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Hydrogen Sulfide formation in Oil and Gas

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Abstract

Hydrogen sulfide (H_2S) can be a significant component of oil and gas upstream production, where H_2S can be naturally generated *in situ* from reservoir biomass and from sulfate containing minerals through microbial sulfate reduction (MSR) and/or thermochemical sulfate reduction (TSR). On the other hand, the technologies employed in oil and gas production, especially from unconventional resources, also can contribute to generation or delay of appearance of H_2S . Steam assisted gravity drainage (SAGD) and hydraulic fracturing used in production of oil sands and shale oil/gas, respectively, can potentially convert the sulfur content of the petroleum into H_2S or contribute excess amounts of H_2S during production. A brief overview of the different classes of chemical reactions involved in the *in situ* generation and release of H_2S is provided in this work. Speciation calculations and reaction mechanisms are presented to explain why TSR progresses at faster rates under low-pH. New studies regarding the degradation of a hydraulic fracture fluid additive (sodium dodecylsulfate) are reported for $T = 200^\circ\text{C}$, $p = 17$ MPa and high ionic strengths. The absence of an ionic strength effect on the reaction rate suggests that the rate limiting step involves the reaction of neutral species, such as elemental sulfur. This is not the case with other TSR studies at $T > 300^\circ\text{C}$. These two different kinetic regimes complicate the goal of extrapolating laboratory results for field specific models for H_2S production.

Keywords: hydrogen sulfide, sulfur, conventional, unconventional, sulfate reduction

Introduction

Over the 50 year history of the Department of Chemistry at the University of Calgary, both industry and academic researchers have enjoyed a strong collaborative interface through Alberta Sulphur Research Ltd. (ASRL). As early as the 1940s, the oil and gas industry had begun reducing SO₂ emissions through H₂S separation and conversion to elemental sulfur through the Claus process. During the 1950s, increased production of sour gas (natural gas containing H₂S) in Canada, brought with it several new challenges, including sulfur deposition, increased corrosion, sulfur handling and transportation logistics. Moreover, a key component of the continued research activity in this field is the need for elemental sulfur or more specifically sulfuric acid, which is necessary to produce the massive quantities of fertilizer required to feed a much larger world population. Still, a compelling fundamental question remains an active area of research: “where is all the H₂S coming from?”

Ignoring the cases where fluids from different subsurface zones become mixed, many hydrocarbon reservoirs contain native H₂S and CO₂ which have been geologically generated *in situ*. On average, sulfur constitutes about 1% of the dry mass of living organisms, with cysteine and methionine amino acids being the major contributors to this portion; therefore, some H₂S can come from the degradation of biomass.¹ Sour gas fluids have been produced with up to 94% H₂S, suggesting that a large portion of H₂S has originated from sulfate minerals, especially in carbonate reservoirs. Other fluids can chemically produce H₂S through the various anthropogenic processes that are used to activate the flow of hydrocarbon through formations and into wellbores. In either case, H₂S must be anticipated for a variety of surface facilities, removed from sales fluids

(treated), chemically scavenged, recovered as elemental sulfur or other sulfur-bearing products, or returned to subterranean formations *via* a process called acid gas injection.

The first portion of this study contains a brief review of three reservoir souring mechanisms: (i) aquathermolysis, (ii) microbial sulfate reduction (MSR) and (iii) thermal sulfate reduction (TSR). All three mechanisms can be responsible for the appearance of native H₂S (natural) and anthropogenic H₂S (caused by production stimulation). With the non-biological cases of H₂S production, there have been several laboratory and field studies aimed at understanding and modelling H₂S production kinetics. In the more recent cases, it has been noted that (a) many laboratory experiments require higher-than-reservoir temperatures to effectively study reaction rates and (b) extrapolating the kinetic results to reservoir temperatures may be flawed due to different mechanisms in various temperature regimes. Further information is required in this area to build fit-for-purpose models to estimate the extent and timing of H₂S concentration changes over the life of commercial production.

New experiments into shale gas souring are reported here, where TSR involving fracture fluid additives can result in (a) the scavenging of native reservoir H₂S during stimulation and (b) the regeneration of H₂S after hydrocarbon production begins. Like previous TSR studies, we have recently investigated reaction rates involving sodium dodecyl sulfate at high-ionic strengths and $T = 200^{\circ}\text{C}$. Results reported in this study show no significant change in reaction rate with increased ionic strength, suggesting that the rate limiting step involves a reaction between two neutral reactants. Alternatively, higher-temperature TSR experiments from literature suggest that ionic strength does increase reaction rates. Re-analyzing the latter results suggest that the

dominant controlling mechanisms for laboratory reactions at $T > 300^{\circ}\text{C}$ is thermolysis rather than S° reduction, dominant at $T < 300^{\circ}\text{C}$. These two different kinetic regimes must be considered and distinguished (if possible) when extrapolating TSR rates from high-temperature laboratory experiments to reservoir conditions.

2. Primary Sources of H_2S in Produced Hydrocarbons

2.1 Aquathermolysis (Cyclic Steam Stimulation and Steam Assisted Gravity Drainage)

While many hydrocarbon reservoirs will contain native or natural H_2S (considered sour), many heavy oil reservoirs are sweet with the majority of sulfides being bound within organosulfur species or metal sulfide. Examples include the oil sands within Northern Alberta and Venezuela. While the later bituminous hydrocarbon reserves do not contain native H_2S , the stimulation of flow by the introduction of high-pressure steam causes the thermochemical production of H_2S , CO_2 , CO , H_2 , CH_4 and other minor hydrocarbons. As a result, the associated sour gases produced at surface often contains up to *ca.* 5% H_2S which must be removed (treated) and converted to elemental sulfur (recovered) to avoid extraneous SO_2 emissions.

