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ASRL CORE RESEARCH PROGRAM
2024 - 2025

Prepared by R. A. Marriott
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LIST OF CORE RESEARCH PROJECTS

1. Correlating thermal oxidizer operating conditions with SO_3 formation
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4. What happens to SO_3 when it crosses a Claus catalyst?
5. High temperature sulfidation of carbon steel and select alloys
6. Degassing kinetics as a function of surface area
7. Ammonium salt vapour pressure under Claus conditions
8. Persistence of SO_3^{2-} and its effect on amine unit operation
9. Kinetic modelling of CS_2 destruction in the Claus furnace
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11. Water entrainment in liquid sulfur
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14. Trace sulfur sampling from hydrocarbon streams
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CRP 1. Correlating thermal oxidizer operating conditions with SO_3 formation

Commercial Objective

Describing conditions which lead to excess SO_3 formation in the thermal oxidizer

Environmental Benefit(s)

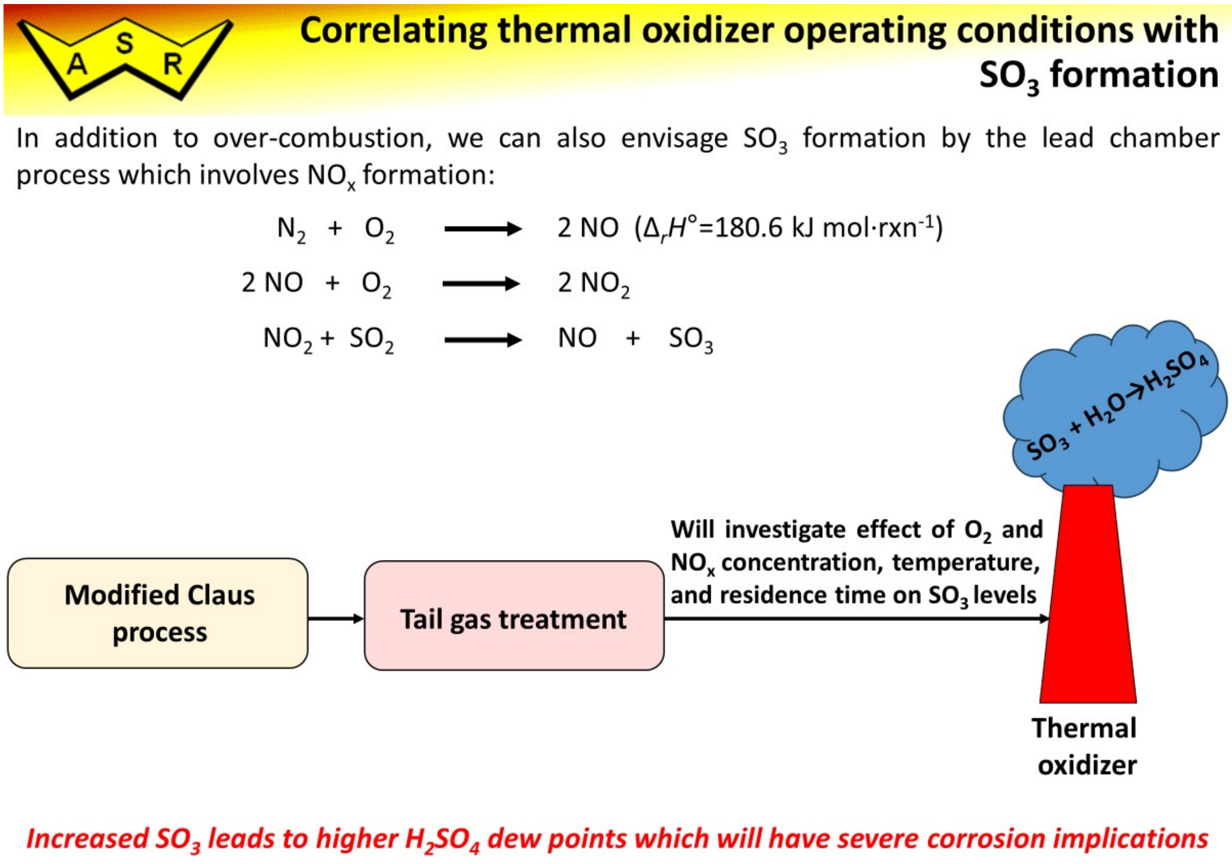
Avoiding harmful environmental release of SO_3 and potential damage to heat recovery systems

