

Sulfur Solvents: Understanding Operating Envelopes Through Laboratory Studies and Field Case Histories

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ABSTRACT

Accumulation of elemental sulfur in sour gas or sour crude oil gathering systems is a challenge Producers encounter. Sulfur blockages can persist throughout a gathering system; problems can occur in the formation, production tubing, pipeline and/or within surface equipment. Predicting where precipitation of sulfur will occur is complicated due to numerous influential factors such as temperature, pressure, and gas and liquid compositions. When solid sulfur is identified, primary concerns become interruptions in production, increased risk associated with sulfur-related corrosion, and the well-being of the surrounding population and environment.

A successful mitigation strategy for sulfur deposition is the application of sulfur solvents on either a continuous or batch frequency. These chemicals are classified as physical or chemical solvents depending on the mechanism used for dissolving sulfur blockages. This paper reviews background information for both types of sulfur solvents, compares product efficacy as determined in laboratory testing performed by Baker Hughes and Alberta Sulfur Research Ltd., and highlights the value and diversity of sulfur solvents through field case histories.

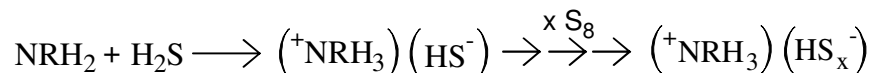
Keywords: Sulfur, Solvent, Precipitation, Deposition, Dissolve, Dissolution, Physical, Chemical, Mechanism, Amine, Polysulfide, Continuous, Batch, Application

INTRODUCTION

Research surrounding sulfur deposition in sour gas gathering systems includes determining the sulfur loading capacity of the sour fluids,^{1,2} combining this information with standard operating conditions of the field to predict at what location elemental sulfur will precipitate and ultimately deposit,²⁻⁴ and finally, determining how to avoid or alleviate the issue to minimize interruption to gas production. The use of sulfur dispersants or solvents is one option for mitigating sulfur deposition in sour gas systems.

Sulfur solvents based on aromatic-containing hydrocarbons dissolve sulfur via a physical mechanism, where interactions between the electron-rich aromatic rings and the crown structure of S₈ allow for dissolution of the solid.^{1,5} For this reason, physical solvents of high aromatic content (*e.g.* doped with naphthalene) illustrate superior sulfur dissolving capability relative to lean hydrocarbons. The physical dissolution of sulfur is an efficient process at elevated temperatures⁶; therefore, these solvents find much use in downhole and tubing wash applications. That being said, large solvent volumes (>600 m³/d for continuous applications and >2 m³ per tubing wash) must be employed to address drawbacks encountered with these solvents. For example, in lean sour gas streams, physical solvents composed of more volatile aromatic compounds will evaporate or 'flash' into the gas phase, significantly reducing the volume of liquid solvent remaining to dissolve downhole sulfur deposits.⁶ Another significant drawback to these types of solvents is the tendency to reprecipitate solid sulfur from saturated solutions at cooler temperatures.⁵ To rectify this, sulfur mitigation strategies are based on the larger volume of solvent required to dissolve sulfur at 25 – 20 °C, not the smaller solvent volume needed to dissolve sulfur at the higher temperatures.⁽¹⁾

Chemical sulfur solvents dissolve elemental sulfur by reacting with the S₈ ring to produce ionic polysulfides, which are soluble in polar fluids such as methanol, water and brine. Amines are a common active ingredient in these types of solvents. In the presence of H₂S, the mechanism for dissolving sulfur is thought to include reaction of an aliphatic amine and H₂S to form an ammonium bisulfide, followed by reaction of the bisulfide anion with elemental sulfur to yield ionic polysulfides.^{1,5}



While support for this reaction mechanism is outlined in the Results & Discussion section of this article, the type of amine present in the sulfur solvent will influence the role of the above reactions in the dissolution of solid sulfur by an amine-based sulfur solvent.

The physical and chemical properties of an amine-based sulfur solvent at various temperatures and under different gaseous environments are outlined in this paper. Procedures to determine sulfur uptake data performed independently by Baker Hughes Incorporated (BHI) and Alberta Sulfur Research Ltd (ASRL) are described, and the results presented within. A comparison of the temperature dependence of a chemical solvent relative to an aromatic physical solvent in a predominately H₂S environment is also presented. Finally, the operating envelope of a BHI amine-based chemical solvent is highlighted through a detailed case history.

EXPERIMENTAL

⁽¹⁾ Paper presented at 5th Annual Alberta Sulfur Research Ltd. Sulfur Deposition Forum (May 2009)

The operating envelopes of two sulfur solvents were explored through sulfur uptake testing. The chemical compositions of the two solvents were as follows:

- Sulfur Solvent 1 (SS1): primary and secondary amines dissolved in a water/alcohol package
- Sulfur Solvent 2 (SS2): heavy aromatic petroleum naphtha containing naphthalene (4-12%)

Sulfur Uptake Testing

Baker Hughes Testing Procedure: The operating envelopes of two sulfur solvents were explored through sulfur uptake testing. Gravimetric analysis was used to determine the amount of sulfur dissolved by each solvent. Glass crucibles were designed with coarse sintered glass frits (250 – 500 μm) that permitted passage of fluids but kept sulfur particles contained within (Figure 1). Thus, the weight of remaining sulfur relative to initial sulfur present could be determined and then converted into sulfur uptake data.

