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An Effective Solution for Elemental Sulfur Deposition in Natural Gas Systems

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An Effective Solution for Elemental Sulfur Deposition in Natural Gas Systems

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Abstract

Natural gas pipelines commonly transport small amounts of sulfur as hydrogen sulfide (H₂S) and mercaptans (RSH) of various types. The mercaptans are added as a safety precaution due to their distinct odors. Because elemental sulfur has a vapor pressure, it can also be transported in the gas phase. The solubility is quite low and therefore the amount transported is also very low, typically in the parts per billion range. However, it is not uncommon for operators to observe a yellow or grey colored powder wherever pressure and temperature changes occur, such as filter elements, filter housing outlet nozzles, flow meters, control valves, and inlet guide vanes of compression equipment. The phenomenon is known as ESD or Elemental Sulfur Deposition. The theoretical understanding of how gases carry elemental sulfur started in the 1960's and is increasing even today. Correlations and prediction methods are becoming more common. Cleaning solvents and cleaning methods abound, but what is lacking is a means of preventing the deposition.

This paper presents test results for a new process for removing elemental sulfur being developed by Bechtel Hydrocarbon Technology Solutions, Inc. (BHTS).

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1. Introduction

1.1. Elemental Sulfur Deposition (ESD)

Reports from industry indicate the detrimental presence of Elemental Sulfur Deposition (ESD) in locations where changes in temperature and pressure occur, such as pipelines, regulators, flow meters, filter housings, pilot operated pressure safety valves, and downstream process equipment. Countries that have reported serious challenges associated with ESD include: Argentina, Australia, Brazil, Canada, Hong Kong, New Zealand, Norway, Russia, Saudi Arabia, the United Kingdom, and USA.

Solid elemental sulfur has a vapor pressure, even at ambient and sub-ambient temperatures. Under the right conditions sublimation will occur from the vapor phase to the solid phase causing the sulfur to deposit in various areas of the natural gas system. Although sulfur is yellow, these deposits are sometimes grey colored due to the presence of other contaminants.

1.2. Problems associated with deposition

The deposition of elemental sulfur can cause problems similar to fine solids being present in the natural gas by plugging small openings which make control systems inoperable or cause mal-operation. This can result in the following:

- Erratic flow meter readings and the associated control problems
- Plugged controls leading to:
 - Poor process control due to hindered valve operation
 - Regulator failure (pilot or main valve)
 - System overpressure if the valve fails to close
 - Frequent maintenance requirements to prevent a shutdown of operations
- Plugged pilot-operated relief valve ports that can result in equipment overpressure
- Rotating equipment can become unbalanced resulting in excessive vibration and damage.

2. History

Publications in the 1960's discussed problems mostly related to upstream production. Some of the early locations were the Harmattan-Leduc field in Canada (Canadian Oil Co.)¹ and the Okotoks field in Canada (Texas Gulf Sulfur Co.)².

By the 1970's a method of handling the problem had been found, which was to let the sulfur deposit and then wash it with a solvent. Some of the solvents that were used included DADS (diaryl disulfides), DMDS (dimethyl disulfides), CS₂ (carbon disulfide), amines, and/or hydrocarbons (diesel, kerosene, etc.). Some of these chemicals contain sulfur, which can lead to off-spec product during re-start, some can cause cancer through worker exposure, and some require special handling and disposal of the used chemicals, which can be very costly.

In the 1980's, the direction of research began to move from wellhead / production problems into the downstream areas - pipelines and pipeline systems. Some research included documenting operator experiences, developing solubility data, developing solubility predictions and trying to understand the deposition mechanism.

The primary researchers that have been doing work on solubility and prediction are Alberta Sulphur Research Ltd. (ASRL) in Canada³, David Pack in Australia⁴, and DB Robinson (now Schlumberger)⁵ in Canada. The research helped generate an understanding of the phenomenon and motivated work on prediction and modeling methods. To help augment the theoretical research, operators shared experiences such as the Lost Cabin Expansion (Dow Chemical)⁶ and in natural gas pipelines (El Paso Pipeline)⁷.

More than 40 papers have been published on ESD covering the following:

- Operating problems
- Theory of the how and why the problem occurs
- Prediction of the problem
- How to minimize the problem, usually with a focus on heating and washing

There was not much accomplished in preventing the problem, aside from minimizing the ingress of oxygen and working with regulator vendors on improved designs.