Because steam reformation is too slow at *in situ* steam stimulation conditions, the steam reformation of hydrogen and subsequent hydrogenation of organosulfur compounds is rarely considered as the major pathway for H_2S production. As a result the hot liquid water phase is thought to be the reactant contributing to H_2S production. High-temperature liquid water undergoes increased dissociation, thereby allowing for several reactions between liquid water and organic molecules which would otherwise not proceed at temperatures less than $T = 200^{\circ}\text{C}$. For $200 < T < 300^{\circ}\text{C}$ (accompanied by high-pressures) the complex reactions between water and

hydrocarbons are referred to as “aquathermolysis” whereas at $T > 300^{\circ}\text{C}$, hydrous pyrolysis or thermal cracking is the major contributor to hydrocarbon reactions.^{2,3,4} These two different chemical regimes were defined through the early work of Clark and Hyne,³ who studied the formation of CO_2 and H_2S through aquathermolysis of alkyl sulfides, thiophenes and sulfide containing asphaltenes. The C-S bond is weak in comparison to C-C bonds; therefore, reaction with high-temperature acidic H_2O or H_2 normally comes at the expense of more organosulfur species when compared to non-sulfur-containing hydrocarbons. Clark *et al.*³ later found that, in general, sulfur containing asphaltenes lead to the majority of produced H_2S . Near 300°C and above, various high-valence cations are also thought to provide a catalytic effect.³ It should be noted that the degradation of organosulfur species and H_2S production through aquathermolysis does not lead to a significant desulfurisation of the oil, *i.e.*, normally not considered worthwhile process for partial oil upgrading.

The produced CO_2 from aquathermolysis comes from two sources: (i) carbonate minerals and (ii) various organic species. Katritzky *et al.*⁴ have provided a detailed review of the reactions associated with oxygen containing organic compounds, where aquathermolysis leads to minor CO_2 production. The majority of produced CO_2 for an *in situ* stimulation is released from carbonate mineral.

From the brief discussion above, one can deduce that the production of H_2S from aquathermolysis (or even thermolysis) is greatly dependent on the temperature, time and composition of the bitumen. Thus, most chemical rate models are developed as fit-for-purpose rather than universal and targeting a wide range of hydrocarbon types. For application to

Athabasca oil sands, Thimm⁵ has provided a simplified model for H₂S/CO₂ production through aquathermolysis and, more recently, Kapadia *et al.* have provided a more complex kinetic model using 7 reaction rate constants.⁶ It should be noted that many laboratory studies of aquathermolysis are completed at $T > 300^{\circ}\text{C}$ in order to increase reaction rates for laboratory measurements. However, at these increased temperatures, thermolysis or cracking becomes a significant contributing mechanism versus aquathermolysis. Those calibrating aquathermolysis models for application to H₂S production from a steam stimulation need to be aware that there are two kinetic regimes. This point was addressed by Kapadia *et al.*,² but also turns out to be relevant when considering H₂S production through thermal sulfate reduction kinetics (discussed later in this study).

2.2 Microbial Sulfate Reduction (Conventional Sour Gas Reservoirs, Water Flooded Oil Reservoirs, Ground Water Wells)

Aqueous sulfate species also can be reduced to hydrogen sulfide through microbial sulfate reduction (MSR). Microbial activities typically are expected in shallow reservoirs or when a deep reservoir is uplifted to shallow depths,^{7,8} where sufficient sulfate supply is provided in order to extract energy for microbial proliferation. MSR also can be responsible for souring reservoirs which undergo water flooding (for enhanced oil recovery), where sulfate rich fluids enter gathering pipelines. Shallow ground water wells within Gypsum-rich earth are susceptible to souring and require periodic treatment. Thus, MSR can be responsible for both native and non-native H₂S with industrial hydrocarbon production. Geological or induced MSR source of H₂S can be confirmed by carbon, oxygen and sulfur isotopic signatures. For example, the ³⁴S isotope fraction within the produced H₂S and the source SO₄²⁻ will differ due to decreased microbial

activity for ^{34}S versus lower mass isotopes.^{9,10} MSR can be responsible for early geological production of H_2S , whereas, for very sour fluids, larger and more recent H_2S levels evolve through geothermal reactions.

The reduction of sulfate to sulfide can be achieved by a variety of living organisms under different environmental, yet anaerobic, conditions. The commonly accepted range of temperature where microbial activity can occur is $T < 80^\circ\text{C}$,⁸ although there have been reports of such activities for temperatures above 100°C .¹¹ Production of H_2S by microbes/bacteria has been a long-time concern of oil and gas industry and is a particular concern when production/enhanced recovery requires pumping water into a reservoir, *e.g.*, hydraulic fracturing of shale reservoirs or water flooding of conventional oil reservoirs. In such cases, there is a chance that microbes from the surface permeate and colonise in the reservoir and feed on the sulfate sources, such as minerals or fracturing additives, and commence production of H_2S . A sulfate concentration of 300 mM is suggested to serve as an additional source of sulfate if sea water is pumped into the well, since sea water is a major source of sodium sulfate.¹² To prevent MSR activity, biocides are added to the injected water, but the effectiveness of biocide in the bulk of the fluids and the biofilms, formed by bacteria on various surfaces, has been a matter of debate and investigation. Chemical additives such as glutaraldehyde and quaternary ammonium chloride are typical biocides utilized in petroleum industry;^{12,13} however, it has recently been demonstrated that compounds such as glutaraldehyde likely serve as a thermal sulfate-reductant under hydrothermal conditions where thermal degradation would reduce its effectiveness as a biocide.¹⁴ The Voordouw group have shown that periodic injection of nitrate can be used to control H_2S production by replacing sulfate reduction with the more favourable nitrate reduction.¹⁵ It should

be noted that CO₂ partial pressures are relatively large in most hydrocarbon reservoirs and this may act as a natural inhibitor to limit the bacterial activity.

2.3 Thermochemical Sulfate Reduction (TSR)

2.3.1 TSR in Conventional Carbonate Reservoirs

Conventional sedimentary basins often contain native sulfate (from receding seawater) along with organic species of various maturity. As implied in the previous section, an initial H₂S concentration can often be attributed to MSR; however, increase in burial depth accompanied with a rise in temperature results in the thermochemical sulfate reduction (TSR) to sulfide at the expense of the reservoir hydrocarbons.¹⁶ A simplified aqueous TSR mechanism for aliphatic hydrocarbons, C_{x+1}H_{2x+4}, in a conventional sour reservoir is given by:¹⁷

where the net reaction for the oxidation of C₂₊ species is

The overall products of TSR, are H₂S, CO₂ and CH₄,^{16,18,19} where the majority of the CO₂ forms carbonate to replace the anhydrite mineral. This is important for the geological development of prolific sour gas reservoirs, as the more malleable anhydrite layers continue to be responsible for the gas containment (cap rock), whereas the internal carbonate-rich zone is more easily fractured

(naturally or through stimulation) for gas production. The produced H_2S may re-enter the TSR reaction and further oxidize the hydrocarbons/organics or it may get fixated through reaction with reservoir rocks; for instance, if iron minerals are available, typically pyrite (FeS_2) deposits are found within the reservoir.