Project Description

Increased SO_3 levels in the thermal oxidizer can lead to sulfuric acid condensation during heat recovery or in the plume. Since 1746 (Roebuck) is has been well known that excess O_2 at very hot temperatures can lead to NO_x which can catalyse the formation of SO_3 from SO_2 through the lead chamber process. In this study we will investigate flame temperature, excess O_2 (2 to 10%), NO_x concentrations and SO_3 formation. The experimental work will look at post flame temperatures from 350 to 800°C with fixed NO_x levels and various residence times. With the help of CFD colleagues to calculate possible NO concentrations, we hope to provide a clearer picture of how much excess oxygen is tolerable in these systems with specific SO_2 concentrations.

Specific Objectives

a) Provide a review of NO and NO_2 formation kinetics
b) Measure SO_3 formation in the presence of predetermined NO_x concentrations at 500 to 800°C and residence times of 0.5 to 2.0 seconds
c) Combine experimental and literature data to describe how excess oxygen and SO_2 can lead to SO_3 formation through the lead chamber process in a thermal oxidiser



Correlating thermal oxidizer operating conditions with SO_3 formation

In addition to over-combustion, we can also envisage SO_3 formation by the lead chamber process which involves NO_x formation:

$$N_2 + O_2 \longrightarrow 2\,NO \quad (\Delta_r H^\circ = 180.6\ \text{kJ mol}\cdot\text{rxn}^{-1})$$

$$2\,NO + O_2 \longrightarrow 2\,NO_2$$

$$NO_2 + SO_2 \longrightarrow NO + SO_3$$

Will investigate effect of O_2 and NO_x concentration, temperature, and residence time on SO_3 levels

Increased SO_3 leads to higher H_2SO_4 dew points which will have severe corrosion implications

CRP 2. COS removal with alkanolamines

Commercial Objective

Measuring parameters to assist in optimising simulation of COS removal during treatment will contribute to designing for total sulfur removal from sour natural gas