3. Theoretical Understanding of Elemental Sulfur in Natural Gas

3.1. Sources of Sulfur

Sources of elemental sulfur in natural gas streams include:

- Elemental sulfur in the hydrocarbon-bearing reservoir
- Sulfate reduction in the reservoir due to production fluid chemistry
- Microbial action in the reservoir or at the surface

- Thermal decomposition of sulfur compounds during compression or other processing steps
- Catalytic decomposition in surface equipment, and
- Catalytic oxidation of H₂S due to oxygen ingress.

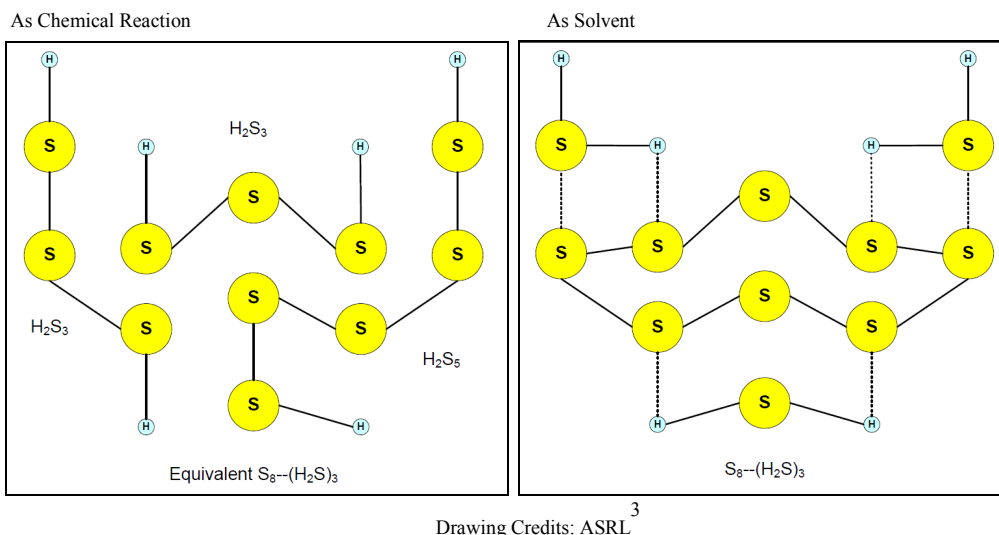
Eliminating the source of the problem is always the best solution from a technical standpoint. It is readily seen that some of these sources are relatively easy to eliminate, such as putting a nitrogen blanket on the tanks of surface chemicals to prevent dissolved oxygen from entering the wellbore or surface piping. That oxygen can then react with any H₂S present to form elemental sulfur. Recall that dissolved oxygen is typically in the single digit ppm range while ESD can occur with sulfur in the ppb range. Thus, eliminating the oxygen eliminates one source of the problem. Similarly, changing production fluids can have an analogous effect.

Most sources are not so easy to eliminate. If elemental sulfur exists in the reservoir it cannot be separated from the production process. Microbes are notoriously difficult to eliminate – mitigation of that problem is normally the best one can hope for. In theory, thermal decomposition can be controlled or mitigated by selection of compression ratios, but it is difficult to accomplish in practice considering economics. Because the catalyst mentioned in two of the items above is iron, it is difficult if not impossible to remove the catalyst from the design of production equipment.

3.2. Carrying of Sulfur by Hydrogen Sulfide (H₂S)

Solid elemental sulfur has a vapor pressure and as such vaporous elemental sulfur can be dissolved in natural gas. This phenomenon will occur with or without H₂S being present, however, H₂S increases the carrying capacity of the natural gas. In fact, pure H₂S can carry three or four orders of magnitude more sulfur than can be carried by methane.⁸

Carrying of vapor phase elemental sulfur by H₂S was first identified as a reaction with H₂S in late 1960's⁹. It was later determined to be by either the H₂S acting as a solvent for the elemental sulfur or as a chemical reaction between the H₂S and the elemental sulfur forming polysulfides (H₂S_x)³.