A very important factor for the overall rate of TSR is the temperature, although TSR is thermodynamically favourable at temperatures as low as 20°C .²⁰ At laboratory time-scales, the kinetics of TSR with aliphatic hydrocarbons is extremely slow. Even at temperatures above 100°C , TSR reactions are normally correspond to geological time-scales. As a result of these slow kinetics, the majority of the laboratory TSR experiments are carried out at temperatures above 250°C up to 600°C in order to obtain enough product to overcome analytical sensitivity.²¹ The reported activation energies for TSR range between $E_a = 77$ and 250 kJ mol^{-1} , depending on the reaction conditions and reactants/products involved.^{20,25,14}

Various laboratory results show that the kinetics of TSR depends on the type of organic reductants, dissolved sulfate species and a variety of intermediate sulfur species.^{22,23,24,7} The mechanism shown in Reactions (1) to (5) implies that steady-state elemental sulfur (S°) is formed from the reaction between bisulfate and H_2S (equilibrium), and then S° is kinetically consumed by oxidation of hydrocarbons (or other organic species). This agrees with the type of hydrocarbon being an important factor through (a) aqueous hydrocarbon solubility and (b) specific hydrocarbon oxidation rate. In other words, it is the oxidation step which is rate limiting and implies a steady state concentration of elemental sulfur in sour gas reservoirs.¹⁷

$$[\text{S}_8] = k_{\text{obs}} \frac{[\text{H}^+][\text{CaSO}_4]^x[\text{H}_2\text{S}]^y}{[\text{C}_{2+}]^z}. \quad (7)$$

Reservoirs with remaining anhydrate and very little larger hydrocarbons (beyond methane) often contain steady state elemental sulfur concentrations near saturation, where production can induce sulfur deposition in wellbores and in the reservoir. Sulfur deposition is a major issue for lean sour gas reservoirs (little or no C_{2+}) from both a flow assurance and corrosion perspective. Larger hydrocarbons will oxidise readily at lower temperatures; therefore, the steady state of $[S^0]$ is much lower and sulfur deposition is not observed for rich hydrocarbon fluids.

Also in agreement with the mechanism presented here, previous laboratory studies have shown that presence of low oxidation states of sulfur, sulfide or elemental sulfur, will initiate and catalyze TSR.^{25,26}

2.3.2 The Influence of pH on the overall TSR Reaction Rate

Several authors have demonstrated that pH can significantly influence the rate of TSR, where faster overall TSR rates are observed for $pH < 5$.^{25,26,27} Thus very acidic conditions have allowed for laboratory investigations of TSR which would otherwise be too slow for study. For example, activation energies of 77, 167 and 197 kJ mol^{-1} have been reported for $pH = 2, 4-7$ and 9, respectively.²⁰ This observation agrees with the shift of equilibrium reaction (2) through the higher concentration of bisulfate (HSO_4^-). Some authors have explained the apparent acid catalysis of TSR by stating that HSO_4^- is the more reactive species compared to sulfate, and conclude that conversion of sulfate to bisulfate might be the rate determining step for TSR.^{14,23} An alternative explanation is provided here which is self-consistent with the mechanism above and high-pressure aqueous speciation calculations, *i.e.*, where reaction 3 is the limiting reaction.

It is worthwhile to note that lower pH also favours the equilibrium reaction of HSO_4^- and H_2S to form S° (reaction 2). Therefore the steady-state $[\text{S}^\circ]$ will increase and the overall TSR reaction rate will increase at low pH. The S- H_2O system is complex and involves various sulfur oxidation states from S(-II) to S(VI); therefore, many aqueous sulfur species can potentially form and participate in TSR. MacDonald and Sharifi-Asl²⁸ have recently discussed the complex S- H_2O chemistry by constructing Volt-Equivalent Diagrams (VEDs) for aqueous sulfur species. While the latter authors were interested in long-term management of nuclear waste, similar calculations/diagrams can be used to demonstrate the change in aqueous oxosulfur speciation in high-temperature TSR experiments.

Using VEDs, the thermodynamic stability of various sulfur species can be compared using the volt equivalent difference between any species (*e.g.*, S°) and the line joining two disproportionation species (*e.g.*, H_2S and HSO_4^-). Here the volt equivalent is the equilibrium potential for a species with respect to its element. In the case of bisulfate (HSO_4^-), the reduction reaction to form elemental sulfur is

The equilibrium potential, E° , for reaction 8 is

$$E^e = \frac{-\Delta_f G^\circ}{6F} - \left[\frac{2.303RT}{6F} \right] \log \left[\frac{1}{a_{\text{H}^+}^7 a_{\text{HSO}_4^-}} \right], \quad (9)$$

where $\Delta_f G^\circ$ is the change in standard Gibbs energy, which is both pH and temperature dependant, T is the temperature, and a_i is the activity for species i . The previous equilibrium potential can be calculated for any sulfur species in an aqueous system.

While there are several detailed explanations regarding interpreting and convenience of VEDs for disproportionation reactions,^{28,29,30} a very brief explanation of their interpretation is provided here for clarity. Using the same modified Helgeson, Kirkham and Flower's model (HKF)³¹ as used by MacDonald and Sharifi-Asl,²⁸ we have calculated the $\Delta_f G^\circ$ for multiple species and the corresponding VEDs for the S-H₂O system at pH = 7.0 and 1.0 (Figure 1). The slope of any line joining two species is, by definition, the standard reduction potential. More conveniently, if a third species lies above a line joining two species, then that third species will tend to spontaneously disproportionate to form the two adjoining species on the line. This is shown in Figure 1a, where elemental sulfur, S⁰, is above the line joining H₂S and HSO₄⁻. Thus, at pH = 7 and $T = 200^\circ\text{C}$, equilibrium favours H₂S and HSO₄⁻, or the left hand side of reaction 2. Alternatively, if S⁰ is below the adjoining line, then S⁰ is thermodynamically favoured by reaction of H₂S and HSO₄⁻. If all three species lie on the same line, then all species will be in equilibrium (a reaction quotient of unity). Figure 1b, shows that S⁰ has dropped slightly below the line joining H₂S and HSO₄⁻ or slightly below the equivalence point, *i.e.*, H₂S and HSO₄⁻ are favoured at pH = 7.0; whereas, S⁰ is thermodynamically favoured at pH = 1.0.