In each test, a known amount of sulfur was placed into a glass crucible, which was then inserted into a glass liner (Figure 1). The liner was filled with a predetermined amount of solvent (and production fluids, if required). This apparatus was placed into an autoclave that was filled with the appropriate acid gas composition. The autoclave was subjected to the required test temperature for a predetermined length of time. Upon test completion, the autoclave was degassed and the glass liner was removed. The glass crucible was then extracted from the resulting test solution; remaining sulfur particles were washed, dried and weighed.

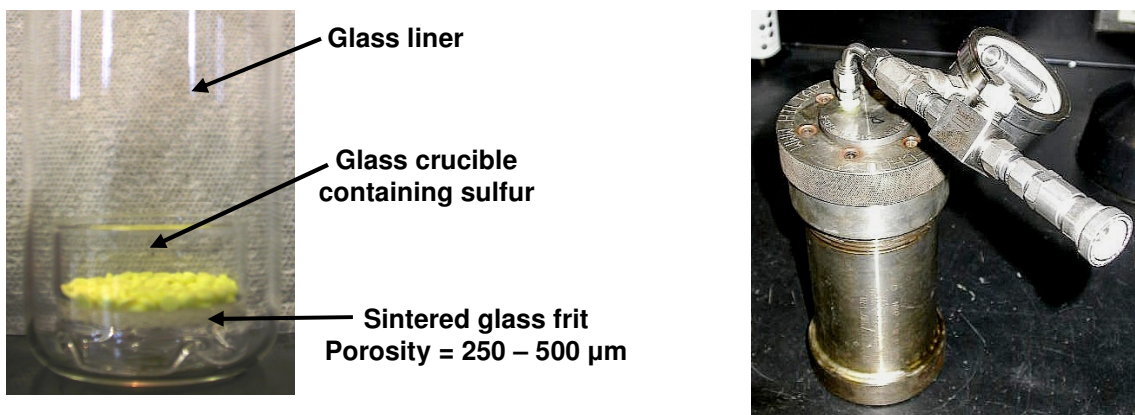


FIGURE 1 – Sulfur Uptake Test Apparatus and 316SS Autoclave

Testing was performed at various temperatures, in environments of varying acid gas compositions, and in the presence of different production fluids (Table 1).

**TABLE 1
SULFUR UPTAKE TESTING PARAMETERS**

Test Parameter	Amounts	Details
Sulfur	10 g	Granular 4 mm “split pea” particles Simulate sulfur deposition
Sulfur Solvent	80 mL	Sulfur Solvent 1 (SS1) Sulfur Solvent 2 (SS2)
H ₂ S Partial Pressure	0 to 200 psi	Subject SS and sulfur to different acid gas compositions
CO ₂ Partial Pressure	0 to 240 psi	

Temperatures	Max: 80 °C Min: 25 °C	Simulated downhole, pipeline and surface equipment temperatures
Flow Regime	No Stirring	Simulated soak application (worst case scenario)
Test Duration	Max: 16 h	Simulated contact times in various soak applications
Fluids	0 or 80 mL	Fresh Water Brine Methanol
Brine Composition	80 mL	75,000 ppm chlorides 2,000 ppm calcium 46,340 ppm sodium Total Dissolved Solids (TDS): 123,340 ppm

Alberta Sulfur Research Ltd. (ASRL) Testing Procedure: Additional sulfur uptake testing for SS1 was completed by ASRL to verify the results determined at Baker Hughes. In the ASRL procedure, sulfur, SS1 and any required co-solvents were placed into a glass vessel that was surrounded by a circulating oil jacket to maintain test temperatures (Figure 2). Gases (N_2 or H_2S) were introduced into the solvent system via a sintered glass frit and expelled from the vessel through an outlet port fitted with a condenser, to limit solvent loss at elevated temperatures. In these experiments, sulfur uptake was determined using a chromatographic technique where aliquots of spent solvent (*i.e.* amine polysulfides) were reacted with triphenylphosphine (TPP) to form a triphenylphosphine-sulfide adduct identifiable by gas chromatography (GC).⁷

Two types of sulfur uptake experiments were performed. In the first, aliquots of the test fluids were sampled at the intervals listed below:

- After 18 h at 40 °C under N_2 to determine sulfur content of virgin solvent
- After exposure to H_2S for two hours at 40 °C
- Followed by another two hours later under H_2S at 40 °C
- Two hours after increasing temperature to 60 °C, still under H_2S
- Two hours later under H_2S at 60 °C
- Two hours after changing purge gas to N_2 and decreasing temperature to 40 °C
- Finally, after 18 h at 40 °C under N_2 to determine the recyclability of the solvent
- Total test time ~ 46 h

This type experiment was repeated with high chloride brine to determine the effect co-solvents have on the sulfur uptake capacity of the sulfur solvent, SS1. Finally, to verify that results from the above experimental procedure were representative of an equilibrium state, a second experiment was performed where the sulfur and the solvent(s) were exposed to H_2S at 40 °C for seven days.