Environmental Benefit

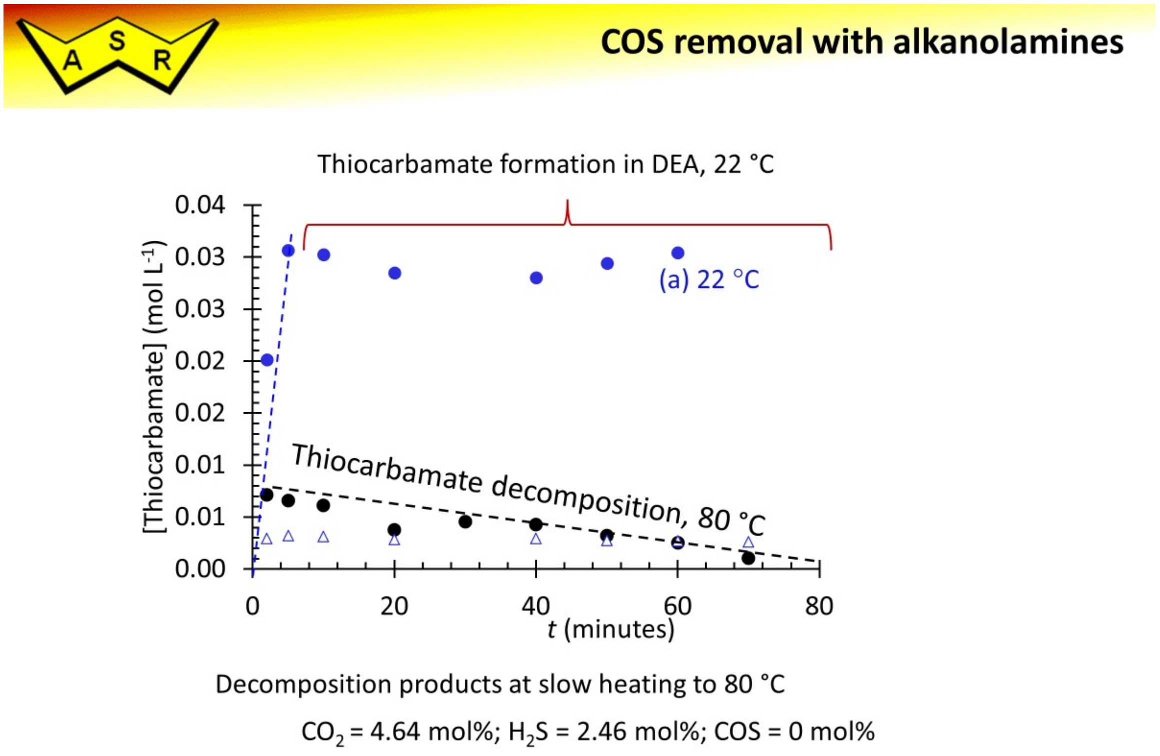
Improving on existing sulfur removal technologies and contributions towards greener processes by educing SO_2 emissions

Project Description

Several investigators have explored the bulk uptake kinetics for COS removal with alkanolamines, but speciation data for COS in alkanolamines are less certain in the liquid. Speciation data for the reaction of carbonyl sulfide (COS) with alkanolamine is important in order to model and design for optimised treating. For example, with MEA, we have found that both hydrolysis and thiocarbamate formation are involved in the uptake kinetics. This research has shown that thiocarbamate is stable up to 60 °C. This research is designed to look at evolving species in various amine solutions through NMR, GC and ESI-MS. An analytical method has been established for measuring speciation during COS absorption and thiocarbamate formation rates and decomposition rates have been measured for diisopropanolamine (DIPA), monoethanolamine (MEA) and diethanolamine (DEA).

Future Objectives

a) Explore regeneration species during stripping at high heating rate
b) Explore flash drum behavior
c) Use automated ESI-MS to follow hydrosulfide formation during simultaneous COS hydrolysis



COS removal with alkanolamines

Decomposition products at slow heating to 80 °C

CO_2 = 4.64 mol%; H_2S = 2.46 mol%; COS = 0 mol%

CRP 3. Towards a better understanding of sulfiding procedures for CoMo tail gas catalysts

Commercial Objective

To help support industry's understanding of what process conditions lead to optimal tail gas catalyst performance and what factors may or may not be detrimental to tail gas catalyst health

Environmental Benefit(s)

