Reservoir Sourcing:
Sulfur Chemistry in Reservoir

by

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Abstract

Reservoir souring is a widespread phenomenon in reservoirs undergoing seawater injection. During this process, the sulfate in the seawater promotes the growth of sulfate reducing bacteria and archaea generating hydrogen sulfide. However, other reactions involving formation of different sulfur species with intermediate valence states such as elemental sulfur, sulfite, polysulfide ions, and polythionates can occur. These sulfur species have implications in both chemical and microbial processes and impact the treatment approaches for soured reservoirs. A predictive reactive model was developed in this study to investigate the chemical reactivity of sulfur species and their partitioning behaviour as a function of temperature, pressure, and pH in a seawater-flooded reservoir. The presence of sulfur species with different oxidation states impacts the amount and partitioning behaviour of H$_2$S. The model predicts at pH values less than 5, sulfur is predominantly in the form of sulfate, polysulfide, hydrogen sulfide and approximately 10% of the total sulfur is thiosalts. There is also elemental sulfur precipitation. At pH above neutral, the bulk of the sulfur is sulfate and thiosalts and less than 10% polysulfide is formed. The amount of sulfur deposited as elemental sulfur is also less compared to pH lower than 5. Without considering sulfur speciation and assuming that all the initial sulfate in the injected seawater (2454 mg/L) is converted to H$_2$S microbially and the formed H$_2$S partitions between phases, the gas phase under test separator conditions on the surface contains 1080 ppm H$_2$S which is in equilibrium with the oil phase containing 295.7 ppm H$_2$S and water phase with H$_2$S content of 8.8 ppm. These values are higher than those obtained from reactivity analysis (i.e., H$_2$S content of the gas, oil, and aqueous
phases are 487 ppm, 134 ppm, and 4 ppm, respectively). Therefore, ignoring sulfur speciation in investigating reservoir souring leads to over-prediction of H$_2$S content of reservoir fluid. The developed reactivity model enables one the investigation of sulfur chemistry when injection of sulfate-containing seawater is used in recovery processes. This model can be used as a tool to study sulfur speciation and H$_2$S amounts as a function of reservoir temperature, pressure and pH and therefore, could be used in developing souring mitigation measures.

**Keywords:** Chemical reactions, Hydrogen sulfide partitioning, Seawater injection, Sulfur speciation, Thermodynamic model
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Nomenclature

\( A \) : Debye-Huckel constant (molality\(^{1/2} \))

\( A_k \): total number of atomic masses of the \( k \)th element in the system in Eq. (3-1)

\( a_i \): activity of component \( i \) (mol/kg)

\( a_{ik} \): number of atoms of the \( k \)th element present in each molecule of chemical species \( i \)

\( C_i \): concentration of species \( i \) (mol/lit)

\( F \): feed flow rate (mol/sec)

\( f_i \): fugacity of component \( i \) (kPa)

\( f_i^\circ \): standard-state fugacity (kPa)

\( \tilde{f}_i \): fugacity of component \( i \) in solution (kPa)

\( G_i^\circ \): standard-state Gibbs energy of species \( i \)

\( G_r^\circ \): standard Gibbs free energy of reaction (J/kg)

\( \tilde{G} \): standard state partial molal Gibbs energy (J/kg)

\( H \): Henry's constant (kPa.kg/mol)

\( H^\circ \): standard enthalpy (J/kg)

\( \tilde{H} \): standard state partial molal enthalpy (J/kg)

\( H_f^\circ \): standard enthalpy of formation (J/kg)

\( I \): ionic strength (molality)

\( k \): salting-out coefficient

\( K \): equilibrium constant

\( k_{i1} \): vapor/liquid 1 equilibrium ratio (species \( i \))

\( k_{i2} \): vapor/liquid 2 equilibrium ratio (species \( i \))

\( L_1 \): water stream concentration (mol)

\( L_2 \): oil stream concentration (mol)

\( L_i \): liquid-phase flow rate (mol/sec)

\( m_S \): concentration of the electrolyte (molality)

\( S_0 \): solubility in pure water (molality)

\( S_S \): solubility in the electrolyte solution (molality)

\( m_i \): molality of species \( i \) in the aqueous phase (mol/kg)

\( n_i \): number of moles of the \( i^{th} \) solute species

\( P \): pressure (kPa)
$P_c$ : critical pressure of species $i$ (Pa)
$P_{c_{\text{sat}}}$ : vapor pressure of species $i$ (kPa)
$R$ : universal gas constant (8.314 kJ/kmol.K)
$r_i$ : reaction rate (mol/lit.sec)
$S^\circ$ : standard entropy (J/kg.K)
$S^\circ$ : standard state partial molal entropy (J/kg.K)
$T$ : absolute temperature (K)
$T_c$ : critical temperature of species $i$ (K)
$u$ : fluid velocity (m/sec)
$V$ : vapor-phase flow rate (mol/sec)
$V_i^{\infty}$ : partial molar volume of species $i$ in water at infinite dilution (m$^3$/kmol)
$v$ : fluid velocity (m/sec)
$x$ : distance (m)
$x_{i}^{L1}$ : mole fraction of species $i$ in $L_1$
$x_{i}^{L2}$ : mole fraction of component $i$ in $L_2$
$y_i$ : mole fraction of species $i$ in the gas phase
$Z$ : compressibility factor
$z$ : number of electrons transferred
$z_i$ : charge on the ion
$z_i$ : the initial mole fraction of species $i$

Greek letters
$\gamma_i$ : activity coefficient of species $i$
$\lambda_k$ : Lagrange's multipliers in Eq. (3-2)
$\phi_i$ : fugacity coefficient of component $i$
$\nu_i$ : stoichiometric coefficient of species $i$
$\mu_i$ : chemical potential of species $i$
$\epsilon_j$ : reaction coordinate for reaction $j$
$\omega$ : acentric factor
$\omega$ : total number of elements comprising the system in Eq. (3-1)
$\Psi$ : phase split (gas stream concentration/feed stream concentration)
$\xi$ : liquid phase split
CHAPTER ONE

INTRODUCTION
1.1. Overview

The formation of hydrogen sulfide (H$_2$S) in originally sweet reservoirs is known as reservoir souring. The amount of hydrogen sulfide in the gas phase under test separator conditions is an indicator of the extent of souring. Typically, a reservoir with a produced gas stream containing more than 3 ppmv H$_2$S (measured at 0°C and 1 atm) is considered soured (Eden et al., 1993). Hydrogen sulfide is a malodorous and toxic gas that is harmful to human health. The presence of H$_2$S in reservoirs or in topside processing facilities lowers the value of the products, increases corrosion rates, presents a safety risk, and creates issues of sulfur deposition in near wellbore (blocking pores and reducing permeability) and in production equipment, decreasing oil productivity (Hua et al., 2013; Shedid and Zekri, 2002). These issues and the limited space for equipment to treat or mitigate souring on offshore platforms represent a cost and logistical problem.

Thermochemical sulfate reduction, thermal hydrolysis of organic sulfur compounds, hydrolysis of metal sulfides, and desorption of H$_2$S from the aqueous phase could cause an increase in the concentration of H$_2$S in produced fluids. H$_2$S could also be generated due to the activity of some bacteria and archaea. This biogenic H$_2$S generation is a widespread phenomenon in reservoirs undergoing seawater injection and is of major concern to the oil industry. The injection of sulfate-containing seawater into an oil reservoir, for increasing the recovery and/or pressure maintenance, promotes the growth of sulfate reducing bacteria (SRB) and archaea near the injection wells, leading to the reduction of sulfate to sulfide (Khatib and Salanitro, 1997; Machel, 2001; Voordouw et al., 2007; Kaster et al., 2007; Hubert, 2010; Holubnyak et al., 2011; Stemler, 2012).
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 sulfur oxyanions, 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 (+6) and sulfide (-2) and therefore, they are usually referred to as intermediate sulfur species (Witter and Jones, 1998; Miranda-Trevino et al., 2013; Miranda-Trevino, 2013). These intermediate sulfur species have implications in both chemical and microbial processes (Hissner et al., 1999; O'Reilly et al., 2001; Warren et al., 2008; Tang et al., 2009; Reid and Warren, 2016); the reduced forms of sulfur take part in various oxidation-reduction (redox) reactions influencing the souring/scaling process. The level and types of sulfur species (i.e., sulfur speciation) is a function of temperature, pressure, pH, and composition, therefore, as conditions change within flowlines and unit operations, these species could degrade to corrosion causing and health and safety problematic compounds (Xu and Schoonen, 1995; Xu et al., 2000; Druschel et al., 2005; Miranda-Trevino et al, 2013). The distribution of sulfur compounds is important to determine the effectiveness of souring mitigation measures in either preventing the formation of sulfide or lowering the amount of sulfide already presents.

1.2. Motivation and Objectives

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 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 (beyond the formation of hydrogen sulfide and some common sulfur species) in seawater-flooded reservoirs. Therefore, identifying the origins, reactivity, and the partitioning behaviour of these compounds is a critical step in developing promising souring control strategies.

The focus of this work is to study sulfur speciation in reservoirs undergoing seawater injection in an attempt to assess the relative impact of different sulfur species on hydrogen sulfide formation and, therefore on the extent of reservoir souring. This study could be used as a screening tool for evaluating the sulfur chemistry in seawater-flooded reservoirs and incorporated into existing reservoir simulators, enabling one to estimate the sulfur speciation and hence souring of the produced fluid as a result of seawater injection. The following approach is followed in this study to investigate sulfur chemistry in a reservoir undergoing sulfate-containing seawater injection:

- Identification of key sulfur compounds involved in reservoir souring through literature review and equilibrium analysis to predict their partitioning behaviour in the reservoir fluid.

- Investigation of the chemical reactivity of sulfur species in a seawater-flooded reservoir as temperature, pressure, and pH change during production through development of a predictive reactive model including both equilibrium and kinetic reactions.

First a general overview of the known reservoir souring mechanisms during recovery methods is provided in Chapter 2. The focus of this section is, however, souring at temperatures below 100°C where sulfide is generated as a result of microbial activity to
highlight the importance of understanding the sulfur chemistry in these types of reservoirs.

The major sulfur species in the reservoir fluid/seawater mixture are then identified through a comprehensive literature review and Gibbs energy analysis and their behaviour is studied as a function of temperature, pressure and pH in the system at equilibrium (Chapter 3). Sulfur chemistry in a soured reservoir (due to seawater injection) is then assessed through a predictive reactive model considering equilibrium and kinetic chemical reactions involving sulfur species (Section 3.3). The chemical reactivity of intermediate valence state sulfur species is studied through this reactive model, considering the reacting system as a plug flow reactor under steady-state conditions with constant velocity. This approach simplifies the flow regime and decouples the complex transport phenomena within the reservoir from the chemical reactions and phase behaviour, allowing the reacting system to be studied. The effects of the secondary dehydrogenation and oxidation reactions of sulfide with organic compounds and their impact on distribution of sulfur between oil and water are not taken into account. The developed model was validated against the analytical MIN3KIN model.

Upon formation, H$_2$S could partition to the gas, water or oil phases depending on pressure, temperature and/or composition. As such a 3-phase flash partitioning model is developed to study the phase partitioning behaviour of H$_2$S in a multi-phase system. The details of the developed model are outlined in Chapter 4. During oil production, both temperature and pressure decrease resulting in a change in sulfur solubility in the aqueous phase and therefore, possible sulfur deposition. An equilibrium analysis is therefore
performed to investigate the partitioning behaviour of elemental sulfur (Chapter 4). The results of equilibrium analysis and chemical reactivity could be found in Chapters 4 and 5, respectively.
References


CHAPTER TWO

LITERATURE REVIEW
2.1. Introduction

A general overview of the known reservoir souring mechanisms including, thermochemical sulfate reduction, thermal hydrolysis of organic sulfur compounds, bacterial sulfate reduction, hydrolysis of metal sulfides, redox reactions involving oxygen scavengers, and desorption of H₂S from aqueous phase is presented in this chapter. The main focus of this chapter is reviewing sulfur speciation as a result of injection of sulfate-containing seawater at low to moderate temperatures (i.e., below 100°C).

2.2. Mechanisms of reservoir souring

2.2.1. Thermochemical sulfate reduction

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 at temperatures above 250°C (Toland, 1960; Kiyosu and Krouse, 1990; Krouse et al., 1988; Machel, 1987; Orr, 1977; Belkin et al., 1985; Worden and Smalley, 1996). This thermal redox reaction, or thermochemical sulfate reduction (TSR) can result in high concentrations of H₂S in the reservoir fluid (more than 10% of reservoir fluid). Other reduced sulfur compounds, carbonate minerals such as calcite and dolomite, carbon dioxide, elemental sulfur, and water are also formed during TSR. The Devonian Nisku Formation in Western Canada (Anderson and Machel, 1988), Devonian and Mississippian sour gas fields in Western Canada (Krouse et al., 1988; Hutcheon et al., 2009), the Jurassic Smackover Formation of the United States (Orr, 1977; Heydari and Moore, 1989; Sassen, 1988), and the Permian Khuff Formation of Abu Dhabi (Worden
and Smalley, 1996; Worden et al., 1995) are examples of reservoir souring as a result of TSR.

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. (Krouse et al., 1988; Orr, 1977; Worden and Smalley, 1996; Anderson and Machel, 1988; Hutcheon et al., 2009; Heydari and Moore, 1989; Sassen, 1988; Worden et al., 1995; Ligthelm et al., 1991; Goldstein and Aizenshtat, 1994; Worden et al., 2000; Chen et al., 2009; Zhang et al., 2007; Amrani et al., 2008; Zhang et al., 2008; Tuan et al., 2013)).

During TSR, sulfur is reduced from $S^{6+}$ to $S^{2-}$ through the formation of sulfur with intermediate valence states in the form of elemental sulfur, polysulfides, thiosulfate, and sulfite. Although TSR is thermodynamically possible at temperatures as low as 25°C (due to large negative free energy changes of reaction), the reaction rates at temperatures below 100-140°C (i.e., a minimum temperature range determined for TSR) are relatively slow compared to other souring mechanisms (Machel, 1998a; Mougin et al., 2007). Based on thermodynamic calculations, significant accumulations of H$_2$S due to TSR requires temperatures higher than 150°C (Goldhaber and Orr, 1995; Machel, 1998a).

Once generated, H$_2$S acts as a catalyst in TSR and its catalytic effect is enhanced at low pH values (i.e. pH~3-3.5) where the sulfate ion is activated and bisulfate ion is generated for reaction with hydrocarbon (Orr, 1974; Worden and Smalley, 1996; Zhang et al., 2008; Chen et al., 2009; Marriott et al., 2016). It is proposed that elemental sulfur is first generated from the reaction between calcium sulfate and H$_2$S (associated with
reservoir) and then oxidizes hydrocarbons to carbon dioxide leading to the generation of
H$_2$S and water (Worden and Smalley, 1996; Marriott et al., 2016). Since the TSR
environments are often hydrodynamically closed, the generated water (by-product of
TSR) may dilute the formation water which in turn impacts the rate of TSR as well as
gas/oil ratio (Worden and Smalley, 1996). The water catalyzes the TSR reaction as it
results in a decrease in salinity and hence, an increase in the solubility of hydrocarbon
and hydrogen sulfide.