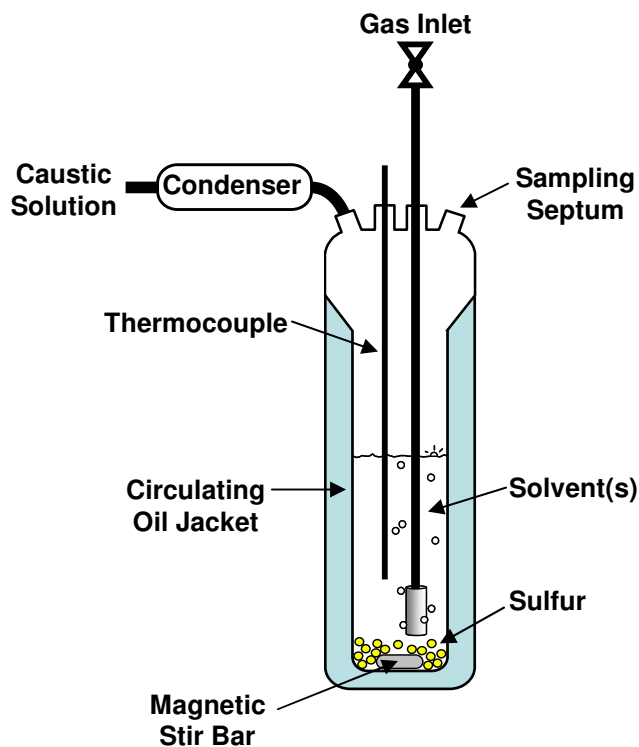


FIGURE 2 – Alberta Sulfur Research Ltd. Sulfur Uptake Test Apparatus

Product Stability and Compatibility Testing

Thermal Stability: Product stability at elevated temperatures ($> 150\text{ }^{\circ}\text{C}$) is relevant to chemical applications at gas coolers within molecular sieve regeneration systems where gas inlet temperatures can reach $275\text{ }^{\circ}\text{C}$. To investigate this, samples of SS1 were heated to various temperatures (max. $300\text{ }^{\circ}\text{C}$) under N_2 (50 psi). At each temperature, the sample was held for 30 minutes. Following cool down, the individual solutions were visually inspected for solids and analyzed by FT-IR. Finally, to confirm chemical integrity, elemental sulfur was treated with the heated products at ambient conditions and visually inspected for the formation of amine polysulfides, which was identified by a red/orange color change.^{8,9}

Metals: Compatibility with 316 stainless steel (SS) and Duplex SS was investigated by performing thermal stability and compatibility testing at $150\text{ }^{\circ}\text{C}$. Three test tubes were prepared as follows: (a) neat SS1, (b) SS1 + 316SS metal coupon and (c) SS1 + Duplex SS metal coupon. The three test tubes were then placed in an autoclave and charged with 500 psi of N_2 . Following a one week long static test at $150\text{ }^{\circ}\text{C}$, the solutions were visually inspected for solids and the metal coupons analyzed for corrosion.

Two short term compatibility tests with 1018 carbon steel (CS) were also performed. In the first test, CS coupons were subjected to neat chemical at $90\text{ }^{\circ}\text{C}$ under 100 psi N_2 for 96 h. In the second test, CS coupons were subjected to high chloride water and acid gases at $55\text{ }^{\circ}\text{C}$ for a 72 h period. The selected testing conditions are outlined in Table 2:

**TABLE 2
PARAMETERS FOR METALS COMPATIBILITY TESTING**

Parameter	Value
Acid Gas Composition	200 psi H ₂ S / 100 psi CO ₂
Brine Composition	75,000 ppm chlorides 2,000 ppm calcium 46,340 ppm sodium Total Dissolved Solids (TDS): 123,340 ppm
Brine Volume	300 mL
Temperature	55 °C
Test Duration	72 h
Flow Regime	Medium Stirring
Filming Step	Dip the coupon in sulfur solvent for 10 seconds, allow to drip dry for 1 minute
Sulfur	None
16 h Pre-Corrode Step	None

Amine Polysulfides: The properties of SS1-generated amine polysulfide solutions were examined through a series of autoclave corrosion tests completed at two different temperatures. The three day experiments were performed in predominately sour environments with elemental sulfur, SS1 and high chloride brine present in the testing cells. Specific testing conditions are listed in Table 3:

**TABLE 3
PARAMETERS FOR AMINE POLYSULFIDE PROPERTIES TESTING**

Parameter	Value
Acid Gas Composition	200 psi H ₂ S / 50 psi CO ₂
Brine Composition	75,000 ppm chlorides 2,000 ppm calcium 46,340 ppm sodium Total Dissolved Solids (TDS): 123,340 ppm
Brine Volume	275 mL
SS1 Volume	25 mL (7.5%)
Temperatures	80 and 50 °C
Test Duration	72 h
Flow Regime	Medium Stirring
Sulfur	0 – 2.5 g
Metal Coupons	1018 Carbon Steel Disc Coupons
16 h Pre-Corrode Step	None

1% = 10,000 ppm

RESULTS AND DISCUSSION

Sulfur Uptake Testing

Baker Hughes Testing Results: In these experiments, the amount of sulfur dissolved by a solvent was gravimetrically determined by comparing the initial weight of elemental sulfur to the final weight of solid sulfur remaining at completion of the test. The weight percent uptake by a solvent was calculated as the amount of sulfur dissolved relative to the weight of the solvent used (*i.e.* g sulfur dissolved / 100 g solvent).

When exposed to amines, sulfur molecules are converted to ionic amine polysulfides of varying chain lengths, with the most stable being S₄²⁻ and S₅²⁻.^{8,9} These polysulfide molecules are oils that are soluble in polar solvents such as water, brine, MeOH or mixtures thereof. Granular sulfur was employed in these solubility tests because relative to prill sulfur, the larger particles better simulated sulfur deposits, and could be easily separated from produced amine polysulfide oils by washing with a 2:1 water/methanol mixture (Figure 3).

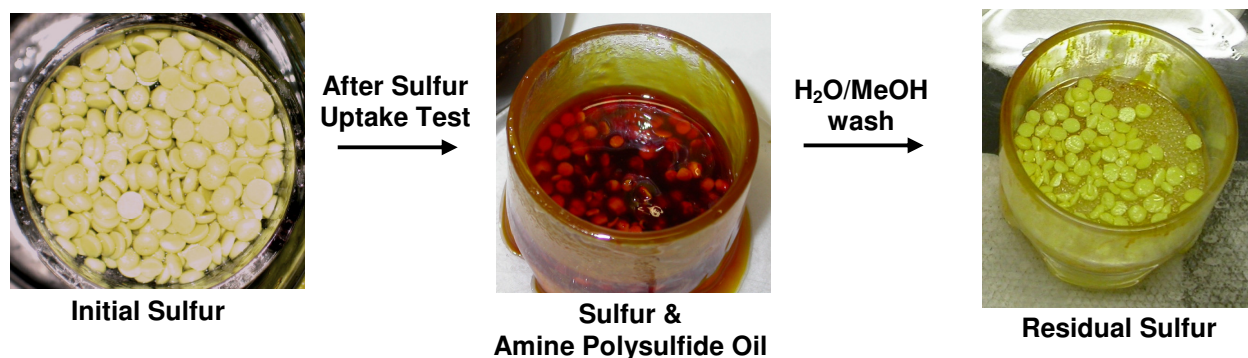


FIGURE 3 – Gravimetric Determination of Sulfur Uptake

The sulfur uptake results for the following three experiments can be found in Table 4.

Sulfur Uptake Results in Inert Environment – N₂: Sulfur uptake testing performed in inert environment provides the ‘virgin sulfur uptake’ values for a sulfur solvent. That is, the percent sulfur uptake with no assistance or impediment by included acid gases. As expressed in the Introduction, amines present in chemical solvents can react with H₂S.^{1,5} Likewise, amines can react with CO₂ to form carbamate salts^{10a} as well as alcohols present in solvent packages to yield alkoxide ions.^{10b} Therefore, the amount of sulfur dissolved by an amine-based solvent depends on the rate of formation of these by-products, and if formed, their reactivity towards elemental sulfur. In these experiments, autoclaves were pressurized with 240 psi N₂ and the test temperature was 80 °C.

Results showed the virgin sulfur uptake for SS1 in the inert environment was 2.7 wt% (*i.e.* 2.7 g sulfur / 100g solvent).

Sulfur Uptake Results in Sour Environment – High H₂S: The acid gas composition used in this experiment was 200 psi H₂S & 50 psi CO₂, and the test temperature was 80 °C. Compared to sulfur uptake experiments performed in the inert atmosphere, a dramatic increase in the sulfur uptake of SS1 was observed under sour conditions (7.5 wt% vs 2.7 wt%, respectively). These results support the idea that H₂S assists amines in dissolving solid sulfur deposits. As outlined in the Introduction, the mechanism for H₂S participation likely includes reaction of an aliphatic amine and H₂S to form an ammonium bisulfide, followed by reaction of the bisulfide anion with elemental sulfur.^{1,5}

