Elemental Sulfur and Di-thiazine Formation in Natural Gas Pipelines

Developed By:

The NAPSR / PHMSA Distribution Team

Distribution Team Mission Statement

The NAPSR / PHMSA Distribution Team is a collaboration of State and Federal Regulators to support improvements in the integrity of the Nations' gas distribution pipeline systems through the conduct of investigations and research to develop educational materials as well as improving our inspection methods and guidance for evaluation of Operator's Distribution systems

Disclaimer

The document is intended to provide clarity to the public regarding existing pipeline safety standards. The contents of this document do not have the force and effect of law and are not meant to bind the public in any way, but pipeline operators must comply with the underlying safety standards.

The materials contained in this work product are for educational and awareness purposes only.

Elemental Sulfur and Di-Thiazine Formation in Natural Gas Pipelines

- The Issue
- Research Papers
- Recent Occurrences
- Incidents and Failures
- Regulatory Requirements
- Path Forward

The Issue

- In 2019 deposits of what appeared to be sulfur (visually and by smell in some cases) was identified by Regulators as being the cause of equipment failures in natural gas transmission and distribution pipelines
- Regulators began investigating these solids formations to understand the cause and scope of the issue
- Samples of the solids formed in pipelines have not been regularly collected for testing, and chemical composition of deposits and location of deposit is not well documented

Photographs of Recent Deposits

Varying Appearances and Odors of Solid Deposits

- Observed colors of deposits vary from white to yellow to yellow-brown apparently depending on constituents in the gas stream and where the deposits forms (condenses) in pressure reduction equipment
- In some cases, the only odor is a normal pipeline odor or in a distribution system only the smell of odorant.
- H_2S has a rotten egg smell, and the lack of a rotten egg smell should not alleviate the need for analysis of the deposits

Photographs of Sulfur Deposits

The following photographs illustrate the ESD phenomenon:

- Flow Restrictors

- Compressor inlets

- Filter housing outlets

- Valves (Valve Cage)

Four Photo credits: Dr. David Pack

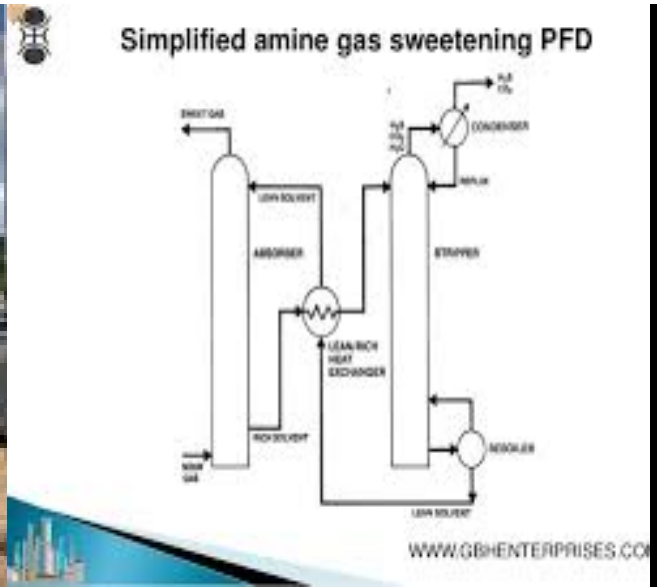
- Image from An Effective Solution for Elemental Sulfur Deposition in Natural Gas Systems, Kimtantas and Taylor, 2014, Bechtel Hydrocarbon Technology Solutions, Inc.