3.3. Equations of State

A number of methods have been developed to help predict when and where ESD will occur. The first correlations were published around 1968¹⁰ and the first equation of state was published in 1985¹¹. Early equations of state were somewhat crude since they frequently used empirical field data correlations. More advanced, fugacity based equations of state have developed starting in 2005. There are now at least five methods of predicting the saturation points of elemental sulfur in a gas stream:

- ASRL (Correlation)¹¹
- ASRL (Equation of State)¹¹
- David Pack^{8, 12}
- DB Robinson (now Schlumberger)⁴
- LaTep / ENSGTI¹³

4. Practical Understanding of Elemental Sulfur

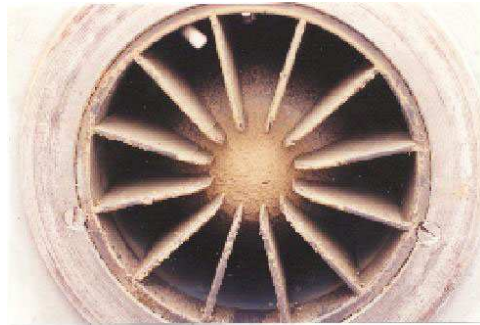
Operators will see a yellow powder (often grey colored due to contaminants) form at the locations when ESD occurs. Frequently the filtration system is blamed, although no filter in the world is capable of removing this problem. There is no expectation that a filter would remove dissolved water vapor or carbon dioxide vapor, and one should not expect it to remove vapor-phase elemental sulfur either. As referred to in Section 1.1, the filter itself represents a pressure drop (plus any associated Joule-Thomson cooling) which can cause more sulfur to come out of the vapor phase. It is true that adding an additional filter in series would remove the elemental sulfur created by the first filter. But due to the saturation phenomenon, the pressure drop caused by the second filter would also cause more sulfur to sublime. Additional filtration is not the answer.

The following photographs illustrate the ESD phenomenon:

- Flow Restrictors



- Compressor inlets



- Filter housing outlets



- Valves (Valve Cage)



Four Photo credits: Dr. David Pack

5. Cleaning of Equipment and Instrumentation

5.1. Current Techniques

Upstream producers tend to deal with ESD by allowing the sulfur to deposit and then cleaning it with regularly-scheduled solvent washings.

Pipeline operators also tend to rely on regular cleaning of the deposits or sometimes try to move the problem downstream by using line heaters to increase the gas temperature and thereby increase the sulfur solubility in the gas. Heating is not always practical due to the high temperatures required and the large volumes of gas being heated for transportation. A disadvantage to the heating-only approach is that it can lead to deposition between the last regulator or line heater and the end user due to heat losses.

The sulfur in the natural gas may then be burned by the end user with the formation of sulfur dioxide (SO₂), typically in low ppm or even ppb levels.

Once the natural gas reaches saturation, any additional pressure drop and/or cooling will result in additional deposition. This can be a very big problem for cryogenic facilities such as LNG plants. Line heating does not help because the stream eventually must reach cryogenic temperatures. The inevitable cooling and fouling create significant performance and economic penalties.

It has been documented that there is a kinetic aspect to the elemental sulfur deposition.¹⁴ In pipelines where there is a long slow decline in pressure and an almost steady temperature, deposition can be delayed to well below saturation levels (i.e., supersaturated). Such deposition can be delayed for up to 3.5 km (2.2 miles) downstream of the saturation point.¹⁵

Solvent cleaning involves a number of operations, which can include:

- Pumping solvent(s) through the system
- Cooling the solvent(s) after washing the affected equipment
- Filtering of the solvent(s) to remove the sulfur deposits
- Heating the solvent(s) before reuse

Vendors have been developing solutions that focus on better cleaning methods or equipment design, such as:

- Better solvent spray nozzles
- Use of longer solvent residence times
- Different solvents or mixtures of solvents

In all cases, however, current approaches to solving the elemental sulfur deposition problem treat the symptom and not the underlying cause.

5.2. Disadvantages of Current Cleaning Techniques

Cleaning-only approaches have a number of challenges that can increase the cost and complexity of dealing with the problem, such as: maintenance of heat exchangers, pumps, compressors, etc.; filter change-outs; and maintenance of instrumentation at pressure let-down stations and pressure safety devices. There are also problems with exposure of workers to hazardous materials and the disposal of hazardous materials. Cleaning usually involves a shutdown of the facility, resulting in lost revenue.

