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REALLY YOUR ALLY?**

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ABSTRACT

Elemental sulfur shares the same Group on the Chemical Periodic Table as oxygen and, like oxygen, is a powerful oxidant. In the oil and gas industry, oxygen and elemental sulfur are recognized as aggressive corrosion accelerators, particularly for pitting and other forms of localized corrosion.

Elemental sulfur is commonly formed in sour oil and gas systems from some of the following mechanisms: differential solubility of sulfur in high pressure sour gas, destabilization of hydrogen polysulfides present in sour gas, oxygen ingress that reacts with H₂S to yield sulfur and the decomposition of aqueous polysulfide solutions. The presence of a hydrocarbon phase such as condensate has typically been considered beneficial because the condensate will oil-wet the metal and also help to dissolve some of the sulfur that is present.

Recent laboratory autoclave work incorporating elemental sulfur dissolved in a hydrocarbon phase has shown enhanced localized corrosion compared to tests which had no sulfur present. The experimental data are presented in this paper along possible mechanistic pathways.

Keywords: Elemental sulfur, sour gas, hydrogen sulfide, sulfanes, polysulfides, condensate, pitting corrosion

INTRODUCTION

Even though the corrosive properties of elemental sulfur in oil and gas production have been well documented for more than 30 years^{1,2}, the increased corrosion threat associated with the presence of sulfur continues to attract attention in the scientific literature^{3,4,5,6}. Sulfur shares the same Group on the Chemical Periodic Table with oxygen and, like oxygen, is a powerful oxidant. The strong oxidizing properties associated with elemental sulfur explain the particularly aggressive pitting corrosion which occurs when wet sulfur contacts bare carbon steel.

Pure, dry elemental sulfur in contact with carbon steel does not constitute a corrosion threat to steel. However, if water is added to the equation, severe corrosion occurs. The presence of other corrosion accelerators such as chloride ions and iron sulfide solids escalate the severity of corrosion even more⁵. There are several mechanisms that have been identified which explain the transport and deposition of elemental sulfur in sour gas systems. A brief description of these various mechanisms is provided in the following sections.

The focus of this paper involves a potentially new mechanism that involves elemental sulfur dissolved in a hydrocarbon phase (e.g., field condensate). Condensate has traditionally been viewed as an “ally” in systems where elemental sulfur precipitation occurs because it oil wets the pipe surface and dissolves small amounts of elemental sulfur and thereby reduces the amount of sulfur that could settle out on the bottom of the pipeline where water will also accumulate.

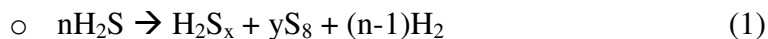
As part of developing new products for sour gas systems containing elemental sulfur, Baker Hughes conducted a series of stirred and high speed (i.e. rotating cage) autoclave tests that incorporated various concentrations of sulfur dissolved in field and synthetic condensate. The results obtained were quite surprising and suggested that very low amounts of sulfur, completely dissolved in a hydrocarbon phase, will increase general corrosion rates compared to tests done with no sulfur in the hydrocarbon phase. General corrosion rates are those determined by overall weight loss when coupons are used. For tests using Linear Polarization Resistance (LPR), the general corrosion rate is obtained by averaging the LPR data over the duration of the test. Dissolved sulfur also increases the probability of localized corrosion and/or pit initiation. Some mechanistic pathways are suggested to account for these findings.

Baker Hughes believes that it is important to share these learnings with industry and thereby stimulate further research in this area.

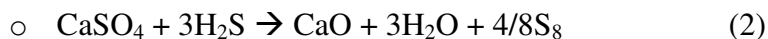
Origin of Sulfur in Sour Gas Systems

Probably the most extensive documentation explaining the origin of sulfur in sour gas has been assembled by Alberta Sulfur Research Ltd.⁷. Various mechanisms have also been proposed that can also be used to explain the formation and transport of elemental sulfur in sour gas systems:

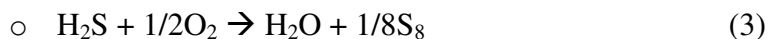
- Poly condensation of H₂S at high temperatures and pressures



- Thermochemical sulfate reduction



- Air oxidation of H₂S



- Ionic Polysulfides formed by dissociation of sulfanes, H₂S_x



- Oxidation of Aqueous Sulfide Solutions
- Dissolution of elemental sulfur in hydrocarbon liquids

A more detailed discussion of some these mechanisms is presented below.

Setting the Stage – a Primer on Sulfur Chemistry

The chemistry of sulfur is complex. Sulfur is one of the few elements that readily bonds to itself to form chain-like molecules with a variety of configurations. The terms “catenate” and “concatenate” are used to describe this phenomenon. The stable form of sulfur at room temperature and atmospheric conditions is one where eight sulfur atoms catenate to form a crown-shaped, eight-membered ring denoted as S₈ (see Figure 1).

These S₈ molecules crystallize to form the well-known yellow solid that is stable below about 95°C and is also chemically robust in the presence of air.

