Reservoir Souring:

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_2S. 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_2S microbially and the formed H_2S partitions between phases, the gas phase under test separator conditions on the surface contains 1080 ppm H_2S which is in equilibrium with the oil phase containing 295.7 ppm H_2S and water phase with H_2S content of 8.8 ppm. These values are higher than those obtained from reactivity analysis (*i.e.*, H_2S 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_2S 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_2S 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 kth element in the system in Eq. (3-1)

a_i : activity of component i (mol/kg)

a_{ik}: number of atoms of the kth 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^o: standard-state fugacity

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

G_i^o: standard-state Gibbs energy of species i

G_r° : standard Gibbs free energy of reaction (J/kg)

$\overline{G}^\circ$: standard state partial molal Gibbs energy (J/kg)

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

H° : standard enthalpy (J/kg)

$\overline{H}^\circ$: standard state partial molal enthalpy (J/kg)

H_f° : standard enthalpy of formation (J/kg)

I : ionic strength (molality)

k : salting-out coefficient

K : equilibrium constant

k_i^1 : vapor/liquid 1 equilibrium ratio (species i)

k_i^2 : vapor/liquid 2 equilibrium ratio (species i)

L_1 : water stream concentration (mol)

L_2 : oil stream concentration (mol)

L_1 : 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 ith solute species

P : pressure (kPa)

P_{ci}: critical pressure of species i (Pa)

P_i^{sat}: vapor pressure of species i (kPa)

R : universal gas constant (8.314 kJ/kmol.K)

r_i: reaction rate (mol/lit.sec)

S°: standard entropy (J/kg.K)

$\overline{S}^\circ$: standard state partial molal entropy (J/kg.K)

T : absolute temperature (K)

T_{ci}: critical temperature of species i (K)

u : fluid velocity (m/sec)

V : vapor-phase flow rate (mol/sec)

$\overline{V}_i^\infty$: partial molar volume of species i in water at infinite dilution (m^3/kmol)

v: fluid velocity (m/sec)

x : distance (m)

$x_i^{L_1}$: mole fraction of species i in L$_1$

$x_i^{L_2}$: 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

γ_i : activity coefficient of species i

λ_k: Lagrange's multipliers in Eq. (3-2)

φ_i : fugacity coefficient of component i

ν_i : stoichiometric coefficient of species i

μ_i : chemical potential of species i

ε_j : reaction coordinate for reaction j

ω: acentric factor

ω: total number of elements comprising the system in Eq. (3-1)

Ψ : phase split (gas stream concentration/feed stream concentration)

ξ: liquid phase split

CHAPTER ONE

INTRODUCTION

1.1. Overview

The formation of hydrogen sulfide (H_2S) 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_2S (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_2S 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_2S from the aqueous phase could cause an increase in the concentration of H_2S in produced fluids. H_2S could also be generated due to the activity of some bacteria and archaea. This biogenic H_2S 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 $100^{\circ}C$ 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_2S 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_2S 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.

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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 H_2S 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 H_2S 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_2S due to TSR requires temperatures higher than 150°C (Goldhaber and Orr, 1995; Machel, 1998a).

Once generated, H_2S 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_2S (associated with

reservoir) and then oxidizes hydrocarbons to carbon dioxide leading to the generation of H_2S 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_2S (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_2S 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_2S 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).
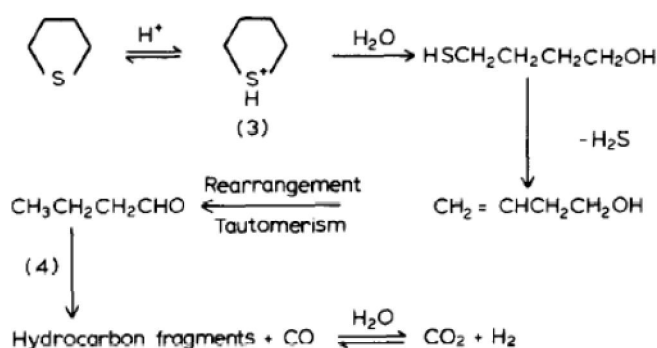
Fig. 2- 1 Reaction pathway for the hydrolysis of tetrahydrothiophene (Clark *et al*., 1983)

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, dihyrothienylthiophene, alkyldihyrothienylthiophene, and butanethiol.

The H_2S 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_2S production during thermal recovery processes. A kinetic model assuming that H_2S 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_2S (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_2S during water flooding or steam injection (Marsland *et al*., 1989; Hutcheon, 1998).

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

Reductive dissolution: $MS + 2H^+ + yR \rightarrow M^{2+} + H_2S + yO$ (2- 2)
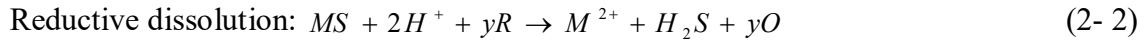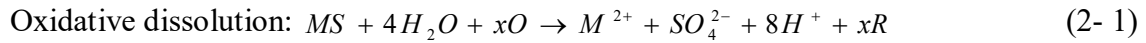
MS represents sulfide mineral, *M* is the metal base, and *O* and *R* are some oxidized and reduced state of some appropriate redox couple, respectively. The acidic components come from the injection water or the degradation of injected biocides and corrosion and scale inhibitors (Khatib and Salanitro, 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 H_2S are (Peters, 1976):

$$FeS_2 + 2H^+ \rightarrow Fe^{2+} + H_2S + S^0 \tag{2-3}$$

$$FeS_2 + 4H^+ + 2R \rightarrow Fe^{2+} + 2H_2S + 2R \tag{2-4}$$

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):

$$FeS_2 + 4OH^- \rightarrow 1/3Fe_3O_4 + 11/6S^{2-} + 1/6SO_4^{2-} + 2H_2O \tag{2-5}$$

$$FeS_2 + 2O \rightarrow Fe^{2+} + 2S^0 + 2O \tag{2-6}$$

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_2S. 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_2S (Eden *et al*., 1993). Another possibility for the increase in the concentration of H_2S 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_2S.

2.2.5. Desorption of H_2S 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_2S. As reservoir pressure decreases during production, the solubility of H_2S in water decreases. This ultimately leads to the liberation of H_2S 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_2S in the production wells (Seto and Beliveau, 2000). This is an important phenomena, as it could in part explain the observation of H_2S in produced fluids even after a reservoir 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_2S. Biogenic sulfide production results in soured oil and gas in the reservoir and topside processing facilities including oil-water separation units, water storage tanks for produced water, and flowlines. There are various comprehensive reviews on the types of sulfate reducers (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_2S, bisulfide, bicarbonate, carbon dioxide, calcite, and dolomite may be produced during bacterial sulfate reduction. The amount of H_2S 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_2S scavenger as it reacts with sulfide resulting in the generation of elemental sulfur and nitrogen (Sturman and Goeres, 1999). Microbial competition between NRB and SRB for electron donors (oil-derived organics or H_2) and nitrate-driven sulfide oxidation are the two mechanisms proposed for the NRB-facilitated souring control (Sunde *et al*., 2004; Dolfing and Hubert, 2017). There are concerns that nitrate treatment shifts the corrosion risk from production to injection wells due to the oxidizing potentials of nitrate and nitrite (Martin, 2008; Hubert *et al*., 2005). Depending on the ratio of nitrate to sulfide, fully

oxidized sulfate or partially oxidized sulfur-polysulfides may be generated; Sulfide is oxidized to sulfate at high nitrate to sulfide ratios with the reduction of nitrate to nitrite, while at low ratios, sulfur-polysulfide formation is favored (Sturman and Goeres, 1999). The latter conditions can be encountered at oilfield topside at low temperatures (4-85°C) (Dolfing and Hubert, 2017). These intermediate sulfur species could also be formed rapidly by chemical reactions, when soured produced water containing substantial sulfide concentrations is exposed to air (Johnston $et\ al.$, 2010). The oxidation of sulfide to sulfate is a kinetically slow reaction that requires a biological catalyst to occur at a significant rate. Therefore, partially oxidation of sulfide to elemental sulfur and other intermediate sulfur species is a more probable reaction pathway. The formed intermediate sulfur compounds may cause corrosion. The corrosive nature of these compounds has been well-documented (Dowling, 1992; Alekseev $et\ al.$, 1990; Fang $et\ al.$, 2011). Polysulfide, for example, acts as an oxidizer that receives electrons from steel surfaces to form sulfide (Ramo $et\ al.$, 2003). Sulfur can react rapidly with metallic iron to form iron sulfide and other iron sulfur compounds such as greigite (Fe_3S_4) and pyrite (FeS_2) (Johnston $et\ al.$, 2010; Dronen $et\ al.$, 2014). The formed iron sulfide is essentially insoluble in aqueous solution leading to high local corrosion rates. Partially oxidized sulfur species can acidify natural waters (O'Reilly $et\ al.$ 2001). 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 H_2S 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).
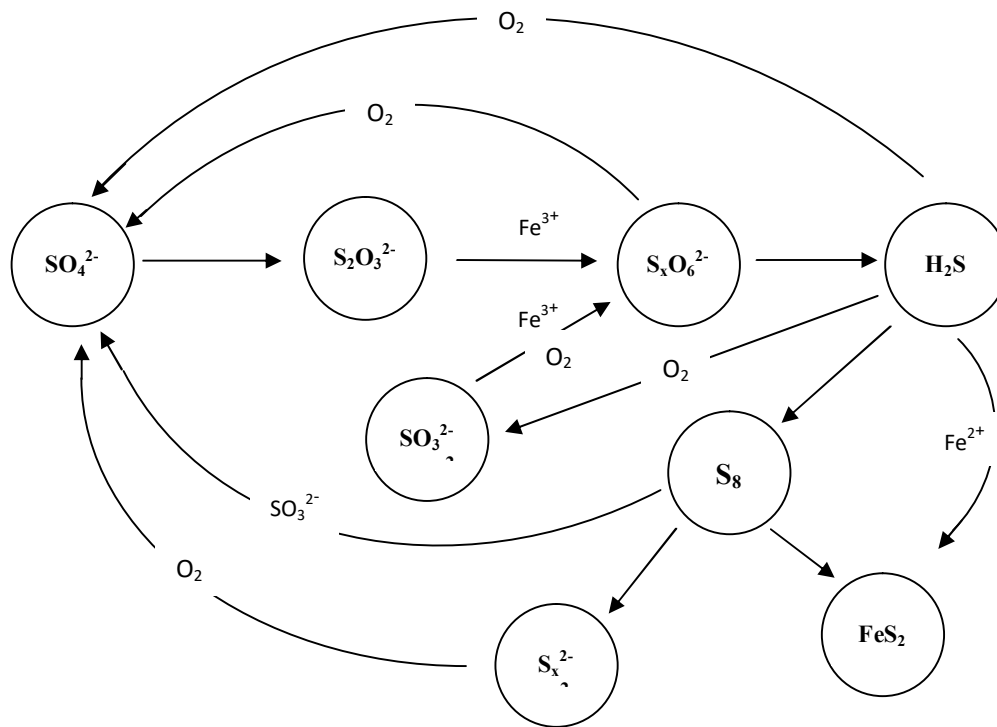
Fig. 2- 2: Oxidation reduction reactions in sulfur cycle from (Miranda-Trevino *et al*., 2013) with modification

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_2S, 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_2S to sulfur may occur in low-temperature aerobic environments, where

molecular oxygen presents, and in high-temperature anaerobic environments, excess sulfate acts as the oxidant. Intermediate sulfur species can also be reduced to sulfide due to the SRB activity. Some sulfate reducers can reduce sulfur compounds such as thiosalts, sulfite, and sulfur (Muyzer and Stams, 2008; Barrett and Clark, 1987; Moura *et al.*, 1997; Dalsgaard and Bak, 1994) 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:

$$H_2S \leftrightarrow H^+ + HS^- \tag{2-7}$$

$$HS^- \leftrightarrow H^+ + S^{2-} \tag{2-8}$$
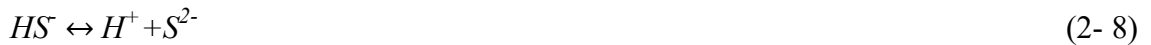
Rate constants for the oxidation of sulfide in seawater and formation of sulfite, sulfate, and thiosulfate were determined as a function of pH, temperature, and salinity. The reactions are overall second-order reactions, first-order with respect to both sulfide and oxygen. The kinetic model accounting for the distribution of the reactants and products is based on the following reactions (Zhang and Millero, 1993):

$$H_2S + 1.5O_2 \xrightarrow{\ k_1\ } SO_3^{2-} + 2H^+ \tag{2-9}$$

$$SO_3^{2-} + 0.5O_2 + H_2 \xrightarrow{\ k_2\ } SO_4^{2-} + 2H^+ \tag{2-10}$$

$$H_2S + SO_3^{2-} + 0.5O_2 \xrightarrow{\ k_3\ } S_2O_3^{2-} + H_2O \tag{2-11}$$

$$\frac{d[H_2S]}{dt} = -k_1[H_2S][O_2] - k_3[H_2S][SO_3^{2-}][O_2] \tag{2-12}$$

$$\frac{d[SO_3^{2-}]}{dt} = k_1[H_2S][O_2] - k_2[SO_3^{2-}]^2[O_2]^{1/2} - k_3[H_2S][SO_3^{2-}][O_2] \tag{2-13}$$

$$\frac{d[S_2O_3^{2-}]}{dt} = k_3[H_2S][SO_3^{2-}][O_2] \tag{2-14}$$

$$\frac{d[SO_4^{2-}]}{dt} = k_2[SO_3^{2-}]^2[O_2]^{1/2} \tag{2-15}$$

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

$$\ln k_1 = -4.71 + 0.914pH - 0.0289pH^2 \tag{2-16}$$

$$\ln k_2 = 3.87 + 1.51pH - 0.103pH^2 \tag{2-17}$$

$$\ln k_3 = -9.09 + 3.01pH - 0.177pH^2 \tag{2-18}$$

In low-temperature diagenetic settings (T<100°C), where oxygen is available and pH conditions are favourable, sulfide can be oxidized to elemental sulfur. It is believed that the dissolution of elemental sulfur in aqueous sulfide solutions is the precursor for the formation of polysulfide anions (Petre and Larachi, 2006):

$$S_n + HS^- + OH^- \Leftrightarrow S_{n+1}^{2-} + H_2O \tag{2-19}$$

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

$$(n-1)S_{n+1}^{2-} + HS^- + OH^- \Leftrightarrow nS_n^{2-} + H_2O \qquad n = 2-5 \tag{2-20}$$
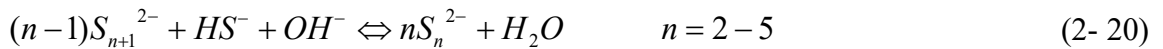
In the presence of oxygen, the autoxidation of the polysulfides also occurs rapidly which results in thiosulfate formation:

$$S_n^{2-} + 3/2O_2 \rightarrow S_2O_3^{2-} + [(n-2)/8]S_8 \qquad (2\text{-}21)$$

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_2S when exposed to water and temperature and pressure change. A decrease in temperature and pressure also leads to the decomposition of polysufides (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):

$$S_n^{2-} + H^+ \Leftrightarrow HS_n^- \Leftrightarrow HS^- + [(n-1)/8]S_8 \qquad (2\text{-}22)$$

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:

$$H_2S_n + HCO_3^- \Leftrightarrow HS_n^- + H_2O + CO_{2(g)} \qquad (2\text{-}23)$$

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):

$$nHS^- + (n-1)/2O_2 \Leftrightarrow S_n^{2-} + H_2O + (n-2)OH^- \tag{2-24}$$

$$S_n^{2-} + 3/2O_2 \Leftrightarrow S_2O_3^{2-} + (n-2)/8S_8 \tag{2-25}$$

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

$$SO_3^{2-} + 1/2O_2 \Leftrightarrow SO_4^{2-} \tag{2-27}$$
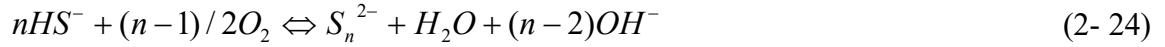
In the presence of a transition metal, like Fe^{3+}, the overall process of sulfide oxidation may be represented as:

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

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_2S 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).