2.2.2. Thermal hydrolysis of organic sulfur compounds

Thermolysis and/or aquathermolysis of organosulfur compounds such as thiophene and
tetrahydrothiophene in heavy oil also produces H$_2$S (Clark et al., 1983, 1984; Clark and
Hyne, 1984; Marcano et al., 2013; Hoffmann and David, 2018). 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
and kinetics of H$_2$S production by thermal decomposition of oil is proportional to the
sulfur content of the oil. Thiols, sulfide, disulfides, polysulfides, thiophenes,
benzothiophenes, and dibenzothiophenes are typical sulfur species in bitumen with
disulfides and thiols as the most reactive and benzothiophenic compounds as the most
stable sulfur species. Due to the limited organic sulfur compounds, typically less than 5%
H$_2$S is produced during aquathermolysis.

The reactivity of organosulfur compounds, the possible reaction products, and the
effect of metal cations on decomposition of these compounds during in-situ steam
injection in heavy oil recovery has been studied extensively by Clark et al. (Clark et al.,
1983, 1984, 1987; Clark and Hyne, 1984). Hydrolysis of thiophene-type organic compounds, produces significant quantities of carbon dioxide with the water as the source of oxygen in the system, whereas in thermolysis (i.e. higher temperature than hydrolysis and in the absence of water), the formation of small molecular weight compounds is favoured and no CO$_2$ detected (Figure 2.1).

Fig. 2-1 Reaction pathway for the hydrolysis of tetrahydrothiophene (Clark et al., 1983)

Hydrolysis of organosulfur compounds is influenced by the pH of the system (Clark and Hyne, 1984). Under acidic conditions, the rate of hydrolysis is dramatically increased compared to neutral conditions probably due to the presence of protons and the sulfate anion which acts as an oxidizing agent. The acidic hydrolysis of organosulfur compounds produced small quantities of soluble organics including alkylthiophene, dihyrothiénylthiophene, alkylidihyrothienylthiophene, and butanethiol.

The H$_2$S production during steam injected processes has been predicted from aquathermolysis experimental results and simulation (Freitag et al., 2006; Anaya et al., 2010; Barroux et al., 2013; Lin et al., 2016). Kapadia et al. (Kapadia et al., 2010, 2012)
have developed a thermo-kinetic model for reservoir simulation of the H$_2$S production during thermal recovery processes. A kinetic model assuming that H$_2$S yield is mainly due to the steam-induced cracking of the organosulfur components of resin and asphaltene fractions has also been developed by Lamoureux et al. (Lamoureux-Var and Lorant, 2007; Lamoureux-Var et al., 2010; Barroux et al., 2013).

Kinetic studies of aquathermolysis of heavy oils have shown the catalytic effect of the reservoir mineral components on the conversion of organosulfur components of heavy oil to CO$_2$ and H$_2$S (Fan et al., 2004; Guangshou et al., 2009). Aqueous solutions of first-row transition-metals, as well as aluminum cations, were used to investigate the effect of metal ions on decomposition of organosulfur compounds (Clark et al., 1987).

### 2.2.3. Hydrolysis of metal sulfides

Oxidative and reductive dissolution of metal sulfides under acidic conditions may also produce sulfate ions (a source for SRB growth) and H$_2$S during water flooding or steam injection (Marsland et al., 1989; Hutcheon, 1998).

Oxidative dissolution:

$$MS + 4H_2O + xO \rightarrow M^{2+} + SO_4^{2-} + 8H^+ + xR$$  \hspace{1cm} (2-1)

Reductive dissolution:

$$MS + 2H^+ + yR \rightarrow M^{2+} + H_2S + yO$$  \hspace{1cm} (2-2)

MS represents sulfide mineral, $M$ is the metal base, and $O$ and $R$ are some oxidized and reduced state of some appropriate redox couple, 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, 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 favourable decomposition reactions for pyrite at low pH values (pH<7) and under reducing conditions, generating H₂S are (Peters, 1976):

\[
\begin{align*}
FeS_2 + 2H^+ & \rightarrow Fe^{2+} + H_2S + S^0 \quad (2-3) \\
FeS_2 + 4H^+ + 2R & \rightarrow Fe^{2+} + 2H_2S + 2R \quad (2-4)
\end{align*}
\]

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

\[
\begin{align*}
FeS_2 + 4OH^{-} & \rightarrow 1/3Fe_3O_4 + 11/6S^{2-} + 1/6SO_4^{2-} + 2H_2O \quad (2-5) \\
FeS_2 + 2O & \rightarrow Fe^{2+} + 2S^0 + 2O \quad (2-6)
\end{align*}
\]

2.2.4. **Redox reactions involving oxygen scavengers**

During water flooding oil recovery, surface water with dissolve oxygen is injected downhole, which can induce oxygen-related corrosion and pitting and increase in the deposition of iron oxides (Eden et al., 1993). As such, control of oxygen in oilfield applications is required to improve the environment, health and safety compliance, maximize throughput, improve water quality and operational reliability. Dissolved oxygen can be controlled in injected and produced water using oxygen scavengers including bisulfites and sulfites. Although the injected bisulfite is readily reduced to
sulfide, it is unclear if it could be the principal sulfur source for H\textsubscript{2}S. It is likely, however, that the bisulfite could either stimulate the growth of SRB or serve as a catalyst in the conversion of some other sulfur-containing substances, generating H\textsubscript{2}S (Eden et al., 1993). Another possibility for the increase in the concentration of H\textsubscript{2}S as a result of injection of bisulfite could be the modification of the surface of the metal sulfides in the reservoir to making it more reactive in generating H\textsubscript{2}S.

2.2.5. Desorption of H\textsubscript{2}S from aqueous phase

Reservoir pores contain both water and hydrocarbons and as the hydrocarbons are produced, capillary forces result in water retention in the small pores of the reservoir rock. This initial water saturation in reservoir pores may vary from 5 to 50% (Katz, 1959; Standing, 1977; Eden et al., 1993). The in-situ formation water has the capacity to absorb (from soured reservoir fluids) and potentially store H\textsubscript{2}S. As reservoir pressure decreases during production, the solubility of H\textsubscript{2}S in water decreases. This ultimately leads to the liberation of H\textsubscript{2}S from the stationary aqueous phase into the produced fluids. This is a potential mechanism for souring the fluids, even if souring mitigation measures have been put in place upstream. Seto and Beliveau first proposed this as a potential mechanism for reservoir souring in the Caroline field where the other microbial or abiotic souring mechanisms seemed unlikely to explain the source of increased H\textsubscript{2}S in the production wells (Seto and Beliveau, 2000). This is an important phenomena, as it could in part explain the observation of H\textsubscript{2}S in produced fluids even after a reservoir had been treated to prevent souring (e.g. nitrate injection).
2.2.6. Microbial sulfate reduction

Sulfate can be reduced bacterially by hydrocarbons in low-temperature diagenetic environments (commonly up to 60-80°C) (Worden and Smalley, 1996; Machel and Foght, 2000; Machel, 2001). 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$_2$S. 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 (Orphan et al., 2000; Muyzer and Stams, 2008; Grigoryan et al., 2008; Fauque and Barton, 2009; Bodtker et al., 2008; Wei et al., 2010; Agrawal et al., 2010; Kumaraswamy et al., 2011), bioreaction mechanisms, products, and geochemical characteristics of BSR (Machel, 1987; Morse et al., 1987; Machel, 1992; Machel et al., 1995; Goldhaber and Orr, 1995; Noth, 1997).

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. SRB are found in both acidic and basic environments where sulfate is present (Nilsen et al., 1996; Sen and Johnson, 1999; Knittel et al., 2003; Webster et al., 2006). 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 (Stetter et al., 1993; Wilhelms et al., 2001),
temperature (Kaster et al., 2007; Voordouw et al., 2009;), and sources of carbon and other nutrients (Grigoryan et al., 2008). High salinities (more than 10%) and high temperatures (>100°C) in reservoirs limit microbial activity. The injection of sulfate rich seawater, cools the reservoir and alters the physical and chemical conditions of the produced water and the reservoir, creating a favourable environment for the growth of some mesophilic seawater bacteria. Scale and corrosion inhibitors, demulsifier, and wax inhibitors can provide nutrients to SRB. At temperatures above 80°C, almost all SRB cease to metabolize (Machel, 2001), however some hyperthermophilic SRB metabolize at temperatures as high as 100°C (Jorgensen et al., 1992; Stetter et al., 1993; Beeder et al., 1994; Rees et al., 1995; Beeder et al., 1995; Dang et al., 1996; Lien et al., 1998; Feio et al., 2004).

Depending on the availability of reactants, formation water chemistry, and wettability, different species such as H$_2$S, bisulfide, bicarbonate, carbon dioxide, calcite, and dolomite may be produced during bacterial sulfate reduction. The amount of H$_2$S generated by SRB is limited by the availability of organic reactants, sulfate and the presence of base and transition metals, such as Fe, Pb, Zn, and Mn (Bailey et al., 1973; Orr, 1977). When the system runs out of reactive hydrocarbons, the elemental sulfur that is not reduced to sulfide, accumulates as the net reaction product.

2.3. 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) phosphoniumsulfate (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$_2$S 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 et al., 2003). Sulfur can react rapidly with metallic iron to form iron sulfide and other iron sulfur compounds such as greigite (Fe₃S₄) and pyrite (FeS₂) (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). Theses 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 favourable 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.

2.4. Sulfur chemistry and reservoir souring

Most studies use hydrogen sulfide concentration in production fluids to indicate the rate and type of reservoir souring. However, other sulfur species including sulfite, polysulfides, and sulfur oxyanion compounds has been detected in several produced water samples (Witter and Jones, 1998; Druschel et al., 2003). The average oxidation state of these sulfur species is between that of sulfate (+6) and sulfidic (-2) and therefore, they are usually referred to as intermediate sulfur species (Figure. 2.2). These sulfur species could affect the microbial communities (e.g., microbially-influenced corrosion) and will impact the effectiveness of any souring treatment process. In addition, the presence of these sulfur species can result in operational, environmental and treatment problems. These sulfur compounds not only impact the amount of H₂S in the various phases but also the overall reactivity of the produced fluids in terms of sulfur. Sulfur oxyanions may also play a role in the transport of metals (Druschel et al., 2003).
The presence of intermediate sulfur species in produced fluids indicates that there are microbial and chemical reactions occurring as the reservoir fluids flow from injection to production wells. The possible origins of these compounds have been studied under different temperature and pH conditions (Muyzer and Stams, 2008; Orphan et al., 2000; Gieg et al., 2011; Tang et al., 2009; Takano et al., 1994; Zhang and Millero, 1993; Chen and Morris, 1972; Xu et al., 2000; Barrett and Clark, 1987; Moura et al., 1997; Dalsgaard and Bak, 1994). The incomplete redox reactions involving H$_2$S, sulfur dioxide, or sulfate are likely causes of the generation of sulfur oxyanions (Machel, 1987, 2001; Takano et al., 1994; Zhang and Millero, 1993; Chen and Morris, 1972; Xu et al., 2000). Partial reoxidation of H$_2$S 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) and thermophilic sulfur reducers and thiosulfate reducers have been isolated from produced water at temperatures ranging from 60-90°C (Orphan et al., 2000; Gieg et al., 2011). A mesophilic SRB has been detected in oil fields at temperatures of 30°C and pH 7 and reduced sulfate, sulfite, and thiosulfate in the presence of lactate (Gieg et al., 2011).

The intermediate sulfur species have implications in both biology and geology and, therefore, understanding the mechanism of chemical reactions involving these compounds is critical. The chemical reactivity of these sulfur compounds under different temperature and pH conditions is reviewed in the following.

Hydrogen sulfide is a weak acid in water and depending on the pH of the environment, it may exist as bisulfide or sulfide ions:

\[ H_2S \leftrightarrow H^+ + HS^- \]  \hspace{1cm} (2-7)
\[ HS^- \leftrightarrow H^+ + S^{2-} \]  \hspace{1cm} (2-8)

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. The kinetic model accounting for the distribution of the reactants and products is based on the following reactions (Zhang and Millero, 1993):

23
The rate constants of the distribution of products from the oxidation of sulfide in seawater as a function of pH are obtained as follows:

\[
\ln k_1 = -4.71 + 0.914pH - 0.0289pH^2
\]  (2-16)

\[
\ln k_2 = 3.87 + 1.51pH - 0.103pH^2
\]  (2-17)

\[
\ln k_3 = -9.09 + 3.01pH - 0.177pH^2
\]  (2-18)
In the presence of oxygen, the autoxidation of the polysulfides also occurs rapidly which results in thiosulfate formation:

\[ S_n^{2-} + 3/2O_2 \rightarrow S_2O_3^{2-} + [(n-2)/8]S_8 \]  

(2-21)

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).