Sulfur Uptake Results in Sour Environment – High CO₂: The acid gas composition used in this experiment was 10 psi H₂S & 240 psi CO₂, and the test temperature was 80 °C. The sulfur uptake value for the amine-based solvent in CO₂-dominated environment was lower than that for predominantly H₂S environment (4.7 wt% vs 7.5wt%, respectively). The CO₂ present competed with H₂S for the amine molecules present in SS1. Kinetically, CO₂ and H₂S react at similar rates with primary amines. Selectivity between the two gases improves as the number of substituents on the amine molecule increases, with tertiary amines demonstrating the highest preference towards H₂S.^{10a} These results suggest sulfur solvents based on primary or secondary amines are not the preferred choice for wells rich in carbon dioxide.¹¹

TABLE 4
SS1 SULFUR UPTAKE DATA FOR VARYING ATMOSPHERES

Atmosphere	Gas Composition	Sulfur Uptake Data
Inert	240 psi Nitrogen	2.7 wt%
H ₂ S-dominant	200 psi H ₂ S & 50 psi CO ₂	7.5 wt%
CO ₂ -dominant	10 psi H ₂ S & 240 psi CO ₂	4.7 wt%

wt% = g sulfur dissolved / 100 g solvent

Test temperature = 80 °C

Other Sulfur Uptake Results in Sour Environment

Co-solvent Influence: The performance of SS1 in the presence of various co-solvents was studied under acid gas conditions (200 psi H₂S & 50 psi CO₂). The results are listed in Table 5. In general, the sulfur uptake of SS1 increased when a polar co-solvent was present. This effect was attributed to the dissolution of amine polysulfides into the polar co-solvents; removal of the viscous amine polysulfide material allowed unreacted SS1 amine molecules to access and react with residual sulfur pellets, increasing the overall sulfur uptake of the solvent.

TABLE 5
SS1 SULFUR UPTAKE DATA WHEN CO-SOLVENTS PRESENT

Conditions	Sulfur Uptake Data
Neat Chemical	7.5 wt%
Chemical + Brine	9.2 wt%
Chemical + MeOH	8.3 wt%

wt% = g sulfur dissolved / 100 g solvent

Gas Composition: 200 psi H₂S & 50 psi CO₂

Temperature: 80 °C

Temperature Dependence: The performances of SS1 and SS2 at various temperatures were compared in the presence of acid gases (200 psi H₂S & 50 psi CO₂). Temperatures were chosen to simulate three different locations in sour gas gathering systems: production tubing (80 °C), wellhead (50 °C) and surface equipment (25 °C). Results for the series of tests are listed in Table 6.

**TABLE 6
TEMPERATURE DEPENDENT SULFUR UPTAKE DATA**

Temperature	Sulfur Uptake Data SS1	Sulfur Uptake Data SS2
80 °C	7.5 wt%	12.9 wt%*
50 °C	7.0 wt%	5.5 wt%
25 °C	2.4 wt%	1.7 wt%

*2.3 wt% sulfur recrystallized from the solvent at 25 °C
wt% = g sulfur dissolved / 100 g solvent

As anticipated, the aromatic physical solvent, SS2 displayed greater sulfur uptake performance at elevated temperatures (80 °C) relative to the amine-based solvent, SS1 (12.9 wt% vs 7.5 wt%).⁽²⁾ One drawback to this impressive sulfur uptake was the recrystallization of 2.3 wt% sulfur from the aromatic solution as the temperature cooled to 25 °C. In the field, this outcome is avoided by basing aromatic sulfur solvent mitigation strategies on the volume of solvent required to dissolve sulfur at 25 – 20 °C.⁽¹⁾ It should also be noted that, as expected, no sulfur drop-out was observed for SS1 because amine polysulfides convert back to elemental sulfur when exposed to acidic conditions or high oxygen environments^{6,8,12}, not as a result of temperature decline.

Comparison of the results for sulfur uptake at 80 °C and 50 °C illustrates the significant effect temperature has on the performance of aromatic solvents. The sulfur uptake for SS2 declined from 12.9 wt% at 80 °C to 5.5 wt% at 50 °C. In contrast, the performance of SS1 remained relatively consistent regardless of the 30 degree temperature decline; 7.5 wt% at 80 °C decreasing slightly to 7.0 wt% at 50 °C.

At the lowest test temperature, 25 °C, the performance of both solvents plummeted; 2.4 wt% for SS1 and 1.7 wt% for SS2. In this temperature range, disulfide solvents still prevail as the most effective for dissolving elemental sulfur, with sulfur uptakes in the range of 150 wt%.¹³

With respect to all sulfur uptake tests described in the above sections, it is important to note these tests measured the amount of solid sulfur completely dissolved by the solvent in a stagnant environment. In field applications, the dissolution of sulfur blockages is accompanied by softening of the deposit, which allows portions of the solid sulfur to break into smaller particles that disperse into system fluids and can be carried downstream by production flow. Consequently, the volume of solvent required to dissolve sulfur in these laboratory settings can be significantly larger than the volume used in the field, based on trial application results.