$$FeS_2 + 6Fe^{3+} + 3H_2O \rightarrow 7Fe^{2+} + 6H^+ + S_2O_3^{2-}$$ (2- 29)

$$FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2H^+ + 2SO_4^{2-}$$ (2- 30)
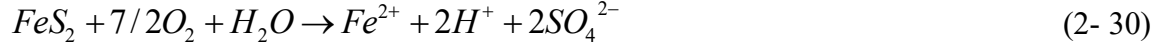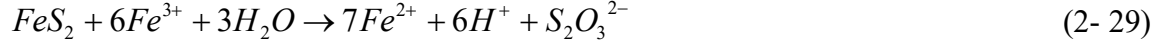
In acidic aqueous solutions at temperatures between 4-30°C, thiosulfate is further oxidized to tetrathionate as follows (Takano *et al.*, 1994; Zhang and Millero, 1993; Chen and Morris, 1972; Xu *et al.*, 2000; Miranda-Trevino *et al.*, 2013):

$$2S_2O_3^{2-} + 2H^+ + 1/2O_2 \rightarrow S_4O_6^{2-} + H_2O$$ (2- 31)

$$2S_2O_3^{2-} + 2Fe^{3+} \rightarrow S_4O_6^{2-} + 2Fe^{2+}$$ (2- 32)
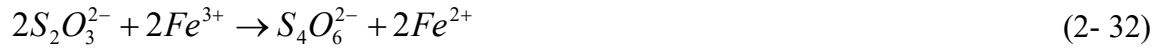
The decomposition of thiosulfate under both acidic and basic conditions are determined as follows:

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

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

$$3S_2O_3^{2-} + FeS_2 \rightarrow S_4O_6^{2-} + FeS + H_2S$$ (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:

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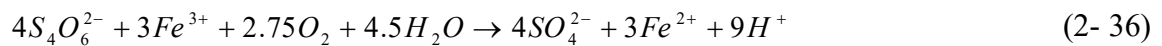
$$-\frac{d[S_4O_6^{2-}]}{dt} = 2.5 \times 10^{-7} [Fe^{3+}]^{0.06} [S_4O_6^{2-}]^{0.3} \qquad pH : 4, \quad T : 70°C \qquad (2\text{-}37)$$

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

$$4S_4O_6^{2-} + 6OH^- \rightarrow 5S_2O_3^{2-} + 2S_3O_6^{2-} + 3H_2O \qquad pH : 9, \quad T : 4-30°C \qquad (2\text{-}38)$$
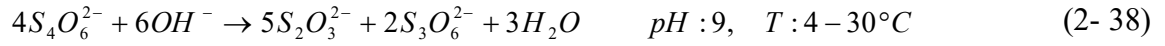
At pH 3.5 to 4 and temperatures between 20 and 70°C, trithionate and pentathionate are formed from tetrathionate decomposition through a second order reaction (Miranda-Trevino, 2013; Zhang and Jeffrey, 2010):

$$2S_4O_6^{2-} \rightarrow S_5O_6^{2-} + S_3O_6^{2-} \qquad (2\text{-}39)$$

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

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

$$3S_3O_6^{2-} \rightarrow S_4O_6^{2-} + 1/8S_8 + 2SO_4^{2-} + 2SO_2 \qquad (2\text{-}41)$$
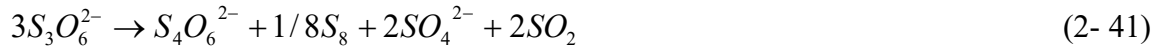
$$-\frac{d[S_3O_6^{2-}]}{dt} = 3.2 \times 10^{-2} s^{-1} [S_3O_6^{2-}] \qquad pH : 4, \quad T : 35°C \qquad (2\text{-}42)$$

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

$$S_3O_6^{2-} + H_2O \rightarrow S_2O_3^{2-} + SO_4^{2-} + 2H^+ \qquad (2\text{-}43)$$

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

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

$$S_3O_6^{2-} + 2Fe^{3+} + 1/2O_2 \rightarrow S_2O_3^{2-} + SO_4^{2-} + 4Fe^{2+} \qquad pH : 7-9, \quad T : 30°C \qquad (2\text{-}45)$$
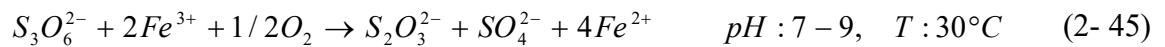
The oxidation of trithionate at pH below 7 and in highly basic solutions (pH around 12) follows the same reaction (reaction 1-46). However, in acidic conditions, the produced thiosulfate is further oxidized to tetrathionate and sulfite. At pH between 3.5 and 4 and temperatures between 20 and 70°C, trithionate is first decomposed to tetrathionate and sulfate and then to sulfur dioxide and sulfur.

$$S_3O_6^{2-} + 2OH^- \rightarrow S_2O_3^{2-} + SO_4^{2-} + 2H_2O \hspace{3cm} (2\text{-}46)$$

As indicted 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_2S in the various phases but also they affect the overall reactivity of the produced fluids in terms of sulfur. The incomplete redox reactions involving H_2S, sulfur dioxide, or sulfate are likely causes of the generation of sulfur oxyanions. The isolation of some sulfur and thiosulfate reducing bacteria from produced waters indicates that although H_2S 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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CHAPTER THREE

RESEARCH METHODOLOGY

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^t) 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:

$$\sum_i n_i a_{ik} = A_k \qquad k = (1,2,...\omega)$$
(3- 1)

Where ω 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 kth element in the system. Further, a_{ik} is the number of atoms of the kth element present in each molecule of chemical species i. Next, the Lagrange's multipliers λ_k are introduced for each element:

$$\lambda_k \left(\sum_i n_i a_{ik} - A_k \right) = 0$$
(3- 2)

Summation of these equations over k gives:

$$\sum_k \lambda_k \left(\sum_i n_i a_{ik} - A_k \right) = 0$$
(3- 3)

Then a function F is formed by:

$$F = G^t + \sum_i \lambda_k \left(\sum_i n_i a_{ik} - A_k \right)$$
(3- 4)

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

$$\left(\frac{\partial F}{\partial n_i} \right)_{T,P,n_j} = \left(\frac{\partial G^t}{\partial n_i} \right)_{T,P,n_j} + \sum_k \lambda_k a_{ik} = 0 \qquad (i = 1,2,..., N)$$
(3- 5)

The first term on the right side is the definition of the chemical potential. The chemical potential is also given by:

$$\mu_i = G_i^\circ + RT \ln(\hat{f}_i / f_i^\circ)$$ (3- 6)

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

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

$$\Delta G_{f_i}^\circ + RT \ln(x_i \gamma_i f_i / f_i^\circ) + \sum_k \lambda_k a_{ik} = 0 \qquad (i = 1,2,...,N)$$ (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.

$$F = \Delta G_{f_i}^\circ / RT + \sum_l \lambda_l \left(b_l - \sum_k a_{lk} x_k^s - \sum_k \sum_a a_{lk} x_k^a \right) + \lambda_e \left(\sum_j \sum_a z_j x_j^a \right)$$ (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 γ_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 (ε) by:

$$x_i = \frac{n_{i0} + \sum_j v_{i,j}\varepsilon_j}{n_0 + \sum_j v_j\varepsilon_j}$$

(3- 9)

Where, ε_j applies to each reaction and $v_{i,j}$ designates the stoichiometric number of species i in reaction j. Summation over all species yields: $v_j = \sum_i v_{i,j}$. 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:

$$\Delta G_r^{\circ} = -RT \ln K$$

(3- 10)

Where, the standard molal Gibbs free energy of the reaction (ΔG_r^0) is defined by Eq. (3-11) (Smith *et al.*, 2005):

$$\Delta G_r^{\circ} = \sum_i v_{i,r} \Delta G_i^{\circ}$$

(3- 11)

where, v_i is the stoichiometric coefficient and ΔG_i^0 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:

$$\frac{d(\Delta G^{\circ} / RT)}{dT} = \frac{-\Delta H^{\circ}}{RT^2}$$

(3- 12)

The standard enthalpy change of reaction (ΔH°) is related to temperature:

$$\Delta H^{\circ} = \Delta H_0^{\circ} + R \int_{T_0}^{T} \frac{\Delta C_P^{\circ}}{R} dT$$

(3- 13)

Similarly, the standard entropy change of reaction is developed as follow:

$$\Delta S^\circ = \Delta S_0^\circ + R \int_{T_0}^{T} \frac{\Delta C_P^\circ}{R} \frac{dT}{T} \tag{3-14}$$

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:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{3-15}$$

$$\Delta G^\circ = \Delta H_0^\circ - \frac{T}{T_0}(\Delta H_0^\circ - \Delta G_0^\circ) + R \int_{T_0}^{T} \frac{\Delta C_P^\circ}{R} dT - RT \int_{T_0}^{T} \frac{\Delta C_P^\circ}{R} \frac{dT}{T} \tag{3-16}$$

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:

$$G_i^\circ = \Gamma_i(T) + RT \ln f_i^\circ \tag{3-19}$$

The difference between these two equations gives:

$$\mu_i - G_i^\circ = RT \ln \frac{\hat{f}_i}{f_i^\circ} \tag{3-20}$$

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

$$\prod_i (\hat{f}_i / f_i^\circ)^{\nu_i} = K \tag{3-21}$$

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 $P^{°}$ of 1 bar.

$$\hat{f}_i = \hat{\phi}_i y_i P \tag{3-22}$$

$$\prod_i (y_i \hat{\phi}_i)^{\nu_i} = \left(\frac{P}{P^{°}}\right)^{-\nu} K \tag{3-23}$$

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:

$$\hat{f}_i = \gamma_i x_i f_i \tag{3-24}$$

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

$$\frac{\hat{f}_i}{f_i^{°}} = \frac{\gamma_i x_i f_i}{f_i^{°}} = \gamma_i x_i \left(\frac{f_i}{f_i^{°}}\right) \tag{3-25}$$

Where, this ratio is approximated as:

$$\ln \frac{f_i}{f_i^{°}} = \frac{V_i(P - P^{°})}{RT} \tag{3-26}$$

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

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

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:

$$\prod_i (\hat{f}_i / f_i^{\circ})^{\nu_{i,j}} = K_j \qquad\qquad (3\text{-}28)$$

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.

$$\frac{\partial C_i}{\partial t} = -\frac{\partial (uC_i)}{\partial x} - \frac{\partial J_i}{\partial x} + r_i \qquad (3\text{-}29)$$

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:

$$0 = -\frac{\partial (uC_i)}{\partial x} + r_i \qquad (3\text{-}30)$$

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

$$u \frac{d(C_i)}{dx} = r_i \qquad (3\text{-}31)$$

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.
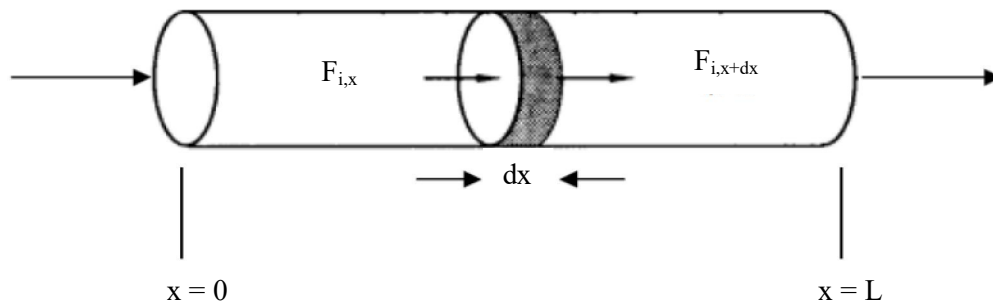

Fig. 3- 1: A schematic diagram of a plug flow reactor

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)

	pH	Temperature (^{o}C)
$H_2S \leftrightarrow H^+ + HS^-$	5-8	-
$HS^- \leftrightarrow H^+ + S^{2-}$	>7	-
$S_2O_3^{2-} + H_2O \rightarrow H_2S + SO_4^{2-}$	12	>70
$S_2O_3^{2-} + 2O_2 + H_2O \rightarrow 2SO_4^{2-} + 2H^+$	>7	25
$nS^{2-} + 2(n-1)H_2O \rightarrow S_n^{2-} + 2(n-1)OH^- + (n-1)H_2$	>7	>70
$HS^- + 2Fe^{3+} \rightarrow 1/8S_8 + H^+ + 2Fe^{2+}$	5-8	-
$S_n^{2-} + 3/2O_2 \rightarrow S_2O_3^{2-} + [(n-2)/8]S_8$	-	-
$S_3O_6^{2-} + 2OH^- \rightarrow S_2O_3^{2-} + SO_4^{2-} + 2H_2O$	>7	-
$HS^- + SO_3^{2-} + 0.5O_2 \rightarrow S_2O_3^{2-} + OH^-$	5-8	-
$nHS^- + (n-1)/2O_2 \rightarrow S_n^{2-} + H_2O + (n-2)OH^-$	-	-
$4S_4O_6^{2-} + 4H_2O \rightarrow 6S_2O_3^{2-} + S_3O_6^{2-} + SO_4^{2-} + 8H^+$	<7	25-70
$S_2O_3^{2-} + O_2 \rightarrow S_4O_6^{2-} + SO_3^{2-}$	<7	25
$3S_3O_6^{2-} \rightarrow S_4O_6^{2-} + 1/8S_8 + 2SO_4^{2-} + 2SO_2$	4	35
$HS^- + 2O_2 \rightarrow SO_4^{2-} + H^+$	8	10

Table 3- 2: Kinetically-controlled 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)

Kinetic reaction	Rate coefficient	Rate order
$S_3O_6^{2-} + Fe^{3+} + 1/2O_2 \rightarrow S_2O_3^{2-} + SO_4^{2-} + Fe^{2+}$	3.2×10^{-2} s^{-1}	$[S_3O_6^{2-}]$
$4S_4O_6^{2-} + 6OH^- \rightarrow 5S_2O_3^{2-} + 2S_3O_6^{2-} + 3H_2O$	6.1×10^{-3} s^{-1}	$[S_4O_6^{2-}]$
$2S_4O_6^{2-} + 6OH^- \rightarrow 3S_2O_3^{2-} + 2SO_3^{2-} + 3H_2O$	5.1×10^{-3} M^{-1} s^{-1}	$[S_4O_6^{2-}]^2$
$H_2S + 1.5O_2 \rightarrow SO_3^{2-} + 2H^+$	k_1^*	$[H_2S][O_2]$
$SO_3^{2-} + 0.5O_2 + H_2 \rightarrow SO_4^{2-} + 2H^+$	k_2^{**}	$[SO_3^{2-}]^2[O_2]^{0.5}$
$H_2S + SO_3^{2-} + 0.5O_2 \rightarrow S_2O_3^{2-} + H_2O$	k_3^{***}	$[H_2S][SO_3^{2-}][O_2]$
$2S_2O_3^{2-} + 2Fe^{3+} \rightarrow S_4O_6^{2-} + 2Fe^{2+}$	0.66 M^{-1} s^{-1}	$[S_2O_3^{2-}]^2$
$2S_2O_3^{2-} + 2H^+ + 0.5O_2 \rightarrow S_4O_6^{2-} + H_2O$	1.48×10^{-3} s^{-1}	$[S_2O_3^{2-}]$
$S_3O_6^{2-} + H_2O \rightarrow S_2O_3^{2-} + SO_4^{2-} + 2H^+$	2.6×10^{-2} s^{-1}	$[S_3O_6^{2-}]$
$4S_4O_6^{2-} + 3Fe^{3+} + 2.75O_2 + 4.5H_2O \rightarrow 4SO_4^{2-} + 3Fe^{2+} + 9H^+$	4.4×10^{-2} M^{-1} s^{-1}	$[S_4O_6^{2-}]^2$
$2S_4O_6^{2-} \rightarrow S_5O_6^{2-} + S_3O_6^{2-}$	0.4×10^{-2} s^{-1}	$[S_4O_6^{2-}]$

* $\ln k_1 = -4.71 + 0.914\,pH - 0.0289\,pH^2$ (M^{-1} s^{-1})

** $\ln k_2 = 3.87 + 1.51\,pH - 0.103\,pH^2$ (M$^{-1.5}$ s^{-1})

*** $\ln k_3 = -9.09 + 3.01\,pH - 0.177\,pH^2$ (M^{-2} s^{-1})

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). The

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_2S 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 3- 3: Initial and reservoir conditions for studying H_2S partitioning behaviour (Stemler, 2012)

Pressure (MPa)	1 – 35
Temperature (°C)	15 – 85
Oil API gravity	34
Gas-oil ratio	135
Water-cut (%)	30
Water production (m^3/d)	20,000
Distance from injection to producer (m)	600
H_2S (based on sulfate concentration in seawater concentration of 2454 mg/L) (mg/L)	869
Test separator pressure (kPa)	690
Test separator temperature (°C)	65