Sulfur is in the same chemical family as oxygen which means it has the same orbital ability to acquire two electrons and act as an oxidizing agent in a chemical reaction. From a chemist’s perspective, sulfur is different from oxygen because it has a set of empty d-orbitals available in its valence shell that give sulfur more flexibility and options with respect to the kinds of chemical bonding it can achieve. However, at room temperature, it is not as reactive as oxygen for several reasons.

- Sulfur’s ability to take electrons away from other chemical species (i.e., its oxidizing power) is less than that for oxygen but is still significant in relative terms.
- Sulfur is a solid at room temperature. From a simple mechanical standpoint, this hinders its ability to react with other solids such as pipeline steel.

- The cyclic chemical form of sulfur at room temperature is chemically stable. In order for sulfur to react, the eight-membered ring must be opened to render the sulfur “kinetically active”.

The situation changes considerably as the temperature is increased or if the sulfur is mobilized by circumstances such as being dissolved into a suitable solvent or rendered into other mobile species that facilitate chemical reaction mechanisms.

- The S₈ molecule has more tendency to vaporize as the temperature increases. The gaseous molecules are no longer hindered mechanically as they were in the solid and are free to react with other chemical species.
- The yellow solid eventually melts at about 112°C. This partially removes the mechanical hindrance imposed by the solid crystalline form.
- After melting, the eight-membered rings begin to break open. The resulting opened chains are much more chemically reactive than the closed rings.
- Sulfur will dissolve into hydrocarbon solvents at low temperatures and continue to exist as eight-membered rings. At this point, the mechanical hindrance imposed by the crystalline solid is removed and these eight-membered rings become more chemically reactive.

Hydrogen Polysulfides

Hydrogen polysulfides, sometimes referred to as “sulfanes”, are denoted by the chemical formula H₂S_x. In the laboratory, mixtures of hydrogen polysulfides are fairly easy to prepare; however, the pure compounds are relatively unstable and are easily decomposed in the presence of bases, sand, rough surfaces, and traces of water. Hydrogen sulfide gas is very soluble in liquid sulfur; this solubility increases dramatically in the temperature range of 120 to 200°C. This remarkable solubility increase is attributed to the formation of hydrogen polysulfides via the following reaction:



Since H₂S and elemental sulfur occur together in natural gas reservoirs, it is not unreasonable to assume that hydrogen polysulfides will also exist under these high temperature and pressure conditions. The formation of hydrogen polysulfides is described by an equilibrium reaction; it is therefore reasonable to expect that decreases in the temperature and/or pressure will lead to decomposition and formation of elemental sulfur. Depending on the temperature, sulfur may precipitate as a solid and cause plugging in the reservoir, well bore and/or surface facilities.

The enthalpies of vaporization, defined as kJ/mole, of hydrogen polysulfides (chain length $n = 2$ to 5) at ambient conditions (293°K) have been described by the following linear relationship⁸.

$$\Delta_v H^\circ_{293} = 10.67 + 11.54 * n$$

The enthalpy of vaporization for elemental sulfur is considerably lower (i.e. 9.62 kJ/mole) than that for the hydrogen polysulfides, but, at the high temperatures encountered in many sulfur-bearing reservoirs, the vapor pressure of hydrogen polysulfides will increase substantially. This increased volatility at downhole conditions allows hydrogen polysulfides to travel with the gas in the vapor phase. When sour gas is produced up the tubing, the temperature and partial pressure of H_2S decrease. This shifts the equilibrium in Equation 5 to the left and leads to the formation of elemental sulfur. Thermodynamics dictate the formation of sulfur, but the kinetics of the precipitation reaction often determines where the sulfur precipitates (i.e. in the reservoir, wellbore, tubing or surface equipment).

Exposure of hydrogen polysulfides to water at reservoir conditions can lead to the formation of ionic, water-soluble species. These ionic polysulfides offer another transport mechanism for sulfur; this is discussed in greater detail in the next Section.

Ionic Polysulfides

All hydrogen polysulfides behave as relatively strong acids in the gas phase.



Ab-initio molecular orbital calculations suggest that the gas phase acidities of hydrogen polysulfides increases with increasing chain length⁸. Experimental data supports the molecular orbital calculations; this shown Table 1 below⁹.

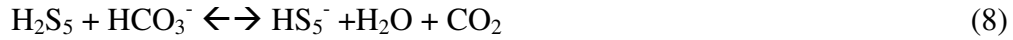
Table 1
Acid Dissociation Constants of Sulfanes

Species	K_{a1}	$\text{p}K_{a1}$	K_{a2}	$\text{p}K_{a2}$
H_2S	1.5×10^{-7}	6.83	1.0×10^{-14}	14.0
H_2S_2	1.0×10^{-5}	5.0	2.0×10^{-10}	9.7
H_2S_3	6.3×10^{-5}	4.2	3.2×10^{-8}	7.5
H_2S_4	1.6×10^{-4}	3.8	5.0×10^{-7}	6.3
H_2S_5	3.2×10^{-4}	3.5	2.0×10^{-6}	5.7

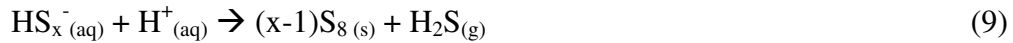
Decreasing $\text{p}K_a$ values indicate that increasingly acidic solutions are formed when hydrogen polysulfides dissolve in water. For example, a 0.1 molar solution of H_2S_5 gives

a solution with a pH of approximately 2. This is considered a very acidic solution that will be quite corrosive toward carbon steel.