Figure 1. The Volt-Equivalent Diagrams for the S-H₂O system at $T = 200^{\circ}\text{C}$ and pH = 7.0 (a) and 1.0 (b). $\Delta_f G^{\circ}$ for all species have been calculated using the modified Helgeson, Kirkham and Flower's model (HKF).³¹

Figure 2 shows the equivalence point for reaction 5 as function of temperature and pH, where S° is favoured at pH below the zero volt equivalence difference (below the solid line) and disproportionation is favoured high pH (above the solid line). Both Figures 1 and 2 demonstrate that a decrease in pH will increase the concentration of S° and the overall TSR reaction rate, *i.e.*, acid catalysed results do not necessarily imply that HSO_4^- is the catalyst, because low-pH suggests a higher concentration of S° , which is a reactant in the limiting reaction (reaction 3). The assumption that HSO_4^- is the catalyst at low-pH, would require that no H_2S be present. These calculations also agree with the observation that the addition of S° to neutral H_2O will react to form H_2S and HSO_4^- until the equilibrium pH is achieved. The calculations shown here imply that that formation of S° is fundamental to the development of any TSR rate model and to the interpretation of laboratory results.

While the pH in a traditional carbonate gas reservoir is typically not very acidic ($pH > 5$), the above calculations imply that a near-wellbore region which has undergone acid stimulation may experience higher-than-native levels of sulfur during early gas production. This may complicate analytical results and could even increase the severity of sulfur deposition during early production.

Figure 2. The aqueous sulfur disproportionation (reaction 5) as a function of temperature and pH. The solid line represents the equivalence point for the reaction of $\text{H}_2\text{S}(\text{aq}) + \text{HSO}_4^-(\text{aq})$. $\Delta_f G^\circ$ for all species have been calculated using the modified Helgeson, Kirkham and Flower's model (HKF).³¹

2.3.2 The Influence of Ionic-strength on the High-temperature TSR Reaction Rate

Similar to the previous studies regarding thermolysis, some studies have argued that the presence of di- and tri-valent cations such as magnesium and aluminum, provide catalysts for the overall TSR reaction. Thus, another method for increasing the reaction rate in the laboratory has been to add high-valence metal sulfates, *e.g.*, MgSO_4 . He *et al.* have provided some recent and comprehensive results in this area, where they conclude that HSO_4^- is the reactive species (based on pH observations) and observed that MgCl_2 and AlCl_3 lead to increased reaction rates.³² The

authors also note that their results are for $T > 300^{\circ}\text{C}$. Because the majority of commercial sour gas production is from reservoirs at $T < 180^{\circ}\text{C}$, the same reaction mechanisms and catalytic species must be assumed relevant at lower-temperature, in order to extrapolate to typical reservoir conditions. At $T > 300^{\circ}\text{C}$, the kinetics may be controlled by thermal cracking (thermolysis).

He *et al.*³² studied the reaction of $n\text{-C}_{16}\text{H}_{34}$ and MgSO_4 in the presence of various concentration of NaCl , MgCl_2 and AlCl_3 at $T = 360^{\circ}\text{C}$; however, we note that the observed increased gas yields with MgCl_2 and AlCl_3 versus NaCl , does not necessarily imply that Mg^{2+} or Al^{3+} are active catalysts. Depending on the charge of the reactants involved in formation of the activation complex, the ionic strength of a solution alone can influence the stability of the activation complex, which influences the overall rate of the reaction. This point is explored further within the results and discussion section of this study.

2.3.3 The delayed H_2S production from Shale Gas Reservoirs

With the progress in exploration and production from unconventional reserves such as shale reservoirs, initial impressions were that all these low permeability reservoirs were sweet (did not contain H_2S).³³ But it turns out that many shale gases may contain up to thousands of ppm H_2S which can present itself months after gas production begins.³³ The geochemical reaction of native and immature organic sulfur compounds could be the major source of the observed H_2S ;⁷ however, H_2S is observed within mature fluids (insignificant hydrocarbon content beyond methane). MSR from microbial and sulfate contamination during reservoir stimulation is a commonly suggested as the cause of souring. TSR is often ruled out because shales are often

deficient in sulfate minerals.¹⁴ Recent studies from our group have shown that the additives used in hydraulic fracturing can undergo TSR reactions under hydrothermal conditions of a shale reservoir ($T > 120^\circ\text{C}$).^{26,14} Furthermore, oxygen ingress upon fracturing could cause the oxidation of native H_2S , which would slowly regenerate through the sulfur oxidation of hydrocarbons (reaction 3). These results suggest that the process of fracturing is the likely cause for the temporary sweetening (reduction in H_2S) of the production fluid and, subsequent, early flow tests show insignificant H_2S levels. In other words, the shale reservoir likely contained a native amount of H_2S or metal sulfide before production flow was stimulated.

Different chemicals were previously examined including ammonium persulfate, glutaraldehyde and ethylene glycol which are used as gel breaker, biocide and scale inhibitor, respectively.¹⁴ The majority of our recent work has focused on sodium dodecyl sulfate (SDS), an anionic surfactant also known as sodium lauryl sulfate (SLS), which is usually used in slick water fracturing.¹⁴ It was demonstrated that upon hydrolysis of SDS into 1-dodecanol ($\text{C}_{12}\text{H}_{25}\text{OH}$) and sodium bisulfate (NaHSO_4), these intermediate products can undergo TSR and produce H_2S and a variety of organic sulfur compounds.^{26,14} The presence of bisulfate would then cause an early scrubbing affect and result in false negative tests for well fluids just after flow-back for water recovery. We note that our earlier examinations of this chemistry involved only the degradation of aqueous SDS and did not include any initial sulfide; therefore, all sulfide was generated from SDS degradation alone. The following simplified set of equations has been suggested:

where the net reaction is

In the case of native H_2S , the elemental sulfur produced with reaction 5 can react with the 1-dodecanol, or other hydrocarbon species in the hydraulic fracturing or from the reservoir, and regenerate H_2S . With only SDS, our reaction mixtures extracted post-TSR were highly acidic and elemental sulfur had been found in the mixtures.^{26,14} These observations explain the rate at which the shale gas wells go sour in the fields.