Investigating the sulfur chemistry in reservoirs undergoing seawater flooding is conducted as summarized in Figure 3.2:
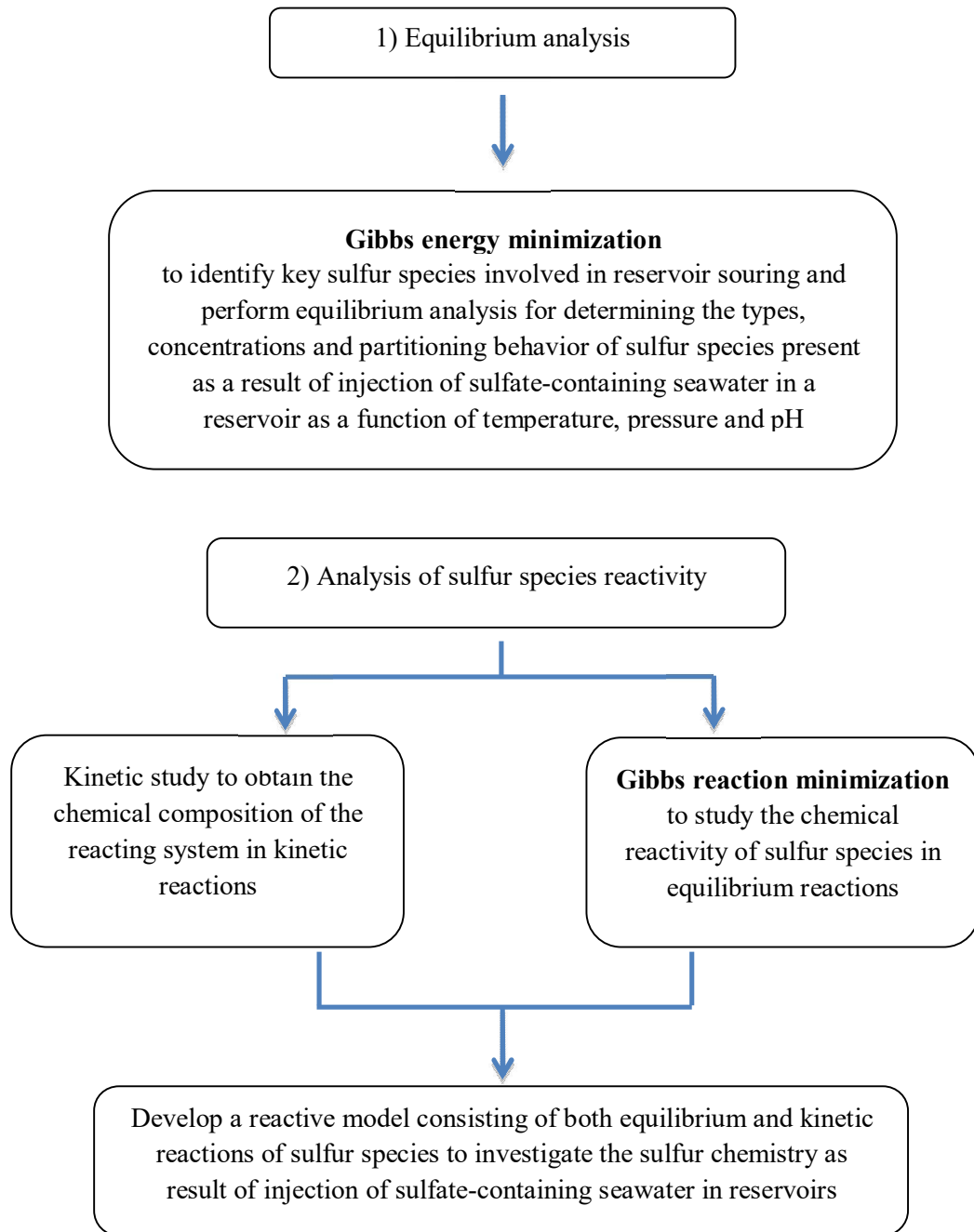

Fig. 3- 2: A schematic diagram of the algorithm followed in this study to investigate sulfur chemistry in a reservoir undergoing seawater injection process

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^oC 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)

Chemical kinetic reactions	Rate Coefficient	Rate order
$4NO_3^- + S_2O_3^{2-} + H_2O \rightarrow 4NO_2^- + 2SO_4^{2-} + 2H^+$	10^3 mol^{-1}yr^{-1}	$[NO_3^-][S_2O_3^{2-}]$
$4FeS_{2(s)} + 14NO_2^{2-} + 6H^+ + 3H_2O \rightarrow$ $4S_2O_3^{2-} + 4Fe(OH)_{3(s)} + 7N_2O_{(g)}$	4.0 yr^{-1}	$[NO_2^-][FeS_{2(s)}]$
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.
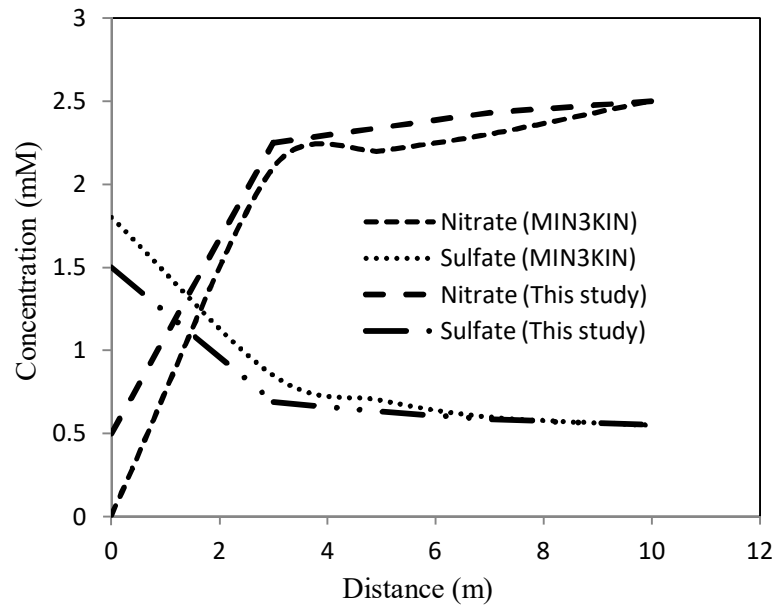
(a)
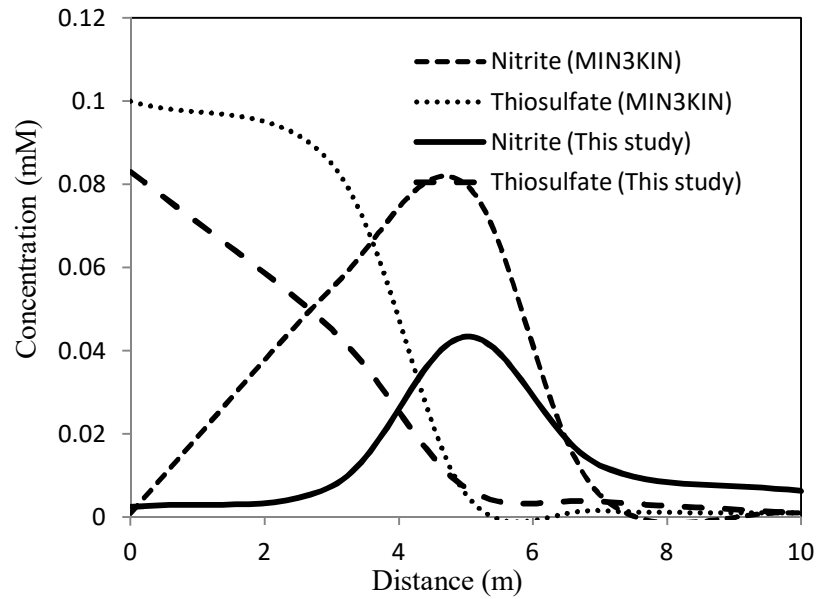
(b)

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.

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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_2S 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 ($S_2O_3^{2-}$, $S_3O_6^{2-}$, $S_4O_6^{2-}$, $S_5O_6^{2-}$), 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.
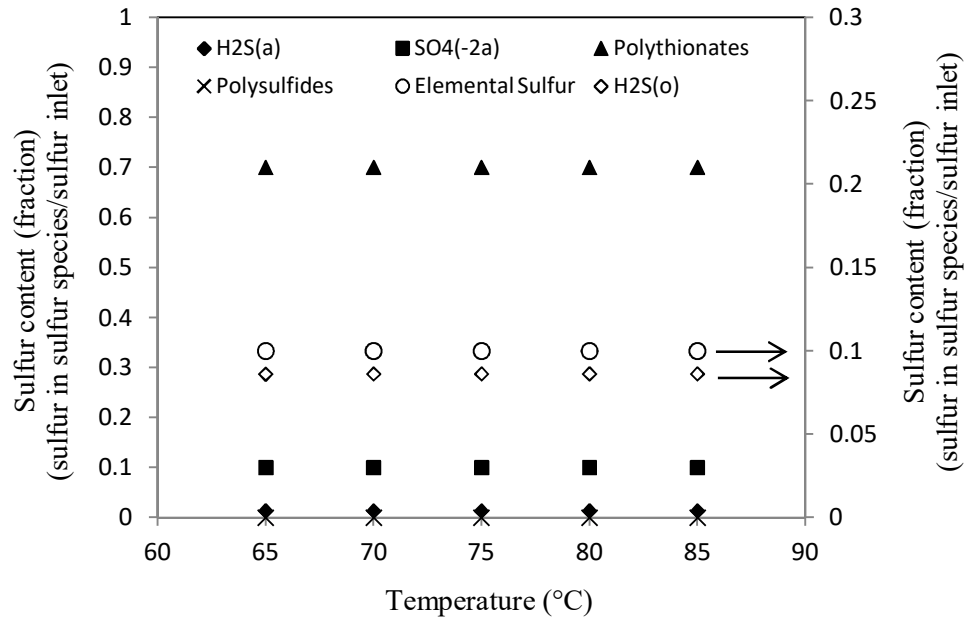
(a)
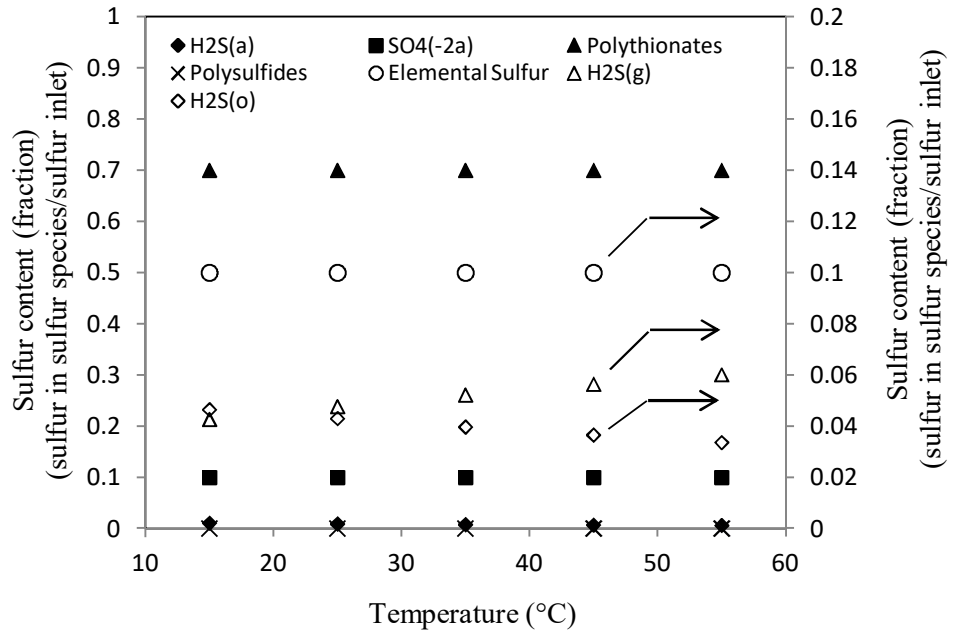
(b)

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) (◊, ○, □, Δ 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 H_2S 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.
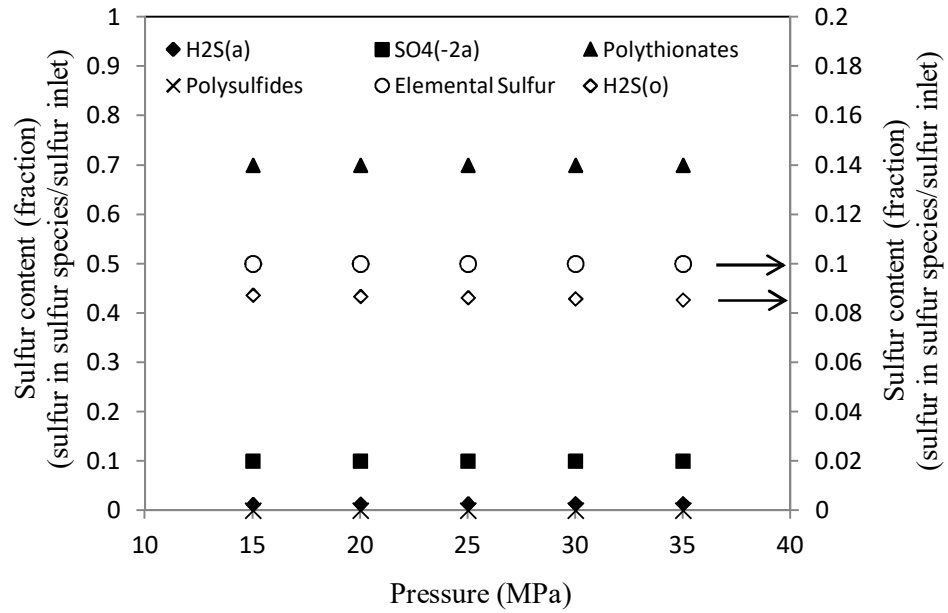
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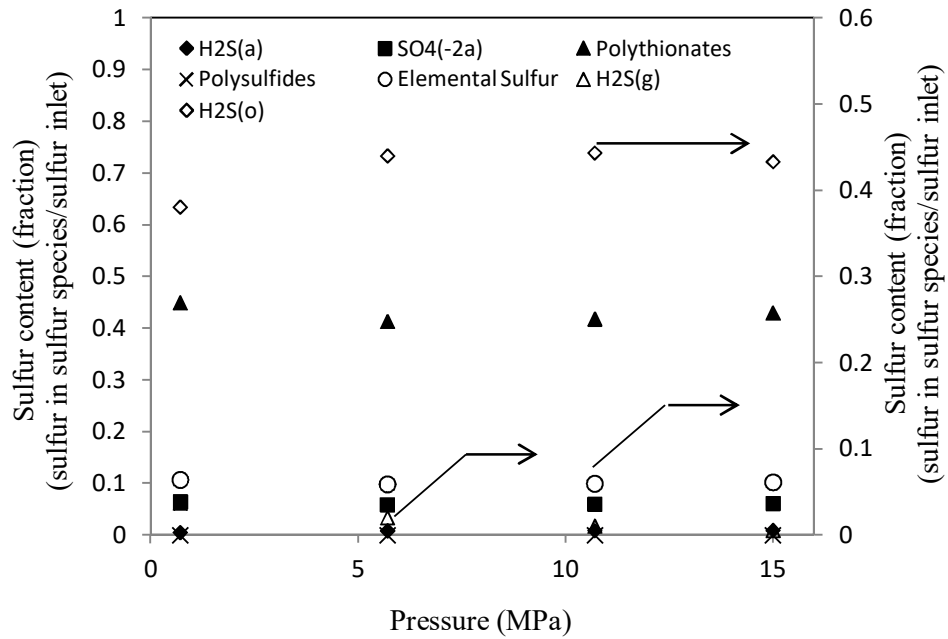
(b)

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)