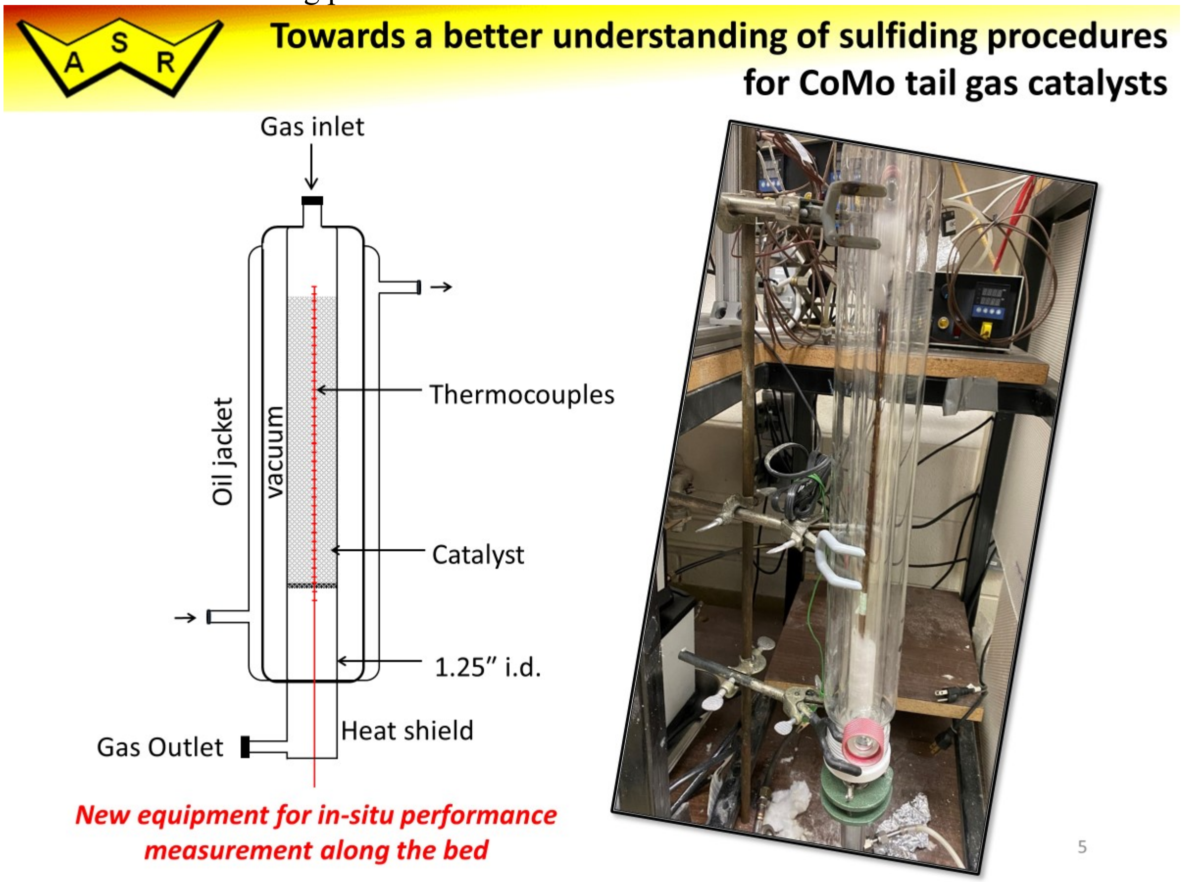
Increased sulfur recoveries / less release of SO_2 to the atmosphere through ensuring optimal performance of tail gas treatment units

Project Description

Usef of our isothermal catalyst system led to some key findings in this research program regarding H_2S concentration during sulfiding, effect of H_2 exposure, effect of O_2 ingress, and the relative effects of the support material (Al_2O_3 versus TiO_2). At lower temperatures, the TiO_2-supported catalysts offered higher activity than the Al_2O_3-supported counterpart. In addition to differences in pore structure and activity levels for COS hydrolysis, this was attributed to a more efficient CoMo sulfiding and reduction procedure promoted by the TiO_2 support. Future directions for this project will further scrutinize various sulfiding conditions *(i.e.*, GHSV, temperature, H_2S concentration, and order of gas introduction) in our newly furnished lab-scale pseudo-adiabatic reactor. The pseudo-adiabatic reactor allows us to accurately track reaction exotherms across the catalyst bed which will offer valuable insight during sulfiding and performance tests. This project is partially funded through NSERC.

Specific Objectives

a) While monitoring catalyst bed exotherms, perform catalyst sulfiding with different H_2S concentrations, GHSVs, and finishing temperatures
b) While monitoring catalyst bed exotherms, check catalyst performance in a standardized test after each sulfiding procedure from above



Towards a better understanding of sulfiding procedures for CoMo tail gas catalysts

New equipment for in-situ performance measurement along the bed

CRP 4. What happens to SO_3 when it crosses a Claus catalyst?