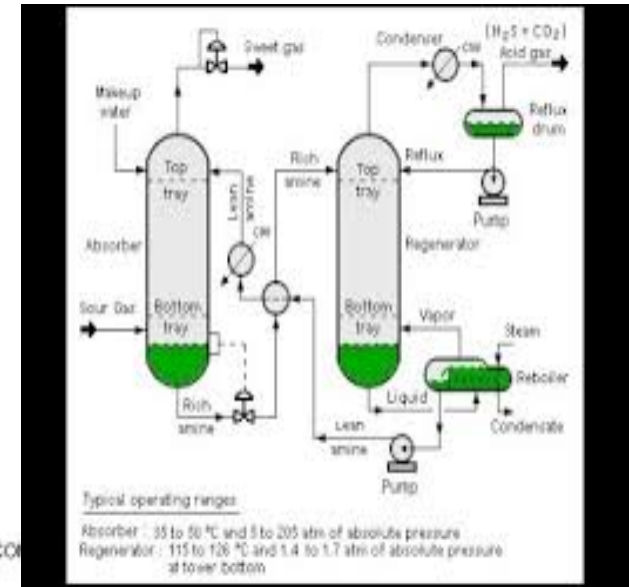
Composition of Solid Deposits

- In the PRCI Project PR-616-17607 report, chemical compositions of deposits from the same gas stream varied depending on the type of pressure reduction equipment used.
- The location of the deposit in the equipment varied depending on the body style (globe versus in-line evaluated in the report) of pressure reduction equipment used.
- Constituents of the deposits analyzed in the report primarily included elemental Sulfur, Di-thiazine, and lubricating oil.
- Observations document that elemental Sulfur and Di-thiazine appear to form as deposits in pressure reduction equipment as gas streams experience a reduction in pressure and vapors turn to solids.

Di-thiazine is a result of H_2S scavengers

- Di-thiazine is a common result of many H_2S scavengers based on cyclic amine called Triazine (water soluble) which react with the H_2S to form the insoluble compound Di-thiazine.
- The Triazine scavengers are prevalent in the natural gas industry to treat gas streams containing Sulfur by either injecting Triazine scavengers directly into the transmission pipelines or by bubbling the gas through amine treater towers.





Di-thiazine Solids Formation

- While the Triazines are effective H_2S Scavengers capable of eliminating the hazards of H_2S and neutralizing the H_2S corrosivity, Di-thiazine and Sulfur vapors that are produced entrain in the gas stream.
- Elemental Sulfur and Di-thiazine solids form from vapors where pressure and flow are reduced and form as solids within pipelines and can cause equipment failure.
- Industry practices for removing Di-thiazine solids include mechanical and chemical cleaning processes or equipment replacement if solids cannot be removed efficiently.
- Internets searches using phrases such as “Di-thiazine solids formation in pipelines” yield useful information on issues and solutions.

Research Papers

- Elemental Sulfur Formation in Natural Gas Transmission Pipelines, David Pack, 2005, Thesis for PhD, University of Western Australia.
- An Effective Solution for Elemental Sulfur Deposition in Natural Gas Systems, Kimtantas and Taylor, 2014, Bechtel Hydrocarbon Technology Solutions, Inc.
- Sulfur Condensation in Pressure Reduction Equipment, David Pack, 2019, PRCI project PR-616-17607.
- Internet searches yield other articles and papers on the subject of solids formation in the pipeline and processing industries.

Recent Events

- Regulators have reached out to stakeholders to gather information on the scope of “issue” and identify any similarities in source of gas and area/region where “issue” may be most common
- Occurrence of “Sulfur” deposits identified as a cause or contributing cause in failures in natural gas pressure reduction equipment in Western, Central, and Southern Regions of USA
- Gas streams/feeds where the “issue” has occurred have been identified as originating from transmission pipelines from US and Canada production and storage fields
- Deposits appear to be from a Sulfur vapor that can “de-sublimate out as solid elemental Sulfur and then combine with other particle matter and trace liquids in the gas stream to form the observed contamination deposits.” (PRCI Project PR-616-17607 report excerpt)
  - Primary constituents include: elemental Sulfur, Di-thiazine, lubricating oils

Recent Incidents and Failures

- PHMSA Form F 7100.2 Incident Report – Gas Transmission And Gathering Systems
  - No. 20170011- 16784, Incident Date: 01/13/2017, Location – Gem County, Idaho
  - No. 20190109 – 32765, Incident Date: 09/04/2019, Location – Spokane, Washington
- Several equipment failures have been observed by Regulators during inspections and investigations across the country
  - Failures may/should require accelerated maintenance schedules or sometimes equipment replacement

Regulatory Requirements: §192.617

- Operators are required to investigate failures, collect samples, identify cause(s), and take action to prevent recurrence.
  - §192.617 Investigation of failures. Each operator shall establish procedures for analyzing accidents and failures, including the selection of samples of the failed facility or equipment for laboratory examination, where appropriate, for the purpose of determining the causes of the failure and minimizing the possibility of a recurrence.
- Operators are required to have procedures for analyzing accidents and failures
  - Failure is defined in ASME/ANSI B31.8S as a general term used to imply that a part in service: has become completely inoperable, is still operable but is incapable of satisfactorily performing its intended function; or has deteriorated seriously, to the point that it has become unreliable or unsafe for continued use.