($\Diamond$, $\circ$, $\square$, Δ from right axis; $\blacklozenge$, $\blacksquare$, $\blacktriangle$, $\times$ 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_2S in a multi-phase system in that a significant amount of aqueous H_2S might be formed as sulfate and polythionates resulting in less H_2S 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.
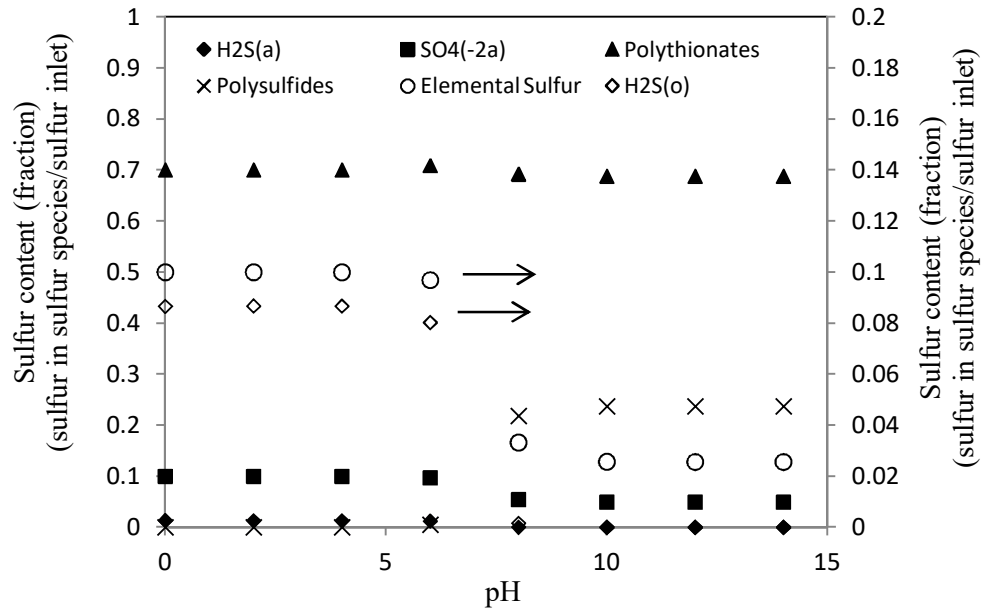
(a)
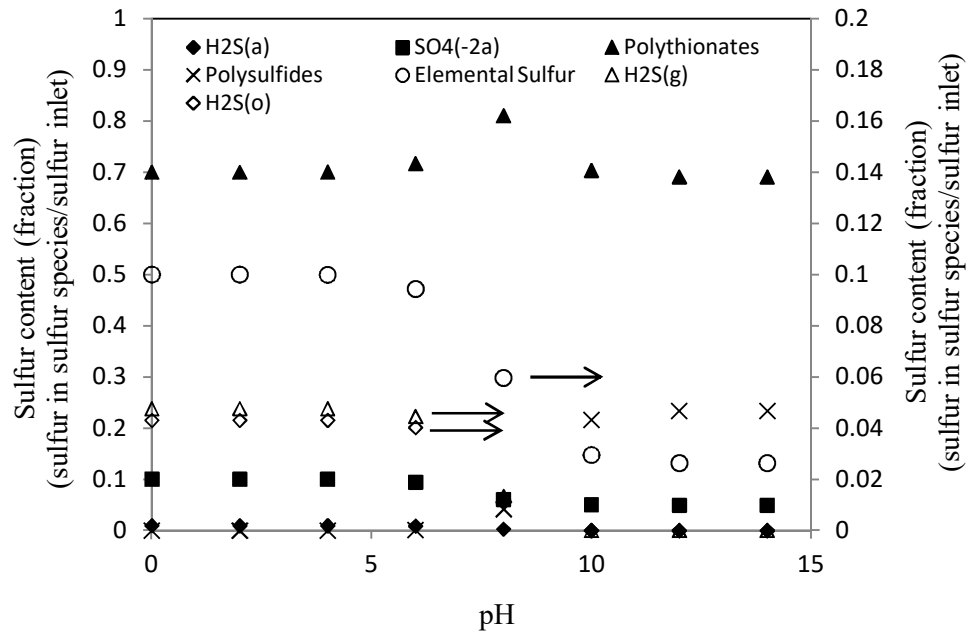
(b)

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), (◊, ○, □, Δ 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_2S 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_2S 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_2S 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_2S partitioning behaviour in a multi-phase system

Upon formation, H_2S 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_2S in a multi-phase system.

Several models have been developed to predict the partitioning behaviour of H_2S in reservoir fluids and to investigate the effects of temperature, pressure, fluids composition, ionic strength, and water pH on the H_2S mass production rate (Eden *et al.*, 1993; 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 H_2S 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 H_2S in water at high pressures and high solute concentrations is determined through a complete form of Henry's law as follow:

$$y_i \hat{\varphi}_i P = x_i \gamma_i H_i \exp\left[\frac{\overline{V}_i^{\infty}\left(P - P_i^{sat}\right)}{RT}\right] \tag{4-1}$$

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 ($\overline{V}_i^{\infty}$) in water is approximately 35 cm^3/mol. The Henry's law constant for H_2S 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):

$$\ln H_{H_2S,water} = 315.722 + 0.05303T - 12224.4/T - 49.7825 \ln T \tag{4-2}$$

The equality of fugacity of each species in all phases at equilibrium is also used for evaluating the distribution of H_2S 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):

$$\log\left(\frac{S_0}{S_S}\right) = kI \tag{4-3}$$

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

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

- Ionization

The dissolution of H_2S in water involves a series of chemical reactions: the dissociation of the molecular H_2S to bisulfide and sulfide ions and the self-ionization of water (Burger et al., 2013):

$$H_2S_{(aq)} \overset{K_1}{\leftrightarrow} HS^- + H^+ \tag{4-5}$$

$$HS^- \overset{K_2}{\leftrightarrow} S^{2-} + H^+ \tag{4-6}$$

$$H_2O \overset{K_3}{\leftrightarrow} OH^- + H^+ \tag{4-7}$$

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

$$K_1 = \frac{a_{H^+} a_{HS^-}}{a_{H_2S_{(aq)}}} = \frac{\gamma_{H^+} \gamma_{HS^-}}{\gamma_{H_2S_{(aq)}}} \frac{m_{H^+} m_{HS^-}}{m_{H_2S_{(aq)}}} \tag{4-8}$$

$$K_2 = \frac{a_{H^+} a_{S^{2-}}}{a_{HS^-}} = \frac{\gamma_{H^+} \gamma_{S^{2-}}}{\gamma_{HS^-}} \frac{m_{H^+} m_{S^{2-}}}{m_{HS^-}} \tag{4-9}$$

$$K_3 = \frac{a_{H^+} a_{OH^-}}{a_{H_2O}} = \frac{\gamma_{H^+} \gamma_{OH^-}}{\gamma_{H_2O}} \frac{m_{H^+} m_{OH^-}}{m_{H_2O}} \tag{4-10}$$

71

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

$$\ln \gamma_i = A|z_i|\sqrt{I} \qquad \text{(4- 11)}$$

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

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

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:

$$t_{H_2S_{(aq)}} = m_{H_2S_{(aq)}} + m_{HS^-} + m_{S^{2-}} \qquad \text{(4- 13)}$$

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

$$pH = -\log\left(a_{H^+}\right) \approx -\log\left(m_{H^+}\right) \qquad \text{(4- 14)}$$

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:

$$F = V + L_1 + L_2 \qquad \text{(4- 15)}$$

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

$$z_i F = y_i V + x_i^{L_1} L_1 + x_i^{L_2} L_2 \qquad \text{(4- 16)}$$

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

$$\Psi = \frac{V}{F} \qquad \text{(4- 17)}$$

$$\xi = \frac{L_1}{L_1 + L_2} \tag{4-18}$$

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

$$K_i^1 = \frac{y_i}{x_i^{L_1}} \tag{4-19}$$

$$K_i^2 = \frac{y_i}{x_i^{L_2}} \tag{4-20}$$

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

$$y_i = \frac{z_i}{\dfrac{\xi(1-\Psi)}{K_i^1} + \dfrac{(1-\Psi)(1-\xi)}{K_i^2} + \Psi} \tag{4-21}$$

$$x_i^{L_1} = \frac{z_i}{\xi(1-\Psi) + (1-\Psi)(1-\xi)\left(\dfrac{K_i^1}{K_i^2}\right) + \Psi K_i^1} \tag{4-22}$$

$$x_i^{L_2} = \frac{z_i}{\xi(1-\Psi)\left(\dfrac{K_i^2}{K_i^1}\right) + (1-\Psi)(1-\xi) + \Psi K_i^2} \tag{4-23}$$

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:

$$\sum_i \frac{z_i(1-K_i^1)}{\xi(1-\Psi) + (1-\Psi)(1-\xi)\dfrac{K_i^1}{K_i^2} + \Psi K_i^1} = 0 \tag{4-24}$$

$$\sum_i \frac{z_i\left(1-\dfrac{K_i^1}{K_i^2}\right)}{\xi(1-\Psi)+(1-\Psi)(1-\xi)\dfrac{K_i^1}{K_i^2}+\Psi K_i^1} = 0 \qquad (4\text{-}25)$$

These two equations are solved simultaneously by Newton-Raphson method to calculate the two unknowns Ψ and ξ.

The amount of molecular H_2S in each phase can be determined based on the Henley-Rosen algorithm as shown in Figure 4.4. Once the amount of molecular H_2S 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).
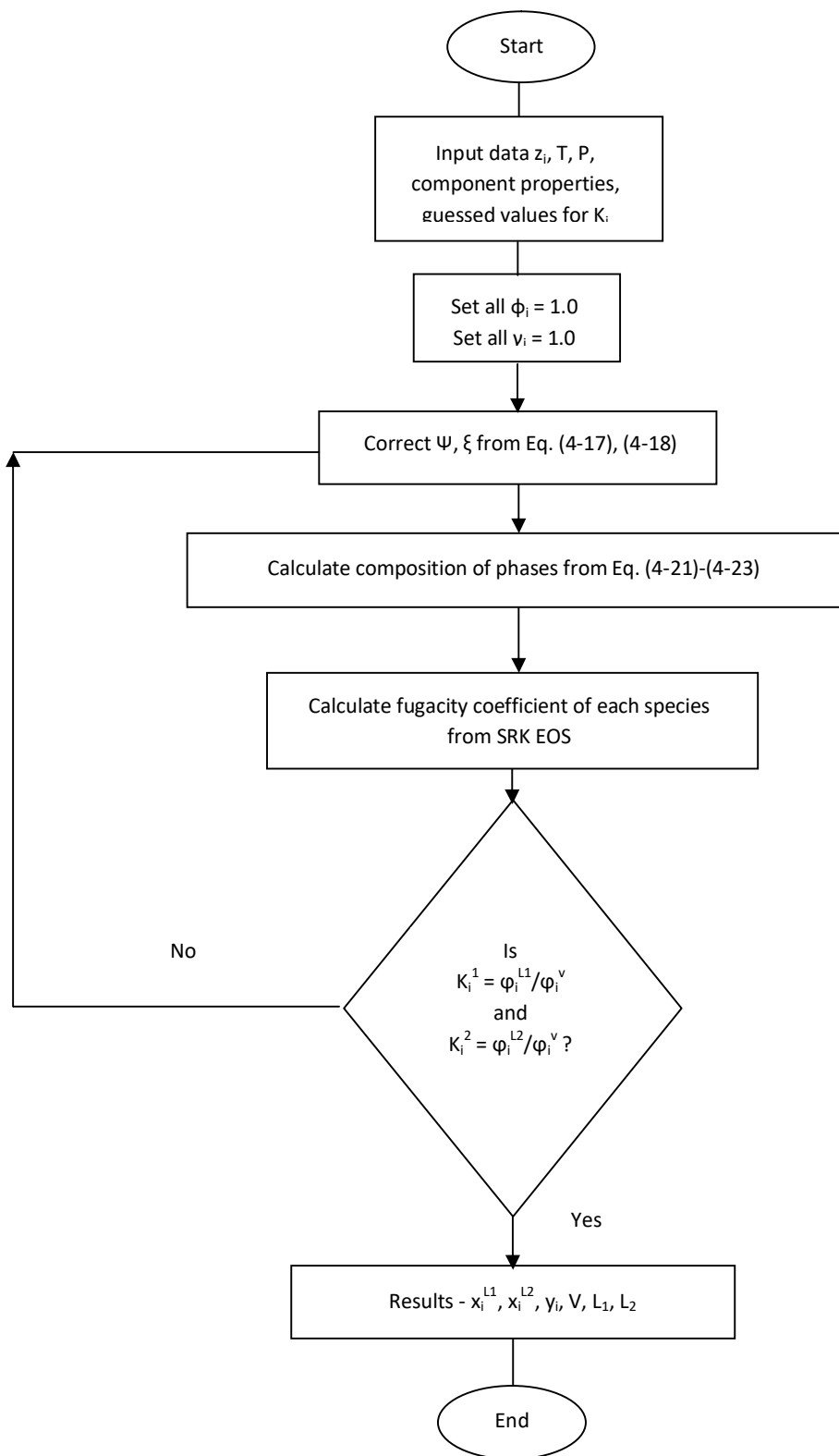
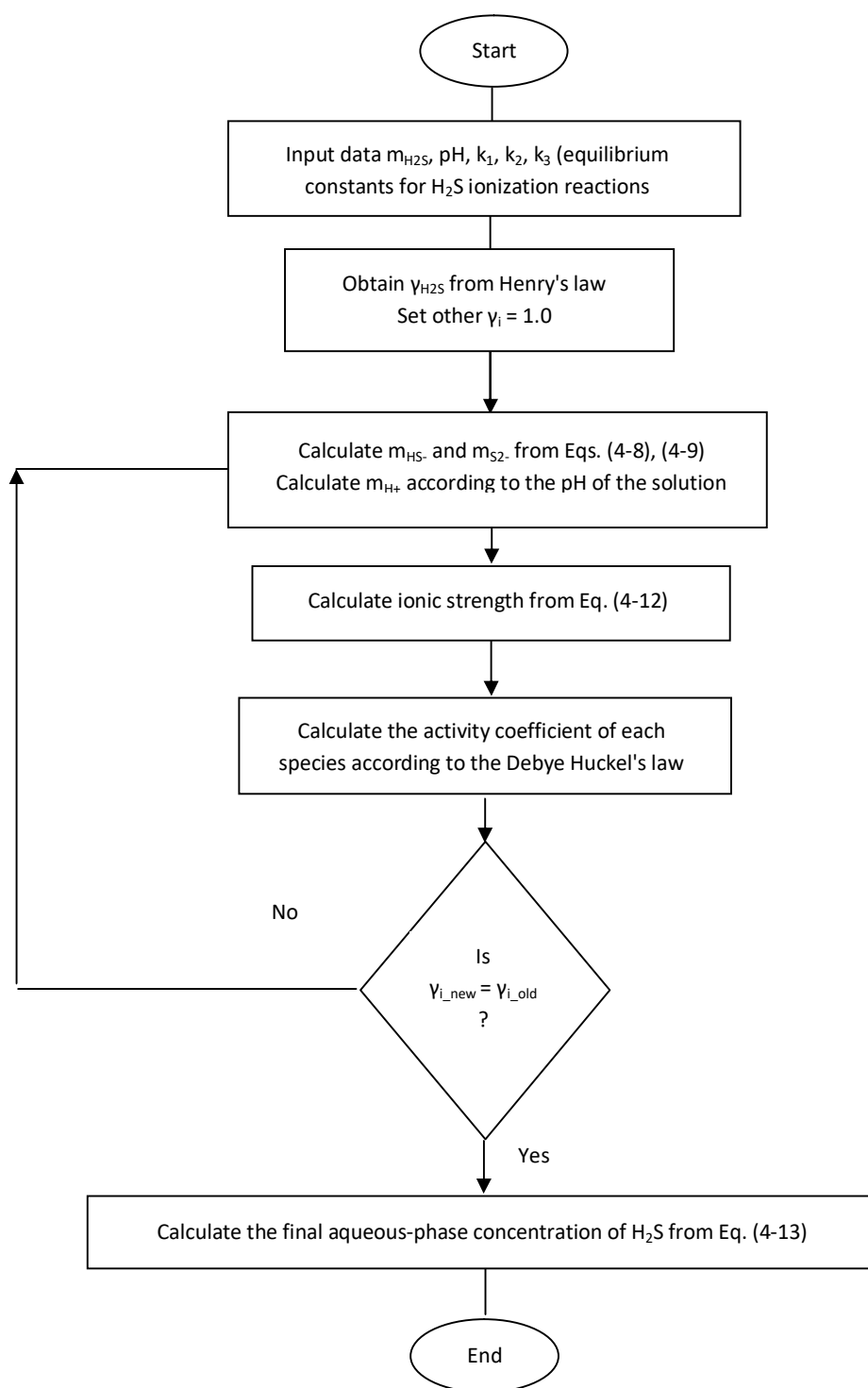Fig. 4- 4: The Henley-Rosen algorithm for studying H_2S partitioning behaviour

```
                        ┌─────────┐
                        │  Start  │
                        └────┬────┘
                             │
         ┌───────────────────▼───────────────────┐
         │  Input data m_{H2S}, pH, k_1, k_2, k_3 (equilibrium │
         │  constants for H_2S ionization reactions │
         └───────────────────┬───────────────────┘
                             │
         ┌───────────────────▼───────────────────┐
         │  Obtain γ_{H2S} from Henry's law       │
         │  Set other γ_i = 1.0                   │
         └───────────────────┬───────────────────┘
                             │
         ┌───────────────────▼───────────────────┐
         │  Calculate m_{HS-} and m_{S2-} from Eqs. (4-8), (4-9) │
         │  Calculate m_{H+} 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 Huckel's law │
         └───────────────────┬───────────────────┘
                             │
                      Is γ_{i_new} = γ_{i_old} ?
                        No ◄──── / Yes ▼
```

Fig. 4- 5: The general algorithm for studying H_2S partitioning behaviour considering ionization reactions

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):

$$f_1^s = \hat{f}_1^l \tag{4-26}$$

The fugacity of the solid can be written as follow:

$$f_1^s = \phi_1^{sat} P_1^{sat} \exp \frac{V_1^s (P - P_1^{sat})}{RT} \tag{4-27}$$