Commercial Objective

To study the fate of SO_3 across a Claus catalyst bed under representative conditions

Environmental Benefit(s)

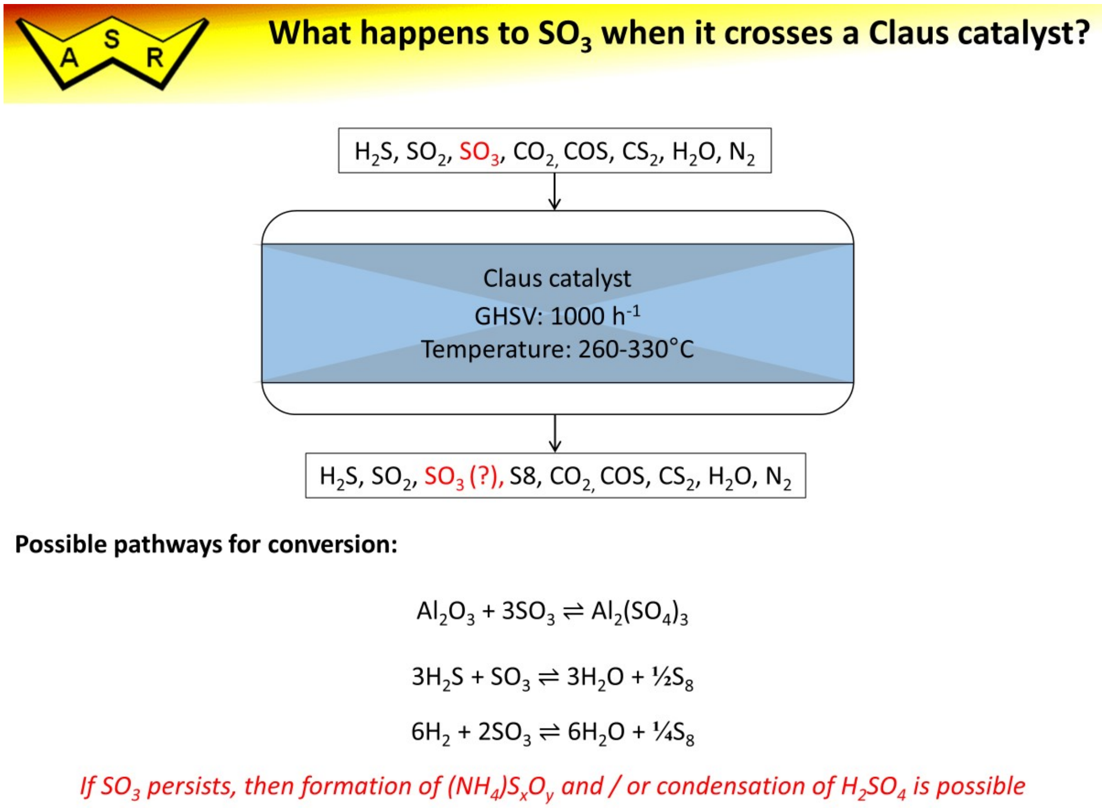
Savings in energy and material by less frequent plant failure / shut down due to corrosion and / or ammonium salt deposition (plant or refinery sustainability)

Project Description

Improperly operated acid gas fired reheaters can lead to the formation of SO_3 which, if able to persist, can lead to undesirable consequences. In the presence of NH_3, it has been shown the persistence of SO_3 leads to facile formation of ammonium salts. Additionally, in the presence of H_2O vapour, persistence of SO_3 can result in condensation of corrosive H_2SO_4. Both issues arise in colder areas; thus, while SO_3 might be generated at a reheater, the issues are located after the catalyst bed. Laboratory data on the fate of SO_3 across a Claus catalyst bed under representative conditions, or otherwise, is scarce. In this context, ASRL will perform a systematic laboratory to investigate the fate of SO_3 across Claus catalysts under first, second, and third converter conditions. The impact of temperature, H_2S concentration, space velocity, and Claus alumina versus titania will be considered. The controlled condensation method will be utilized to trap any residual SO_3 in the reactor effluents as H_2SO_4 which will be analyzed for using anion chromatography.