High temperatures and pressures favour polysulfide formation. Polysulfides are relatively unstable and are easily decomposed to elemental sulfur and H\(_2\)S when exposed to water and temperature and pressure change. 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 protonated 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):

\[ S_n^{2-} + H^+ \rightleftharpoons HS_n^- \rightleftharpoons HS^- + [(n-1)/8]S_8 \]  

(2-22)

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

\[ H_2S_n + HCO_3^- \rightleftharpoons HS_n^- + H_2O + CO_{2(g)} \]  

(2-23)
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, and decreases in more alkaline solutions (Machel, 1992; Wang et al., 2013):

\[
nHS^- + (n-1)/2O_2 \leftrightarrow S_n^{2-} + H_2O + (n-2)OH^- \tag{2-24}
\]

\[
S_n^{2-} + 3/2O_2 \leftrightarrow S_2O_3^{2-} + (n-2)/8S_8 \tag{2-25}
\]

\[
S_n^{2-} + 3/2O_2 \leftrightarrow SO_3^{2-} + (n-1)/8S_8 \tag{2-26}
\]

\[
SO_3^{2-} + 1/2O_2 \leftrightarrow SO_4^{2-} \tag{2-27}
\]

In the presence of a transition metal, like Fe\(^{3+}\), the overall process of sulfide oxidation may be represented as:

\[
HS^- + 2M^{n+} \rightarrow S^0 + H^+ + 2M^{(n-1)+} \tag{2-28}
\]

Thiosalts are other forms of intermediate sulfur species which are undesirable in the environment as they can acidify natural waters (Witter and Jones, 1998; Druschel et al., 2003a; O'Reilly et al., 2001; Millero, 1986; Wang et al., 2013; Miranda-Trevino et al., 2013; 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 Fe\(^{3+}\), catalyze the chemical breakdown of polythionates to thiosulfate and sulfite (Schippers and Sand, 1999). Thiosalts formed in the reservoir could rapidly react to form H\(_2\)S or other sulfur species on the topsides (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 (reaction 2-29), and the latter is more important at neutral pH (reaction 2-30) (Schippers and Sand, 1999; Schippers et al., 1996).

\[
FeS_2 + 6Fe^{3+} + 3H_2O \rightarrow 7Fe^{2+} + 6H^+ + S_2O_3^{2-} \tag{2-29}
\]

\[
FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2H^+ + 2SO_4^{2-} \tag{2-30}
\]

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

\[
2S_2O_3^{2-} + 2H^+ + 1/2O_2 \rightarrow S_4O_6^{2-} + H_2O \tag{2-31}
\]

\[
2S_2O_3^{2-} + 2Fe^{3+} \rightarrow S_4O_6^{2-} + 2Fe^{2+} \tag{2-32}
\]

The decomposition of thiosulfate under both acidic and basic conditions are determined as follows:

\[
- \frac{d[S_2O_3^{2-}]}{dt} = 0.66 M^{-2}s^{-1}[S_2O_3^{2-}]^2 \quad pH : 2.9, \quad T : 25°C \tag{2-33}
\]

\[
- \frac{d[S_2O_3^{2-}]}{dt} = 1.48 \times 10^{-3} s^{-1}[S_2O_3^{2-}] \quad pH : 12, \quad T : 125°C \tag{2-34}
\]

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

\[
3S_2O_3^{2-} + FeS_2 \rightarrow S_4O_6^{2-} + FeS + H_2S \tag{2-35}
\]

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:

\[
4S_4O_6^{2-} + 3Fe^{3+} + 2.75O_2 + 4.5H_2O \rightarrow 4SO_4^{2-} + 3Fe^{2+} + 9H^+ \tag{2-36}
\]
\[- \frac{d[S_4O_6^{2-}]}{dt} = 2.5 \times 10^{-7} [Fe^{3+}]^{0.06} [S_4O_6^{2-}]^{0.3}, \quad pH : 4, \quad T : 70^\circ C \]  \hfill (2-37)

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

\[4S_4O_6^{2-} + 6OH^- \rightarrow 5S_2O_5^{2-} + 2S_4O_6^{2-} + 3H_2O, \quad pH : 9, \quad T : 4 – 30^\circ C \]  \hfill (2-38)

At pH 3.5 to 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):

\[2S_4O_6^{2-} \rightarrow S_5O_4^{2-} + S_5O_6^{2-} \]  \hfill (2-39)

\[- \frac{d[S_4O_6^{2-}]}{dt} = 5.1 \times 10^{-3} s^{-1} [S_4O_6^{2-}] \quad pH : 9, \quad T : 4 – 30^\circ C \]  \hfill (2-40)

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

\[3S_3O_6^{2-} \rightarrow S_4O_6^{2-} + 1/8S_8 + 2SO_4^{2-} + 2SO_2 \]  \hfill (2-41)

\[- \frac{d[S_3O_6^{2-}]}{dt} = 3.2 \times 10^{-2} s^{-1} [S_3O_6^{2-}] \quad pH : 4, \quad T : 35^\circ C \]  \hfill (2-42)

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

\[S_3O_6^{2-} + H_2O \rightarrow S_2O_5^{2-} + SO_4^{2-} + 2H^+ \]  \hfill (2-43)

\[- \frac{d[S_3O_6^{2-}]}{dt} = 2.6 \times 10^{-2} s^{-1} [S_3O_6^{2-}] \quad pH : 2 – 4, \quad T : 70 – 150^\circ C \]  \hfill (2-44)

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

\[S_3O_6^{2-} + 2Fe^{3+} + 1/2O_2 \rightarrow S_2O_5^{2-} + SO_4^{2-} + 4Fe^{2+} \quad pH : 7 – 9, \quad T : 30^\circ C \]  \hfill (2-45)
The oxidation of trithionate at pH below 7 and in highly basic solutions (pH around 12) follows the same reaction (reaction 1-46). 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.

\[ S_3O_6^{2-} + 2OH^- \rightarrow S_2O_3^{2-} + SO_4^{2-} + 2H_2O \]  

(2- 46)

As indicated previously, thiosalts are also 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. It is therefore important that a more complete understanding of how sulfur partitions and chemically reacts is required to control reservoir souring and topsides damage/safety concerns.

2.5. Summary

Reservoir souring may be originated from microbial and non-biogenic mechanisms which are of importance in producing excessive amounts of H₂S in oil field reservoirs. Other combination of sulfur species including sulfite, polysulfides, polythionates, and thiosulfate has also been detected in some produced water samples, 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 effectiveness of treatment approaches for sour reservoirs. The presence of sulfur species in produced
oil and gas results in operational, environmental and treatment problems. Not only do these sulfur compounds impact the amount of H$_2$S 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$_2$S, sulfur dioxide, or sulfate are likely causes of the generation of sulfur oxyanions. The isolation of some sulfur and thiosulfate reducing bacteria from produced waters indicates that although H$_2$S is mostly generated by SRB and archaea close to the injection well, and as the reservoir fluids flow from injection to production wells, formation of sulfur species with valence states between those of sulfate and sulfide occurs due to changes in temperature, pressure, and pH of the environment.

Managing the formation of sulfide or lowering the amount of sulfide already present due to the microbial activity requires a more comprehensive understanding of the sulfur compound reactivity and partitioning behaviour as a function of the temperature, pressure, and pH at reservoir conditions associated with SRB activity. An assessment of the sulfur speciation is also necessary for evaluating topsides handling of oil, gas, and produced water.
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3.1. Overview

Sulfur speciation is critical in assessing the potential problems associated with the injection of sulfate-containing seawater within oil reservoirs and also for developing the promising treatment approaches for soured reservoirs. In the first part of this study, the major sulfur species present in a system containing reservoir fluid and injected seawater and the corresponding reactions involving these species will be identified through literature and equilibrium analysis; and in the second part, the reactivity will be analyzed through developing a predictive model based on both equilibrium and kinetic reactions.

3.2. Equilibrium analysis for determining sulfur species equilibrium concentration

In order to determine the type and equilibrium amount of sulfur species present/reacting in the reservoir and topsides, the partitioning behaviour of the various species in a multi-phase system must be determined as a function of temperature, pressure, and pH. This is accomplished through equilibrium analysis (Eden et al., 1993; Burger et al., 2005; Burger and Jenneman, 2009).

Management of soured reservoirs to control corrosion and improve production, requires identification of the major sulfur species in the sulfur cycle (i.e., reduction of sulfate to sulfide and oxidation of sulfide to sulfate). The focus of this work is on sulfur speciation in an oil reservoir where sulfate-containing seawater is injected and where sulfate reducing bacteria and archaea are present. Equilibrium analysis is a useful tool in identifying and screening key reacting species and end products, and the respective phases involved.
There are two approaches to analyzing equilibrium reactions: Gibbs energy minimization and Gibbs reaction minimization. In the former, no reaction mechanism is given and only the feedstock and possible products are known. The Gibbs energy is then minimized for the system and species concentrations are determined based on their relative Gibbs free energies. The advantage of this approach is that the knowledge of the specific reactions is not required, which is useful for systems where the mechanisms are either too complex or unknown. The disadvantage is the need for information about the major products; if products are not included in the phase, the concentration will not be calculated. In the second approach, the reactions must be known and Gibbs energy of each reaction calculated and based on these values concentrations of various products are determined. The two approaches for minimizing Gibbs energy are introduced here. In the first part of this study, the major sulfur species present in the system will be identified through Gibbs energy minimization method and in the second part, where the chemical reactivity of sulfur species is studied, the Gibbs reaction minimization method is used in combination with the kinetic study.

### 3.2.1. Gibbs energy minimization

The Gibbs energy minimization method is used to find the most probable chemical speciation at steady state. The total Gibbs energy of a reacting system is a function of the composition of the system. Based on the fact that at equilibrium the total Gibbs energy of the system has its minimum value, the problem is to find the composition that minimizes the total Gibbs energy ($G^\circ$) for specified temperature and pressure. The solution is based on the method of Lagrange's multipliers which lead to a system of non-linear equations.
These equations can be solved numerically by Newton-Raphson method (Mougin et al., 2007; Smith et al., 2005):

The first step is to write the material balance on each element \( k \):

\[
\sum_i n_i a_{ik} = A_k \quad k = (1, 2, \ldots, \omega)
\]  

Where \( \omega \) is the total number of elements comprising the system and subscript \( k \) identifies a particular atom. \( A_k \) is defined as the total number of atomic masses of the \( k \)th element in the system. Further, \( a_{ik} \) is the number of atoms of the \( k \)th element present in each molecule of chemical species \( i \). Next, the Lagrange's multipliers \( \lambda_k \) are introduced for each element:

\[
\lambda_k \left( \sum_i n_i a_{ik} - A_k \right) = 0
\]  

Summation of these equations over \( k \) gives:

\[
\sum_k \lambda_k \left( \sum_i n_i a_{ik} - A_k \right) = 0
\]  

Then a function \( F \) is formed by:

\[
F = G' + \sum_k \lambda_k \left( \sum_i n_i a_{ik} - A_k \right)
\]  

By differentiating this equation and setting the result equal to zero one would obtain:

\[
\left( \frac{\partial F}{\partial n_i} \right)_{T,P,n_j} = \left( \frac{\partial G'}{\partial n_i} \right)_{T,P,n_j} + \sum_k \lambda_k a_{ik} = 0 \quad (i = 1, 2, \ldots, N)
\]  

The first term on the right side is the definition of the chemical potential. The chemical potential is also given by:
\[ \mu_i = G_i^\circ + RT \ln(\hat{f}_i / f_i^\circ) \quad (3-6) \]

\(\hat{f}_i\) is fugacity of component \(i\) in solution, \(f_i^\circ\) is the standard-state fugacity, \(R\) is the universal gas constant, \(T\) is temperature, and \(G_i^\circ\) is the standard-state Gibbs energy of species \(i\).

For the liquid phase, the fugacity is eliminated in favour of the activity coefficient (\(\gamma_i\)). Therefore, equation (3-5) can be written as:

\[ \Delta G_i^\circ + RT \ln(x_i \gamma_i \hat{f}_i / f_i^\circ) + \sum_k \lambda_k a_{ik} = 0 \quad (i = 1,2,\ldots,N) \quad (3-7) \]

In multiphase reacting systems, the numbers of moles of each species in all coexisting phases should be considered in the previous equations. In addition, in the presence of ionic species, the electroneutrality constraint should also be taken into account.

\[ F = \Delta G_i^\circ / RT + \sum_l \lambda_l \left( b_l - \sum_k a_{lk} x_k^a - \sum_k \sum_a a_{lk} x_k^a \right) + \lambda_e \left( \sum_j z_j x_j \right) \quad (3-8) \]

In this approach, the number of phases at equilibrium needs to be known in advance. The calculations are initiated with \(\gamma_i = 1\) for all species. A preliminary set of \(\{x_i\}\) is then provided by solving Eq. 3-7. An activity model is used together with calculated composition to give a new set for \(\gamma_i\) for use in Eq. 3-7. Then a new set \(\{x_i\}\) is determined. The process is repeated until successive iterations produce no significant change in \(\{x_i\}\).

In the first part of equilibrium analysis, the HSC Chemistry 9.0 is used for solving the system of nonlinear equations (Eq. 3-8).

3.2.2. Gibbs reaction minimization
When two or more independent reactions proceed simultaneously, the equilibrium mole fractions of \((x_i)\) of the species present are related to the reaction coordinate \((\varepsilon)\) by:

\[
{x_i} = \frac{n_{i0} + \sum_j^n v_{i,j} \varepsilon_j}{n_0 + \sum_j^n v_j \varepsilon_j}
\] (3-9)

Where, \(\varepsilon_j\) applies to each reaction and \(v_{i,j}\) designates the stoichiometric number of species \(i\) in reaction \(j\). Summation over all species yields: \(\varepsilon_j = \sum_v v_{i,j}\). \(n_{i0}\) is the initial concentration of species \(i\) and \(n_0\) is the initial concentration of the reacting system.

The equilibrium constant for a reaction can be evaluated as follow:

\[
\Delta G^o_r = -RT \ln K
\] (3-10)

Where, the standard molal Gibbs free energy of the reaction \((\Delta G^o_r)\) is defined by Eq. (3-11) (Smith et al., 2005):

\[
\Delta G^o_r = \sum_i v_{i,r} \Delta G^o_i
\] (3-11)

where, \(v_i\) is the stoichiometric coefficient and \(\Delta G^o_i\) is the Gibbs free energy of formation for species \(i\). The standard Gibbs free energy change of reaction vary with the equilibrium temperature and can be evaluated as follow:

\[
\frac{d(\Delta G^o / RT)}{dT} = -\frac{\Delta H^o}{RT^2}
\] (3-12)

The standard enthalpy change of reaction \((\Delta H^o)\) is related to temperature:

\[
\Delta H^o = \Delta H^o_0 + R \int_{T_0}^T \frac{\Delta C_p^o}{R} dT
\] (3-13)

Similarly, the standard entropy change of reaction is developed as follow:
\[
\Delta S^o = \Delta S^o_0 + R \int_{t_0}^T \frac{\Delta C_p^o}{R} \frac{dT}{T} \tag{3-14}
\]

Finally, based on the definition of the Gibbs free energy (Eq. 3-15), the standard Gibbs free energy change of reaction would be as Eq. 3-16:

\[
\Delta G^o = \Delta H^o - T \Delta S^o \tag{3-15}
\]

\[
\Delta G^o = \Delta H^o_0 - \frac{T}{T_0} (\Delta H^o - \Delta G^o_0) + R \int_{t_0}^T \frac{\Delta C_p^o}{R} \frac{dT}{T} - RT \int_{t_0}^T \frac{\Delta C_p^o}{R} \frac{dT}{T} \tag{3-16}
\]

The equilibrium constant is also related to the composition of the reacting system. The uniformity of temperature, pressure and chemical potential of each component throughout all the coexisting phases at equilibrium leads to (Smith et al., 2005):

\[
\sum_i \nu_i \mu_i = 0 \tag{3-17}
\]

According to the definition of the fugacity of a species in solution:

\[
\mu_i = \Gamma_i(T) + RT \ln \hat{f}_i \tag{3-18}
\]

For pure species \(i\) in its standard state at the same temperature, this equation reduces to:

\[
G_i^o = \Gamma_i(T) + RT \ln f_i^o \tag{3-19}
\]

The difference between these two equations gives:

\[
\mu_i - G_i^o = RT \ln \frac{\hat{f}_i}{f_i^o} \tag{3-20}
\]

Combining the Eq. (3-17) with Eq. (3-18) and using the definition of equilibrium constant (Eq. (3-10)), result in:

\[
\prod_i (\hat{f}_i / f_i^o)^{\nu_i} = K \tag{3-21}
\]
Defining the fugacity as Eq. (3-22), Eq. (3-21) is written as Eq. (3-23) for a gas phase, provided that the standard state for a gas is the ideal-gas state of the pure gas at the standard-state pressure \( P^0 \) of 1 bar.

\[
\hat{f}_i = \phi_i y_i P
\]  
(3-22)

\[
\prod_i (y_i \phi_i)^{\gamma_i} = \left( \frac{P}{P^0} \right)^{v_i} K
\]  
(3-23)

For a reaction occurring in the liquid phase, the fugacity of a species in solution is related to its fugacity \( f_i \) in the pure state at the temperature and pressure of the equilibrium mixture as follow:

\[
\hat{f}_i = \gamma_i x_i f_i
\]  
(3-24)

The fugacity ratio in Eq. (3-21) can now be expressed as:

\[
\frac{\hat{f}_i}{f_i^0} = \frac{\gamma_i x_i f_i}{f_i^0} = \gamma_i x_i \left( \frac{f_i}{f_i^0} \right)
\]  
(3-25)

Where, this ratio is approximated as:

\[
\ln \frac{f_i}{f_i^0} = \frac{V_i (P - P^0)}{RT}
\]  
(3-26)

Finally, combining equations (3-25) and (3-26) with Eq. (3-21) yields:

\[
\prod_i (x_i \gamma_i)^{v_i} = K \exp \left[ \frac{(P^0 - P)}{RT} \sum_i (v_i V_i) \right]
\]  
(3-27)

When there are two or more independent chemical reactions in a system, the equilibrium composition can be found by extension of the methods developed for single reactions. In this case, a separate equilibrium constant is evaluated for each reaction \( j \):
In equations (3-23) and (3-27), the mole fractions may be eliminated in favour of
the equilibrium value of the reaction coordinate according to equation (3-9). This results
in a system of non-linear algebraic equations where the number of equations needed to be
solved is equal to the number of reactions considered in the system.