Where, P_1^{sat} is the saturation vapor pressure at temperature T and V_1^s is the molar volume of the solid. The fugacity of the solute in the liquid phase is related to its mole fraction:

$$\hat{f}_1^l = x_1 \hat{\phi}_1 P \tag{4-28}$$

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

$$x_1 = \frac{P_1^{sat}}{P} F_1 \tag{4-29}$$

Where,

$$F_1 = \frac{\phi_1^{sat}}{\hat{\phi}_1} \exp \frac{V_1^s (P - P_1^{sat})}{RT} \tag{4-30}$$

In this equation, the quantity $\hat{\phi}_1$ could be computed from a PVT equation of state such as PR:

$$\ln \hat{\phi}_i = \frac{b_i}{b}(Z - 1) - \ln(Z - \beta) - \bar{q}_i I \tag{4-31}$$

Where:

$$\bar{q}_i = q\left(1 + \frac{\bar{a}_i}{a} - \frac{b_i}{b}\right) \tag{4-32}$$

$$\bar{a}_i = -a + 2\sum_j x_j a_{ji} \tag{4-33}$$

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

$$a_i(T) = \Psi \frac{\alpha(T_{ri})R^2 T_{ci}^2}{P_{ci}} \tag{4-34}$$

$$b_i = \Omega \frac{RT_{ci}}{P_{ci}} \tag{4-35}$$

$$\beta_i \equiv \frac{b_i P}{RT} \tag{4-36}$$

$$q_i \equiv \frac{a_i(T)}{b_i RT} \tag{4-37}$$

Finally:

$$I = \frac{1}{\sigma - \varepsilon} \ln\left(\frac{Z + \sigma\beta}{Z + \varepsilon\beta}\right) \qquad \varepsilon \neq \sigma \tag{4-38a}$$

$$I = \frac{\rho b}{1 + \varepsilon\rho b} = \frac{\beta}{Z + \varepsilon\beta} \qquad \varepsilon = \sigma \tag{4-38b}$$

Written for species i as a liquid:

$$Z_i^l = \beta_i + (Z_i^l + \varepsilon\beta_i)(Z_i^l + \sigma\beta_i)\left(\frac{1 + \beta_i - Z_i^l}{q_i\beta_i}\right) \tag{4-39}$$

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. H₂S 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_2S partitioning between oil, water and gas. The amount of H_2S in reservoir fluid as temperature and pressure change from reservoir to topside facilities can then be determined provided the H_2S concentration in one phase is known (here, the amount of H_2S in the gas phase under test separator conditions). The H_2S 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_2S partition coefficients are calculated and the results are shown in Figures 4.6-4.8.
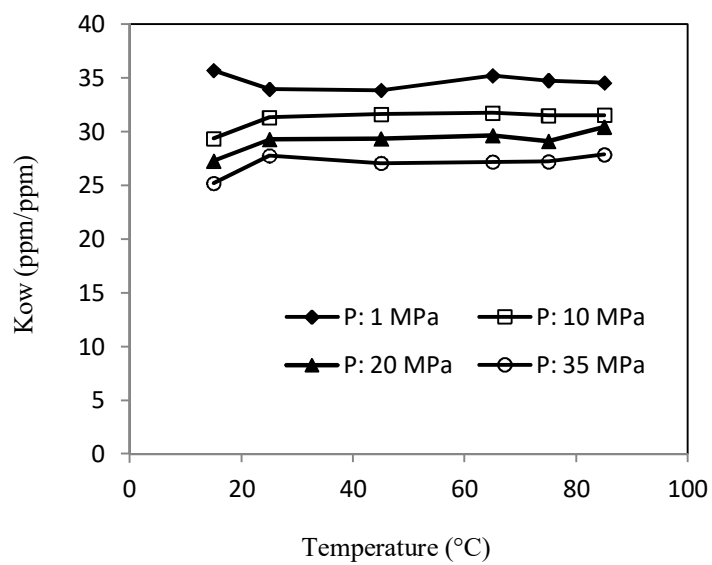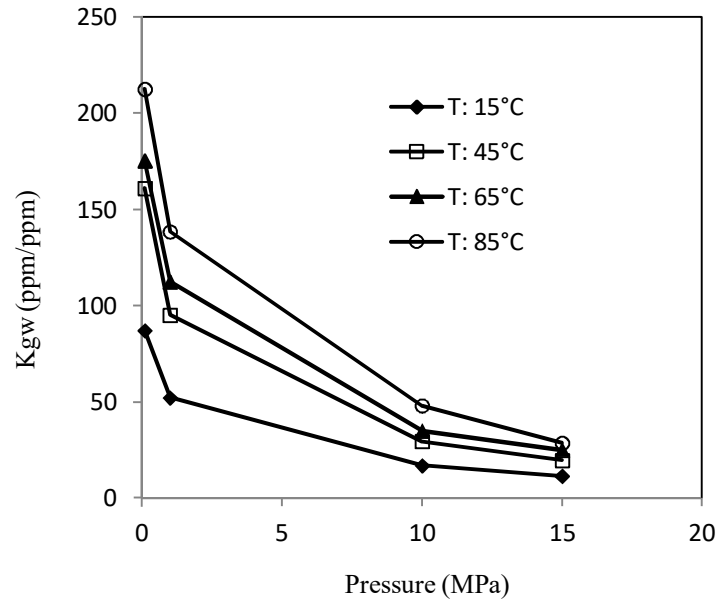
(a)
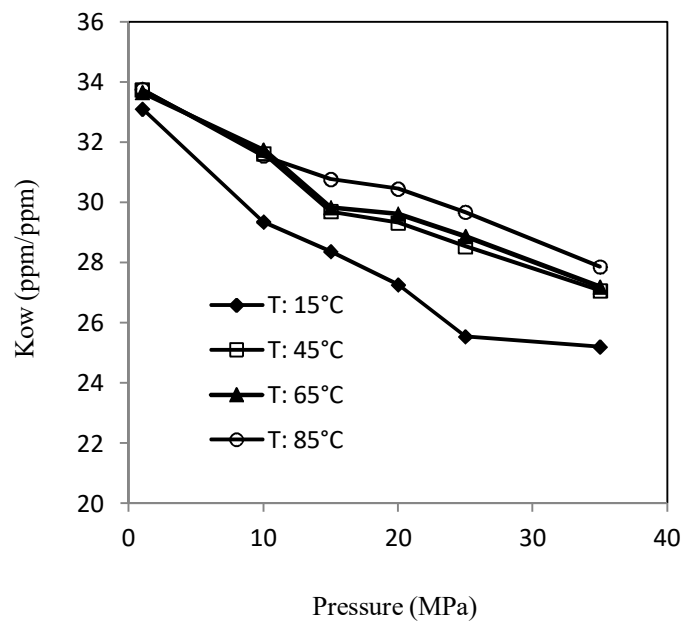
(b)

Fig. 4- 6: H_2S oil-water partition coefficients for the conditions in Table 4.1 as a function of a) temperature, b) pressure
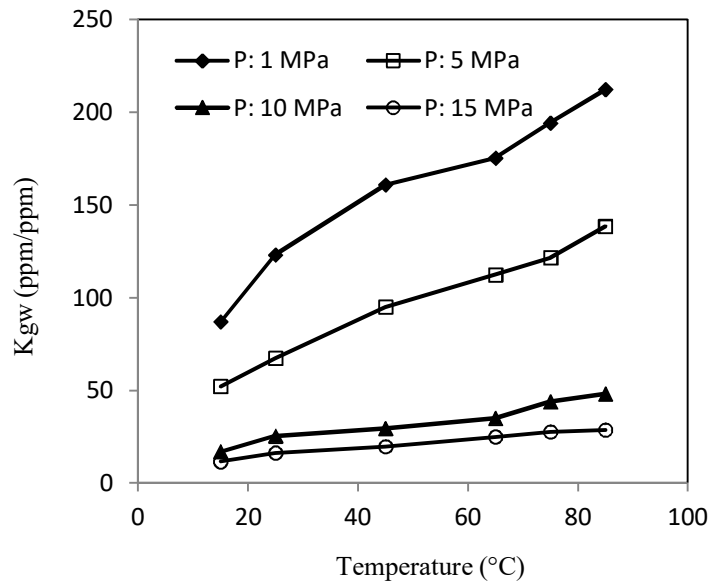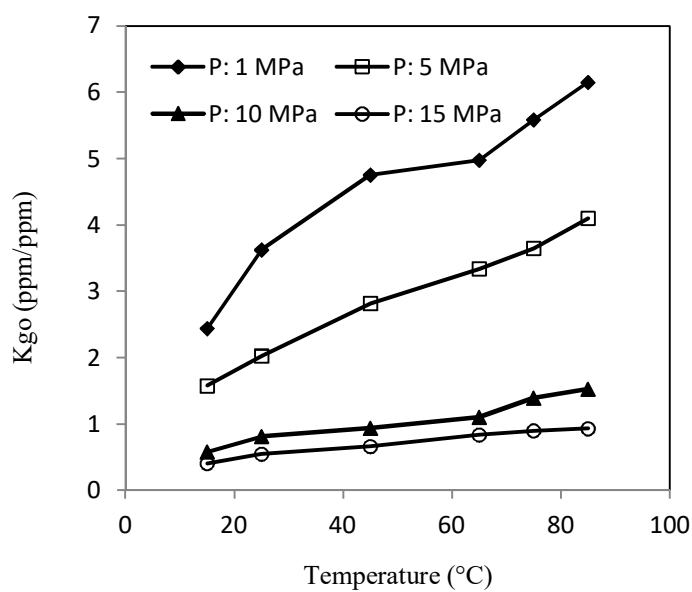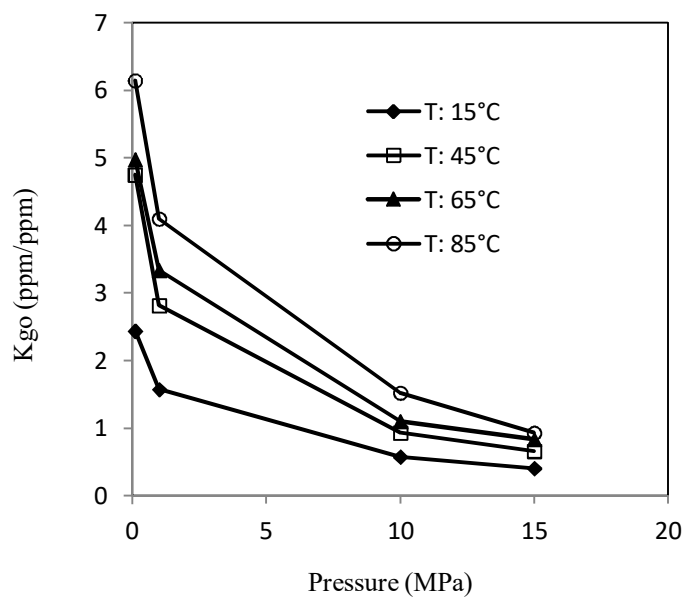
(a)

(b)

Fig. 4- 7: H_2S gas-water partition coefficients for the conditions in Table 4.1, as a function of a) temperature, b) pressure

(a)

(b)

Fig. 4- 8: H_2S 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_2S 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_2S partitions between oil and water. H_2S solubility in the hydrocarbon-rich phase is higher than that in the aqueous phase and therefore, above the bubble point pressure, H_2S is mostly found in the oil phase ($K_{ow(H_2S)}$). When pressure is decreased and temperature is increased, the gas phase forms and H_2S 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_2S 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_2S.

Table 4- 1: Partition coefficient for the distribution of hydrogen sulfide between oil and water, K_{ow} in ppmw/ppmw, P=101.3 kPa

T (°C)	30	50	70	90
Experimental value (Eden *et al.*, 1993)	3.00	3.00	3.1	3.20
Model results	3.19	3.23	3.28	3.25

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.
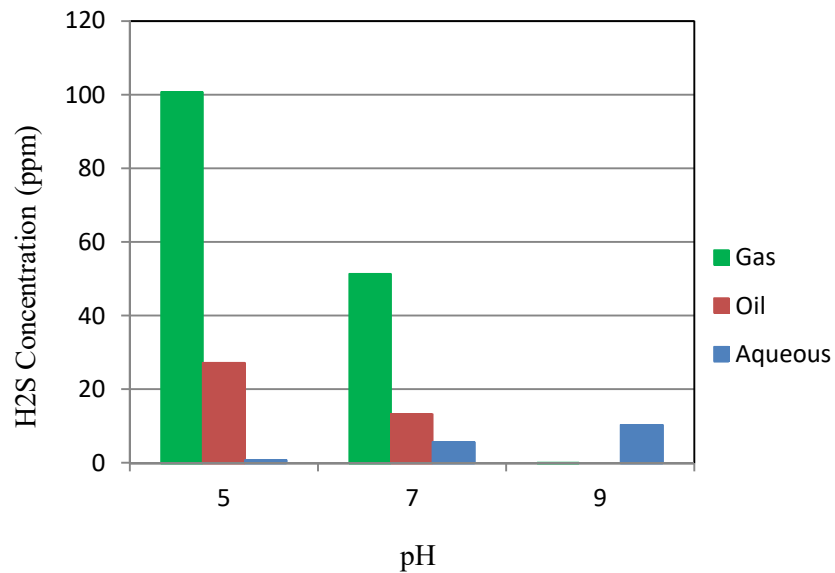
Fig. 4- 9: H_2S partitioning behaviour as a function of pH (Test separator conditions)

The amount of H_2S in the gas phase under test separator conditions is the only measurable quantity of the H_2S produced and is used by industry as an indicator of reservoir souring. One might be interested in predicting the amount of H_2S in reservoir fluid during production. The gas phase H_2S concentration at test separator conditions and the values of partition coefficients were therefore, used to determine the H_2S 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 H_2S presents in reservoir fluids from injection to production well (Figure 4.10).
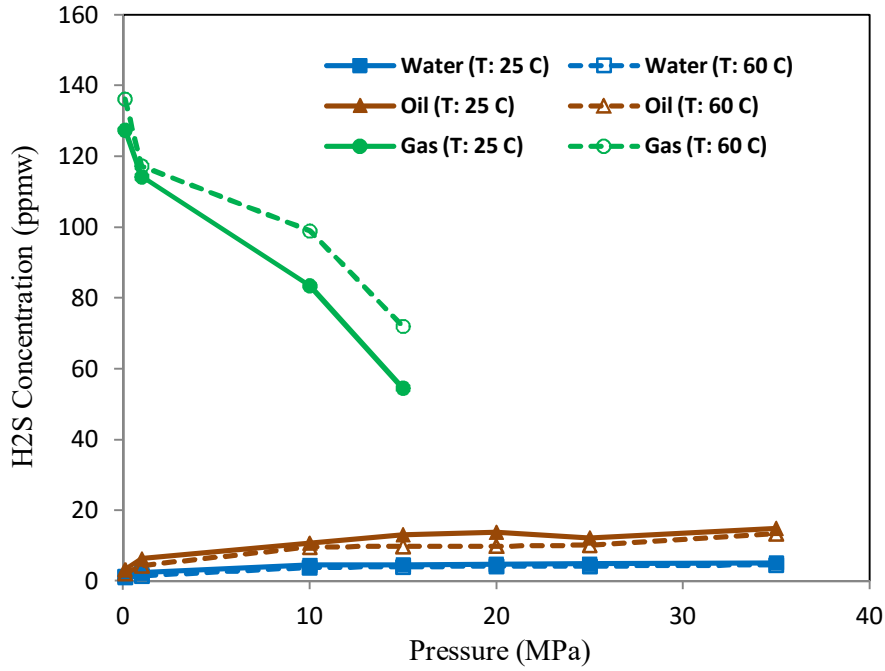
Fig. 4- 10: H_2S concentration in a 3-phase system as a function of temperature and pressure

