviolet (UV) (Bandeekar et al. 1995; Rozan et al. 2000). The detection limits of these methods are typically in the range 10^{-4} to 10^{-2} M which are higher than those of other instruments. Thiosalts have relatively strong UV absorbance and, therefore, more selective direct detection at 214 nm is used (Padaruskas et al. 2000). Thiosulfate, trithionate, tetrathionate, and pentathionate have been detected using indirect UV–Vis detection (Pappoe and Bottaro 2014). Fully ionized pyromellitate ion (PMA) with a high molar absorptivity was used as the chromophoric probe. The method was rapid, sensitive, and selective with limits of detection between 0.02 and 0.12 µg/ml. Total dissolved sulfide in natural waters has also been determined using direct ultraviolet detection of bisulfide ion (Guenther et al. 2001).

Montes-Rosua et al. (2016) proposed an indirect method based on conductivity measurement for determining polythionate concentrations in a sample process water. However, different types of polythionates cannot be discriminated by this method.

A liquid chromatographic separation and polarographic method was developed by Takano and Watanuki (1998) to separate and analyze a mixture of polythionates. Different high-performance liquid chromatography (HPLC) techniques have been used for the separation of polythionates (Chapman and Beard 1973; Takano and Watanuki 1998; Tang and Santschi 2000). The selectivity of these methods is low, especially when samples with complicated matrices are analyzed.

Since the conventional methods are quite time-consuming and difficult to employ in the analysis of sulfur species in very complex matrices, modern techniques based on ion chromatography (IC) and capillary electrophoresis (CE) have been applied with detection sensitivity in the range 10^{-7} to 10^{-5} M (Jeffrey and Brunt 2007; Miura and Watanabe 2001). Sulfate, sulfite, thiosulfate, and sulfide have been determined by IC methods in sulfur speciation studies (e.g., O'Reilly et al. 2001). Moses et al. (1984) determined polythionates indirectly through the determination of thiocyanate. In classical ion-exchange chromatography methods, thiosulfate has been used as an eluent to separate metal ions through the formation of metal-thiosulfate complexes. These classical methods were not able to separate more than five complexes in one analysis. Polythionate separations are easier to achieve using modern anion-exchange and ion-interaction chromatographic methods. The sensitivity of UV detection for trithionate quantification is low and an anion-exchange column is an alternative approach to ion-pair chromatography (Jeffrey and Brunt 2007). Ion chromatography and electrochemical detection with a glassy carbon electrode chemically modified with palladium particles have shown the ability to catalyze sulfide oxidation over wide potential and pH ranges and, therefore, could detect dissolved ions in aqueous solutions (Casella et al. 2000). Sulfate, thiosulfate, and polythionates have been analyzed using IC in hydrothermal waters, while total dissolved sulfide is measured by titration and colorimetry (Kaasalainen and Stefansson 2011).

CE can be used for separation, detection, and quantification of thiosalt species (Buchberger and Haddad 1992; Corr and Anacleto 1996; Daunoravicius and Padaruskas 2002; Haddad et al. 1999; Padaruskas et al. 2000; Motellier and Descostes 2001; O'Reilly et al. 2003; Saeed 2017). CE is a technique for separation of ions based on their size to charge ratio and an attractive alternative to the traditional methods due to its high separation efficiency, low running costs, tolerances for sample matrices with high ionic strength, and the generation of a low amount of waste (O'Reilly et al. 2001). CE is also a rapid method and minimizes sulfur speciation during separation, making it suitable for the analysis of unstable sulfur-containing species. Separation of sulfide, thiosulfate, sulfite, and sulfate has been generally achieved with co-electric-osmotic flow (EOF) through the addition of an EOF modifier to the background electrolyte (BGE). In

this separation mode, sulfide migrates faster than the other ions and thiosulfate has the slowest migration rate. However, increasing the EOF modifier in the BGE reduces sulfide mobility due to the formation of ion-pairs between sulfide and EOF modifier and can change the separation selectivity (Petre and Larachi 2006). Using the anodic oxidation procedure, thiosulfate is completely converted to sulfate, and for this reason, the change in sulfate concentration should also be monitored. Sulfate, however, has no UV absorbance. Indirect UV detection in CE is, therefore, used to detect non-absorbing ions. Due to high UV absorbance, polythionates cannot be detected with indirect CE method and only were sulfate, sulfite, and thiosulfate detected (Padaruskas et al. 2000). In addition, there is a challenge in separating chloride from thiosulfate in saline water samples, implying the necessity of using direct CE method (Saeed 2017).

Other separation techniques for sulfur speciation include planar chromatographic, ion-exclusion chromatography, reversed-phase liquid chromatography, gas chromatography, and capillary electrochromatography. A review of these methods can be found in O'Reilly et al. (2001). Table 2

summarizes the analytical techniques used in sulfur speciation studies.