Additionally, it has been recently suggested that the water used for hydraulic fracturing is saturated with oxygen at atmospheric pressure. Thus, the dissolved oxygen can react with the native H_2S and form elemental sulfur:

The elemental sulfur produced *via* reaction 15 can slowly oxidize organic molecules as suggested by reactions 3, 11 and 12. Evidence of such reactions have recently been presented where it was concluded that CO_2 product provides a more consistent measurement of the reaction rate, as sulfur may be temporary sequestered within organosulfur intermediates.³⁴ Interestingly, unexpected thiol production is also observed during the production of shale fluids.

Whether it is a conventional or unconventional reservoir, it seems one should always plan for the presence of H_2S , although perhaps at very low levels. The additives used in production of wells may act

as a double-edge sword; they may mask the native H_2S but re-release it later, as in the case of shale gas, or they may participate in TSR reactions under hydrothermal conditions of the well and produce H_2S .

A significant increase in reaction rate with our recent studies of SDS at the very low pH has allowed for kinetic studies at more applicable temperatures ($T = 150$ to 200°C). Following He *et al.*'s³² review on the impact of dissolved salt and the hypothesis that the sulfur oxidation reaction provides the limiting rate, we have studied the SDS TSR reactions with various salts. The new experiments were aimed at complimenting He *et al.*'s³² work with $n\text{-C}_{16}\text{H}_{34}$ at $T = 360^\circ\text{C}$ by exploring similar experiments at lower temperatures and with only aqueous SDS. For this work, SDS solutions were allowed to react at constant temperature ($T = 200^\circ\text{C}$) and pressure ($p = 17\text{MPa}$), at excess ionic strengths ranging from $I = 0.1$ to 0.45 mol kg^{-1} of NaCl, KCl, NaBr, MgCl_2 , and CaCl_2 , for $t = 168$ hours. We did not observe a significant ionic strength dependence for the reaction rate at $T = 200^\circ\text{C}$, suggesting that the rate limiting reaction involves two neutral species, *i.e.*, dodecanol oxidation by S° . These results have been compared to previous literature data and suggest that the reaction mechanism is different for the different temperature regimes. These different mechanisms imply that extrapolation of high-temperature laboratory experimentss may not be an appropriate benchmark for developing TSR rate models in reservoirs at $T < 200^\circ\text{C}$.

3. Materials and Methods

The reaction vessels and procedures have been described in detail within a previous publication.²⁶ Briefly, high-pressure reactions were carried out in *ca.* 6 cm^3 grade II titanium vessels. Some recent experiments, not reported here, have been repeated in Gold and Tantalum lined vessels to mitigate some acid dissolution of the vessel walls. The reactions in gold coated

vessels showed no change from earlier results with titanium wetted surfaces. A sampling module with transducer attachment is connected to the reaction vessel to monitor the pressure when vessels are charged at the start of the experiment and during the gas phase sampling at the end of the experiment (after thermal quench). A modified GC oven was used to heat up the vessels to the required temperature of $T = 200^{\circ}\text{C}$, where a type K thermocouple was attached to the vessel skin to monitor the temperature.

Sodium dodecyl sulfate (catalog No. S-329) was obtained from Fisher Scientific Company. Sodium chloride (catalog No. S9888), Calcium chloride (catalog No. C1016) and potassium chloride (catalog No. P9541) were obtained from Sigma Aldrich, and magnesium chloride (catalog No. 12315) was obtained from Alfa Aesar. All chemicals were used without any further purification. The water used to prepare the solution was polished to $18.2\text{ M}\Omega$ and degassed under vacuum for a minimum of 6 hours.

Solutions were gravimetrically prepared shortly before charging each vessel in order to minimize premature hydrolysis of SDS. SDS was dissolved in the water followed by addition of respective chloride salts to prepare the solutions of 0.15 M SDS and desired excess ionic strength. 4 cm^3 of solution was loaded into each evacuated vessel (0.6 mmol of SDS total) followed by some pressurized nitrogen. Once vessels reached target temperature ($T = 200^{\circ}\text{C}$) in the GC oven, they were pressurized further using ultra-high purity nitrogen (99.998%, Praxair) to $p = 17\text{ MPa}$. All experiments were held at temperature for $t = 168$ hours before being quenched to room temperature and analysed.

The head-space gas mixture was sampled by transferring multiple aliquots of the gas mixture through a sampling module to a GC/SCD/FID/TCD. Following the sampling of the head-space gas, the reaction vessel was pressurized with nitrogen to build backpressure in order to extract the aqueous mixture. A 100 μL aliquot of the extracted aqueous mixture was diluted to 10 mL using a preservative solution containing 10 mM mannitol and 50 mM sodium hydroxide to prevent oxidation of sulfide anions. This solution was analyzed on a Dionex DX320 with an IonPac AS17 hydroxide-selective anion exchange column with CD25 conductivity detector and parallel AD25 absorbance detector for quantitative analysis of anions in the aqueous mixture. Potassium hydroxide concentration gradient from 30 to 70 mM was applied to elute anions from the column.

Following the extraction of the aqueous mixtures, each vessel was rinsed with quantitative amounts of xylene and deionized water, respectively. S° within the xylene extract was quantified by reaction with triphenylphosphine and analysed with GC/PFPD.³⁵ The aqueous rinse was added to the drained aqueous mixture for IC analyses.

4. Results and Discussion

The results from the aqueous SDS experiments have been reported in Table 1, where a significant quantity of H_2S and CO_2 have been found after $t = 168$ hours and $T = 200^\circ\text{C}$. The concentrations of H_2S and CO_2 leading to the overall products reported were *ca.* 500 and 1000 ppm respectively. These concentrations are well within our analytical sensitivity (GC). We note that H_2S is not produced in excess of the CO_2 , as would be expected for the balanced TSR reactions presented earlier. Earlier studies suggest that sulfur is sequestered within organosulfur

Table 1. The products of 0.60 mmol SDS(aq) degradation after $t = 168$ hours at $T = 200^{\circ}\text{C}$ and $p = 17$ MPa (rapid hydrolysis followed by TSR).