Based on the equilibrium analysis, the K-values for H_2S partitioning between oil, water, and gas phases were fit to a linear expression as a function of temperature and pressure:

$$K_{ow(H_2S)}=4.717+0.3096T+0.6467P \tag{4-40}$$

$$K_{gw(H_2S)}=11.886+1.1186T+1.2523P \tag{4-41}$$

Where, T is in °C and P is in MPa. The partitioning coefficients calculated in this section for H_2S are then used in the plug flow model, described in Chapter 3, to obtain the H_2S 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.
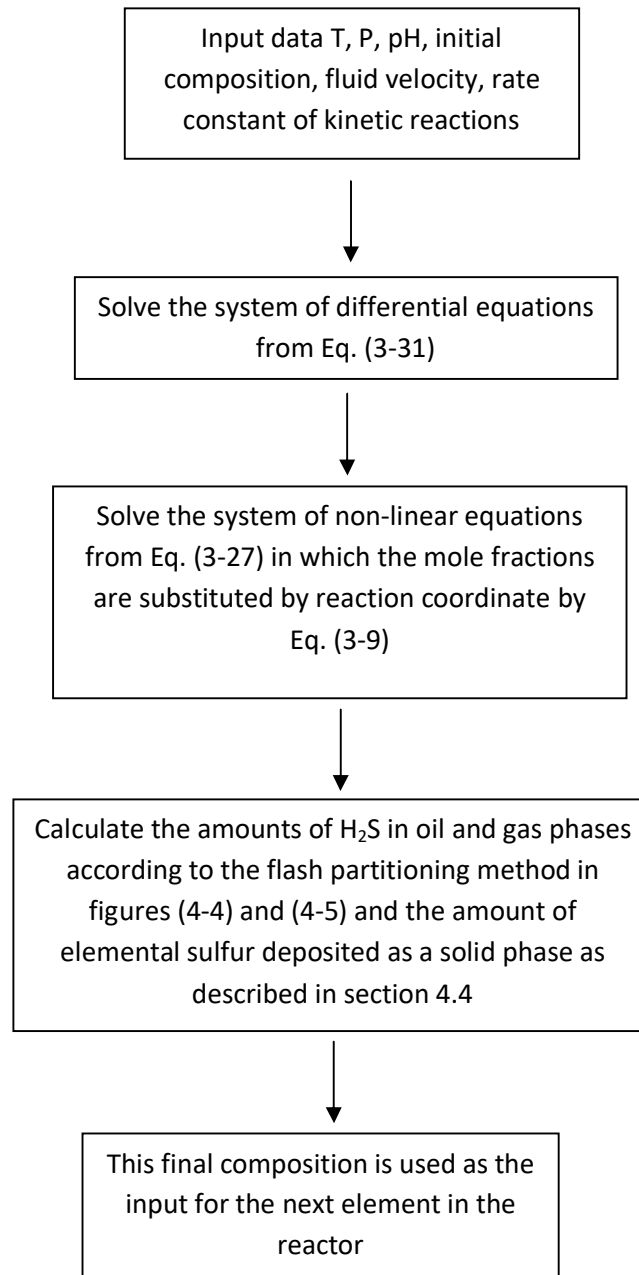
Fig. 4- 11: A schematic diagram of the algorithm followed in this study to investigate sulfur reactivity in the plug flow reactor model

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 H_2S in a multi-phase system in that a significant amount of aqueous H_2S might be formed as sulfate and polythionates resulting in less H_2S 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, H_2S 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_2S 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 H_2S partitioning and elemental sulfur deposition. This provides a more complete picture of the reaction pathways in the reservoir.

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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, trithionate, tetrathionate, 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.
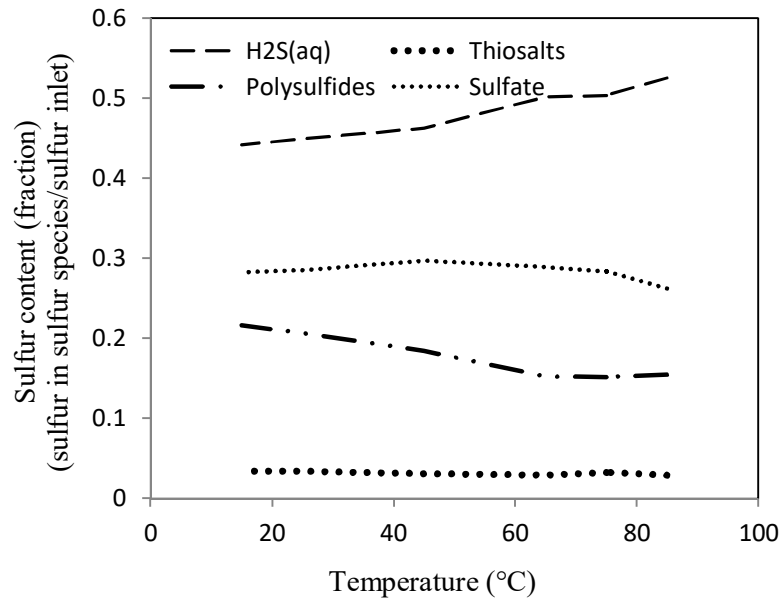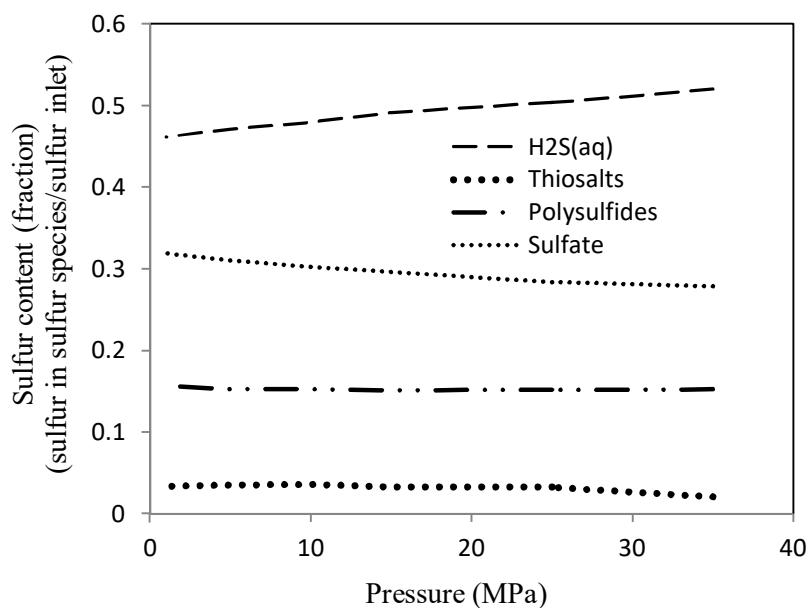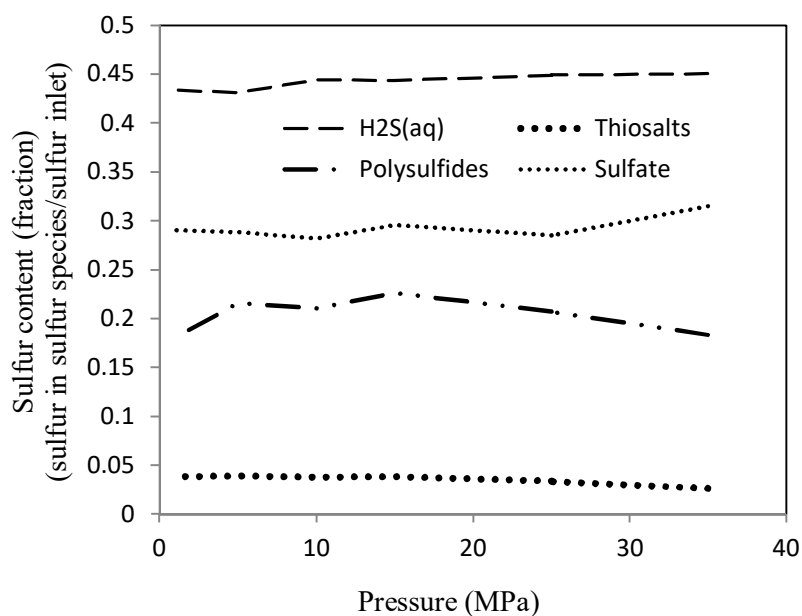

(a)
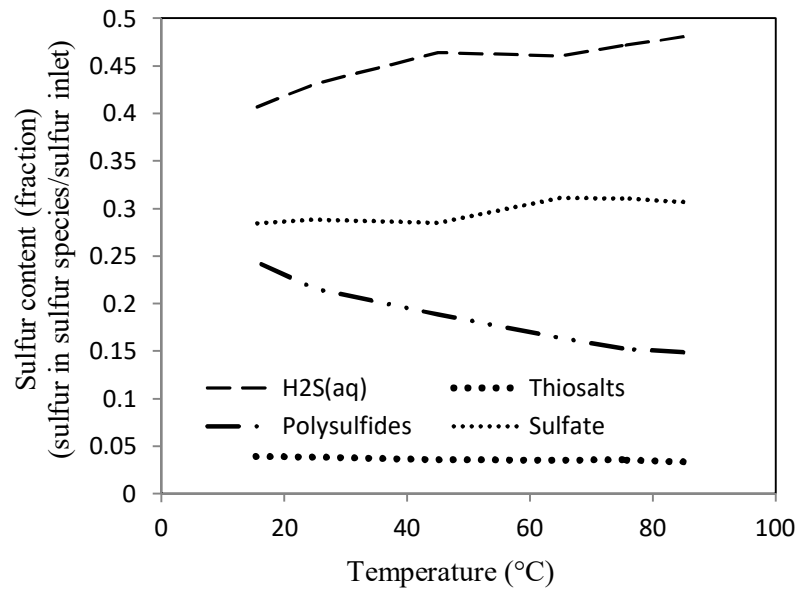
(b)

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
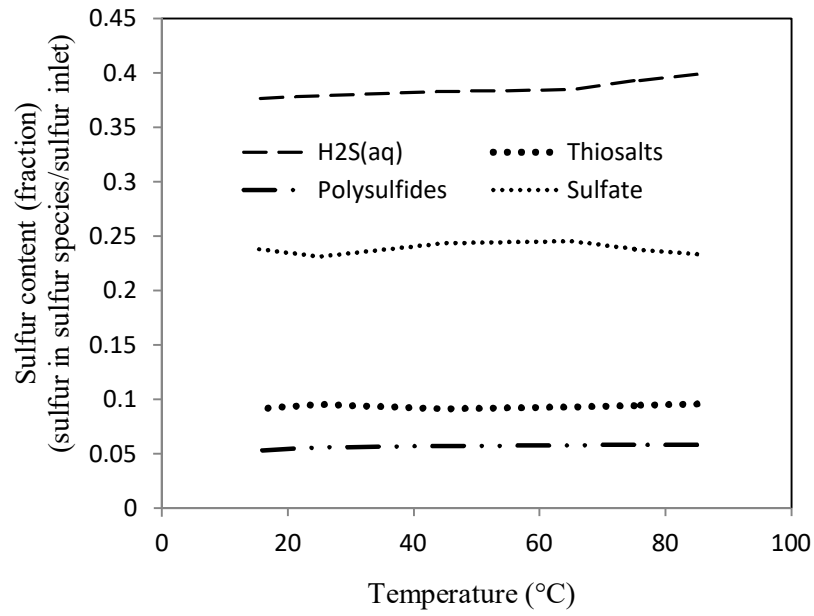

(a)

(b)

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 H_2S, sulfate, and polysulfide ions (S_2^{2-}, S_3^{2-}, S_4^{2-}, and 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 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.
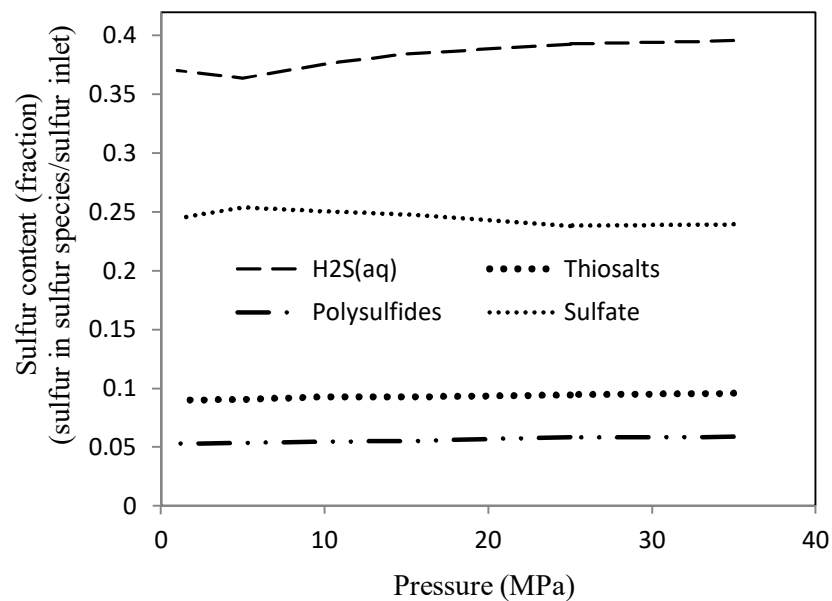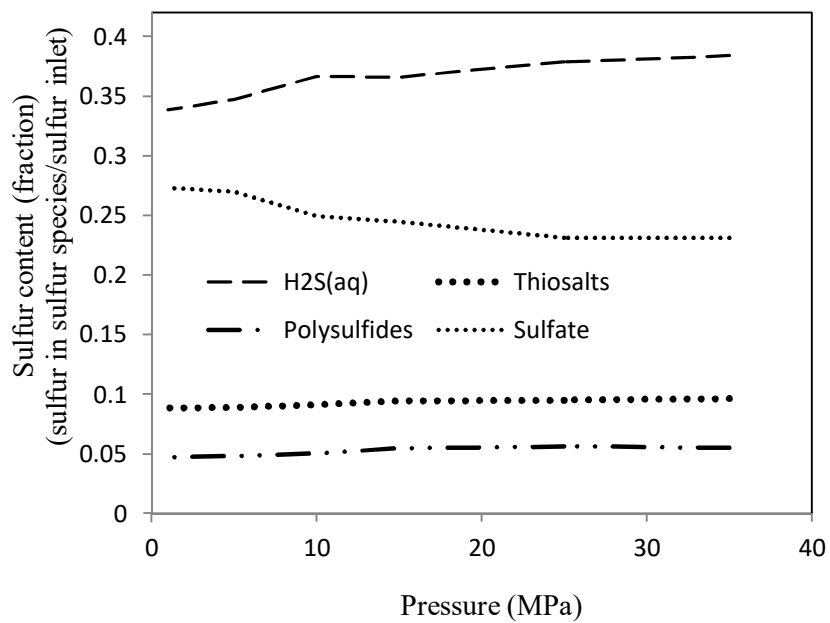
(a)
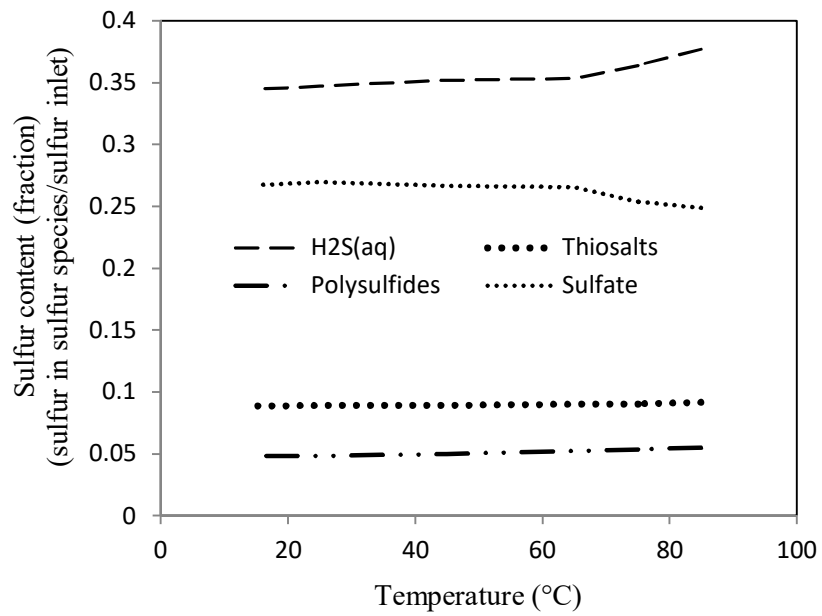
(b)

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
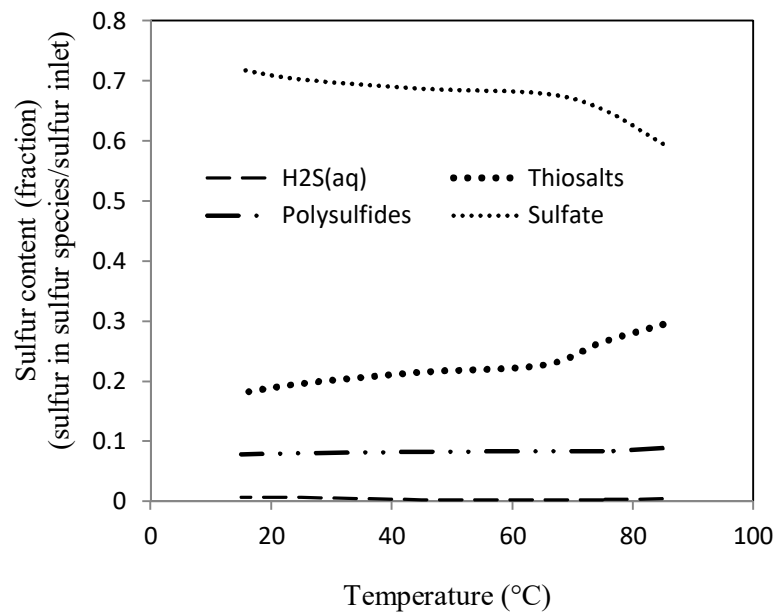
(a)