Alberta Sulfur Research Ltd. Testing Results: Overall, results from the ASRL sulfur uptake testing correlated with the in-house BHI tests. SS1 showed sulfur uptake between 6 – 10 wt% for both the neat and brine samples using TPP-GC methodology¹⁴, a range the results for SS1 agreed with (Tables 4 and 5). Testing in the glass vessel proved useful for making *in-situ* observations. The solvent turned a darker color upon exposure to solid sulfur and then became red once H₂S was introduced into the vessel (Figure 4). Furthermore, following exposure to H₂S at the higher temperature (60 °C), testing fluids tended to separate into two phases; a viscous bottom phase and a less dense upper phase (Figure 4). Based on chromatography results, both phases contained amine polysulfides with the lower

⁽²⁾ For a comprehensive sulfur uptake study on Physical Solvents consult: R.A. Marriott, E. Fitzpatrick, "Physical Sulfur Solvents: The Sulfur Solubility in BTX and the General Solubility Equation for Physical Sulfur Solvents", ASRL Quarterly Bulletin, 145 (April – June 2008) p.1

phase being a more concentrated solution. As a result, sampling of this phase proved problematic after long exposure to H₂S at elevated temperatures, resulting in sub-saturated values for some measurements.¹⁴

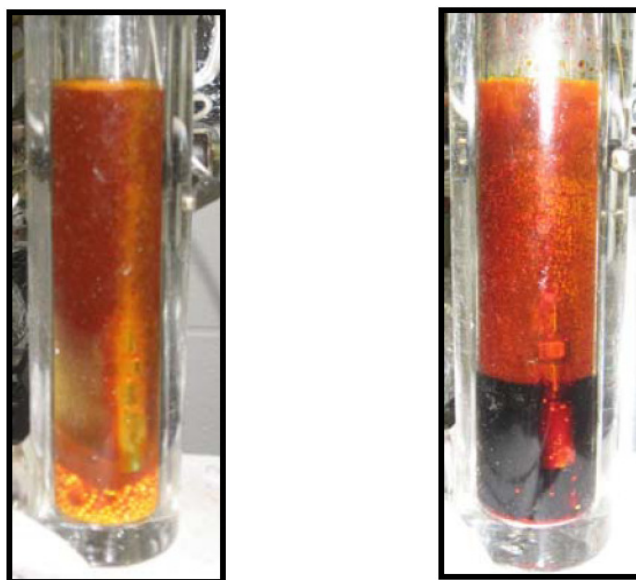


FIGURE 4 – SS1 Sulfur Uptake Testing: ASRL Testing Apparatus¹⁴
Left: SS1 exposed to sulfur in N₂ environment after 16 h – single phase
Right: SS1 exposed to sulfur in H₂S environment after 4 h – two phases

Product Stability and Compatibility Results

Thermal Stability: Individual samples of SS1 were heated at 25 degree increments between 225 – 300 °C; pausing at each temperature for a 30 minute period. The products were allowed to cool, and then analyzed for chemical integrity. In the heated samples, a slight change in color intensity was observed; however, no solids were found, suggesting no decomposition of the product. FT-IR analysis showed no difference between the reference (neat SS1) and heated product (Figure 4), also supporting no chemical decomposition due to heating.

In a final test for chemical integrity at high temperatures, solid sulfur was treated with the heated SS1 solutions. When exposed to amine-based solvents, elemental sulfur converts to amine polysulfides, which are identifiable by their red/orange color.^{7,8} This color change was observed when sulfur was treated with the heated SS1 samples – verifying thermal stability of SS1 up to 300 °C.

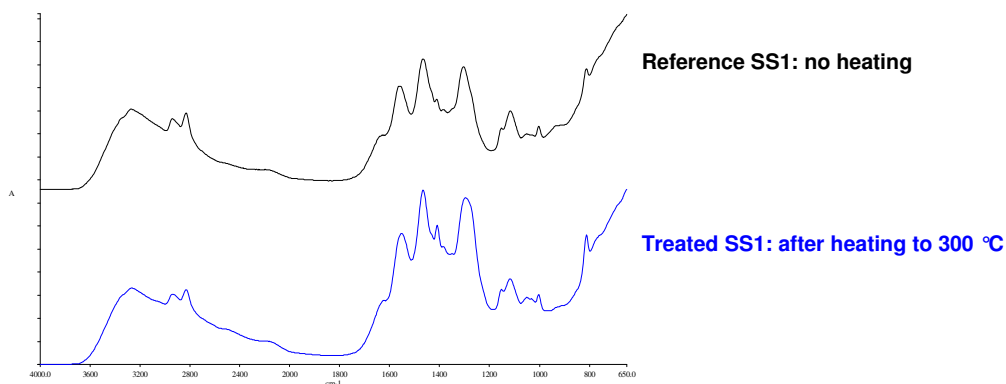


FIGURE 5 – Verification of Thermal Stability Result via FT-IR Analysis

Metals: Results for the week long compatibility testing at 150 °C for SS1 with 316SS and Duplex SS are found in Table 7. In all tests, no solids formation or corrosion of the metal coupons was observed, indicating SS1 is compatible with both 316SS and Duplex SS.