Since hydrogen polysulfides can act as moderately strong acids, they can react with any basic species present. Formation water typically contains bicarbonate ions, which can behave as a base and therefore react with hydrogen polysulfides. Using H_2S_5 as an example, this reaction may be described as follows:



The HS_5^- ion is a water soluble species that will remain in solution, independent of temperature and pressure changes. However, the equilibrium position of Equation 8 is dependent upon the partial pressure of CO_2 and the concentration of bicarbonate in the system. If the pH drops significantly below 7, the HS_5^- ion can decompose into elemental sulfur.



Aqueous polysulfide solutions are typically characterized by a pale to bright canary yellow color. The pH of these solutions is usually slightly basic (i.e. $\text{pH} > 7$).

In a real-life field scenario, mixing sweet production fluids with sour production is not uncommon. If the sour produced water contains ionic polysulfides, elemental sulfur can form when the polysulfide-containing water mixes with the more acidic water from the sweet wells.

Oxidation of Sulfide Solutions

Hydrogen sulfide gas dissolves in water and behaves as a weak acid.



Bisulfide and sulfide ions are thermodynamically unstable in the presence of oxygen. Technical papers dating back more than 40 years have discussed the air oxidation of sulfide solutions to yield polysulfide anions¹⁰. A one electron oxidation of the HS^- ion has been proposed that can be used to explain polysulfide formation in both basic and acidic media¹¹.

Given the wide range of conditions where ionic polysulfides can be formed in solution and the ease by which they can revert to elemental sulfur, the presence of polysulfides in oilfield waters is viewed as a “red flag” that elemental sulfur may be present in the system. Consequently, water samples should be analyzed for ionic polysulfides and greater attention should be paid to the identity of solids that are recovered from pigging operations, chokes, valves, etc. Elemental sulfur in field samples is usually contaminated

with other substances (e.g. iron sulfide) and can vary from grey to green to black in color. Extraction/re-crystallization of the solid from hot toluene or X-Ray Diffraction of the solid can be used to confirm that elemental sulfur is present in the deposit.

EXPERIMENTAL PROCEDURES

Stirred Autoclave Tests (Laminar Flow) – Weight Loss Coupons

Synthetic brine, based on a produced water analysis, was used in the stirred autoclave tests.

Figures 2 and 3 depict the type of equipment typically used for autoclave tests.

Reagent grade inorganic salts dissolved in de-ionized water were used to make the synthetic brine composition is shown in Table 2.

Table 2
Synthetic Brine Composition

Ion	Concentration, ppm
Sodium	27,893
Potassium	376
Magnesium	215
Calcium	862
Strontium	50
Chloride	44,262
Bicarbonate	300
Sulfate	1,140
Acetate	450
TDS	75,548

Field condensate (filtered and unfiltered) and a synthetic condensate were used in these tests. Activated charcoal powder was used to filter the field condensate. 80 mesh sulfur was used to make the sulfur/hydrocarbon solutions. The concentration of elemental sulfur in the hydrocarbon solutions ranged from 0 to 1000 ppm.

The composition of the synthetic condensate is shown in Table 3.

Table 3
Synthetic Condensate Composition

Component	Amount, Volume %
Isopar M	90
Toluene	4
Xylene	6

Corrosion coupons (76.2 mm X 12.7 mm X 1.59 mm, 5LX52 metallurgy) were obtained from Metal Samples in Munford, Alabama. The coupons were configured such that approximately two thirds of the coupon was immersed in the aqueous phase and one third of the coupon was in the hydrocarbon phase.

X-52 and X-65 metallurgies are sometimes used in laboratory studies because they have higher yield strength than carbon steel. Yield strength is related to the microstructure of the steel and is believed to play a role in pit initiation. For this reason, X-52 and X-65 metallurgies were incorporated into the test matrices.

Dissolved air was removed from the brine and hydrocarbon solutions by degassing with carbon dioxide.

The conditions used in the autoclave tests are summarized in Table 4.

Table 4
Stirred Autoclave (Laminar Flow) Test Conditions

Parameter	Value
Brine Volume	240 mL
Hydrocarbon Liquid Volume	60 mL
H ₂ S Pressure	200 psi
CO ₂ Pressure	150 psi
Total Pressure in Autoclave	350 psi
Temperature	75°C
Duration	136 hours
Flow Regime	Gentle Stirring (120 rpm)

Stirred Autoclave Tests (Laminar Flow) – Electrochemical Evaluation

Electrodes (1018CS and X-65) were obtained from Metal Samples in Munford, Alabama. Autoclave tests using an electrochemical method (i.e. LPR) and the same conditions described in Table 4 were also conducted to investigate the corrosivity of elemental sulfur dissolved in a hydrocarbon phase. LPR measurements were performed using Gamry software interfaced with a Gamry multiplexer. Table 5 lists the settings used to measure the electrochemical corrosion rate.