Specific Objectives

a) Investigate fate of SO_3 across Claus Al_2O_3 and TiO_2 under third converter conditions
b) Pending results of above, investigate fate of SO_3 across Claus Al_2O_3 and TiO_2 under first, and second converter conditions



What happens to SO_3 when it crosses a Claus catalyst?

$H_2S, SO_2, SO_3, CO_2, COS, CS_2, H_2O, N_2$

Claus catalyst
GHSV: 1000 h^{-1}
Temperature: 260-330°C

H_2S, SO_2, SO_3 (?), S8, $CO_2, COS, CS_2, H_2O, N_2$

Possible pathways for conversion:

$$Al_2O_3 + 3SO_3 \rightleftharpoons Al_2(SO_4)_3$$

$$3H_2S + SO_3 \rightleftharpoons 3H_2O + \tfrac{1}{2}S_8$$

$$6H_2 + 2SO_3 \rightleftharpoons 6H_2O + \tfrac{1}{4}S_8$$

If SO_3 persists, then formation of $(NH_4)S_xO_y$ and / or condensation of H_2SO_4 is possible

CRP 5. High temperature sulfidation of carbon steel and select alloys

Commercial Objective

To better understand high temperature sulfidation corrosion rates observed in the field under Claus waste heat boiler and molecular sieve regeneration conditions (heat exchanger)

Environmental Benefit(s)

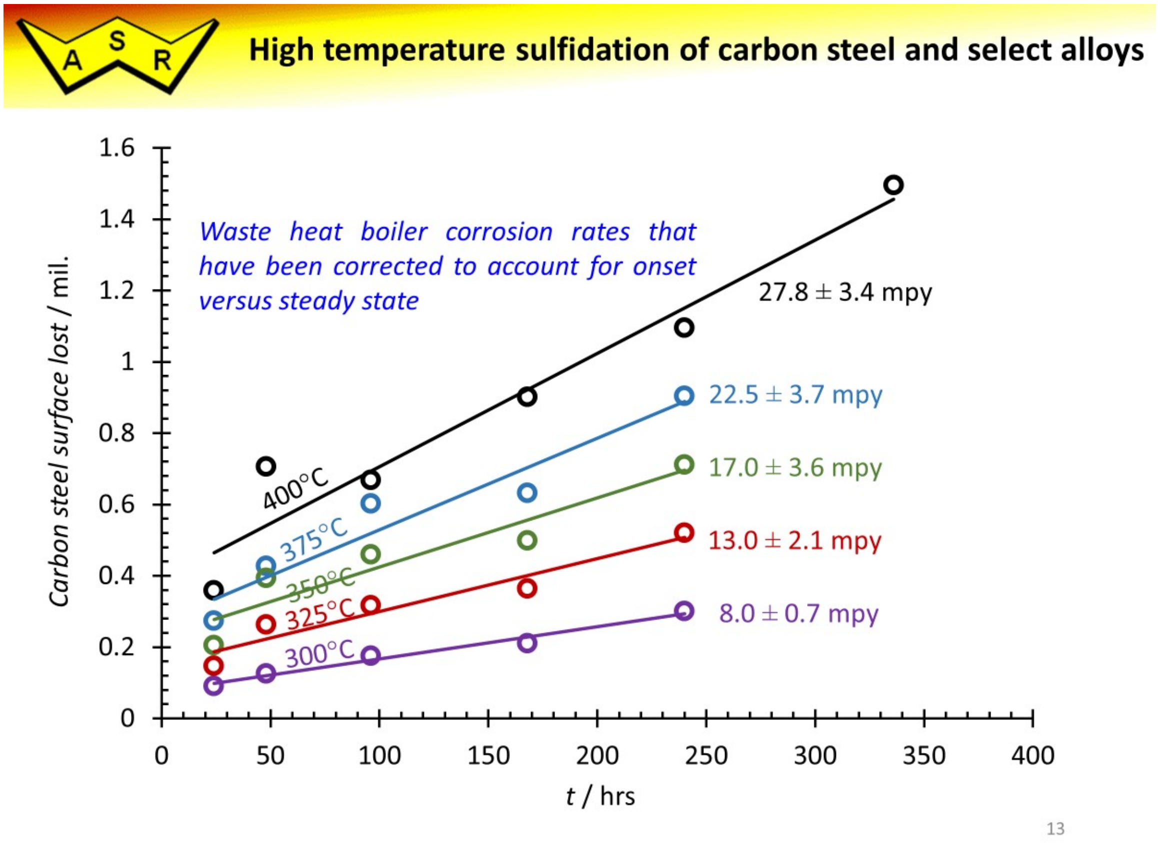
Energy and material savings through increased service lifetime of plant components