**TABLE 7
SS1 COMPATIBILITY RESULTS WITH 316 SS AND DUPLEX SS**

Metal Sample	Coupon weight loss (g)	Observations
None	N/A	None
316SS	0.003	No solids
Duplex SS	0.000	No solids

Corrosion tests for SS1 with 1018CS were performed in two environments; a mild, inert nitrogen atmosphere, and a more corrosive environment where the metal and chemical were exposed to high chloride brine in an acid gas environment (test specifics found in Table 2). Low corrosion rates were observed for 1018CS when exposed to the neat chemical at high temperature (Table 8), illustrating the non-corrosive nature of the product. In a more aggressive environment, SS1 did not contribute to the corrosion of 1018CS but reduced the rate relative to the uninhibited test cell (Table 9).

**TABLE 8
SS1 COMPATIBILITY RESULTS WITH 1018CS IN INERT ENVIRONMENT**

Test Temp	Gas	Test Duration	Corrosion Rate (mpy)	Pitting (N/Y)	Observations
93 °C	100 psi N ₂	96 h	2.12	N	No solids
			2.17	N	No solids

**TABLE 9
SS1 COMPATIBILITY RESULTS WITH 1018CS IN ACID GAS ENVIRONMENT**

Temp	Gas	Duration	Test Fluids	Corrosion Rate (mpy)	Pitting (N/Y)
80 °C	200 psi H ₂ S 50 psi CO ₂	72 h	Brine: 300 mL	28.46	N
			Brine: 300 mL SS1: dip & drip	8.13	N

Amine Polysulfides: The corrosive nature of polysulfide solutions is a popular topic when discussing amine-based sulfur solvents. Corrosion attack in an ethylamine (EA) solvent recycling systems have been reported.⁶ In these systems, concentrated solutions of EA-polysulfides were thermally decomposed at very high temperatures (140 °C) to recycle and reuse EA as a downhole sulfur solvent. In non-recyclable EA solvent applications, no corrosion issues were reported for disposal well systems responsible for the removal of produced water containing moderate levels of EA-polysulfides.⁶ There are even literature reports that document the use of polysulfides to control the rate of corrosion in certain sour gas wells.¹⁵

The testing completed here investigated the corrosivity of SS1-generated amine polysulfides towards 1018CS in a sour environment. Formation of amine polysulfides was verified by visually inspecting of the test cells as well as measuring pH of the final solutions (aqueous polysulfide solutions have pH ~7)⁸. Comparing pH values of the blanks (*i.e.* Brine only and Brine + S₈) to those for test cells containing SS1 illustrates this point (Tables 10 & 11). Regardless of test temperature, significant decline in general corrosion rates, relative to the blanks were found when SS1 was present. Lower corrosion rates were even observed in the 50 °C cells, where solid sulfur was still present following the test (Table 10). The results presented in Tables 10 & 11 suggest amine polysulfides generated by SS1 in these testing conditions do not pose a great corrosion threat to 1018CS.

TABLE 10
RESULTS FOR AMINE POLYSULFIDE PROPERTIES TESTING at 50 °C

Test Cell	Description	S ₈ (g)	Final pH	Corrosion Rate (mpy)	Pitting (Y/N)	Residual S ₈
1	Brine only	0	4.5	17.02	N	---
2	Brine + S ₈	2	4.5	27.83	Y	Y
3	7.5% SS1	1.5	6.7	2.53	N	Y
4	7.5% SS1	2	6.6	2.67	N	Y
5	7.5% SS1	2.5	6.7	2.23	N	Y

1% = 10,000 ppm

TABLE 11
RESULTS FOR AMINE POLYSULFIDE PROPERTIES TESTING at 80 °C

Test Cell	Description	S ₈ (g)	Final pH	Corrosion Rate (mpy)	Pitting (Y/N)	Residual S ₈
1	Brine only	0	4.7	17.68	N	---
2	Brine + S ₈	2	4.7	31.85	N - etching	Y
3	7.5% SS1	1.5	6.7	2.22	N	N
4	7.5% SS1	2	6.7	1.97	N	N
5	7.5% SS1	2.5	6.7	2.81	N	N

1% = 10,000 ppm

The testing results presented here, along with others presented in literature^{16,17} illustrate the varying corrosion properties of ionic polysulfide solutions. Factors that may dictate the degree of corrosion risk associated with polysulfide species include: type of polysulfide species (*i.e.* HS_x⁻ vs. S_x²⁻), concentration of polysulfide ions in solution, type of cation associated with the polysulfide ion and its role in stabilizing the ionic species.