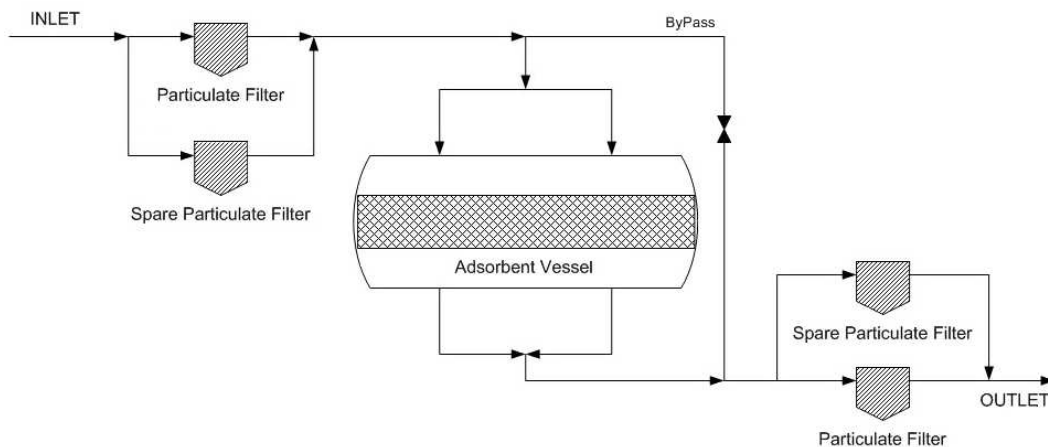
Additionally, the best solvents are sulfur based, leading to off-spec product (especially during restarts) and solvent losses from tank vaporization & filter change-outs.

6. Bechtel Sulfur Adsorbent Technology (BSAT)

The best solution to any problem is to address the root cause and not simply to treat the symptoms. A new patent-pending technology is being developed by Bechtel Hydrocarbon Technology Solutions, Inc. (a technology and front-end design focused subsidiary of Bechtel) that addresses this ESD problem. This technology is called the Bechtel Sulfur Adsorbent Technology (BSAT) and is described in the remainder of the paper. BSAT treats the real problem (the presence of elemental sulfur) instead of treating symptoms (such as plugged equipment).

6.1. Description

BSAT is a very simple system, as described below, and can easily be retrofitted into an existing facility.



The BSAT system should be located downstream of any receiver or slug catcher. The first filter-coalescer is custom designed to mitigate ESD formation in the filter itself. This is followed by the adsorbent bed which captures the elemental sulfur. A second particulate filter prevents any adsorbent from migrating downstream. The advantages of this system are:

- No chemicals are needed for processing other than the solid adsorbent.
- The filter media are the only regular consumables.
- No heating, cooling, or pumping of solvents is required, which results in:
 - low operating expenses,
 - reduced exposure of workers to hazardous environments,
 - minimal operator attention, and
 - increased on-stream time.

When the solid adsorbent has reached the end of its useful life, the adsorbent is replaced with new adsorbent and the spent adsorbent is discarded. Sizing of the adsorbent bed will determine the time between replacements and can be optimized for adsorbent and vessel cost versus the manpower and specialized equipment cost to change the adsorbent.

6.2. Current Status

Over the last several years, BHTS has focused on confirming the effectiveness of the technology by contracting with Alberta Sulphur Research, Ltd. (ASRL) to study elemental sulfur adsorption onto the adsorbent. The results of this laboratory work confirmed the proof of concept over a range of typical pipeline pressures. The laboratory results indicated between 94-100% removal of the inlet sulfur.

If the laboratory removal efficiency is confirmed in the field tests, then there is a very good probability that the natural gas will not become saturated and deposit elemental sulfur in any of the downstream equipment, valving or systems.

The ASRL test reports are available on a confidential basis.

6.3. Commercialization Plan

BHTS is continuing to invest significant effort in proving the effectiveness of the Bechtel Sulfur Adsorbent Technology. A small, portable pilot unit is being designed and fabricated to allow for testing of a client's natural gas at his facility. The pilot testing will provide both visual indication of sulfur removal and quantitative indication of the sulfur removed from the client's natural gas.

The purpose of conducting the field tests and having the adsorbent samples analyzed is to determine the elemental sulfur saturation capacity of the adsorbent, the sulfur breakthrough curve for the adsorbent, and the potential for co-adsorption of other materials. This will allow BHTS to customize equipment sizing parameters based on the field gas in question.

BHTS plans to progress the proof of concept to a commercial reality in 2014. BHTS is looking for owner-operators that have elemental sulfur deposition problems to participate in field pilot testing.

7. Summary

Elemental Sulfur Deposition (ESD) in natural gas pipelines and upstream natural gas processing facilities can occur wherever there is a pressure and temperature change. The yellow or gray elemental sulfur deposits can happen in a variety of locations, such as filter elements, filter housing outlet nozzles, flow meters, control valves, pilot operated pressure safety valves, and inlet guide vanes of compression equipment. Cleaning these devices can be expensive and causes downtime and loss of production.

Bechtel Sulfur Adsorbent Technology effectively treats the real problem (the presence of elemental sulfur) instead of treating symptoms (such as plugged equipment). It is a very simple system and is well-suited to both new and retrofit applications.

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