It should be noted that while equilibrium analysis is useful and has broad
applicability, particularly where there is no kinetic data available, the assumption of
chemical equilibrium may skew the predictions. As such, in addition to equilibrium
analysis, a simulation of the reaction rates of published reactions involving the species of
interest is performed in the developed model. This is combined with the equilibrium
analysis of the reacting species to give a more complete picture of the reaction pathways
in the reservoir. Ideally, only the kinetic rates would be necessary to model the system,
however, given the lack of reaction rate data on key species identified by field and lab
data, the inclusion of both types of analyses is necessary.

3.3. Analysis of sulfur species reactivity

The type of the chemical interactions between substances in a reacting system is essential
as they control the development of the chemical composition of the system. Some of
these reactions occur quickly resulting in the reacting system being under local chemical
equilibrium. These reactions are handled through a set of nonlinear algebraic equations
(Grove and Wood, 1979; Miller and Benson, 1983; Yeh and Tripathi, 1989). Other
reactions, however, occur at a slower rate. Under these conditions, kinetically-controlled
reactions become important when they are fast enough to change the composition of the environment, but cannot be assumed to reach chemical equilibrium.

Various reactive-transport models that consider both equilibrium and kinetic reactions have been developed for simulating subsurface aqueous reacting systems (Grove and Wood, 1979; Miller and Benson, 1983; Walsh et al., 1984; Yeh and Tripathi, 1989; Steefel and Lasaga, 1994; Wernberg, 1998; Robinson et al., 2000; Yeh et al., 2001b; Regnier et al., 2002; Steefel et al., 2005; Zhang et al., 2007; Berk et al., 2015). The kinetic reactions are modeled on the principle of conservation of mass resulting in a system of partial differential equations (PDEs), while the equilibrium reactions are modeled based on equilibrium expression governed by mass action equilibrium equations resulting in a system of non-linear algebraic equations (AEs). These reactive models can be solved through different approaches (Yeh and Tripathi, 1989; Wernberg, 1998; Regnier et al., 2002): 1) considering the system as a set of simultaneous mixed differential and algebraic equations, 2) direct substitution of non-linear chemical reactions into the differential equations and reducing the system to a set of non-linear PDEs, and 3) treating the system as two coupled sequential sets of linear PDEs and non-linear AEs. It has been shown that the last method uses less CPU time and memory (Yeh and Tripathi, 1989). The elimination of equilibrium reactions from the partial differential equations also allows for robust and efficient numerical integration (Zhang et al., 2007). The partial differential equations can be discretized in space to result in a set of ordinary differential equations. The concentration of each species at all nodes is then obtained through applying the non-linear AEs to the spatial nodes.
The behaviour of a multi-component reacting system could be studied through considering the system as a plug flow reactor within which the concentration of species vary with time and position (Figure 3.1). Assuming that the fluid is perfectly mixed in the radial direction, the fluid flowing through a plug flow reactor is considered as a series of infinitely thin plugs travelling in the axial direction.

\[
\frac{\partial C_i}{\partial t} = - \frac{\partial (uC_i)}{\partial x} - \frac{\partial J_i}{\partial x} + r_i \tag{3-29}
\]

Where, \( r_i \) is the rate of chemical reaction of species \( i \) and \( J_i \) is the molar flux of species \( i \) which specifies the diffusion of each species. Under steady-state conditions and assuming that the composition of the reacting system is mainly controlled by convection, the above equation would be as:

\[
0 = - \frac{\partial (uC_i)}{\partial x} + r_i \tag{3-30}
\]

Finally, the mole balance for each component in a plug flow reactor model, assuming constant velocity, is given by the following differential equation:

\[
u \frac{d(C_i)}{dx} = r_i \tag{3-31}
\]

Where, \( u \) is the fluid velocity.

Assuming that the sulfur reactions occur only in the aqueous phase, this equation leads to a system of ordinary differential equations for each species which can be solved numerically. Solving the system of differential equations requires the knowledge of rates of reactions for each chemical species in the reacting system. The chemical reactions
associated with souring as a result of injection of sulfate-containing seawater at low to moderate temperatures are introduced in Chapter 2.

![Fig. 3-1: A schematic diagram of a plug flow reactor](image)

The distance between injection and production is represented as a series of elements and within each element the temperature and pressure are varied. Concentration of each component is calculated by solving the system of differential equations in the first element. However, not all reactions that could occur have published reaction rate equations, therefore where there are reaction rate data gaps, it is assumed the reaction is governed by equilibrium. This ensures we include compounds present in the fluid. After the reaction rate equations are solved, the equilibrium-governed reactions are modeled through solving the system of non-linear equations to get the final concentrations exiting the first element. The equilibrium and kinetic reactions are outlined in Tables 3-1 and 3-2, respectively. These reactions were selected based on first a comprehensive literature review followed by a screening based on equilibrium analysis.
Table 3-1: Equilibrium reactions of sulfur-containing compounds considered in this study (Miranda-Trevino et al., 2013; Wilkin and Barnes, 1996; Moses et al., 1987; Lin et al., 2004; Machel, 1987; Heinen and Lauwers, 1996; Zhang and Millero, 1993, 1991; Zhao et al., 2007; TengShui et al., 2009; Zhang and Jeffrey, 2010)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>pH</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2S \leftrightarrow H^+ + HS^-$</td>
<td>5-8</td>
<td>-</td>
</tr>
<tr>
<td>$HS^- \leftrightarrow H^+ + S^{2-}$</td>
<td>&gt;7</td>
<td>-</td>
</tr>
<tr>
<td>$S_2O_3^{2-} + H_2O \rightarrow H_2S + SO_4^{2-}$</td>
<td>12</td>
<td>&gt;70</td>
</tr>
<tr>
<td>$S_2O_5^{2-} + 2O_2 + H_2O \rightarrow 2SO_4^{2-} + 2H^+$</td>
<td>&gt;7</td>
<td>25</td>
</tr>
<tr>
<td>$nS^{2-} + 2(n-1)H_2O \rightarrow S_n^{2-} + 2(n-1)OH^- + (n-1)H_2$</td>
<td>&gt;7</td>
<td>&gt;70</td>
</tr>
<tr>
<td>$HS^- + 2Fe^{3+} \rightarrow 1/8S_8 + H^+ + 2Fe^{2+}$</td>
<td>5-8</td>
<td>-</td>
</tr>
<tr>
<td>$S_n^{2-} + 3/2O_2 \rightarrow S_2O_3^{2-} + [(n-2)/8]S_8$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$S_2O_6^{2-} + 2OH^- \rightarrow S_2O_3^{2-} + SO_4^{2-} + 2H_2O$</td>
<td>&gt;7</td>
<td>-</td>
</tr>
<tr>
<td>$HS^- + SO_3^{2-} + 0.5O_2 \rightarrow S_2O_3^{2-} + OH^-$</td>
<td>5-8</td>
<td>-</td>
</tr>
<tr>
<td>$nHS^- + (n-1)/2O_2 \rightarrow S_n^{2-} + H_2O + (n-2)OH^-$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$4S_2O_6^{2-} + 4H_2O \rightarrow 6S_2O_3^{2-} + S_3O_6^{2-} + SO_4^{2-} + 8H^+$</td>
<td>&lt;7</td>
<td>25-70</td>
</tr>
<tr>
<td>$S_2O_5^{2-} + O_2 \rightarrow S_4O_6^{2-} + SO_3^{2-}$</td>
<td>&lt;7</td>
<td>25</td>
</tr>
<tr>
<td>$3S_2O_6^{2-} \rightarrow S_4O_6^{2-} + 1/8S_8 + 2SO_4^{2-} + 2SO_2$</td>
<td>4</td>
<td>35</td>
</tr>
<tr>
<td>$HS^- + 2O_2 \rightarrow SO_4^{2-} + H^+$</td>
<td>8</td>
<td>10</td>
</tr>
</tbody>
</table>
It should be noted that the purpose of this study is not to mimic reservoir conditions as a function of distance, but rather to observe the effects of temperature and pressure at reservoir conditions on the speciation of the products. As such, initially two sets of studies are performed. One where temperature is held constant at the production well condition (i.e., 65°C) and pressure varied from 15-35 MPa and repeated at temperature of injection well (i.e., 85°C). These temperatures and pressures are chosen for as they represent the range of conditions in the reservoir (Stemler, 2012).
methodology proposed can be modified based on specified conditions. A second set of studies is conducted where the pressure is held constant at 35 MPa and temperature varied from 65-85°C, then the pressure is decreased to 15 MPa and the simulation repeated. Based on these results, a determination of the relative impact of temperature and pressure can be assessed. The same procedure is followed at lower temperature and pressure values (down to 15°C and 1 MPa) to investigate sulfur speciation from wellbore to surface facilities.

Table 3.3 summarizes the initial conditions used in the current model. It is assumed the initial H$_2$S is the result of complete conversion of sulfate in the seawater (at average seawater value of 2454 mg/L) by sulfate reducing bacteria and archaea. Since the redox reactions involving sulfur species include electron transfer, the system needs to be electroneutral (Wernberg, 1998). As a result, the electron in each redox reaction is considered to be in the aqueous phase. The HSC Chemistry 9.0 database is used for heat capacity and critical data for each sulfur species (Roine and Anttila, 2006).

<table>
<thead>
<tr>
<th>Table 3- 3: Initial and reservoir conditions for studying H$_2$S partitioning behaviour (Stemler, 2012)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pressure (MPa)</strong></td>
</tr>
<tr>
<td><strong>Temperature (°C)</strong></td>
</tr>
<tr>
<td><strong>Oil API gravity</strong></td>
</tr>
<tr>
<td><strong>Gas-oil ratio</strong></td>
</tr>
<tr>
<td><strong>Water-cut (%)</strong></td>
</tr>
<tr>
<td><strong>Water production (m$^3$/d)</strong></td>
</tr>
<tr>
<td><strong>Distance from injection to producer (m)</strong></td>
</tr>
<tr>
<td><strong>H$_2$S (based on sulfate concentration in seawater concentration of 2454 mg/L) (mg/L)</strong></td>
</tr>
<tr>
<td><strong>Test separator pressure (kPa)</strong></td>
</tr>
<tr>
<td><strong>Test separator temperature (°C)</strong></td>
</tr>
</tbody>
</table>
Investigating the sulfur chemistry in reservoirs undergoing seawater flooding is conducted as summarized in Figure 3.2:

1) Equilibrium analysis

**Gibbs energy minimization**

to identify key sulfur species involved in reservoir souring and perform equilibrium analysis for determining the types, concentrations and partitioning behavior of sulfur species present as a result of injection of sulfate-containing seawater in a reservoir as a function of temperature, pressure and pH

2) Analysis of sulfur species reactivity

Kinetic study to obtain the chemical composition of the reacting system in kinetic reactions

**Gibbs reaction minimization**
to study the chemical reactivity of sulfur species in equilibrium reactions

Develop a reactive model consisting of both equilibrium and kinetic reactions of sulfur species to investigate the sulfur chemistry as result of injection of sulfate-containing seawater in reservoirs

Fig. 3-2: A schematic diagram of the algorithm followed in this study to investigate sulfur chemistry in a reservoir undergoing seawater injection process
3.4. Model evaluation

The numerical approach of coupling the chemical equilibrium and kinetic reactions was compared with a reactive-transport multicomponent multiple reactions MIN3KIN model developed by Wernberg (Wernberg, 1998). The MIN3KIN is a two-dimensional reactive-transport model code coupled with chemical equilibrium and kinetic reactions code, however it does not include partitioning of compounds between phases. Therefore, as an example, a case study of groundwater with a composition with Ca$^{2+}$ (3.55 mM), CO$_3^{2-}$ (0.0325 mM), SO$_4^{2-}$ (0.55 mM), and NO$_3^-$ (2.5 mM) at 10$^\circ$C at 1 bar in a 10 m long vertical cross section was modeled based on the chemical reactions summarized in Table 3-4.
Table 3-4: Chemical equilibrium and kinetic reactions considered in the reacting system (Wernberg, 1998)

<table>
<thead>
<tr>
<th>Chemical kinetic reactions</th>
<th>Rate Coefficient</th>
<th>Rate order</th>
</tr>
</thead>
<tbody>
<tr>
<td>$4NO_3^- + S_2O_3^{2-} + H_2O \rightarrow 4NO_2^- + 2SO_4^{2-} + 2H^+$</td>
<td>$10^3 \text{ mol}^{-1} \text{yr}^{-1}$</td>
<td>$[\text{NO}_3^-][\text{S}_2\text{O}_3^{2-}]$</td>
</tr>
<tr>
<td>$4FeS_2(s) + 14 NO_2^{2-} + 6H^+ + 3H_2O \rightarrow 4S_2O_3^{2-} + 4Fe(OH)_3(s) + 7N_2O(g)$</td>
<td>4.0 yr$^{-1}$</td>
<td>$[\text{NO}_2^-][\text{FeS}_2(s)]$</td>
</tr>
</tbody>
</table>

**Chemical equilibrium reactions**

- $OH^- + H^+ \rightarrow H_2O$
- $FeOH^{2+} + 2H^+ \rightarrow Fe^{3+} + 2H_2O$
- $FeOH_{3(aq)}^- + 3H^+ \rightarrow Fe^{3+} + 3H_2O$
- $FeOH_{4}^- + 4H^+ \rightarrow Fe^{3+} + 4H_2O$
- $CaHCO_{3}^+ \rightarrow CO_{3}^{2-} + H^+ + Ca^{2+}$
- $H_2CO_{3(aq)}^+ \rightarrow CO_{3}^{2-} + 2H^+$
- $HCO_{3}^- \rightarrow CO_{3}^{2-} + H^+$
- $HSO_{4}^- \rightarrow SO_{4}^{2-} + H^+$
- $CaCO_{3(aq)} \rightarrow Ca^{2+} + CO_{3}^{2-}$
- $CaSO_{4(aq)} \rightarrow Ca^{2+} + SO_{4}^{2-}$
- $4S_4O_6^{2-} + 3Fe^{3+} + 2.75O_2 + 4.5H_2O \rightarrow 4SO_4^{2-} + 3Fe^{2+} + 9H^+$

The MIN3KIN results (Wernberg, 1998) are compared with our proposed model in Figure 3.3. The proposed model agrees well with MIN3KIN model.
Fig. 3-3: Concentration profiles for a) nitrate and sulfate, b) nitrite and thiosulfate for the aquifer and comparison with MIN3KIN model (Wernberg, 1998)
The developed model is capable of predicting the overall concentration trends of chemical compounds considered in the system compared to the analytical MIN3KIN model with the maximum deviation calculated as 48% which could be due to the difference in the database used for the chemical compounds. It should also be noted that the transportation of chemical species is not considered in the current study. However, the overall trends match well and therefore the model was used to investigate the sulfur speciation in a soured reservoir considering the occurrence of chemical equilibrium and kinetic reactions associated with the sulfate-containing seawater at low to moderate temperatures.
References


Lin, H., Li, Z., Tohji, K., Tsuchiya, N., Yamasaki, N., Reaction of Sulfur with Water under Hydrothermal Conditions, in 14th International Conference on the Properties of Water and Steam in Kyoto.