Case History

Background: Sour gas well in Northern Alberta was experiencing sulfur deposition in production tubing string, pipeline and gas cooler within the molecular sieve regeneration system. Specifics regarding the well and gathering system are found in Table 12.

**TABLE 12
NORTHERN ALBERTA SOUR GAS WELL INFORMATION**

Item	Parameter	Value
Well Specifics	BHP (est.)	20 – 25 MPa
	BHT	125 °C
	Depth	4,224 m
	Tubing ID	76.0 mm
	WHT	15 – 20 °C
	WHP (est.)	4,500 kPa
Production Data	Gas	200 e ³ m ³ /d
	Water	25 m ³ /d
	Chlorides	55,000 ppm
Gas Composition	H ₂ S	12 mol%
	CO ₂	5 mol%

Original Sulfur Mitigation Strategy: Downhole sulfur deposition was addressed by quarterly tubing washes using an aromatic physical solvent (Solvent A). This solvent was applied in high volume (approximately 2 – 3 m³) with flowback fluids being sent to the inlet separator and collected in liquid storage tanks at the plant. Prior to each tubing wash, a gauge ring was run downhole to tag deposits in the tubing string. Following the wash, removal of deposits was verified by running a subsequent gauge ring. Sulfur deposition in the pipelines was controlled on a continuous basis by applying an amine sulfur dispersant/solvent supplied by Baker Hughes (Solvent B). The injection rate for this application was 30 L/d. Sulfur issues at the regeneration gas cooler were also addressed with continuous application of Solvent B. This injection rate was 10 L/d. Along with application of Solvent B, the regen. cooler was regularly flushed with stabilized condensate every 2 – 3 days to remove any lingering deposits.

Alternative Sulfur Mitigation Strategy: A strategy was designed to replace both incumbent sulfur solvents with SS1. In addition, continuous downhole application of SS1 to control sulfur deposition in the production tubing was introduced in place of the tubing wash methodology. Advantages to a continuous downhole sulfur solvent approach included:

- Eliminating production interruptions caused by quarterly well shut-ins
- Reduced costs associated with transportation of large chemical volumes
- Eliminating costs associated with transporting spent-sulfur solvent because SS1-generated amine polysulfides exit system with produced water
- Reduced risk of sulfur-related corrosion and plugging at surface because decrease in temperature does NOT cause recrystallization of sulfur from SS1-generated amine polysulfides

Sulfur uptake results for SS1 in the presence of brine (Table 4) suggested the large volume of salty water produced by the well (25 m³/d of water with 55,000 ppm chlorides) would not negatively affect the performance of SS1. Continuous downhole application of SS1 was started at 18 L/d.

With sulfur deposition being addressed further upstream, the continuous pipeline injection rate was set at 23 L/d. The injection rate upstream of the regeneration gas cooler remained at 10 L/d. Although no decrease in chemical injected was achieved at this location, the frequency of condensate flushes was extended from every 2 – 3 days to once every 7 – 10 days. A summary of the SS1 sulfur mitigation strategy relative to the original program is found in Table 13.

TABLE 13
SULFUR SOLVENT STRATEGY COMPARISON

	Solvent A	Solvent B	SS1
Chemistry	Aromatic Physical Solvent	Amine Dispersant/Solvent	Amine Chemical Solvent
Application	Tubing Washes 2 – 3 m ³ per wash	Pipeline (30 L/d) Regen. Gas Cooler (10 L/d)	Downhole (18 L/d) Pipeline (23 L/d) Regen. Gas Cooler (10 L/d)
Frequency	Quarterly	Daily	Daily
Volume	8 – 12 m ³ annually Plus Solvent B Volume	14.6 m ³ annually Plus Solvent A Volume	18.6 m ³ annually
Infrastructure Requirements	On-site Separation On-Site Storage or Disposal Well	Chemical Pump Chemical Tank	Capillary String Chemical Pump Chemical Tank
Equipment Requirements	Pumper Truck P-Tank if no On-Site Storage	None	None

CONCLUSIONS

1. The chemical dissolution of sulfur using Sulfur Solvent 1 (SS1) generates amine polysulfide species. Under certain conditions, these ionic polysulfides pose low corrosion risk to carbon steel.
2. In H₂S-predominant environments, the amine-based sulfur solvent SS1 has sulfur uptake values in the range of 6 – 10 wt% based on testing completed by Baker Hughes and Alberta Sulfur Research Ltd.
3. The presence of water, brine or methanol as co-solvents aids the sulfur uptake performance of SS1 because the amine polysulfides products are soluble in polar fluids.
4. Decline in temperature does not cause sulfur to recrystallize from amine polysulfide solutions. Ionic polysulfides convert back to solid sulfur when exposed to environments of low pH or high oxygen content.
5. The case history presented here illustrates the versatility of SS1. The product successfully controlled sulfur deposition in the production tubing, pipeline and in surface equipment.

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