(b)

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

H$_2$S 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.
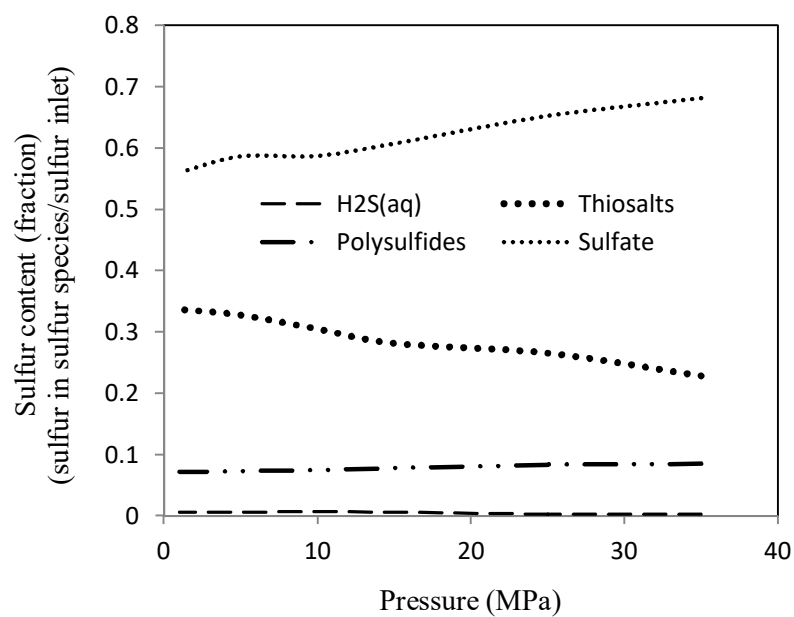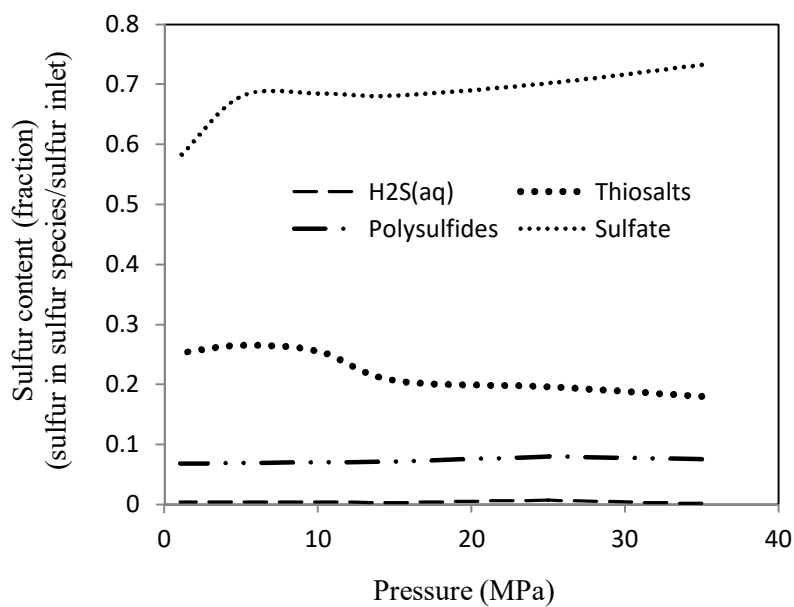
(a)
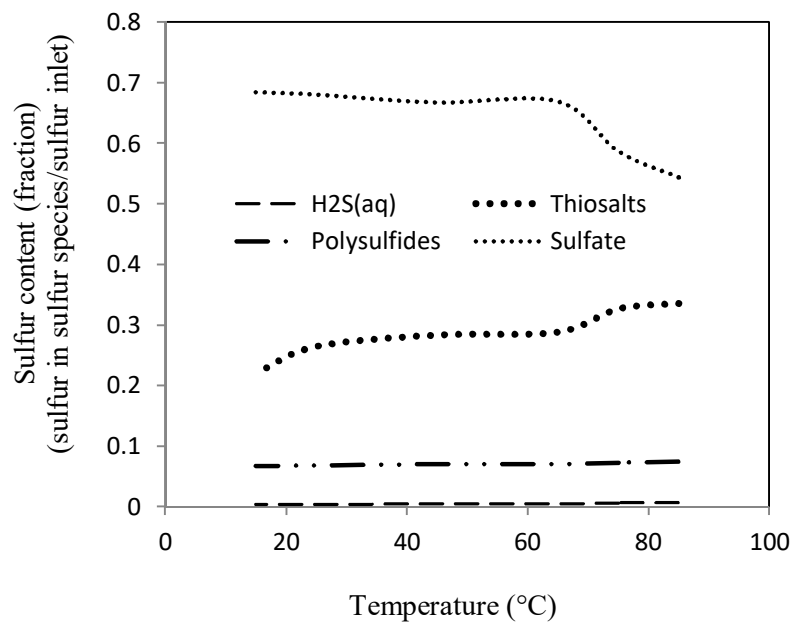
(b)

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

(a)

(b)

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 H_2S dissociation reaction under basic conditions, the amount of molecular H_2S 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 H_2S value on the topsides, the phase partitioning behaviour of H_2S and elemental sulfur were studied. The K-values for H_2S 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.
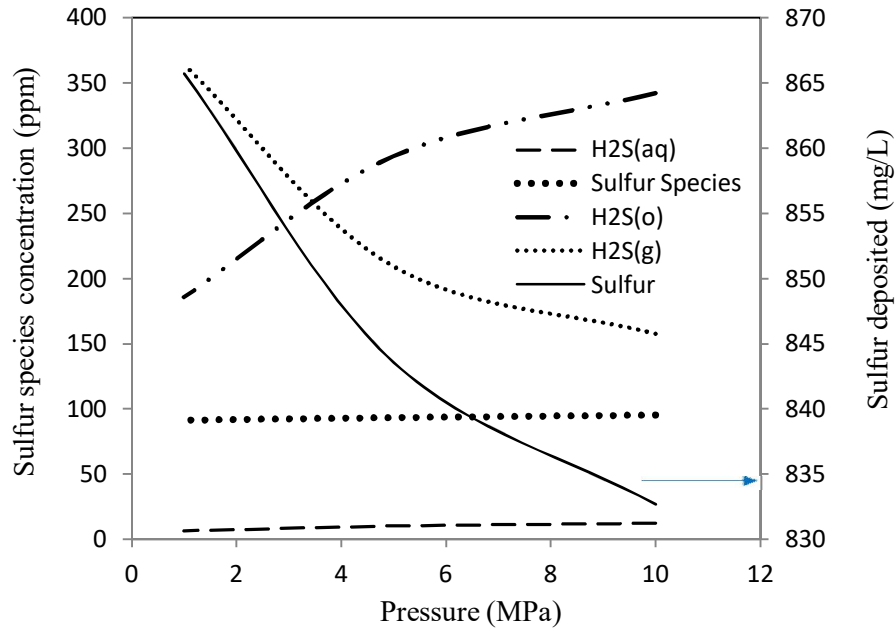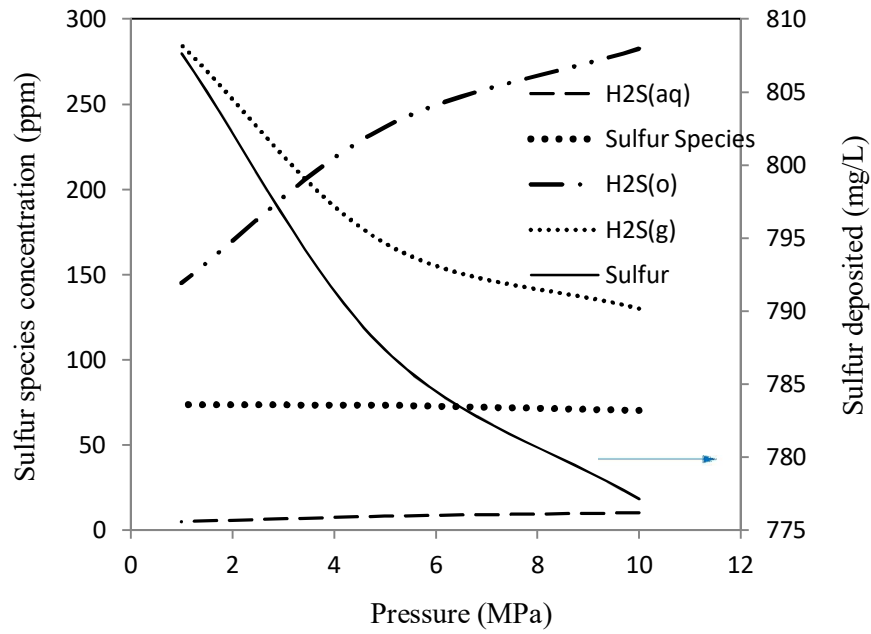
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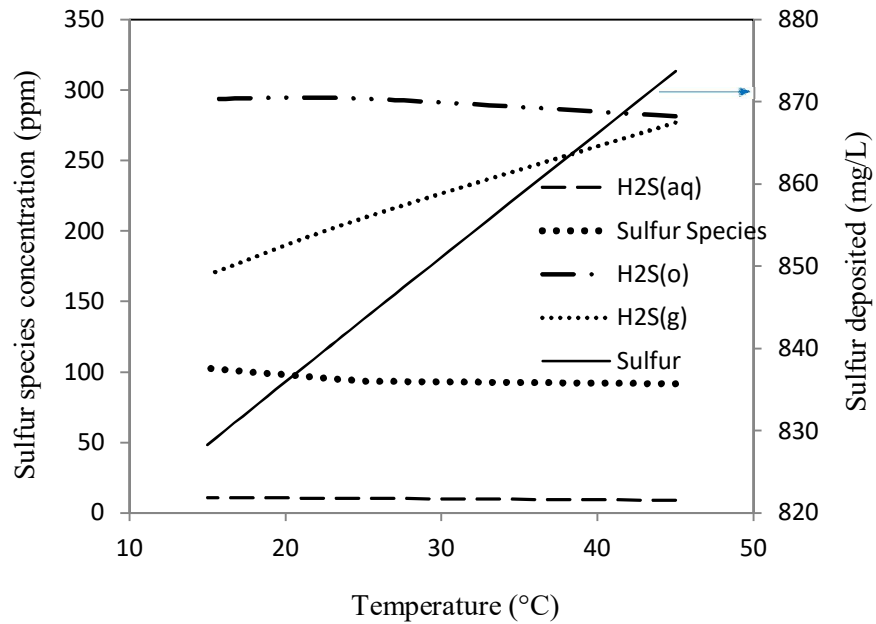
(b)

Fig. 5- 7: The effects of temperature and pressure on sulfur speciation, solid phase formation, and H₂S 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 H_2S in the gas phase from the model at test separator conditions, is 487 ppm, while the H_2S 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 (*i.e.*, assuming that all the initial sulfate in the injected seawater is converted to H_2S 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 H_2S.

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_2S to bisulfide at pH values near neutral, the amount of molecular H_2S in the aqueous phase and therefore, the amount in oil and gas phases in equilibrium decreases.
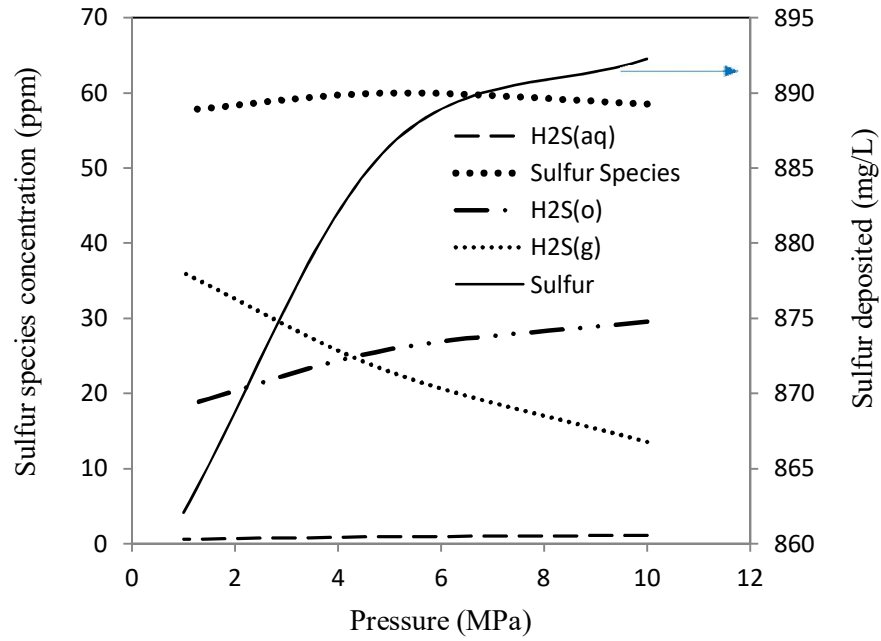
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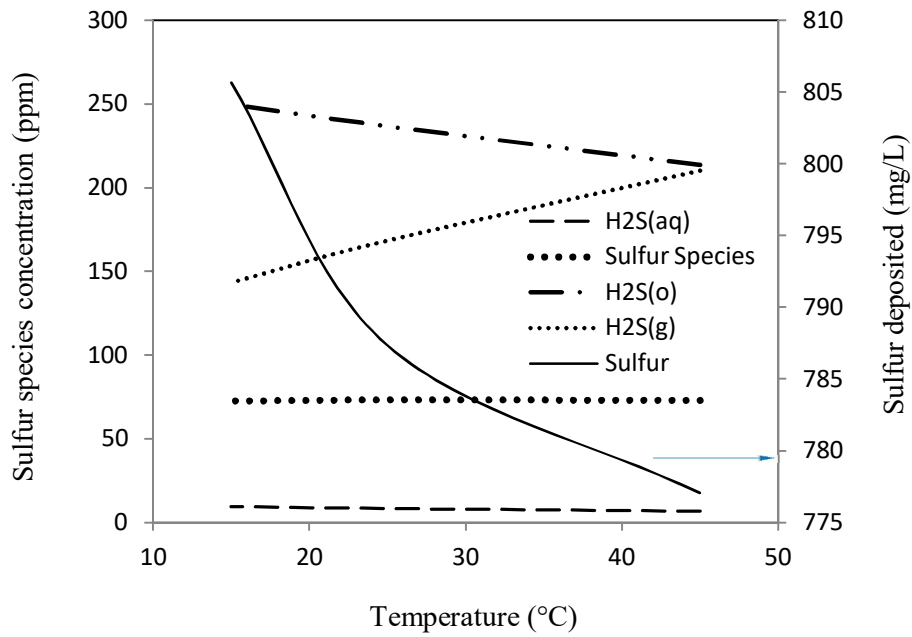
(b)

Fig. 5- 8: The effects of temperature and pressure on sulfur speciation, solid phase formation, and H$_2$S 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)
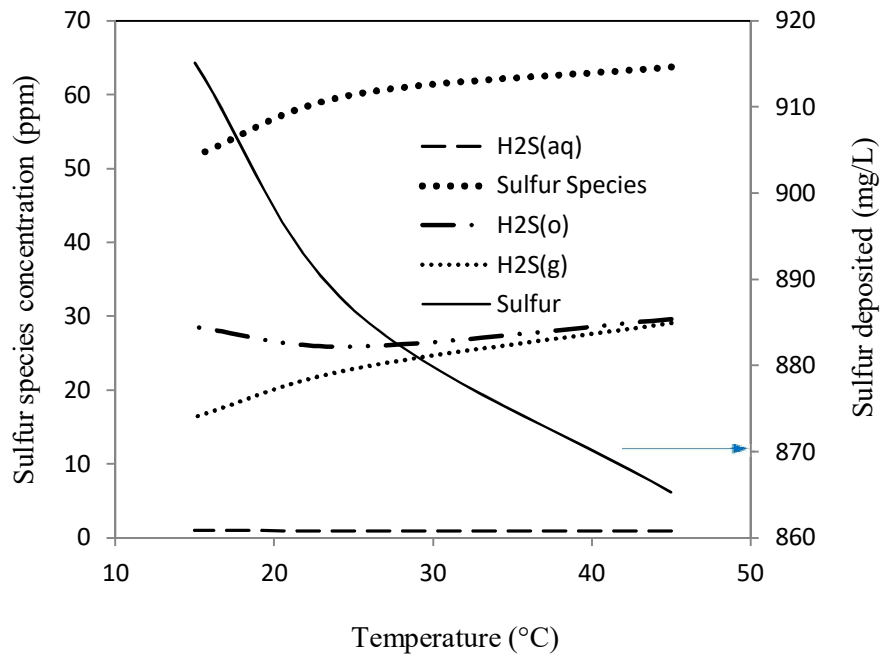
(a)

(b)

Fig. 5- 9: The effects of temperature and pressure on sulfur speciation, solid phase formation, and H$_2$S 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_2S.