Conclusions

The presence of sulfur species in produced oil and gas results in operational, environmental, and treatment problems. Combination of sulfur species including sulfite, polysulfides, polythionates, and thiosulfate has been detected in some produced water samples along with hydrogen sulfide, likely a result of phase partitioning, and chemical and microbial reactions. These intermediate sulfur species have implications in both biology and geology and could impact the treatment approaches for sour reservoirs. Not only do these sulfur compounds impact the amount of H_2S in the various phases, but also they affect the overall reactivity of the produced fluids in terms of sulfur. The incomplete redox reactions involving H_2S , sulfur dioxide, or sulfate are likely causes of the generation of sulfur oxyanions. Understanding the sulfur chemistry is important to define the gaps in the souring reactions and phase behaviour occurring in soured

Table 2 Analytical methods for the determination of inorganic sulfur species in aqueous mixtures

Species detected	Detection	Detection limit	References
S^{2-} , $S_2O_3^{2-}$, SO_3^{2-} , SO_4^{2-} , $S_4O_6^{2-}$	CE, and direct and indirect UV (214 nm)	–	Saeed (2017)
Total polythionates	Conductivity measurement	0.04–2.28 g/l	Montes-Rosua et al. (2016)
SO_4^{2-} , SO_3^{2-} , $S_2O_3^{2-}$, $S_4O_6^{2-}$, $S_5O_6^{2-}$, $S_6O_6^{2-}$	IC	1–8 μ mol/kg	Kaasalainen and Stefansson (2011)
S^{2-}	Titration and colorimetry	0.02–52.7 mmol/kg	Kaasalainen and Stefansson (2011)
S^{2-} , $S_2O_3^{2-}$, SO_3^{2-} , SO_4^{2-}	CE	–	Lin et al. (2010)
$S_2O_3^{2-}$, $S_4O_6^{2-}$, $S_5O_6^{2-}$, $S_6O_6^{2-}$	IC	0.05–1 μ M	Jeffrey and Brunt (2007)
Polysulfides	HPLC and UV	15–70 nM	Kamyshny et al. (2006)
$S_2O_3^{2-}$, $S_4O_6^{2-}$, SO_3^{2-} , SO_4^{2-} , S^{2-}	CE	–	Petre and Larachi (2006)
$S_2O_3^{2-}$, SO_3^{2-} , SO_4^{2-}	CE	0.45–1.0 μ g/l	Liang (2001)
$S_2O_3^{2-}$, $S_4O_6^{2-}$, $S_5O_6^{2-}$, $S_6O_6^{2-}$	CE, and direct and indirect UV (214 nm)	5 mM	Padaruskas et al. (2000)
$S_2O_3^{2-}$, $S_3O_6^{2-}$, $S_4O_6^{2-}$, $S_5O_6^{2-}$	IC and UV absorbance	15–30 nM	Miura and Kawaoui (2000)
Polysulfides, S^0	Voltammetry	–	Rozan et al. (2000)
S^{2-}	Classical	200–4000 ppb	Pawlak and Pawlak (1999)
S^{2-} , $S_2O_3^{2-}$, SO_3^{2-} , SO_4^{2-}	ICP-MS	35–270 μ g/l	Divjak and Goessler (1999)
$S_2O_3^{2-}$, SO_3^{2-} , SO_4^{2-}	Indirect and direct UV (214 and 254 nm)	0.17–0.5 mg/l	Hissner et al. (1999)
S^{2-}	IC	0.14–16 ppb	Miura et al. (1998)
$S_2O_3^{2-}$, SO_3^{2-} , S_x^{2-}	IC and UV (320 nm)	~0.1 μ M	Witter and Jones (1998)
S^{2-}	UV–Vis	0.1–32 ppb	Wall et al. (1997)
$S_3O_6^{2-}$, $S_4O_6^{2-}$, $S_5O_6^{2-}$	UV (205 nm)	–	Weir et al. (1994)
S^{2-} , $S_2O_3^{2-}$, SO_3^{2-} , SO_4^{2-} , S_x^{2-}	Suppressed conductivity and UV (220 nm)	4.9–68 μ M	Zhou et al. (1993)
$S_2O_3^{2-}$, SO_3^{2-} , SO_4^{2-}	Suppressed conductivity	15–75 μ g/l	Weidenauer et al. (1996)
S^{2-}	Potentiometric	3–32 ppm	Raba et al. (1992)
$S_2O_3^{2-}$, $S_3O_6^{2-}$, $S_4O_6^{2-}$, $S_5O_6^{2-}$	IC, suppressed conductivity, and amperometry	< 1 μ M	Steudel and Holdt (1986)
$S_2O_3^{2-}$, SO_3^{2-} , SO_4^{2-}	IC and UV (335 nm)	0.05–0.1 mM	Story (1983)

reservoirs, especially those undergoing seawater injection recovery processes which are common offshore. Furthermore, an assessment of the sulfur speciation is necessary for evaluating topsides handling of oil, gas, and produced water. Various separation techniques are available for determining sulfur anions in aqueous mixtures. Due to the rapid changes that could occur during the analysis of sulfur species, the selection of the proper analytical technique is important. The method used needs to be quick and reliable. Sample management is also important for the success of sulfur speciation studies.

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