CHAPTER FOUR

EQUILIBRIUM ANALYSIS
4.1. Overview
The first step in studying sulfur chemistry is to investigate the partitioning behaviour of the various sulfur species present as a function of temperature, pressure, and pH. This can be accomplished through equilibrium analysis to determine partition coefficients in a multi-phase, multi-component system. The equilibrium analysis assumes that all reactions go to completion and there is no kinetic limitations.

4.2. Equilibrium analysis for investigating the partitioning behaviour of sulfur species
Sulfur intermediates such as elemental sulfur, polythionates, polysulfides, and sulfite have been detected in several produced waters and are important as there is potential for H$_2$S production, corrosion, and scaling. They can also be further oxidized to form sulfuric acid leading to low pH and increased corrosion rates (Salanitro and Khatib, 1997; Xu and Schoonen, 1995; Miranda-Trevino et al., 2013). These issues highlight the importance of studying sulfur chemistry in reservoirs undergoing recovery operations.

In order to identify the possible sulfur compounds that may be present during seawater injection and investigate their partitioning behaviour, sulfur speciation in an aqueous phase in the presence of a hydrocarbon-rich phase has been studied as a function of temperature, pressure and pH using Outotec's HSC Chemistry software. The Gibbs free energy minimization method, described in Chapter 3, is used to find the most probable chemical system at steady state. A sample seawater containing 2454 mg/L sulfate is considered in contact with an oil phase with API gravity of 34 (Table 3.3). Based on literature, sulfur species with different valence states including, sulfate,
elemental sulfur, sulfite, polysulfides ($S_2^{2-}$, $S_3^{2-}$, $S_4^{2-}$, $S_5^{2-}$), polythionates ($S_2O_5^{2-}$, $S_3O_6^{2-}$, $S_4O_6^{2-}$, $S_5O_6^{2-}$), and sulfides ($H_2S$, $HS^-$, $S^{2-}$) are considered in this system to investigate sulfur chemistry during production as a function of temperature, pressure and pH.

It is assumed that the oil and water phases are flowing from injection to the production well and temperature and pressure vary accordingly. The temperature and pressure ranges considered are summarized in Table 3.3. These ranges are chosen for as they represent the range of conditions in the reservoir (Stemler, 2012). For the purpose of this study and to observe the effects of temperature and pressure on sulfur speciation, a simple linear relationship between temperature and pressure is considered as the reservoir fluid moves from injection well to topside processing facilities. Therefore, the relative impact of temperature and pressure can be assessed.

Above bubble point pressure (15 MPa), no separate gas phase is formed. The equilibrium composition of this system as temperature changes is shown in Figure 4.1.
Fig. 4-1: Concentration profile of sulfur species under equilibrium conditions  a) above bubble point pressure (P: 25 MPa), b) below bubble point pressure (P: 1 MPa) 
(◊, ○, □, ∆ from right axis; ♦, ■, ▲, ✗ from left axis)
Above the bubble point pressure and at high temperatures (higher than the production well temperature), sulfate and polythionates are the dominant sulfur species in the aqueous phase (Figure 4.1(a)). Among polythionates, thiosulfate is the major component and a small amount of sulfur (less than 1%) is present as trithionate and teterathionate. Hydrogen sulfide is more soluble in oil than in water and therefore, is mostly found in the hydrocarbon-rich phase. A fraction of initial sulfur (approximately 10%) is formed as elemental sulfur and is found as a separate solid phase. A similar speciation behaviour is observed below bubble point pressure and at low temperatures (below 60°C), where one would expect the formation of a gas phase (Figure 4.1(b)). Under these conditions, molecular H₂S partitions between oil, water, and gas phases.

The equilibrium composition of this reacting system as a function of pressure is shown in Figure 4.2.
Fig. 4-2: The effect of pressure on sulfur speciation

(a) no separate gas phase (T: 75°C)
(b) gas phase is formed (T: 25°C)

(◊, ○, □, ∆ from right axis; ♦, ■, ▲, × from left axis)
It can be concluded that the pressure does not have a significant effect on the equilibrium composition below the bubble point. Sulfate, polythionates, hydrogen sulfide in the oil phase, and elemental sulfur in the solid form are the major sulfur species above bubble point pressure (Figure 4.2(a)). At pressures lower than the bubble point pressure and at low temperatures, however, most of the initial sulfur is formed as hydrogen sulfide in the oil phase (Figure 4.2(b)). Based on the results, the presence of different sulfur species with different valence states affect the partitioning behaviour of H$_2$S in a multi-phase system in that a significant amount of aqueous H$_2$S might be formed as sulfate and polythionates resulting in less H$_2$S partitioning to other phases.

The effect of pH on the partitioning behaviour of sulfur species below and above the bubble point pressure is shown in Figure 4.3.
Fig. 4-3: The effect of pH of the solution on sulfur speciation a) above bubble point pressure (T: 75°C, P: 20 MPa), b) below bubble point pressure (T: 25°C, 1 MPa), (◊, ○, □, △ from right axis; ♦, ■, ▲, × from left axis)
As was expected, sulfur speciation is significantly influenced by the pH of the solution. Increasing the pH from acidic to basic is accompanied with the formation of polysulfides. At low pH values, H\(_2\)S exists in the molecular form and partitions between oil, water and gas phases below bubble point pressure. It is, however, dissociated to sulfide and bisulfide with increasing the pH resulting in the decrease in the H\(_2\)S content of all phases in equilibrium. In addition, one would expect a decrease in the formation of solid elemental sulfur under basic conditions. Polythionates are the major sulfur species below and above the bubble point pressure.

Based on the equilibrium analysis, the sulfur oxyanions primarily remain in the aqueous phase, while H\(_2\)S and elemental sulfur are distributed between phases. Therefore, there is a need to investigate the partitioning behaviour of these components in order to couple the results of equilibrium analysis with the reactivity model.

4.3. **Equilibrium analysis for studying H\(_2\)S partitioning behaviour in a multi-phase system**

Upon formation, H\(_2\)S could partition to the gas, water or oil phases depending on pressure, temperature and/or composition. As such a 3-phase flash partitioning model is developed to study the phase partitioning behaviour of H\(_2\)S in a multi-phase system.

Several models have been developed to predict the partitioning behaviour of H\(_2\)S in reservoir fluids and to investigate the effects of temperature, pressure, fluids composition, ionic strength, and water pH on the H\(_2\)S mass production rate (Eden et al., 1993; Schofield and Stott, 2012; Ligthelm et al., 1991; Burger et al., 2005; King and Al-Najjar, 1977; Sunde et al., 1993; Tyrie and Ljosland, 1993). Carroll and Mather presented
a model taking into account the non-ideality of the vapor phase to determine the solubility of $\text{H}_2\text{S}$ in water at pressures up to 1 MPa (Carroll and Mather, 1989). They did not, however, consider the non-idealities in the liquid phase and assumed that the Henry's law could be applied. This assumption is only valid at low pressures (usually less than 1 MPa). Therefore, the extended form of Henry's law is used in this study.

The solubility of molecular $\text{H}_2\text{S}$ in water at high pressures and high solute concentrations is determined through a complete form of Henry's law as follow:

$$y_{i} \phi_{i} P = x_{i} y_{i} H_{i} \exp \left( \frac{V_{i}^{\infty} (P - P_{i}^{\text{sat}})}{RT} \right)$$  \hspace{1cm} (4-1)

Where, $H$ is the Henry's constant which is a function of temperature and the solute-solvent pair.

For hydrogen sulfide, the partial molal volume at infinite dilution ($V_{i}^{\infty}$) in water is approximately 35 cm$^3$/mol. The Henry's law constant for $\text{H}_2\text{S}$ in water in the temperature range of 0 to 90°C, based on the study of Carroll and Mather (1989), was calculated according to the following equation used by Burger et al. (2013):

$$\ln H_{\text{H}_2\text{S},\text{water}} = 315.722 + 0.05303T - 12224.4 / T - 49.7825 \ln T$$  \hspace{1cm} (4-2)

The equality of fugacity of each species in all phases at equilibrium is also used for evaluating the distribution of $\text{H}_2\text{S}$ between oil and water phases and the SRK equation of state is used for calculating the fugacity coefficients of species in the non-aqueous phases (Burger et al., 2013).

- Salting-out effect
The solubility of dissolved gases in a salt solution decreases as the ionic salts 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):

\[
\log \left( \frac{S_0}{S_s} \right) = kI
\]  

(4- 3)

The salting-out coefficients for hydrogen sulfide in sodium chloride can be obtained as a function of temperature as follows (Millero, 1986):

\[
10^3k = 65.3214 - 0.41302T + 6.6066 \times 10^{-4}T^2
\]  

(4- 4)

--- Ionization

The dissolution of H\(_2\)S in water involves a series of chemical reactions: the dissociation of the molecular H\(_2\)S to bisulfide and sulfide ions and the self-ionization of water (Burger *et al.*, 2013):

\[
\begin{align*}
H_2S_{(aq)} & \rightleftharpoons K_1 HS^- + H^+ \\
HS^- & \rightleftharpoons K_2 S^{2-} + H^+ \\
H_2O & \rightleftharpoons K_3 OH^- + H^+
\end{align*}
\]  

(4- 5)  

(4- 6)  

(4- 7)

The equilibrium relation, the so-called "mass action" relations, for each of these reactions are given as:

\[
K_1 = \frac{a_{HS^-}a_{H^+}}{a_{H_2S_{(aq)}}} = \frac{\gamma_{HS^-}\gamma_{H^+}}{\gamma_{H_2S_{(aq)}} m_{H_2S_{(aq)}}}
\]  

(4- 8)

\[
K_2 = \frac{a_{S^{2-}}a_{H^+}}{a_{HS^-}} = \frac{\gamma_{S^{2-}}\gamma_{H^+}}{\gamma_{HS^-} m_{HS^-}}
\]  

(4- 9)

\[
K_3 = \frac{a_{OH^-}a_{H^+}}{a_{H_2O}} = \frac{\gamma_{OH^-}\gamma_{H^+}}{\gamma_{H_2O} m_{H_2O}}
\]  

(4- 10)
The activity coefficients in solution where the concentration of ionic species is low is estimated by Debye-Huckel's law:

$$\ln \gamma_i = A|z_i|\sqrt{I}$$  \hspace{1cm} (4-11)

Where, $A$ is the Debye-Huckel constant, $z_i$ is the charge on the ion and the ionic strength ($I$) is calculated as follow:

$$I = 1/2 \sum m_i z_i^2$$  \hspace{1cm} (4-12)

The Debye-Huckel constant is independent of the solute and is derived from the physical properties of the solvent. For water at 25°C its value is -1.17 (Burger et al., 2013).

The total hydrogen sulfide concentration in the aqueous solution is typically obtained from the summation of the concentrations of the various sulfide species:

$$t_{H_2S(aq)} = m_{H_2S(aq)} + m_{HS^-} + m_{S^{2-}}$$  \hspace{1cm} (4-13)

Finally, the concentration of $H^+$ ion is obtained from the definition of pH of the solution:

$$pH = -\log(a_{H^+}) \approx -\log(m_{H^+})$$  \hspace{1cm} (4-14)

The Henley-Rosen algorithm is used to solve the above mentioned 3-phase flash separation. The overall mass balance in the system is given by:

$$F = V + L_1 + L_2$$  \hspace{1cm} (4-15)

$F$, $V$, and $L$ are the flow rates of feed stream, vapor-phase, and liquid-phases, respectively. For each component the mass balance is:

$$z_i F = y_i V + x_i^{L1} L_1 + x_i^{L2} L_2$$  \hspace{1cm} (4-16)

The phase splits can be defined as equations (4-17) and (4-18):

$$\Psi = \frac{V}{F}$$  \hspace{1cm} (4-17)
\[ \xi = \frac{L_1}{L_1 + L_2} \quad (4-18) \]

At equilibrium, the relationship between the components in the three phases are given by the equilibrium ratios as:

\[ K_i^1 = \frac{y_i}{x_i^{L_1}} \quad (4-19) \]

\[ K_i^2 = \frac{y_i}{x_i^{L_2}} \quad (4-20) \]

The composition of the three phases can then be calculated as follows:

\[ y_i = \frac{z_i}{\xi(1 - \Psi) + \frac{(1 - \Psi)(1 - \xi)}{K_i^1} + \Psi} \quad (4-21) \]

\[ x_i^{L_1} = \frac{z_i}{\xi(1 - \Psi) + (1 - \Psi)(1 - \xi) \left( \frac{K_i^1}{K_i^2} \right) + \Psi K_i^1} \quad (4-22) \]

\[ x_i^{L_2} = \frac{z_i}{\xi(1 - \Psi) \left( \frac{K_i^2}{K_i^1} \right) + (1 - \Psi)(1 - \xi) + \Psi K_i^2} \quad (4-23) \]

Applying the summation rule \( \sum_i x_i^{L_1} = \sum_i x_i^{L_2} = \sum_i y_i = 1 \), the two Henley-Rosen equations should be solved are:

\[ \sum_i \frac{z_i(1 - K_i^1)}{\xi(1 - \Psi) + (1 - \Psi)(1 - \xi) \left( \frac{K_i^1}{K_i^2} \right) + \Psi K_i^1} = 0 \quad (4-24) \]
These two equations are solved simultaneously by Newton-Raphson method to calculate the two unknowns $\Psi$ and $\xi$.