Table 5- 1: Comparison of the results of sulfur speciation for 3 cases, T: 15 °C, P: 1 MPa

pH	Sulfur compounds concentration (ppm)						Sulfur deposited (mg/L)
	Polysulfides*	Sulfate	Thiosalts**	H_2S (aq)	H_2S (g)	H_2S (o)	
5	38.5	48.7	7.3	6	272.4	201.3	831
7	22.7	60.8	16	5.29	240.4	177.3	835
9	11.8	104.2	32.3	0.06	2.6	1.6	868
Base case***	–	–	–	12.5	567.5	420	–

* polysulfide ions is the summation of S_2^{2-}, S_3^{2-}, S_4^{2-}, S_5^{2-}

** thiosalts is the summation of $S_2O_3^{2-}$, $S_3O_6^{2-}$, $S_4O_6^{2-}$, $S_5O_6^{2-}$

*** base case: all the initial sulfate forms H_2S, 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_2S dissociates to sulfide and bisulfide and therefore, the amount of molecular H_2S in the aqueous phase and that in the oil and gas phases decreases. Again, in this case, one might estimate 0.5 ppm H_2S in the aqueous phase, 22.5 ppm H_2S in the gas phase, and 13.4 ppm H_2S in the oil phase with ignoring sulfur speciation which leads to over prediction of H_2S 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.
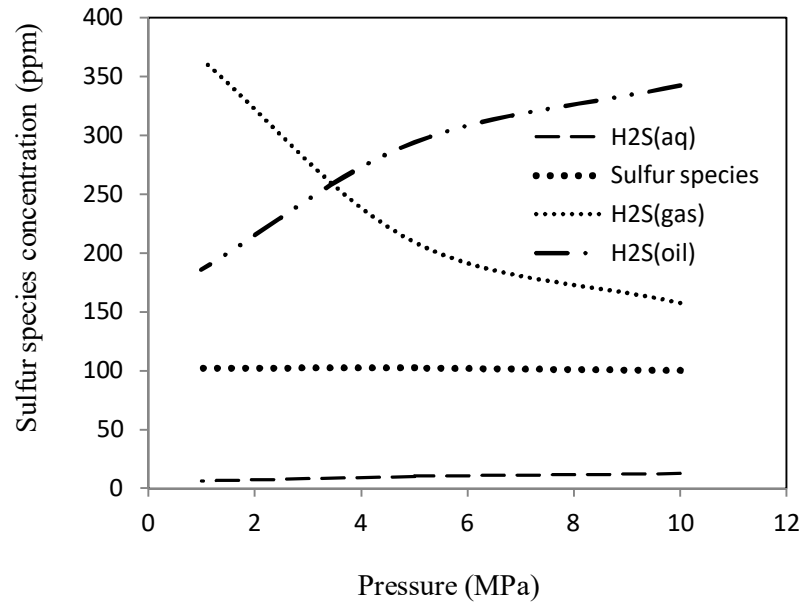
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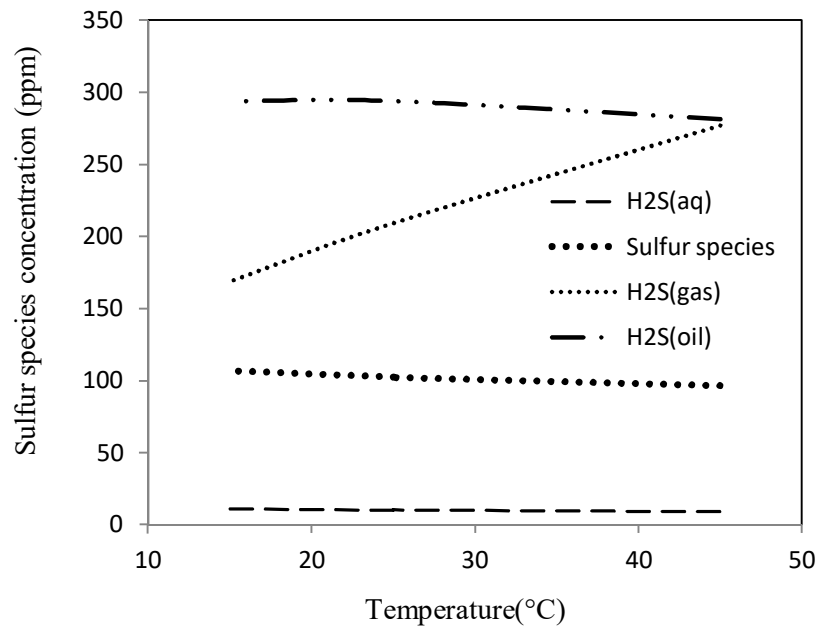
(b)

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)
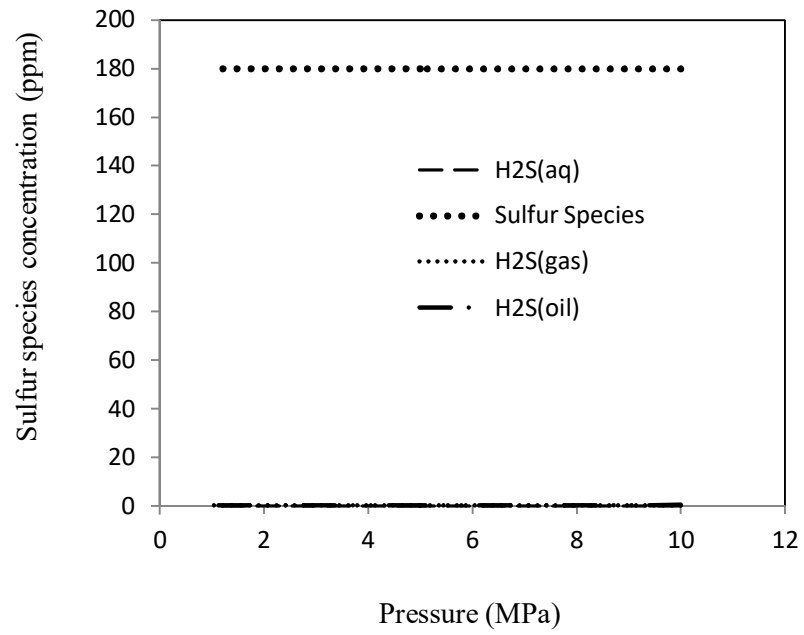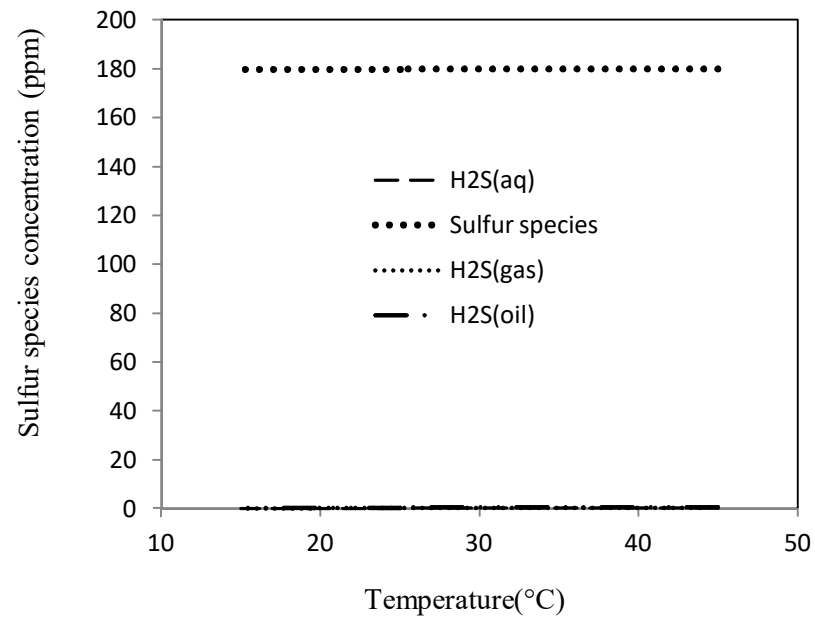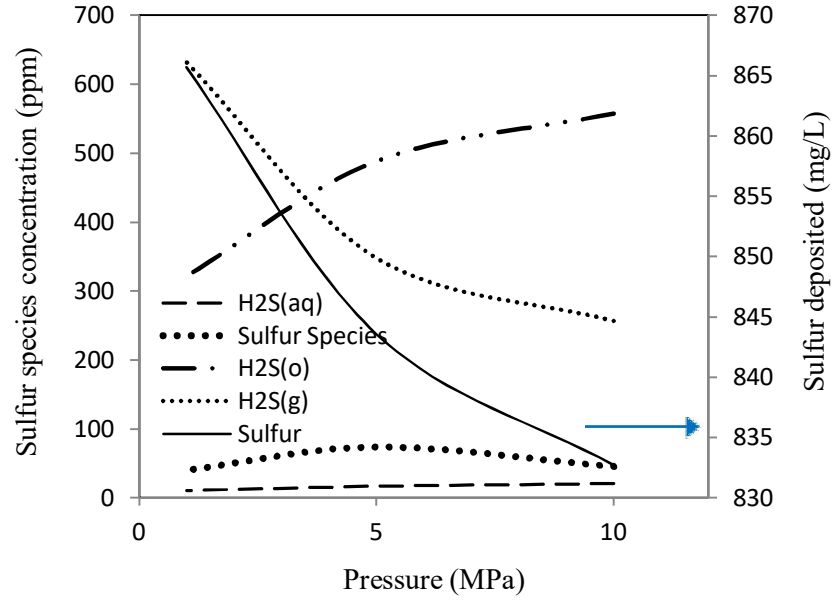
(a)

(b)

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_2S 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_2S dissociates to sulfide and bisulfide decreasing the molecular H_2S 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_2S 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_2S 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.

(a)
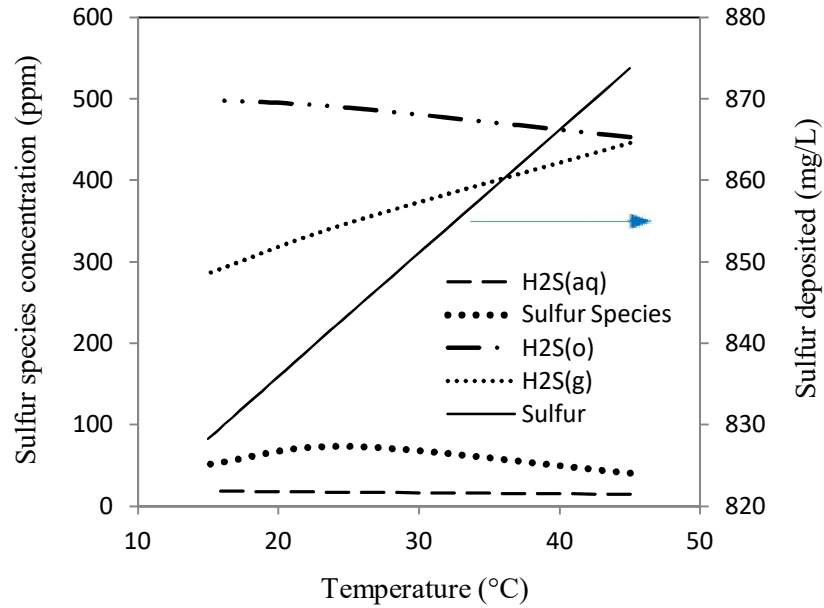
(b)

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
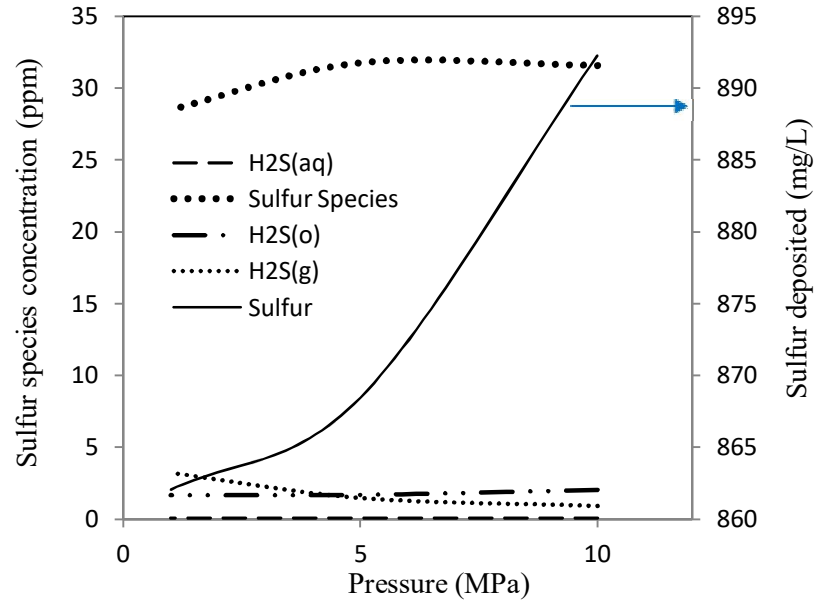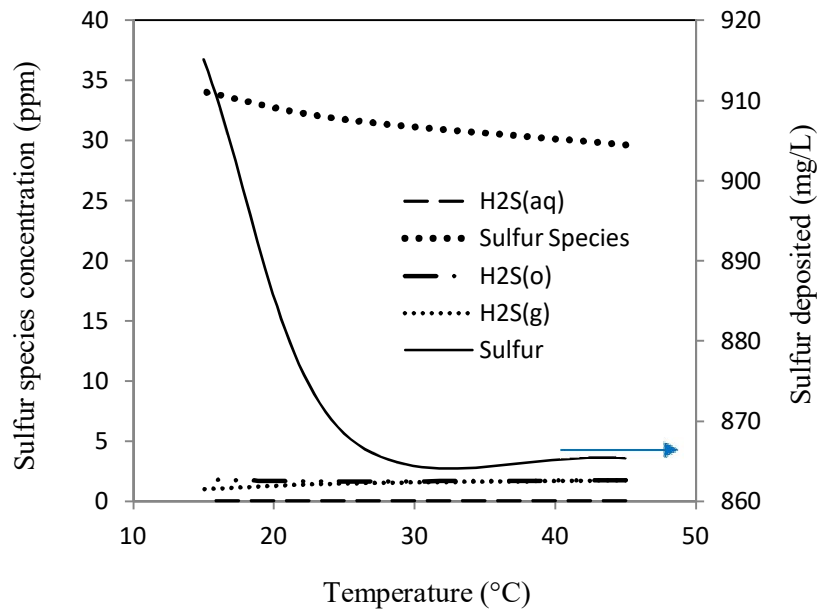(Sulfur Species is the total concentration of sulfate, sulfite, polysulfide ions, and thiosalts)

(a)

(b)

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_2S below bubble point. It also increases the possibility of formation of a solid phase containing elemental sulfur. A significant amount of H_2S dissolves in the oil phase leaving a small amount of molecular H_2S 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.

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

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 S^{2-}) 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 (S_2^{2-}, S_3^{2-}, S_4^{2-}, and S_5^{2-}). 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

	Sulfur content of aqueous phase (%)			
	sulfate	Thiosulfate	Polysulfides[*]	HS⁻, S²⁻
Experimental value (Witter and Jones, 1998)	56	2	3	39
Model results	58	1.8	3.7	31
Deviation (%)	3.6	10	23.3	20.5

[*] polysulfide ions is the summation of S_2^{2-}, S_3^{2-}, S_4^{2-}, S_5^{2-}

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.

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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, H_2S could partition to the gas, water or oil phases depending on pressure, temperature and/or composition. However, depending on the pH, H_2S could dissociate to bisulfide and sulfide ions which remain in the aqueous phase and do not partition between phases affecting the amount of H_2S 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 H_2S 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_2S 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_2S in a multiphase system in that a significant amount of aqueous H_2S might be formed as sulfate and polythionates resulting in a lower overall amount of H_2S.

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_2S 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_2S 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). H_2S solubility in the hydrocarbon-rich phase is higher than that in the aqueous phase and therefore, above the bubble point pressure, H_2S 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 H_2S forms, while the H_2S 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 H_2S which partitions between phases is decreased significantly. The sulfur reactivity results in the formation of 7 ppm H_2S 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 H_2S. This results in the potential for over prediction of H_2S in the reservoir fluids. For instance in this study, the gas phase under test separator conditions on the surface would contain 1080 ppm H_2S, the oil phase contains 235 ppm H_2S, and water

phase contains 7 ppm H_2S 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_2S 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_2S 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.