Table 5
Electrochemical Experimental Parameters

Parameter	Value
Scanning Potential	+/- 5 mv
Scan Rate	0.5 mv/s
Scanning Frequency	Hourly
Electrodes	Working – 1018CS or X-65; Reference and Counter Electrodes - Hastelloy
Test Duration	72 hours

In the electrochemical experiments, the electrodes were completely immersed in the aqueous phase. These experiments were carried out using the synthetic condensate described in Table 3. After the experiment was complete, the electrodes were examined under a microscope to determine if localized/pitting corrosion was present.

High Speed Autoclave Tests (Very Turbulent Flow)

High Speed Autoclave Tests (HSAT), also described as “rotating cage” tests, typically incorporate four corrosion coupons mounted vertically on two Teflon^R holders. This coupon configuration, which gives the appearance of a “cage”, is mounted on a shaft that is rotated at a speed that simulates the wall shear stress in the pipeline. Figure 4 shows the shaft and Teflon^R mounting plates with one coupon in place.

X52 coupons (Metal Samples) were sand blasted prior to use. Before addition to the autoclave, all fluids were sparged continuously with CO₂ to eliminate the presence of any oxygen. The total autoclave volume is 4 liters. During operation, the autoclave is filled with 3 liters of liquid, which leaves a 1 liter gas headspace. The rotational speed used in these experiments was 400 rpm and was defined by the customer. In this case, superficial gas and liquid velocities were not provided by the customer. Baker Hughes has modified the classical equations to define shear stress using classical boundary theory to estimate the flow at the leading edge of the coupon. In this particular case, at a distance of 0.001 inches from the leading edge of the rotating cage and at a rotational speed of 400 rpm, the shear stress can reach 108 Pa¹².

Localized / Pitting Corrosion Determination

Optical profiling is a Vertical Scanning Interferometric (VSI) technique that accurately creates a three dimensional image of an electrode’s surface. A WYKOTM NT 9100 optical profiler (white light interferometer) from Veeco Instruments Inc. equipped with various objectives and an automated stage was employed to assess the corrosion damage on the HSAT coupons. The white light interferometer is essentially an optical microscope with a parallel mirror interferometer below the objective lens. Figure 5 shows a schematic of the VSI technique.

By scanning the lens towards the surface (vertical scanning interferometry – VSI), the height of all pixels in the image can be determined with high precision using software that has the ability to acquire images and analyze the topographic data. This technique has a depth resolution of 3 nm.

RESULTS AND DISCUSSION

Stirred Autoclave (Laminar Flow) Test Results

The results of the stirred autoclave tests are summarized in Table 6. This Table contains the general corrosion rates as a function of the various sulfur concentrations in both the

field and synthetic hydrocarbon phases that were evaluated. Evidence of localized and/or pitting corrosion was present in all the tests except those where no elemental sulfur was present. Also noteworthy is the fact that the majority of the corrosion damage was located at the brine/hydrocarbon interface (Note: recall that the coupons were submerged in both the brine and hydrocarbon layers).

At this point, it is appropriate to discuss the concept of localized and pitting corrosion. In some of the tests, distinct, separate pits were clearly visible to the naked eye and under the microscope. However, in some cases deep etching was present at different locations on the coupon surface. This localized form of corrosion is believed to be a “transition zone” from general corrosion to well-defined pitting corrosion. For this reason, the localized corrosion that was observed in all the tests is considered to represent an increased corrosion threat and has been grouped together with pitting corrosion. There are some gaps in Table 6. Equipment availability and project deadlines did not allow every condition to be tested.

**Table 6
Summary of Stirred Autoclave Test Data**

Type of Hydrocarbon	Pitting/Localized Corrosion	General Corrosion Rate, mpy						
		Sulfur Content of Hydrocarbon Phase, ppm						
		0	10	25	50	100	200	1000
Synthetic	Yes	-	5.2	5.3	5.8	5.6	6.7	11.1
	No	14.7	-	-	-	-	-	-
Field	Yes	-	-	-	3.7	3.9	6.3	19.7
	No	3.0	-	-	-	-	-	-

Figure 6 depicts the corrosion damage observed with variable amounts of sulfur dissolved in synthetic condensate or field oil. The condensate/water interface is clearly visible on the coupon.

Figure 7 shows the damage associated with 200 ppm dissolved sulfur in filtered field condensate.

Electrochemical Autoclave Test Results

The results of the autoclave LPR tests are shown in Tables 7 and 8.

**Table 7
LPR Autoclave Results – 1018 Carbon Steel Electrodes**

Dissolved Sulfur Concentration, ppm	General Corrosion Rate, mpy	Microscopic Evaluation of Coupon Surface
0	29.61	General corrosion
100	38.47	Localized etching
200	40.19	General corrosion

Table 8
LPR Autoclave Results – X-65 Electrodes

Dissolved Sulfur Concentration, ppm	General Corrosion Rate, mpy	Microscopic Evaluation of Coupon Surface
0	25.0	Localized etching
100	30.6	Trace etching by O-ring
200	37.3	Moderate etching with defined pits present

As noted in the experimental section, in this set of experiments, the electrodes were completely immersed in the aqueous phase. Some significant observations should be noted:

- For both 1018CS and X-65 steel, the general corrosion rate steadily increases as the amount of dissolved sulfur increases
- Localized etching was apparent on one of the carbon steel electrodes where dissolved sulfur was present
- More localized etching/pitting corrosion was evident on the X-65 electrodes

High Speed Autoclave Test Results

The results of the HSAT tests are summarized in Table 9. Once again, equipment availability and project deadlines did not allow every condition to be tested; this explains the missing data in Table 9.