The amount of molecular $\text{H}_2\text{S}$ in each phase can be determined based on the Henley-Rosen algorithm as shown in Figure 4.4. Once the amount of molecular $\text{H}_2\text{S}$ in each phase is obtained, the impacts of salting-out and ionization should also be taken into account to determine the total concentration of hydrogen sulfide (Figure 4.5).
Fig. 4- 4: The Henley-Rosen algorithm for studying H2S partitioning behaviour

Start

Input data \( z_i, T, P \), component properties, guessed values for \( K_i \)

Set all \( \phi_i = 1.0 \)
Set all \( \gamma_i = 1.0 \)

Correct \( \Psi, \xi \) from Eq. (4-17), (4-18)

Calculate composition of phases from Eq. (4-21)-(4-23)

Calculate fugacity coefficient of each species from SRK EOS

Yes

Is

\[ K_i^1 = \frac{\phi_i^{L_2}}{\phi_i^v} \]
and
\[ K_i^2 = \frac{\phi_i^{L_2}}{\phi_i^v} \]

No

Results - \( x_i^{L_1}, x_i^{L_2}, y_i, V, L_1, L_2 \)

End
Fig. 4-5: The general algorithm for studying H\textsubscript{2}S partitioning behaviour considering ionization reactions

- **Start**
  - Input data \(m_{\text{H}_2\text{S}}, \text{pH}, k_1, k_2, k_3\) (equilibrium constants for H\textsubscript{2}S ionization reactions)
  - Obtain \(y_{\text{H}_2\text{S}}\) from Henry's law
  - Set other \(y_i = 1.0\)

- **Obtain** \(y_{\text{H}_2\text{S}}\) from Henry's law
  - Set other \(y_i = 1.0\)

- **Calculate** \(m_{\text{H}_2\text{S}}\) and \(m_{\text{H}_2\text{O}}\) from Eqs. (4-8), (4-9)
  - Calculate \(m_{\text{H}_2\text{O}}\) according to the pH of the solution

- **Calculate** ionic strength from Eq. (4-12)

- **Calculate** the activity coefficient of each species according to the Debye-Hückel's law

- **Is** \(y_{i,\text{new}} = y_{i,\text{old}}\)

- **Yes**
  - Calculate the final aqueous-phase concentration of H\textsubscript{2}S from Eq. (4-13)

- **End**
During oil production, both temperature and pressure decrease resulting in a change in sulfur solubility in the aqueous phase and therefore, possible sulfur deposition. An equilibrium analysis is therefore performed as follow to investigate the partitioning behaviour of elemental sulfur.

4.4. **Equilibrium analysis for determining elemental sulfur deposition**

The solubility of sulfur in solution is mainly controlled by temperature and pressure and it has been shown that high bottom hole temperatures and low wellhead pressures provide favourable 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; Kuo and Colsmann, 1966).

In order to determine the amount of sulfur precipitated during recovery operations, there is a need to evaluate the maximum amount of sulfur dissolved in the aqueous phase at different reservoir temperatures and pressures. For this purpose, the equilibrium of a pure solid sulfur with a binary liquid mixture containing sulfur (species 1) and water (species 2) was considered (Smith *et al*., 2005):

\[ f_i^s = f_i^l \]  \hspace{1cm} (4- 26)

The fugacity of the solid can be written as follow:

\[ f_i^s = \phi_i^{sat} P_i^{sat} \exp \frac{V_i^s (P - P_i^{sat})}{RT} \]  \hspace{1cm} (4- 27)

Where, \( P_i^{sat} \) is the saturation vapor pressure at temperature \( T \) and \( V_i^s \) is the molar volume of the solid. The fugacity of the solute in the liquid phase is related to its mole fraction:
\( \hat{f}_i' = x_i \hat{\phi}_i P \)  \hspace{1cm} (4-28)

Finally, the sulfur solubility in water can be calculated by combining the three preceding equations:

\[
x_i = \frac{P_{i,\text{sat}}}{P} F_i
\]  \hspace{1cm} (4-29)

Where,

\[
F_i = \frac{\phi_i^{\text{sat}}}{\hat{\phi}_i} \exp \left( \frac{V_i^{\text{sat}}(P - P_{i,\text{sat}})}{RT} \right)
\]  \hspace{1cm} (4-30)

In this equation, the quantity \( \hat{\phi}_i \) could be computed from a PVT equation of state such as PR:

\[
\ln \hat{\phi}_i = \frac{b_i}{b} (Z - 1) - \ln(Z - \beta) - \bar{q}_i I
\]  \hspace{1cm} (4-31)

Where:

\[
\bar{q}_i = q \left( 1 + \frac{\overline{a}_i}{a} - \frac{b_i}{b} \right)
\]  \hspace{1cm} (4-32)

\[
\overline{a}_i = -a + 2 \sum_j x_j a_{ji}
\]  \hspace{1cm} (4-33)

Evaluation of parameters \( a_i \) and \( b_i \) requires values for \( T_{ci} \), \( P_{ci} \), and \( \omega_i \) which can be found in a handbook or from literature.

\[
a_i(T) = \Psi \frac{\alpha(T, \omega_i) R^2 T_{ci}^2}{P_{ci}}
\]  \hspace{1cm} (4-34)

\[
b_i = \Omega \frac{RT_{ci}}{P_{ci}}
\]  \hspace{1cm} (4-35)

\[
\beta_i = \frac{b_i P}{RT}
\]  \hspace{1cm} (4-36)
\[ q_i = \frac{a_i(T)}{b_iRT} \quad (4-37) \]

Finally:

\[ I = \frac{1}{\sigma - \varepsilon} \ln \left( \frac{Z + \sigma \beta}{Z + \varepsilon \beta} \right) \quad \varepsilon \neq \sigma \quad (4-38a) \]

\[ I = \frac{\rho b}{1 + \varepsilon \rho b} = \frac{\beta}{Z + \varepsilon \beta} \quad \varepsilon = \sigma \quad (4-38b) \]

Written for species \( i \) as a liquid:

\[ Z_i = \beta_i + (Z_i^i + \varepsilon \beta_i)(Z_i^i + \sigma \beta_i) \left( \frac{1 + \beta_i - Z_i^i}{q_i \beta_i} \right) \quad (4-39) \]

Once the amount of sulfur generated during kinetic and equilibrium reactions is obtained, one would be able to compute the amount of sulfur deposited as temperature and pressure change during production through evaluating the solubility of sulfur in the aqueous phase and subtracting the value from the corresponding value of elemental sulfur formed.

### 4.5. H\(_2\)S partitioning behaviour in a multi-phase system

The flash-partition model described in Section 4.2.2 is used to demonstrate the effects of temperature, pressure, and pH on the H\(_2\)S partitioning between oil, water and gas. The amount of H\(_2\)S in reservoir fluid as temperature and pressure change from reservoir to topside facilities can then be determined provided the H\(_2\)S concentration in one phase is known (here, the amount of H\(_2\)S in the gas phase under test separator conditions). The H\(_2\)S partitioning behaviour is studied for a sample crude oil of Terra Nova offshore oil fields in Newfoundland and Labrador (Table 3.3) (Stemler, 2012). The H\(_2\)S partition coefficients are calculated and the results are shown in Figures 4.6-4.8.
Fig. 4-6: \( \text{H}_2\text{S} \) oil-water partition coefficients for the conditions in Table 4.1 as a function of a) temperature, b) pressure
Fig. 4-7: H$_2$S gas-water partition coefficients for the conditions in Table 4.1, as a function of a) temperature, b) pressure
Fig. 4-8: H$_2$S gas-oil partition coefficients for the conditions in Table 4.1, as a function of a) temperature, b) pressure
First, the pH of the solution is assumed to be below neutral conditions, so all the initial H$_2$S is in the molecular form and is distributed between phases. The bubble point pressure of the reservoir fluid was calculated to be approximately 15 MPa. Above this pressure, no separate gas phase is evolved and H$_2$S partitions between oil and water. H$_2$S solubility in the hydrocarbon-rich phase is higher than that in the aqueous phase and therefore, above the bubble point pressure, H$_2$S is mostly found in the oil phase ($K_{ow}$). When pressure is decreased and temperature is increased, the gas phase forms and H$_2$S partial pressure increases in the gas phase resulting in an increase in the $K_{gw}$ and $K_{go}$ partition coefficients. $K_{gw}$ was calculated as 10 (ppm in gas/ppm in water) at 15°C and 15 MPa, while at 85°C and 1 MPa it was 220 (ppm in gas/ppm in water). The H$_2$S partition coefficient between oil and water is not significantly influenced by temperature and pressure and varies from 25 (ppm in oil/ppm in water) at 15°C/35MPa, to 35 (ppm in oil/ppm in water) at 85°C/1MPa.

The hydrogen sulfide partition coefficients between oil and water were compared with those measured by Eden et al. (1993) at atmospheric pressure and between 20-90°C (Table 4.1). The measured values of $K_{ow}$ were essentially independent of temperature. As shown in Table 4.1, The model predictions are in good agreement with experimental values. The small difference in K-values between the study of Eden et al. and the current study could be due to the difference in the type of organic compound used (API gravity of 46 in the study of Eden et al. vs. API gravity of 34 in the current study) which affects the solubility of H$_2$S.
Table 4-1: Partition coefficient for the distribution of hydrogen sulfide between oil and water, $K_{ow}$ in ppmw/ppmw, $P=101.3$ kPa

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>30</th>
<th>50</th>
<th>70</th>
<th>90</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental value (Eden et al., 1993)</td>
<td>3.00</td>
<td>3.00</td>
<td>3.1</td>
<td>3.20</td>
</tr>
<tr>
<td>Model results</td>
<td>3.19</td>
<td>3.23</td>
<td>3.28</td>
<td>3.25</td>
</tr>
</tbody>
</table>

Once the pH of the solution is increased from acidic to neutral, $H_2S$ dissociates to bisulfide ($HS^-$) and a small amount of sulfide ($S^{2-}$). A further increase in the pH to basic conditions, is accompanied with an elevation in the proportion of sulfide. This dissociation process, reduces the amount of molecular $H_2S$ in the aqueous phase and therefore, less $H_2S$ is found in the oil and gas phases in equilibrium with the aqueous phase. The effect of pH on the amount of $H_2S$ one would expect in a multi-phase system under test separator conditions is shown in Figure 4.9. It should be noted that the amount of $H_2S$ in the aqueous phase is the summation of all the molecular $H_2S$ and $HS^-$ and $S^{2-}$ ions.
Fig. 4-9: H₂S partitioning behaviour as a function of pH (Test separator conditions)

The amount of H₂S in the gas phase under test separator conditions is the only measurable quantity of the H₂S produced and is used by industry as an indicator of reservoir souring. One might be interested in predicting the amount of H₂S in reservoir fluid during production. The gas phase H₂S concentration at test separator conditions and the values of partition coefficients were therefore, used to determine the H₂S in oil and water phases in equilibrium with the gas phase in topside processing facilities as temperature and pressure change. The same approach was applied to study the H₂S presents in reservoir fluids from injection to production well (Figure 4.10).
Based on the equilibrium analysis, the K-values for H$_2$S partitioning between oil, water, and gas phases were fit to a linear expression as a function of temperature and pressure:

\[
K_{ow(H_2S)} = 4.717 + 0.3096T + 0.6467P \quad (4-40)
\]

\[
K_{gw(H_2S)} = 11.886 + 1.1186T + 1.2523P \quad (4-41)
\]

Where, T is in °C and P is in MPa. The partitioning coefficients calculated in this section for H$_2$S are then used in the plug flow model, described in Chapter 3, to obtain the H$_2$S content of each phase and therefore, the composition of the reacting system at the end of each element. Figure 4.11 illustrates the general steps followed in the reactivity study. The results of sulfur chemistry study are discussed in the next Chapter.

Fig. 4- 10: H$_2$S concentration in a 3-phase system as a function of temperature and pressure
Input data $T$, $P$, pH, initial composition, fluid velocity, rate constant of kinetic reactions

Solve the system of differential equations from Eq. (3-31)

Solve the system of non-linear equations from Eq. (3-27) in which the mole fractions are substituted by reaction coordinate by Eq. (3-9)

Calculate the amounts of $H_2S$ in oil and gas phases according to the flash partitioning method in figures (4-4) and (4-5) and the amount of elemental sulfur deposited as a solid phase as described in section 4.4

This final composition is used as the input for the next element in the reactor

Fig. 4-11: A schematic diagram of the algorithm followed in this study to investigate sulfur reactivity in the plug flow reactor model
4.6. Conclusions

The partitioning behaviour of sulfur species present as a result of seawater injection as a function of temperature and pressure was investigated in this study. The Gibbs energy minimization method was used to find the most probable chemical system at steady state. It was concluded that the pressure did not have a significant effect on the equilibrium composition below the bubble point. Sulfate, polythionates, hydrogen sulfide in the oil phase, and elemental sulfur in the solid form are the major sulfur species above bubble point pressure. At pressures lower than the bubble point pressure and at low temperatures, however, most of the initial sulfur is formed as hydrogen sulfide in the oil phase. Based on the results, the presence of different sulfur species with different valence states affect the partitioning behaviour of $\text{H}_2\text{S}$ in a multi-phase system in that a significant amount of aqueous $\text{H}_2\text{S}$ might be formed as sulfate and polythionates resulting in less $\text{H}_2\text{S}$ partitioning to other phases.

Sulfur speciation is significantly influenced by the pH of the solution. Increasing the pH from acidic to basic is accompanied with the formation of polysulfides. At low pH values, $\text{H}_2\text{S}$ exists in the molecular form and partitions between oil, water and gas phases below bubble point pressure. It is, however, dissociated to sulfide and bisulfide with increasing the pH resulting in the decrease in the $\text{H}_2\text{S}$ content of all phases in equilibrium. In addition, one would expect a decrease in the formation of solid elemental sulfur under basic conditions.

Although identifying key reacting species and the phases involved in a multi-phase, multi-component reacting system could be accomplished through equilibrium
analysis, the assumption of chemical equilibrium may skew the predictions. As such, in
addition to equilibrium analysis for identifying the possible sulfur species as a result of
injection of sulfate-containing seawater in an oil reservoir, a simulation of the reaction
rates of published reactions involving the species of interest is performed to investigate
the full extent of sulfur speciation. This reactivity analysis is the scope of the next
Chapter where a plug flow based reactor model is used for evaluating sulfur speciation in
a multi-phase multi-component reacting system. The reactivity analysis is coupled with
the results of equilibrium analyses of H₂S partitioning and elemental sulfur deposition.
This provides a more complete picture of the reaction pathways in the reservoir.
References


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CHAPTER FIVE

REACTIVITY ANALYSIS
5.1. Overview

The plug flow based reactor model developed in Chapter 3 is used to analyze the reactivity of sulfur species in reservoirs undergoing recovery operations by sulfate-containing seawater injection. This chemical reactivity analysis could help one screen sulfur chemistry during production in soured reservoirs.

5.2. Reactivity analysis for investigating sulfur speciation in reservoirs undergoing seawater injection

According to the results of equilibrium analyses performed and based on the literature, the key reacting species and end-products identified are sulfate, sulfite, sulfide, bisulfide, polythionates including thiosulfate, thronionate, tetrahionate, and pentathionate, polysulfides ($S_n^{2-}, n = 2-5$) and hydrogen sulfide. These compounds have been found to participate in different oxidation-reduction reactions depending on temperature and pH.