Project Description

An important aspect that has come to light during this research program is the correction of our measured laboratory rates to account for “onset” versus “steady-state” corrosion rates. This requires multiple experiments with varying exposure times. However, even when applying this correction factor, our results indicate higher corrosion rates compared to some existing correlations and what field observation would suggest is realistic; particularly at higher temperatures and sulfur concentrations. There are ongoing experiments to help decipher why this may be the case. Our initial experiments point towards a water partial pressure dependence and less dependence on H_2. In parallel with probing how each component in the Claus environment impacts the overall corrosion rate, we have begun testing some select higher alloys (310 stainless steel and HR-160). These materials have required much higher temperatures, compared to carbon steel, to observe appreciable corrosion rates.

Specific Objectives

a) Continue to probe influence of individual Claus components, particularly water and CO_2
b) Examine if silica leaching from thermal reactor ceramics and deposition within waste heat boiler components may have a protective effect with respect to high temperature sulfidation
c) Longer term objective here is to combine corrosion rates found in an extensive literature survey with our laboratory findings to develop a comprehensive model



High temperature sulfidation of carbon steel and select alloys

CRP 6. Degassing kinetics as a function of surface area

Commercial Objective

To refine kinetic rates for degassing and off-gassing for liquid sulfur

Environmental Benefit

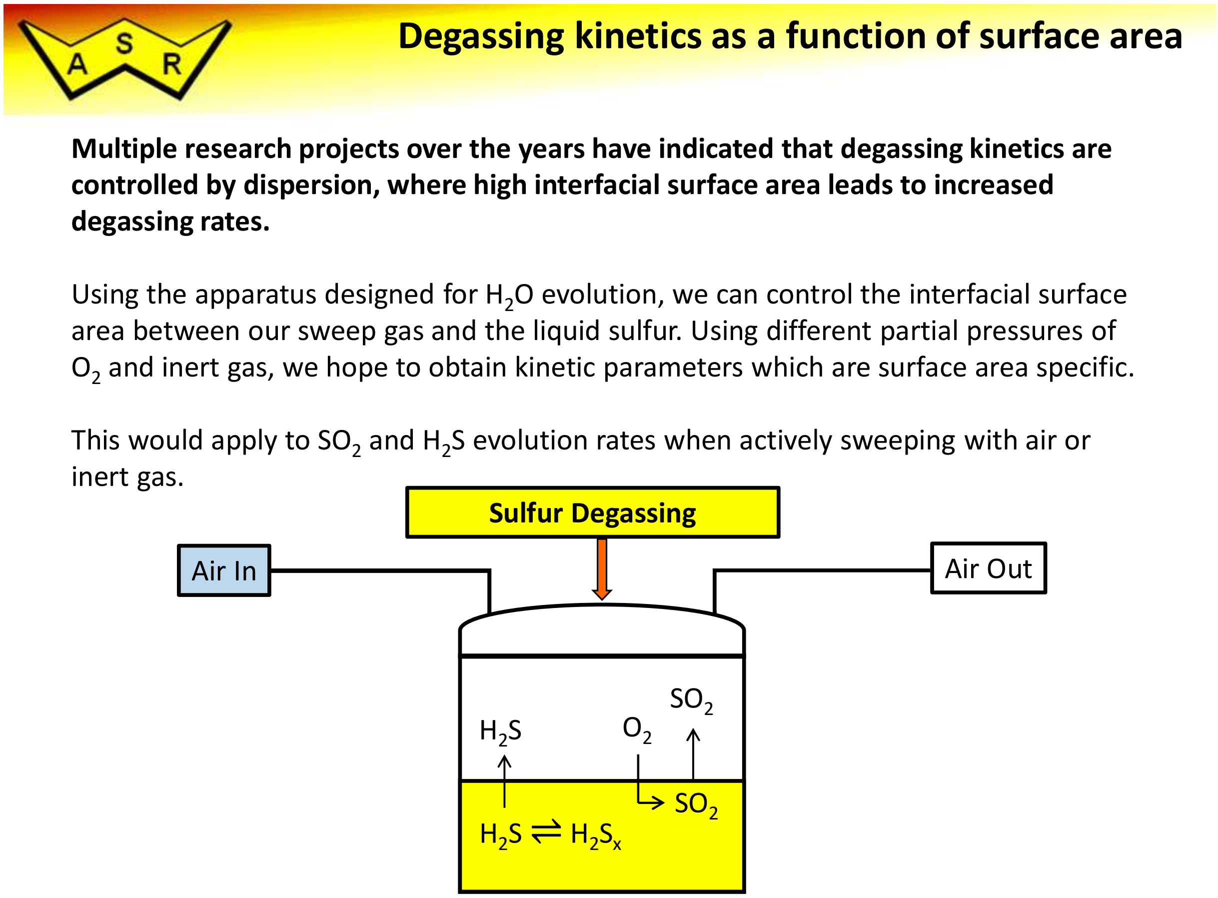
Lowering the risk of emissions and exposure to toxic gases during storage and transport of liquid sulfur

Project Description