^a $I / \text{mol kg}^{-1}$	$10^3 \cdot \text{SO}_4^{2-} / \text{mol}$	$10^7 \cdot \text{H}_2\text{S} / \text{mol}$	$10^7 \cdot \text{CO}_2 / \text{mol}$	% recovery
0.0000		1.9 ± 1.8	35.3 ± 1.8	
		<u>NaCl</u>		
0.0254	0.53	1.2	36.8	88
0.0254	0.54	2.8	43.7	90
0.1512	0.52	2.0	34.9	87
0.3008	0.50	3.9	36.1	83
0.4510	0.68	4.9	29.0	64
0.4510	0.40	4.9	37.1	68
		<u>NaBr</u>		
0.1503	---	---	35.5	---
0.1503	---	---	35.2	---
		<u>KCl</u>		
0.0253	---	0.2	37.6	---
0.0253	---	0.5	34.3	---
0.1024	0.51	0.7	37.0	100
0.1534	0.60	0.4	32.9	70
		<u>MgCl₂</u>		
0.3050	0.44	0.5	35.7	73
0.3050	0.40	3.9	36.1	68
0.4525	0.53	1.1	37.9	88
0.4525	0.49	1.0	31.5	81
		<u>CaCl₂</u>		
0.0306	---	0.4	37.8	---
0.1513	0.46	1.1	33.8	77
0.1513	0.48	1.1	33.7	79
0.3037	0.17	1.3	30.0	29
0.3037	0.16	0.8	28.4	27

^aIonic strength is calculated in excess of the concentration of hydrolysed SDS. % recovery excludes organosulfur intermediates, but does include elemental sulfur. Zero excess salt experiments are reported for an average of five runs, with uncertainties estimated at 95% confidence. In five cases, IC was not performed due to loss of aqueous phase after depressurization. An error with the SCD detector during the sampling of the NaBr experiments resulted in no H₂S measurement.

species (thiols), which lowers the observed H₂S during the initial reaction time.²⁶ Longer reaction times have been shown to produce larger the H₂S/CO₂ ratios, which are more consistent with other TSR studies. Also with our earlier studies, a more consistent ratio was observed when sulfur or sulfide was added to initiate the reaction (similar to a reservoir containing native H₂S).²⁶

Because the reactions studied here were not influenced by the disproportionation of initial sulfur or sulfite, the rate of reaction for these results are more appropriately followed using the produced CO₂. Thus initial reaction rates can be followed from the CO₂ increase. The rate of disproportionation and mixing effects will be addressed with future studies, which will be necessarily for fit-for-purpose reservoir kinetics.

To assess the influence of extraneous aqueous ions, a rate constant k can be related to ionic strength, I , of a solution by implementing the extended Debye-Hückel equation in the Bronsted-Bjerrum relation:³⁶

$$\log k = \log k^0 + \frac{Az_A z_B \sqrt{I}}{1 + \sqrt{I}}, \quad (16)$$

where A is the Debye-Hückel constant, z_A and z_B are the charge valence for the ions forming the activated complex, and $I = \frac{1}{2} \sum m_i z_i^2$. Based on this relationship, by plotting $\log (k/k^0)$ versus $\sqrt{I}/(1+\sqrt{I})$, the non-zero slope of a linear fit illustrates whether or not the limiting step of the reaction involves charged reactant species, *i.e.*, a Livingston plot.

Figure 3 shows a Livingston plot of the produced CO₂ from the degradation of SDS with various salts. The plot also shows the theoretical slope one would expect at $T = 200^\circ\text{C}$ for a reaction complex associated with two monovalent ions. The Debye-Hückel constant was taken from Helgeson and Kirkham for water at $T = 200^\circ\text{C}$ and saturation.³⁷

Figure 3. The Livingston plot for CO_2 produced from the degradation of aqueous SDS after $t = 168$ hours, in the presence of excess ionic strength, at $T = 200^\circ\text{C}$ and at $p = 17$ MPa. $\blacktriangle$, the addition of 1:1 salts [$\text{NaCl}(\text{aq})$, $\text{NaBr}(\text{aq})$ or $\text{KCl}(\text{aq})$]; $\bullet$, the addition of 2:1 salts [$\text{MgCl}_2(\text{aq})$ or $\text{CaCl}_2(\text{aq})$]. The theoretical slopes for charged monovalent ions were calculated using the Debye-Hückel constant of Helgeson and Kirkham for saturated water at $T = 200^\circ\text{C}$.³⁷

The absence of a significant correlation with ionic strength, suggests that the rate limiting reaction is associated with a reaction between two neutral species. This observation is consistent with the hypothesis that the limiting reaction can be S° reacting with a neutral organic species. While several neutral species can conceivably be involved with this rate limiting step, a strong correlation should be observed when charged species are involved. In addition, unlike the studies of TSR for $n\text{-C}_{16}\text{H}_{34}$,³² none of the anions or cations added to the SDS reactions appear to be catalytic.

Figure 4 shows a Livingston plot of He *et al*'s kinetic data.³² The theoretical slope for the reaction for monovalent ions ($z_A=z_B$) has been shown for saturated water at $T = 350^\circ\text{C}$ and is consistent with the slopes of both the H_2S and CO_2 yield observed by these authors. In fact, a least squares regression shows a slope of 1.8 ± 0.3 for the CO_2 yields, which is in very close to the theoretical slope of 1.9 at $T = 350^\circ\text{C}$. The analysis *via* the Livingston plot has two implications: (i) the limiting rate at $T = 360^\circ\text{C}$ does not appear to be a redox reaction between neutral sulfur and hydrocarbon species (reaction 3, as suggested earlier) and (ii) the increased reaction rate at $T = 360^\circ\text{C}$ is not a cation specific catalysis. Versus a cation specific catalysis, *i.e.*, $\text{Mg}^{2+}(\text{aq})$ or $\text{Al}^{3+}(\text{aq})$, the limiting rate appears to be controlled by long-range coulombic interactions of ions pair, which are de-shielded by high-ionic strength alone (high-valence ions simply contribute a greater charge density). The observation that these reactions appear to follow different kinetic controls in two different temperature regimes, complicates any extrapolation of high-temperature laboratory results to fit-for-purpose reservoir simulations.

While some studies have verified S° as an intermediate state that appears to have a critical role in the TSR reaction rate, ionic strength correlations at high-temperature would suggests otherwise. As noted within aquathermolysis versus thermolysis discussions, S° can form radicals which can dehydrogenate and form unsaturated hydrocarbons, and likely become more reactive.^{22,38} Thus, the extrapolation of TSR reaction rates from very high-temperatures may not be directly applicable to lower-temperature reservoirs where the limiting reactions may be quite different.