Table 9
Summary of HSAT Test Data

Type of Hydrocarbon	Pitting/Localized Corrosion	General Corrosion Rate, mpy						
		Sulfur Content of Hydrocarbon Phase, ppm						
		0	10	25	50	100	200	1000
Synthetic	Yes	9.4	10.7	26.1*	29.2	42.6*		39.0
	No	10.4, 9.5**				11.9**		
Field	Yes	-	-	-	-	-	-	-
	No	3.0	-	-	-	-	-	-

* Lost pressure

** Pressure dropped

Figures 8 and 9 depict VSI scans the front and back views of the coupon that was exposed to 50 ppm dissolved sulfur in synthetic condensate. The mottled blue locations on the coupon represent areas of localized corrosion attack.

The presence of pitting/localized corrosion in the majority of the stirred autoclave and HSAT experiments that contained elemental sulfur completely dissolved in the hydrocarbon phase was unexpected. The presence of a hydrocarbon phase in a sour gas pipeline has typically been considered beneficial when elemental sulfur precipitation occurs in sour gas systems. Field condensate, particularly with a high percentage of aromatic components, is expected to reduce the aggressive impact of elemental sulfur for the following reasons:

- The ability to dissolve small amounts of sulfur
- Oil-wetting the pipe wall
- Liquid phase to assist sulfur transport and reduce deposition (flow regime dependent)

The data presented in this paper suggest that the first bullet listed above may no longer be valid. Low levels of sulfur dissolved in condensate which is in contact with an aqueous phase may increase the risk of pitting corrosion or localized damage in a pipeline. Of particular concern are pipelines where only small amounts of elemental sulfur are present and where the producer is not even aware that sulfur is present in the system.

The Sulfur Transport Mechanism in Liquid Hydrocarbons

Transport mechanisms that “deliver” active forms of sulfur to metal surfaces are too complex to discuss in this paper. Multi-step disproportionation reactions involving electron transfers and chemical bond re-arrangements are used to model the variety of chemical species resulting from the interaction of H₂S and sulfur. However, it is important to visualize how these different species can be distributed between the three phases in a producing system. This is simply depicted in Figure 10.

It is noteworthy that molecular sulfur can be present as a solid, as a species dissolved in a hydrocarbon phase, as a gaseous species dissolved in the gas phase or as combinations of these three situations. Reactions between H₂S and sulfur occur in all three phases and the complex species resulting from these interactions are also distributed between those three phases depending on their chemical nature.

Generally speaking, we can say that S₈ is activated by the presence of H₂S and converted to a variety of species that contain “active” forms of sulfur. Both the activated forms of sulfur and the H₂S derivatives can migrate to and react with metal surfaces more easily than the original solid. That activation is a strong function of the partial pressure of H₂S and temperature.

In a turbulent three-phase system, sulfur will tend to dissolve into an available hydrocarbon phase until it reaches a saturation point and then it will start to accumulate as a solid in the water phase. That saturation point is a function of the partial pressure of H₂S, the temperature and the composition of the hydrocarbon phase. In many situations, there is not enough sulfur present to saturate the hydrocarbon phase so there will be no solid sulfur present. In two-phase systems where no hydrocarbon phase is present (as for

lean gas production), sulfur will be present as a gas and a solid because it is not soluble in water to any significant extent but the H₂S derivatives will still form and will be distributed between those two phases.

When sulfur does form in a flow regime where pools of stagnant water exist, the sulfur can settle out of the water onto the pipe surface and lead to aggressive attack with potentially catastrophic consequences. .

The “inherent corrosivity” of ionic polysulfide solutions has also been a topic discussion for many years. There is data that supports the fact that polysulfides increase the corrosivity of oilfield waters⁵. However, there is also literature that suggests that polysulfides can control the corrosion rate under certain conditions¹. The varying corrosivity of ionic polysulfide solutions may be related the type of cations present in solution. Smaller, alkali metal cations (e.g. Na⁺, K⁺) would be expected to be less stabilizing than large cations. Polysulfide solutions, generated from amine-based sulfur solvents, contain larger, stabilizing amine cations and have been shown to exhibit very low corrosivity toward carbon steel¹³.

It is often difficult to identify a precise failure mechanism in sour gas systems; there are typically a number of contributing factors (e.g. H₂S/CO₂ ratio, chloride content of the water, pitting accelerators – S₈, oxygen). The data presented in this paper points to another possible mechanism by which small amounts of sulfur can be transported to the metal surface.