The equilibrium and kinetic reactions considered in the model are summarized in Tables 3.1 and 3.2, respectively. The distance from injection to production, as will be discussed later, is divided into 3 elements. Within each element, temperature and pressure are varied to observe the effects of operating conditions on the speciation of products. Similar to the equilibrium analyses, and to observe the effects of temperature and pressure on sulfur speciation, a simple linear relationship between temperature and pressure is considered as the reservoir fluid moves from injection well to topside processing facilities. The plug flow based reactor model is used for simulating those reactions for which there is published kinetic data. Once the concentration of each component is calculated from solving the system of differential equations, the
equilibrium analysis is established by solving the system of non-linear equations to get the final concentrations at the end of each element.

It should be noted that the stability of the numerical method depends on the number of elements considered in the model. As the step sizes increase, the reliability of the results of combining kinetic with equilibrium model decreases. During equilibrium reactions, the concentration of some sulfur species decreases significantly and using these small values in the kinetic component of the model makes the system unstable. It was concluded that the maximum number of 3 elements could be used for simulating the distance from injection to the production. This also leads to less CPU time and memory. In addition, according to the literature, in high temperature anaerobic environments sulfate acts as the oxidant. Therefore, the oxidation reactions listed in Tables 3.1 and 3.2 could take place in the reservoir and as the reservoir fluid moves to top sides.

The salinity of seawater was taken as 3.5% (Stemler, 2012). The operating conditions are summarized in Table 3.3. In order to study sulfur speciation in the sample seawater-flooded oil reservoir, the initial pH of the solution at the injection point was varied; Case 1: initial pH = 5 (acidic), Case 2: initial pH = 7 (neutral), Case 3: initial pH = 9 (basic). The pH of the solution, as the temperature and pressure change, was tracked to examine the reactivity/speciation effect on the pH.

5.2.1. Sulfur species reactivity in the aqueous phase for Case 1

A simple linear relationship between temperature and pressure is assumed to model the reservoir fluid from injection well to topside processing facilities. The results of the sulfur species reactivity analysis for case 1 (assuming an initial pH of 5) as a function of
temperature for the range of pressures (reservoir conditions to surface conditions) are shown in Figure 5.1. Figure 5.2 illustrates the sulfur speciation as a function of pressure for the range of temperatures.
Fig. 5-1: Sulfur reactivity as a function of temperature from injection to top surface, initial pH: 5, a) P: 25 MPa, b) P: 1 MPa

Fig. 5-2: Sulfur reactivity as a function of pressure from injection to top surface, initial pH: 5, a) T: 75°C, b) T: 25°C
As the figures outline, under these conditions molecular $\text{H}_2\text{S}$, sulfate, and polysulfide ions ($\text{S}_2^{2-}$, $\text{S}_3^{2-}$, $\text{S}_4^{2-}$, and $\text{S}_5^{2-}$) dominate. A fraction of sulfide is converted into sulfur and thiosalts, predominantly thiosulfate, tetrathionate, and pentathionate. Thiosulfate, however, partially decomposes to sulfate at high temperatures and pressures. At temperatures below 70°C, tetrathionate is formed from thiosulfate and trithionate. Oxidation of hydrogen sulfide (in the presence of oxygen or $\text{Fe}^{3+}$ as oxidant) results in the formation of sulfite and thiosulfate. However, sulfite is not stable in the system and is further oxidized to sulfate. This was also observed by Zhang and Millero (1993), where at pH values below 7, sulfate was the primary product of sulfide oxidation in an aqueous solution. Polysulfides form in aqueous solutions containing sulfide at low pH values (Chen and Morris, 1972). As the temperature and pressure decrease, oxidation of sulfide to elemental sulfur and subsequent reactions with sulfide yield polysulfides. At low pH values, degradation of polythionates also occurs leading to the formation of a small amount of elemental sulfur. As the pressure and temperature decrease, sulfate, thiosalts, and sulfide concentrations increase. The concentration of hydrogen ion was tracked to topside facilities to observe the variation in the pH of the solution in the reacting system. The pH of the solution varied slightly as the chemical reactions occurred. The initial pH increased from 5 to 5.2 as the pressure and temperature decreased from 35 MPa and 85°C to 1 MPa and 15°C.

5.2.2. Sulfur species reactivity in the aqueous phase for Case 2

Sulfur species reactivity analysis, assuming that the solution is initially at pH 7, is summarized in Figures 5.3 and 5.4.
Fig. 5-3: Sulfur reactivity as a function of temperature from injection to top surface, initial pH: 7, a) P: 25 MPa, b) P: 1 MPa
Fig. 5-4: Sulfur reactivity in the aqueous phase as a function of pressure from injection to top surface, initial pH: 7, a) T: 75°C, b) T: 25°C
H₂S dissociates to bisulfide and a small amount of sulfide at pH values close to neutral. This is followed by a limited number of reactions involving sulfide oxidation and intermediate sulfur species formation. However, sulfides and sulfate are still the dominant sulfur species. Direct oxidation of sulfide to thiosulfate and elemental sulfur occurs at pH values near neutral leading to an increase in the concentration of thiosalts and a decrease in the amount of polysulfide ions in the solution compared to acidic conditions. Chen and Morris (1972) observed this behaviour where the minimum in the rate of sulfide oxidation at near neutral pH values was attributed to the formation of thiosulfate. The pH of the reacting system increased very slightly from 7 to 7.06 as the pressure and temperature change from 35 MPa and 85°C to 1 MPa and 15°C.

5.2.3. **Sulfur species reactivity in the aqueous phase for Case 3**

Sulfur species reactivity was also assessed for solution pH of 9. The corresponding results for the range of pressures and temperatures are shown in Figures 5.5 and 5.6, respectively.
Fig. 5- 5: Sulfur reactivity as a function of temperature from injection to top surface, initial pH: 9, a) P: 25 MPa, b) P: 1 MPa
Fig. 5-6: Sulfur reactivity as a function of pressure from injection to top surface, initial pH: 9, a) T: 75°C, b) T: 25°C
At high pH values, hydrogen sulfide dissociates to sulfide and bisulfide which are further oxidized to thiosalts and polysulfide ions and finally to sulfate. Increasing the temperature and decreasing pressure cause a decrease in the concentration of sulfate and an increase in the amount of thiosalts. Furthermore, due to $\text{H}_2\text{S}$ dissociation reaction under basic conditions, the amount of molecular $\text{H}_2\text{S}$ in the aqueous phase decreases. Thiosalts increase significantly at high pH values as more sulfite is formed and is oxidized to thiosalts. High temperatures and low pressures favour the formation of more thiosalts under basic conditions. The formed sulfite is oxidized to sulfate and also reacts with polysulfide ions leading to the formation of more thiosalts and a decrease in the concentration of polysulfide ions (Chen and Morris, 1972). At high temperatures and high pH values, thiosalts degrade to sulfite and sulfate and therefore, more sulfate is found in the solution under basic conditions than under acidic conditions. The pH of the reacting system decreases from 9 to 8.7 as the pressure and temperature change from 35 MPa and 85°C to 1 MPa and 15°C.

5.2.4. Sulfur speciation with coupled chemical equilibrium and kinetics as a function of temperature, pressure, and pH

In order to investigate the impact of sulfur chemistry on key parameters such as the final $\text{H}_2\text{S}$ value on the topsides, the phase partitioning behaviour of $\text{H}_2\text{S}$ and elemental sulfur were studied. The K-values for $\text{H}_2\text{S}$ partitioning between oil, water and gas phases, obtained in the equilibrium analysis, are included in the reactivity analysis. The possibility of the formation of a separate solid phase of elemental sulfur is also considered where the amount of elemental sulfur formed in the reacting system is
obtained from the reactive model and then the solubility of sulfur as a function of temperature and pressure is calculated based on the equilibrium analysis to estimate the amount of sulfur precipitated. Figure 5.7 shows the results of sulfur speciation analysis as a function of temperature and pressure for initial pH of 5.
Fig. 5-7: The effects of temperature and pressure on sulfur speciation, solid phase formation, and H$_2$S partitioning, initial pH: 5, a) T: 25°C, b) P: 1 MPa, (Sulfur Species is the total concentration of sulfate, sulfite, polysulfide ions, and thiosalts)
It should be noted that in these figures, sulfur species is the summation of the concentration of sulfide, thiosalts, polysulfide ions, sulfate, and sulfite in the aqueous phase. Decreasing temperature and increasing pressure increase the solubility of sulfur in the aqueous phase. In theory, as the reservoir fluid transfers from reservoir to surface, the temperature and pressure drop and a fraction of total sulfur is converted to elemental sulfur. The solubility of the formed sulfur in the aqueous phase under reservoir conditions is low and therefore, most of the sulfur forms as a separate solid phase and precipitates. An increase in temperature and a decrease in pressure increases the potential for elemental sulfur formation and therefore, sulfur deposition. Sulfur solubility in the aqueous phase also increases with a decrease in temperature. The combination of deposition of sulfur within the reservoir and increased sulfur solubility as the reservoir fluids move toward topsides, means that the amount of elemental sulfur deposited from reservoir to wellhead decreases.

The amount of \( \text{H}_2\text{S} \) in the gas phase from the model at test separator conditions, is 487 ppm, while the \( \text{H}_2\text{S} \) content of oil is 134 ppm and that of water phase is 4 ppm. Other sulfur species including thiosalts, polysulfide ions, sulfate, and sulfite constitute 90 ppm of the total sulfur in the aqueous phase. Elemental sulfur in the form of a separate solid phase is also formed at 965 mg/L. Without considering the formation of other sulfur species (\textit{i.e.}, assuming that all the initial sulfate in the injected seawater is converted to \( \text{H}_2\text{S} \) and partitions between phases), under test separator conditions, the gas phase would contain 1080 ppm, the oil phase contains 235 ppm and water phase contains 7 ppm \( \text{H}_2\text{S} \).
This large difference in the composition of produced fluid highlights the importance of studying sulfur speciation when investigating reservoir souring.

The impacts of temperature and pressure on sulfur speciation for Cases 2 and 3 are summarized in Figures 5.8 and 5.9, respectively. Due to the dissociation of H$_2$S to bisulfide at pH values near neutral, the amount of molecular H$_2$S in the aqueous phase and therefore, the amount in oil and gas phases in equilibrium decreases.
Fig. 5-8: The effects of temperature and pressure on sulfur speciation, solid phase formation, and H₂S partitioning, initial pH: 7, a) T: 25°C, b) P: 1 MPa (Sulfur Species is the total concentration of sulfate, sulfite, polysulfide ions, and thiosalts)
Fig. 5-9: The effects of temperature and pressure on sulfur speciation, solid phase formation, and H₂S partitioning, initial pH: 9, a) T: 25°C, b) P: 1 MPa, (Sulfur Species is the total concentration of sulfate, sulfite, polysulfide ions, and thiosalts)
As the reservoir fluid moves from reservoir to the surface, and the temperature and pressure decrease, elemental sulfur forms. As indicated in the discussion of Cases 1 and 2, the solubility of the elemental sulfur in the aqueous phase decreases with a decrease in temperature and an increase in pressure and therefore, forms as a separate solid phase and precipitates. However, sulfur of oxidation state zero \( (S^0) \) has low chemical stability at high pH values and therefore, less elemental sulfur is formed compared to acidic conditions.

At high pH values, the amount of \( H_2S \) in the aqueous phase decreases as it dissociates to sulfide and bisulfide resulting in an overall decrease in oil and gas phases \( H_2S \) content. The presence of sulfur species with different valence states influences the amount of molecular \( H_2S \) in the aqueous phase and therefore, the amount formed in other phases in equilibrium. At pH values above 7, \( H_2S \) dissociates to sulfide which could be oxidized to thiosulfate (Chen and Morris, 1972) initiating the formation of tetrathionate, polysulfide ions, and elemental sulfur. At these conditions, thiosulfate is converted to sulfide and sulfate (Lin et al., 2004).

The amount of \( H_2S \) in the gas phase from the model at test separator conditions is 7 ppm, while the \( H_2S \) content of oil is 2 ppm and that of water phase is 0.06 ppm. Other sulfur species including thiosalts, polysulfide ions, sulfate, and sulfite make up 65 ppm of the total sulfur aqueous phase. Elemental sulfur in the form of a separate solid phase is also formed (845 mg/L).
Table 5.1 summarizes the results of sulfur speciation for the 3 cases. These results are compared to the base case study where no sulfur speciation is considered and all the sulfur is in the form of H$_2$S.
Table 5-1: Comparison of the results of sulfur speciation for 3 cases, T: 15 °C, P: 1 MPa

<table>
<thead>
<tr>
<th>pH</th>
<th>Polysulfides*</th>
<th>Sulfate</th>
<th>Thiosalts**</th>
<th>H$_2$S (aq)</th>
<th>H$_2$S (g)</th>
<th>H$_2$S (o)</th>
<th>Sulfur deposited (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>38.5</td>
<td>48.7</td>
<td>7.3</td>
<td>6</td>
<td>272.4</td>
<td>201.3</td>
<td>831</td>
</tr>
<tr>
<td>7</td>
<td>22.7</td>
<td>60.8</td>
<td>16</td>
<td>5.29</td>
<td>240.4</td>
<td>177.3</td>
<td>835</td>
</tr>
<tr>
<td>9</td>
<td>11.8</td>
<td>104.2</td>
<td>32.3</td>
<td>0.06</td>
<td>2.6</td>
<td>1.6</td>
<td>868</td>
</tr>
<tr>
<td>Base case***</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>12.5</td>
<td>567.5</td>
<td>420</td>
<td>–</td>
</tr>
</tbody>
</table>

* polysulfide ions is the summation of S$_2^{2-}$, S$_3^{2-}$, S$_4^{2-}$, S$_5^{2-}$.

** thiosalts is the summation of S$_2$O$_3^{2-}$, S$_3$O$_6^{2-}$, S$_4$O$_6^{2-}$, S$_5$O$_6^{2-}$.

*** base case: all the initial sulfate forms H$_2$S, initial pH: 5

When the initial pH of the solution is above neutral conditions (case 3), less polysulfide ions form in the solution, while the amount of sulfate and thiosalts, especially thiosulfate and pentathionate, increase with the pH. H$_2$S dissociates to sulfide and bisulfide and therefore, the amount of molecular H$_2$S in the aqueous phase and that in the oil and gas phases decreases. Again, in this case, one might estimate 0.5 ppm H$_2$S in the aqueous phase, 22.5 ppm H$_2$S in the gas phase, and 13.4 ppm H$_2$S in the oil phase with ignoring sulfur speciation which leads to over prediction of H$_2$S in the reservoir fluid.

In order to study the sensitivity of the model to the type of the reactions in the system, the equilibrium reactions are removed from the analyses and only are the kinetic reactions considered in the model. The results are summarized in the following section.