Figure 4. The Livingston plot for H_2S produced from TSR reaction of $n\text{-C}_{16}\text{H}_{34}$ alkane and 1 M magnesium sulfate at $T = 360^\circ\text{C}$. Open symbols are for $i = \text{H}_2\text{S}$ and filled symbols are for $i = \text{CO}_2$; $\blacktriangle$, NaCl ; $\bullet$, MgCl_2 ; $\blacksquare$, AlCl_3 . Data is from the work published by He *et al.*,³² where experiments were performed at constant temperature of $T = 360^\circ\text{C}$ and pressure of $p = 24.1$ MPa for a $t = 240$ hours. The theoretical slopes for charged monovalent ions were calculated using the Debye-Hückel constant of Helgeson and Kirkham for saturated water at $T = 350^\circ\text{C}$.³⁷

6. Conclusions

A brief review of the potential sources of H_2S in oil and gas production has been provided with summaries of the understanding of (i) aquathermolysis, (ii) MSR and (iii) TSR. All three of these complex chemical reactions can lead to native and non-native H_2S within conventional hydrocarbon production. It should be noted that while H_2S from aquathermolysis is caused by the steam assisted stimulation of heavy oil flow, sulfur containing oils will result in H_2S upon

desulfurization at surface (upgrading and hydrogenation processes). Thus, the H_2S would need to be handled properly, regardless of where and how it is generated.

For TSR, it was shown that steady state S° would increase under very acidic conditions by shifting the disproportionation of the $\text{S-H}_2\text{O}$ system. The later speciation calculation suggests that faster reaction rates at low-pH does not necessarily imply that $\text{HSO}_4^-(\text{aq})$ is the reactant in the rate-limiting step.

Recent research shows that oxidation of native H_2S , followed by slow oxidation of organic species by elemental sulfur, can lead to the delayed appearance of H_2S in unconventional shale gas production. In some cases, chemical additives to hydraulic fracture fluids can act as both oxidant and reductant during the H_2S delay through TSR reactions, *e.g.*, recent research with SDS degradation.^{14,26} New experiments have been reported here, where aqueous SDS degradation was followed with the addition of various salts to increase the ionic strength. These results show no significant change in reaction rate at increasing ionic strength, suggesting that the rate limiting step involves the reaction between two neutral reactants. Indications of neutral reactants further support a mechanism where S° is oxidizing an organic species.

Alternatively, the measurements of He *et al.*³² for $n\text{-C}_{16}\text{H}_{34}$ at $T = 360^\circ\text{C}$ also have been re-interpreted using an ionic strength plot (Livingston plot). The higher-temperature experiments suggest that (i) catalytic activity is not specific to certain cations and (ii) ionic strength (through concentration increase and high-valence ions) does increase reaction rates. The later suggests that the rate-limiting reaction involves two monovalent ions. Similar to studies on aquathermolysis

and thermolysis, the dominant control for reactions at $T > 300^{\circ}\text{C}$, seems to be thermolysis versus S° oxidation in classical TSR. The two different kinetic regimes must be factored in when extrapolating TSR rates from high-temperature laboratory experiments to reservoir conditions.

Our studies on TSR in shale type fluids are continuing, with the eventual goal of developing a kinetic model to aid producers in estimating H_2S production profiles. Eventually models, based on field specific information and fundamental understanding, will contribute to increasing safe and economic approaches to the design of hydrocarbon production, gathering, treatment and recovery schemes.

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References

- (1) Orr, W.L.; Sinninghe Damste, J.S. *Geochemistry of Sulfur in Fossil Fuels*, ACS Symposium Series, **1990**, 429, 2-29.
- (2) Kapadia, P. R.; Kallos, M. S.; Gates, I. D. *Can. J. Chem. Eng.* **2013**, 91, 475-482.
- (3) (a) Hyne, J. B.; Clark, P. D.; Clarke, R.A.; Koo, J.; Greiddanus, J. W.; Tyrer, J. D.; Verona, D. *Revista Tecnica Intevep* **1982**, 2, 87-94. (b) Clark, P. D.; Hyne, J. B.; Tyrer, J. D. *Fuel* **1983**, 62, 959-962. (c) Clark, P. D.; Hyne, J. B.; Tyrer, J. D. *Fuel* **1983**, 63, 125-128. (d) Clark, P. D.; Hyne, J. B. *Fuel* **1984**, 63, 1649-1654. (e) Clark, P. D.; Hyne, J. B. *AOSTRA J. Res.* **1984**, 1, 15-20. (f) Clark, P. D.; Dowling, N. I.; Hyne, J. B.; Lesage, K. L.; Tsang, G. *Fuel* **1987**, 66, 1353-1357. (g) Clark, P. D.; Dowling, N. I.; Lesage, K. L.; Hyne, J. B. *Fuel* **1987**, 66, 1699-1702. (h) Clark, P. D.; Lesage, K. L.; Tsang, G. T.; Hyne, J. B. *Energy and Fuels* **1988**, 2, 578-581. (i) Clark, P. D.; Clarke, R. A.; Hyne, J. B.; Lesage, K. L. *AOSTRA J. Res.* **1990**, 6, 29-39. (j) Clark, P. D.; Kirk, M. J. *Energy and Fuels* **1994**, 8, 380-387.
- (4) Katritzky, A.R.; Allin, S.M.; Siskin, M. *Acc. Chem. Res.* **1996**, 29, 399-406.
- (5) (a) Thimm, H. F. *J. Can. Petroleum Technol.* **2008**, 47, 7-9. (b) Thimm, H. F. *J. Can. Petroleum Technol.* **2009**, 48, 6-8.
- (6) (a) Kapadia, P. R.; Kallos, M. S.; Gates, I. D. *Can. J. Chem. Eng.* **2013**, 91, 475-482. (b) Kapadia, P.R.; Kallos, M. S.; Gates, I. D. *Fuel Process. Tech.* **2015**, 131, 270-289.
- (7) Amrani, A. *Annu. Rev. Earth Planet. Sci.* **2014**, 42, 733-68.
- (8) Shen, Y.; Buick, R. *Earth-Sci. Rev.* **2004**, 64, 243-272.
- (9) Zhelezinskaia, I; Kaufman, A. J.; Farguhar, J.; Cliff, J. *Science* **2014**, 346, 742-744.
- (10) Konhauser, K. O. *Introduction to Geomicrobiology* **2009**, Wiley.
- (11) Jørgensen, B. B.; Isaksen, M. F.; Jannasch, H. W. *Science* **1992**, 258, 1756-1757.
- (12) Barton, L.L.; Fauque, G.D. *Adv. Appl. Microbiol.* **2009**, 68, 41-98.
- (13) FracFocus, <http://www.fracfocus.ca/chemical-use/what-chemicals-are-used>, accessed April 2015.
- (14) Pirzadeh, P.; Lesage, K.; Marriott, R.A. *Energy Fuels* **2014**, 28, 4993-5001.
- (15) (a) Callbeck, C.; Agrawal, A.; Voordouw, G. *Appl. Environ. Microbiol.* **2013**, 79, 5059-5068. (b) Coombe, D; Jack, T.; Voordouw, G.; Zhang, F.; Clay, B.; Miner, K. *J. Can. Petroleum Technol.* **2010**, 49, 19-26. (c) Voordouw, G.; Grigoryan, A. A.; Lambo, A.; Lin, S; Park, H. S.,