Dissolved Sulfur Content of Field Condensate

Analytical Methodology

Sulfur content in field oil is often misunderstood. There are two categories of sulfur in field oil as shown in Figure 11. Typically, “Total Percent Sulfur” is reported in a standard oil analysis. This value can be determined using one of several standard analytical methods such as ASTM 3177. Many organic and inorganic molecules contain sulfur as part of their molecular make up. Examples are given in the left hand column of Figure 11. The amount of “reactive sulfur” is a totally different quantity. Only a few types of these sulfur-containing molecules are considered to be “reactive” from a corrosion standpoint. Two examples are shown on the right side of Figure 11.

It is important to know if there are reactive forms of sulfur present in the produced fluids. Baker Hughes developed an analytical method based on liquid chromatography (HPLC) that can specifically identify and quantify dissolved S₈ in a hydrocarbon phase. Another method, developed by ASRL, uses a gas chromatograph to detect the reaction product between triphenylphosphine and all active forms of sulfur present in the hydrocarbon phases. The liquid chromatographic method works very well with synthetic hydrocarbon phases and indentifies the S₈ molecule specifically. However this method suffers from overwhelming interferences when actual field oils are used. The gas chromatographic method works well in all cases and yields the total amount “active sulfur” as defined in Figure 11.

Analysis of Some Field Condensates

As a follow-up to the laboratory data that were obtained, a number of field condensates from various locations in Alberta were collected under anaerobic conditions and submitted to Alberta Sulfur Research Ltd. (ASRL) for analysis to determine the amount of dissolved sulfur present as per the discussion above.

Table 10 summarizes the results of the condensates that were analyzed.

Table 10
Dissolved Sulfur Content of Various Field Condensates

Sample	Dissolved Sulfur Concentration, mg/L	Comments
1	135	Collected in sample bottle
2	25	Collected in sample bottle
3	215	Collected in pressure cylinder
4	17	Bottle broke in transit
5	26	Condensate was previously charcoal filtered and analyzed in Baker Hughes's lab in Sugar Land using a procedure analogous to ASRL's
6	1210	Collected in sample bottle

All condensate samples were collected to minimize exposure to air and prevent oxidation of dissolved H₂S in the liquid (i.e., as per Equation 3). When sample bottles were used, the bottle was completely filled so that no air remained in the head space of the bottle. Judging by the low levels of dissolved sulfur in some of samples in Table 10, the reaction of H₂S with atmospheric oxygen appears to be a minor contribution to the total dissolved sulfur in the condensate.

The autoclave test data presented in this paper suggest that even very low levels of dissolved sulfur have the capability to increase the risk of pitting and/or localized corrosion in a sour service pipeline. Sulfur dissolved in the hydrocarbon phase creates a "silent threat" because there is no visible evidence that sulfur is present in the system (e.g. as a solid in the pig barrel). Only a careful, specialized analysis of the field hydrocarbon liquid can determine if dissolved sulfur is present. Additional laboratory testing, field monitoring and/or smart pig inspections will probably be required to evaluate the potential corrosion threat associated with the dissolved sulfur.

CONCLUSIONS

1. Gravimetric and electrochemical stirred autoclave tests and high speed autoclave tests incorporating elemental sulfur dissolved in both field and synthetic condensate showed an increased threat of pitting/localized corrosion.
2. The autoclave tests demonstrate the broad spectrum of conditions where elemental sulfur dissolved in a hydrocarbon phase has the ability to increase the general and/or localized corrosion rate:

- a. HSAT tests – turbulent environment where hydrocarbon and brine phases are well mixed
 - b. Metal surface at the hydrocarbon/brine interface under low flow conditions
 - c. Metal surface completely immersed in the brine phase
3. Electrochemical corrosion tests incorporating sulfur dissolved in a hydrocarbon phase showed the following trends:
 - a. Increasing corrosion rates and localized/pitting attack were associated with higher dissolved sulfur concentrations
 - b. X-65 metallurgy displayed more localized attack than carbon steel
4. The presence of a liquid hydrocarbon phase in sour gas systems where sulfur is present may facilitate the transfer of reactive sulfur species to the aqueous phase and thereby increase the internal corrosion threat in the pipeline.
5. Several field condensates were analyzed and contained dissolved sulfur ranging from 17 to 1210 mg/L
6. The absence of solid yellow sulfur does not mean that there are no pernicious sulfur-containing species lurking in the hydrocarbon phase. Elemental sulfur dissolved in hydrocarbon phase poses a “silent threat” since there are no tell-tale solids which can be analyzed to identify sulfur.
7. A complex series of equilibria involving H₂S, elemental sulfur, sulfanes and ionic polysulfides are proposed to explain the transport of reactive sulfur via the hydrocarbon phase to the aqueous phase and explain the pitting/localized corrosion observed in the autoclave studies.
8. It is hoped that the data presented in this paper will provide the basis and stimulus for additional research to investigate the potential corrosivity of low levels of sulfur dissolved in liquid hydrocarbons.

ACKNOWLEDGEMENT

The Authors wish to thank Bake Hughes Inc. for the opportunity and permission to publish this paper.