Investigation of Failures

- Actions when pressure reduction equipment fails to meet its design intent include:
  - Documentation of the findings of the failure investigation per the operator's procedures including:
    - Location of the failure and the origin of the gas stream
    - Type of Equipment involved and portion of the equipment affected
    - Pressure differential (incoming and outgoing pressures, if applicable
    - Determination of the cause of the failure
  - Laboratory analyses of the samples collected (corrosion products, solids, liquids, etc.)
  - Risk mitigation actions identified and implemented to minimize the possibility of a recurrence

Regulatory Requirements - DIMP

Operators must identify potential and existing threats, evaluate and rank the risks, and take risk mitigation actions to address risks

- Since 2011, operators have been required to gather all available information gained from past design, operations, and maintenance to identify threats - *§192.1007(a) Knowledge*
- Regulators clearly see the formations of solid deposits in pressure reducing equipment as a significant threat- *§192.1007(b) Identify threats*.
- To address risks, operators must determine and implement measures (actions) designed to reduce the risks from failure of its gas distribution pipeline - *§192.1007(d) Identify and implement measures to address risks.*

Management Systems Require Communication and Documentation

- Operators are not identifying threats within DIMP resulting in information on the threat not being forwarded to the DIMP group for evaluation and integration.
- Lack of communication of information and data within an operator's organization and lack of documentation requirements have been identified as issues.
- Many times the records do not have a location documented to identify where a failure or threat has occurred.
- An example is regulator station inspections - If a regulator station fails lock-up when first inspected, the DIMP group may not be capturing this as a failure (threat) or is not looking for this.
  - If the regulator failed lock-up, what was the cause? Was the cause Sulfur and/or Di-thiazine deposits, corrosion, etc.?

Perspective

- The issue of solids formations in gas pipelines, upstream processing equipment, and downstream user facilities is well documented and appears to have been occurring for decades.
- There are solutions offered by industry to remove or mitigate the issue of solids formation in pipeline pressure reduction equipment – Sulfur absorbent technology, filters, heating of the gas stream, accelerated maintenance, chemical cleaning, mechanical cleaning, etc.
- Incident reports submitted to PHMSA provide limited data and information on the significance of the threat that Sulfur and/or Di-thiazine deposits pose to pipeline safety.

Findings and Conclusions

- Deposits chemically analyzed in the PRCI project PR-616-17607 report identified that deposits are primarily elemental Sulfur, primarily Di-thiazine, or a combination of both. Lubricating oil was also identified in the deposits.
- These solid deposits in gas distribution pressure reduction equipment are the cause of pipeline incidents and failures
- The deposits of Di-thiazine have also been noted in transmission pipelines along with “black powder” (literature search).
- Regulators expect all gas pipeline operators to investigate failures and take actions to prevent recurrence of identified cause(s).
- Regulators expect gas distribution operators to include potential and existing threats in the DIMP and implement appropriate risk mitigation actions.
- Deposits seem to form irrespective of the origin of the gas stream as long as the gas was processed to remove Sulfur (preliminary finding).

Path Forward

- While the issue of solids formations in gas pipelines, upstream processing equipment, and downstream user facilities is well documented, the recent upward trend in incidents needs to be evaluated and the threat understood
- Regulators will continue to gather information from inspections and investigations into failures and take compliance actions, as appropriate
- Regulators will continue to review DIMP programs for the identification of potential and existing threats, including the reliability of pressure control equipment and formation of solids within the equipment
- PHMSA will review research and development options and continue to learn more about the threat of solids deposition in pressure reducing equipment