- Jack, T. R.; Coombe, D.; Clay, B.; Zhang, F.; Ertmoed, R.; Miner, K.; Arensdorf, J. *J. Environ. Sci. and Technol.* **2009**, *43*, 9512-9518. (d) Grigoryan, A. A.; Lambo, A.; Lin, S.; Cornish, S. L.; Jack, T. R.; Voordouw, G. *J. Can. Petroleum Technol.* **2009**, *83*, 369-376. (e) Hubert, C.; Voordouw, G. *Appl. Environ. Microbiol.* **2007**, *73*, 2644-2652.
- (16) Worden, R.H.; Smalley, P.C.; Cross, M.M. *J. Sediment. Res.* **2000**, *70*, 1210-1221.
- (17) Marriott, R. A.; Davis, P. M.; Clark, P. D. Estimation of sulfur deposition during the production of lean sour gas, *Proceedings of the 3rd International Conference on Sour Oil & Gas Advanced Technology*, Abu Dhabi, April 2007, Dome Exhibitions, UAE, 2007, 121-140.
- (18) King, H.E.; Walters, C.C.; Horn, W.C.; Zimmer, M.; Heines, M.M.; Lamberti, W.A.; Kliewer, C.; Pottorf, R.J.; Macleod, G. *Geochim. Cosmochim. Acta* **2014**, *134*, 210-220.
- (19) (a) Kelemen, S.R.; Walters, C.C.; Kwiatek, P.J.; Freund, H.; Afeworki, M.; Sansone, M.; Lamberti, W.A.; Pottorf, R.J.; Machel, H.G.; Peters, K.E.; Bolin, T. *Geochim. Cosmochim. Acta* **2010**, *74*, 5305-5332. (b) Kelemen, S.R.; Walters, C.C.; Kwiatek, P.J.; Afeworki, M.; Sansone, M.; Freund, H.; Pottorf, R.J.; Machel, H.G.; Zhang, T.; Ellise, G.S.; Tang, Y.; Peters, K.E. *Org. Geochem.* **2008**, *39*, 1137-1143.
- (20) Goldstein, T.P.; Aizenshtat, Z. *J. Therm. Anal.* **1994**, *42*, 241-290.
- (21) Lu, H.; Greenwood, P.; Chen, T.; Liu, J.; Peng, P. *Appl. Geochem.* **2012**, *27*, 96-105.
- (22) Zhang, T.; Ellis, G.S.; Wang, K-s.; Walters, C.C.; Kelemen, S.R.; Gillaizeau, B.; Tang, Y. *Org. Geochem.* **2007**, *38*, 897-910.
- (23) Ma, Q.; Ellis, G.S.; Amrani, A.; Zhang, T.; Tang, Y. *Geochim. Cosmochim. Acta* **2008**, *72*, 4565-4576.
- (24) Amrani, A.; Zhang, T.; Ma, Q.; Ellis, G.S.; Tang, Y. *Geochim. Cosmochim. Acta* **2008**, *72*, 2960-2972.
- (25) (a) Zhang, T.; Ellis, G.S.; Ma, Q.; Amrani, A.; Tang, Y. *Geochim. Cosmochim. Acta* **2012**, *96*, 1-17. (b) Zhang, T.; Amrani, A.; Ellis, G.S.; Ma, Q.; Tang, Y. *Geochim. Cosmochim. Acta* **2008**, *72*, 3518-3530.
- (26) Pirzadeh, P.; Raval, S.; Marriott, R.A. *Org. Geochem.* **2015**, *83-84*, 94-100.
- (27) Kiyoso, Y. *Chem. Geo.* **1980**, *30*, 47-56.
- (28) MacDonald, D. D.; Sharifi-Asl, S. *Corrosion Science* **2014**, *81*, 102-109.
- (29) Wassink, B.; Clark, P. D.; Hyne, J. B., *ASRL QB* **1989**, *XXV 4*, 1-19.

-
- (30) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*, 2nd Ed, **1997**, Elsevier Oxford, 434-438.
- (31) Shock, E. L.; Helgeson, H. C. *Geochim. Cosmochim. Acta* **1988**, 52, 2009-2036.
- (32) He, K.; Zhang, S.; Mi, J.; Hu, G. *Appl. Geochem.* **2014**, 43, 121-131.
- (33) Weiland, R. H.; Hatcher, N. A. *Hydrocarbon. Process.* **2012**, 91, 45-48.
- (34) Warren, G. L.; Bertrand, T. Laurance Reid Gas Conditioning Conference Proceedings, Norman, Oklahoma, USA, Feb 22-25, **2015**, 146-166.
- (35) Clark, P. D.; Lesage, K.L. *J. Chrom. Sci.* **1989**, 27, 259-261.
- (36) (a) Atkins, P.; De Paula, J. *Physical Chemistry*, **2010**, W. H. Freeman and Co.: New York.
(b) Pethybridge, A.; Prue, J. *Progress in Inorganic Chemistry* **1972**, 327-390.
- (37) Helgeson, H. C.; Kirkham, D. H. *Am. J. Sci.* **1974**, 274, 1199-1261.
- (38) Lewan, M. D. *Nature* **1998**, 391, 164-166.