REFERENCES

1. Bruckhoff, W., “New Results in Corrosion Control in Sour Gas Wells”, *Erdoel, Erdgas Zeitschrift*, Vol. 95, No. 3, pp. 82-89, 1979 and references cited therein.
2. Ockelmann, H. and Blount, F., “Ten Years Experience with Sour Gas Production in Germany”, *SPE paper 4663*, 1973 and references cited therein.
3. Moore, J. et al, “Corrosion Inhibitors in the Presence of Elemental Sulfur”, paper 09363, *CORROSION* 2009.
4. Fang, H. et al, “Corrosion of Mild Steel in the Presence of Elemental Sulfur”, paper 08637, *CORROSION* 2008.

5. Gregg, M. et al, "Corrosion Experiences and Inhibition Practices Managing Wet, Salty Sour Gas Pipeline Environments Contaminated With Elemental sulfur Deposits", paper 03174, CORROSION 2003.
6. Gregg, M. and Lerbscher, J., "Inhibitor Developments Providing Mitigating Benefits Against Pitting Corrosion in Sour Production Environments Contaminated With Elemental Sulfur Deposits", NACE Northern Area Western Conference, Calgary, February 3-6, 2003.
7. For example, see: "Sulfur Deposition and Other Aspects of the Chemistry and Technology of Sour Gas Production", presented in Conjunction with ASRL's Sulfur Deposition Forum, University Research Centre, Calgary, June 1, 2006.
8. Steudel, R., "Inorganic Polysulfanes H_2S_n with $n > 1$ ", Topics in Current Chemistry, Vol. 231, pp 99-125, 2003 and references cited therein.
9. Lerbscher, J. et al, "Corrosion Management of Sour Gas Systems that Produce Elemental Sulfur", NACE Northern Area Western Conference, Calgary, March 8-11, 1999.
10. Chen, K. and Gupta, S., "Formation of Polysulfides in Aqueous Solution", Environmental Letters, Vol. 4, pp. 187-200, 1973.
11. Steudel, R., "Mechanism for the Formation of Elemental Sulfur from Aqueous Sulfide in Chemical and Microbiological Desulfurization Processes", Ind. Eng. Chem. Res., Vol. 35, pp. 1417-1423, 1996.
12. Ramachandran, P.; Ramachandran, S.; Greaves, M.; Jovancicevic, V. "Shear Stress Profile in a Rotating Cage" Paper presented at the International CORCON conference at Mumbai, India, September 27, 2007
13. Baker Hughes – unpublished results.

FIGURES

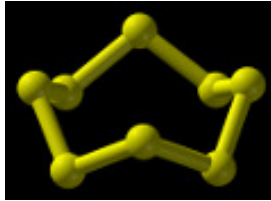


Figure 1
Crown Configuration of Elemental Sulfur



Figure 2
Stirred Autoclave Test in High Temperature Oven



Figure 3
High Temperature and Pressure Hastelloy Autoclave



Figure 4
Typical HSAT Configuration

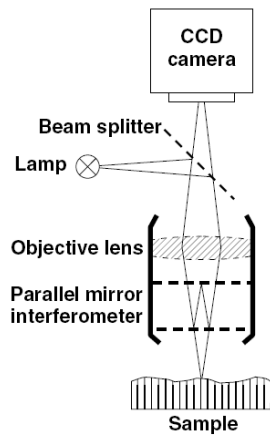


Figure 5
Schematic of Optical Profiling Technique

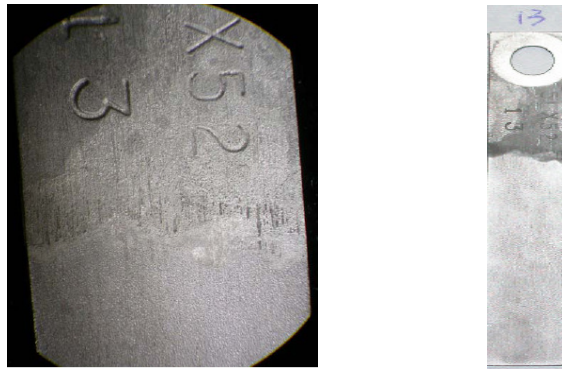


Figure 6
Localized Corrosion Damage – 50 ppm Sulfur in Synthetic Condensate

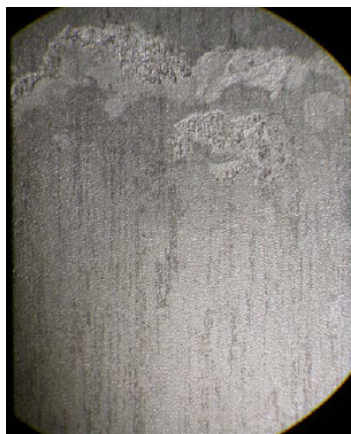


Figure 7
Localized/Pitting Corrosion Damage – 200 ppm Sulfur in Filtered Field Condensate