5.3. Sulfur speciation with chemical kinetics as a function of temperature, pressure, and pH

In the previous simulations, the gap in formation/consumption of sulfur compounds due to lack of kinetic rate expressions was filled assuming the reactions were governed by
equilibrium. To determine how sensitive the output was to ignoring these reactions, a set of simulations was conducted where only kinetic rate expressions were used in the model. The kinetics were solved separately from the non-linear algebraic equations and sulfur speciation was evaluated as a function of temperature and pressure for the initial pH of 5 and 9 (Figures 5.10 and 5.11). It should be noted that in these figures, sulfur species is the total concentration of sulfate, sulfite, polysulfide ions, and thiosalts in the aqueous phase.
Fig. 5-10: Sulfur speciation as a function of temperature and pressure as a result of kinetic reactions, initial pH: 5, a) T: 25°C b) P: 1 MPa
(Sulfur Species is the total concentration of sulfate, sulfite, polysulfide ions, and thiosalts)
Fig. 5-11: Sulfur speciation as a function of temperature and pressure as a result of kinetic reactions, initial pH: 9, a) T: 25°C b) P: 1 MPa (Sulfur Species is the total concentration of sulfate, sulfite, polysulfide ions, and thiosalts)
According to the kinetic model, no polysulfide or elemental sulfur are formed. The H$_2$S concentration decreases significantly and sulfate and a small amount of thiosalts form. At low pH values and as temperature and pressure decrease, the amount of trithionate and tetrathionate decreases, while pentathionate increases. Thiosulfate initially increases with a decrease in temperature and pressure and decreases with the formation of pentathionate. At high pH values, H$_2$S dissociates to sulfide and bisulfide decreasing the molecular H$_2$S content of aqueous phase. More sulfate is formed particularly at low temperatures and high pressures where sulfide exists in the aqueous phase. Considering only the kinetic reactions, the amount of H$_2$S formed is 8.7 ppm in oil, 0.3 ppm in water, and 31 ppm in gas under test separator conditions. At high pH values, however, the concentration of molecular H$_2$S decreases to 0.2 ppm, 0.006 ppm, and 0.7 ppm of the oil, water, and gas phases, respectively. It can be concluded that the inclusion of both types of analyses (i.e., equilibrium and kinetic), rather than only kinetic analysis, in sulfur chemistry study is necessary to provide a comprehensive picture of the system, particularly in the context of sparse kinetic data.

5.4. **Sulfur speciation with chemical equilibrium as a function of temperature, pressure, and pH**

The chemical composition of the reacting system containing sulfur species was also found by solving a set of non-linear algebraic equations assuming that the reactions involving sulfur species reach equilibrium (Figures 5.12 and 5.13). Again, the sulfur species is the total concentration of sulfate, sulfite, polysulfide ions, and thiosalts.
Fig. 5-12: Sulfur speciation as a function of temperature and pressure as a result of equilibrium reactions, initial pH: 5, a) T: 25°C b) P: 1 MPa
(Sulfur Species is the total concentration of sulfate, sulfite, polysulfide ions, and thiosalts)
Fig. 5-13: Sulfur speciation as a function of temperature and pressure as a result of equilibrium reactions, initial pH: 9, a) T: 25°C b) P: 1 MPa (Sulfur Species in the total concentration of sulfate, sulfite, polysulfide ions, and thiosalts)
Increasing temperature and decreasing pressure, causes the formation of a separate gas phase containing H$_2$S below bubble point. It also increases the possibility of formation of a solid phase containing elemental sulfur. A significant amount of H$_2$S dissolves in the oil phase leaving a small amount of molecular H$_2$S in the aqueous phase. Under test separator conditions, more than 13% of the total sulfur content of the aqueous phase is thiosalts, while polysulfide ions form 4% of the sulfur content at low pH values. Once the pH of the solution is increased to basic conditions, the amount of polysulfide ions and sulfate increases and less thiosalts form. As the temperature and pressure are reduced, sulfide is formed as polysulfide ions and a small amount of thiosalts and elemental sulfur, which is precipitated as a separate solid phase due to its low solubility in the aqueous phase.

The results of the coupled equilibrium and kinetic reactions are compared with those obtained from solving the non-linear equations and differential equations separately. The equilibrium study more closely aligns with the coupled equilibrium and kinetic reactions, but still below the combined model. The results of all three scenarios are compared in Table 5.2.
Table 5-2: Comparison of different scenarios; kinetic part, equilibrium part, coupled kinetic and equilibrium. P: 1 MPa, T: 15°C, the initial sulfide concentration: 869 mg/L.

<table>
<thead>
<tr>
<th>Scenario</th>
<th>pH</th>
<th>H₂S concentration (ppm)</th>
<th>Gas phase</th>
<th>Oil phase</th>
<th>Aqueous phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kinetic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>150.4</td>
<td>115.7</td>
<td>3.47</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>143</td>
<td>110.1</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>0.26</td>
<td>0.2</td>
<td>0.006</td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>195.2</td>
<td>144.5</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>181.6</td>
<td>134.4</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>2.33</td>
<td>1.44</td>
<td>0.054</td>
<td></td>
</tr>
<tr>
<td>Kinetic-Equilibrium</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>272.4</td>
<td>201.3</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>240.4</td>
<td>177.3</td>
<td>5.29</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>2.6</td>
<td>1.6</td>
<td>0.06</td>
<td></td>
</tr>
</tbody>
</table>

5.5. Comparing the results with experimental data

Although produced water samples vary in composition depending on their origin, the results of the sulfur speciation obtained in this study were compared with published data of Witter and Jones (1998). Witter and Jones used different analytical approaches for identification and quantification of inorganic sulfur species present in a sample produced water generated during offshore oil production (Witter and Jones, 1998). In general, the measurements of individual sulfur species are influenced by coupled reactions involving sulfur species and polysulfide ions play an important role in these processes. In order to prevent H₂S loss at low pH values, alkaline buffers were used in polarographic methods for sulfide determination. Sulfide, polysulfide ions, thiosulfate, sulfite, and sulfate were measured in the produced water sample. Elemental sulfur and polythionates were not considered. However, it was indicated that elemental sulfur is present in the produced
water sample in low concentrations (Witter and Jones, 1998). More than 39% of the measured inorganic sulfur compounds were sulfide (HS⁻ and S²⁻) making it the second most abundant species after sulfate (56% of the total inorganic sulfur compounds). Polysulfide ions and thiosulfate formed 3% and 2% of the measured sulfur species, respectively. Sulfite accounted for less than 1% of sulfur in the produced water (Witter and Jones, 1998).

According to the proposed model, at atmospheric temperature and pressure and under basic conditions (similar to the conditions in the study of Witter and Jones, 1998), sulfate and thiosalts constitute 58% and 23% of the total sulfur, respectively. Pentathionate accounted for 17% of the total thiosalts. Thiosulfate, trithionate, and tetrathionate constitute 1.8%, 1.5%, and 2.7% of the total sulfur, respectively. Approximately, 4% of the total sulfur was polysulfide ions (S₂⁻, S₃⁻, S₄⁻, and S₅⁻). At high pH values, hydrogen sulfide dissociates to sulfide and bisulfide making up approximately 12% of the total sulfur in the reacting system. Elemental sulfur deposition was 880 mg/L or less than 3% of the total sulfur in the aqueous phase.

The reactivity analysis results are compared with the experimental data by Witter and Jones for a sample produced water (Table 5.3).

Table 5-3: Sulfur speciation at 25°C and 101 kPa, pH = 9

<table>
<thead>
<tr>
<th>Sulfur content of aqueous phase (%)</th>
<th>sulfate</th>
<th>Thiosulfate</th>
<th>Polysulfides*</th>
<th>HS⁻, S²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental value (Witter and Jones, 1998)</td>
<td>56</td>
<td>2</td>
<td>3</td>
<td>39</td>
</tr>
<tr>
<td>Model results</td>
<td>58</td>
<td>1.8</td>
<td>3.7</td>
<td>31</td>
</tr>
<tr>
<td>Deviation (%)</td>
<td>3.6</td>
<td>10</td>
<td>23.3</td>
<td>20.5</td>
</tr>
</tbody>
</table>

* polysulfide ions is the summation of S₂⁻, S₃⁻, S₄⁻, S₅⁻.
The difference in the concentration of sulfide and polysulfides in the proposed model and the experimental data could be due analytical method used for quantification of these sulfur species. Sample preservation impacts speciation and no quantification of intermediate sulfur species (especially thiosalts) was performed in the Witter and Jones study.
References


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CHAPTER SIX

CONCLUSIONS AND RECOMMENDATIONS
The injection of sulfate-containing seawater into an oil reservoir, usually used to maintain the reservoir pressure, can promote the growth of sulfate reducing bacteria and archaea near the injection wells, leading to the reduction of sulfate to hydrogen sulfide. Upon formation, $\text{H}_2\text{S}$ could partition to the gas, water or oil phases depending on pressure, temperature and/or composition. However, depending on the pH, $\text{H}_2\text{S}$ could dissociate to bisulfide and sulfide ions which remain in the aqueous phase and do not partition between phases affecting the amount of $\text{H}_2\text{S}$ one would expect in the gas phase. In addition, the analysis of produced water samples has shown the presence of other sulfur species, with valence states between that of sulfidic-sulfur and sulfate-sulfur, such as polysulfide ions and polythionates.

The objective of this study was to investigate sulfur chemistry in reservoirs undergoing seawater injection. A predictive reactive model was developed for studying the reactivity of sulfur species and their partitioning behaviour as a function of temperature, pressure, and pH. The first step in developing the model was to identify the key sulfur compounds involved in reservoir souring through equilibrium analysis. The key reacting species and end-products identified were sulfate, sulfite, sulfide, bisulfide, polythionates including thiosulfate, trithionate, tetrathionate, and pentathionate, polysulfides ($S_n^{2-}, n = 2-5$) and hydrogen sulfide. A 3-phase flash partitioning model was developed to study the phase partitioning behaviour of $\text{H}_2\text{S}$ in a multi-phase system. An equilibrium analysis was also performed to investigate the partitioning behaviour of elemental sulfur to predict the amount of sulfur deposition.
Above the bubble point pressure and at high temperatures (higher than the production well temperature), sulfate and polythionates are the dominant sulfur species in the aqueous phase. Hydrogen sulfide is more soluble in oil than in water and therefore, is mostly found in the hydrocarbon-rich phase. A fraction of initial sulfur (approximately 10%) is also formed as the elemental sulfur and is found as a separate solid phase. At pressures below the bubble point and at low temperatures (below 60°C), where one would expect the formation of a gas phase, molecular H$_2$S partitions between oil, water, and gas phases. It was concluded that the presence of different sulfur species with different valence states affect the partitioning behaviour of H$_2$S in a multiphase system in that a significant amount of aqueous H$_2$S might be formed as sulfate and polythionates resulting in a lower overall amount of H$_2$S.

Sulfur speciation was significantly influenced by the pH of the solution. Increasing the pH from acidic to basic is accompanied with the formation of polysulfides. At low pH values, H$_2$S exists in the molecular form and partitions between oil, water and gas phases below bubble point pressure. It is, however, dissociated to sulfide and bisulfide with increasing the pH resulting in the decrease in the H$_2$S content of all phases in equilibrium. In addition, one would expect a decrease in the formation of solid elemental sulfur under basic conditions.

In addition to equilibrium analysis, a simulation of the reaction rates of published reactions involving the species of interest was performed to investigate the full extent of sulfur speciation. At low pH values, sulfate, polysulfide ions, and hydrogen sulfide are dominant in the solution. Less than 10% of the total sulfur is formed as thiosalts,
predominantly as thiosulfate and pentathionate. Part of the total sulfur is present as elemental sulfur. The solubility of the formed sulfur in the aqueous phase, in the range of temperature and pressure considered in this study, is not high and therefore, it precipitates as the fluid moves to top surface such that approximately 960 mg/L solid sulfur is deposited at the producer (15 MPa, 65°C). H₂S solubility in the hydrocarbon-rich phase is higher than that in the aqueous phase and therefore, above the bubble point pressure, H₂S is mostly found in the oil phase. Using the developed reactive model for predicting the partitioning behaviour of sulfur species, under test separator conditions, a gas phase containing 487 ppm H₂S forms, while the H₂S content of oil and water phases in equilibrium is 134 ppm and 4 ppm, respectively.

When the pH of the solution is above neutral, most of the total sulfur is found as sulfate and thiosalts. Hydrogen sulfide dissociates to sulfide and bisulfide and less than 10% polysulfide ions forms. The amount of sulfur deposited as elemental sulfur is slightly decreased from 965 mg/L at low pH values to less than 844 mg/L at higher pH values. In addition, at high pH values, the amount of molecular H₂S which partitions between phases is decreased significantly. The sulfur reactivity results in the formation of 7 ppm H₂S in the gas phase, 2 ppm in the oil phase, and 0.06 ppm in the water phase.

Most souring models and management plans do not include sulfur speciation, making the assumption of microbially conversion of all the initial sulfate in the injected seawater to H₂S. This results in the potential for over prediction of H₂S in the reservoir fluids. For instance in this study, the gas phase under test separator conditions on the surface would contain 1080 ppm H₂S, the oil phase contains 235 ppm H₂S, and water
phase contains 7 ppm H\textsubscript{2}S without including sulfur chemistry. Comparison of the results of the sulfur speciation model in the current study with experimental data showed the ability of the developed model in predicting sulfur chemistry during recovery processes as a result of injection of sulfate-containing seawater. Therefore, this study contributes towards understanding sulfur chemistry in reservoirs undergoing seawater injection recovery process as it examined the reactivity, partitioning behaviour and therefore, relative impact of different sulfur species on H\textsubscript{2}S content of produced fluid and finally, on reservoir souring.

There has been no documentation on reservoir souring reactions and phase behaviour occurring at low temperature reservoir conditions associated with SRB activity. A new approach was followed in this study for studying sulfur chemistry in reservoirs undergoing seawater injection in an attempt to fill the gap in addressing reservoir souring-related issues in offshore operations. This study gives one more information on the chemistry, not just the transport, in these systems. Current reservoir models oversimplify the complex sulfur chemistry and developing effective souring control method requires the complete picture. Therefore, the major contribution of this study is identifying the key chemical compounds, reaction schemes, and developing a methodology to incorporate into a more comprehensive reservoir simulator, to model transport and transformation in reservoirs soured via seawater injection.

Some areas to expand on in future work include:
• The proposed model in this study could be incorporated into existing reservoir simulators, allowing the study of sulfur speciation as a function of not only temperature, pressure, and pH but also reservoir transport phenomenon.

• Development of promising souring mitigation methods and also the analytical methods of identification and quantification of sulfur compounds could also benefit from the results of analysis of sulfur species chemical reactivity at different operating conditions.

• During transportation, the reservoir fluid is in contact with the reservoir minerals. There could be some chemical reactions between sulfur species in the fluid and these minerals. H\textsubscript{2}S may be adsorbed on the surface of the reservoir minerals, especially iron-containing minerals. The scavenging effect of these minerals on sulfur speciation could also be included in the reactive model.

• Those reactions for which no kinetic data was found in the literature, were assumed as equilibrium reactions in the current study. Determining the kinetics of these reactions, especially those containing polysulfides, could also be the focus of further sulfur chemistry studies.

• A laboratory-scale experiment could also be designed to study sulfur chemistry under reservoir conditions during seawater injection. This could provide refined data to compare the model outputs with.