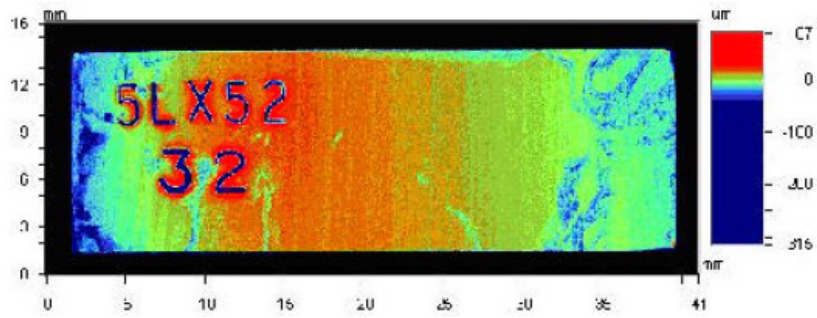


Figure 8
HSAT Coupon Exposed to 50 ppm Dissolved Sulfur

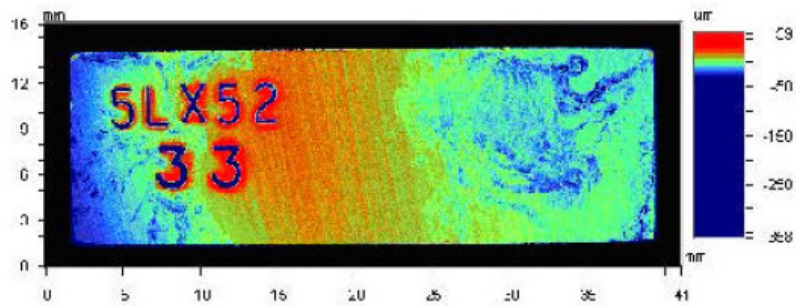


Figure 9
HSAT Coupon Exposed to 50 ppm Dissolved Sulfur

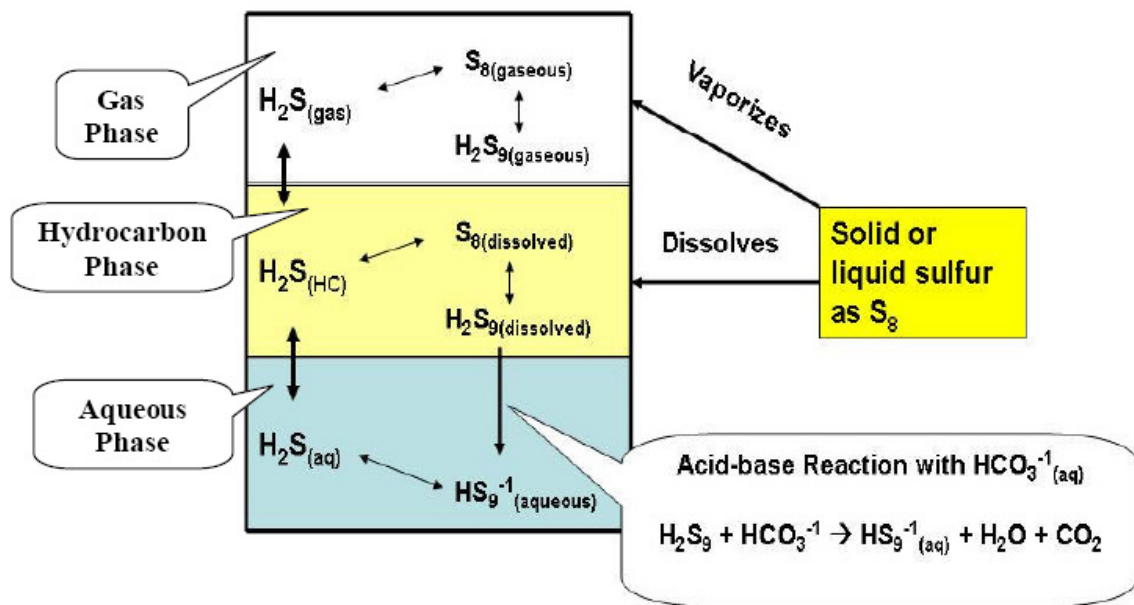


Figure 10
Equilibria and Reaction Pathways for Reactive Sulfur Species

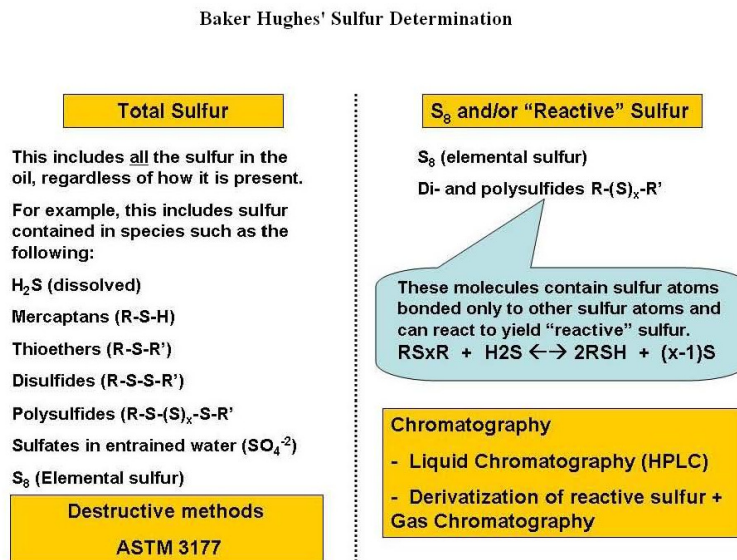


Figure 11
Analytical Determination of Sulfur Species