ASRL has previously conducted several degassing experiments with batch reactors and investigated emissions from static non-swept sulfur. Throughout our learnings over the years, we are more convinced that dispersion (increase on interfacial surface area) is the primary design criteria for degassing schemes without liquid catalysts. The hypothesis is that degassing and oxidation reactions occur at the interface and not in the liquid phase. This suggests that there are emission rates and reaction rates which can be characterized at the surface. In this research we intend to follow dissolved H_2S in liquid sulfur, with a controlled interface between the liquid and gas. Here we hope to determine rates for oxidation and physical dissolution as they change with interfacial area and gas composition. Resulting rate equations can be used to estimate degassing rates at variable pressure, dispersion and gas composition. This can be used to improve and/or understand degassing technologies.

Specific Objectives

a) Through infra red adsorption, follow H_2S composition with a slow sweep of gas containing controlled quantities of H_2S, SO_2, O_2 and N_2.
b) Verify that correlations are scalable to interface, i.e., test the hypothesis that the reactions don't occur in the liquid phase.



Degassing kinetics as a function of surface area

Multiple research projects over the years have indicated that degassing kinetics are controlled by dispersion, where high interfacial surface area leads to increased degassing rates.

Using the apparatus designed for H_2O evolution, we can control the interfacial surface area between our sweep gas and the liquid sulfur. Using different partial pressures of O_2 and inert gas, we hope to obtain kinetic parameters which are surface area specific.

This would apply to SO_2 and H_2S evolution rates when actively sweeping with air or inert gas.

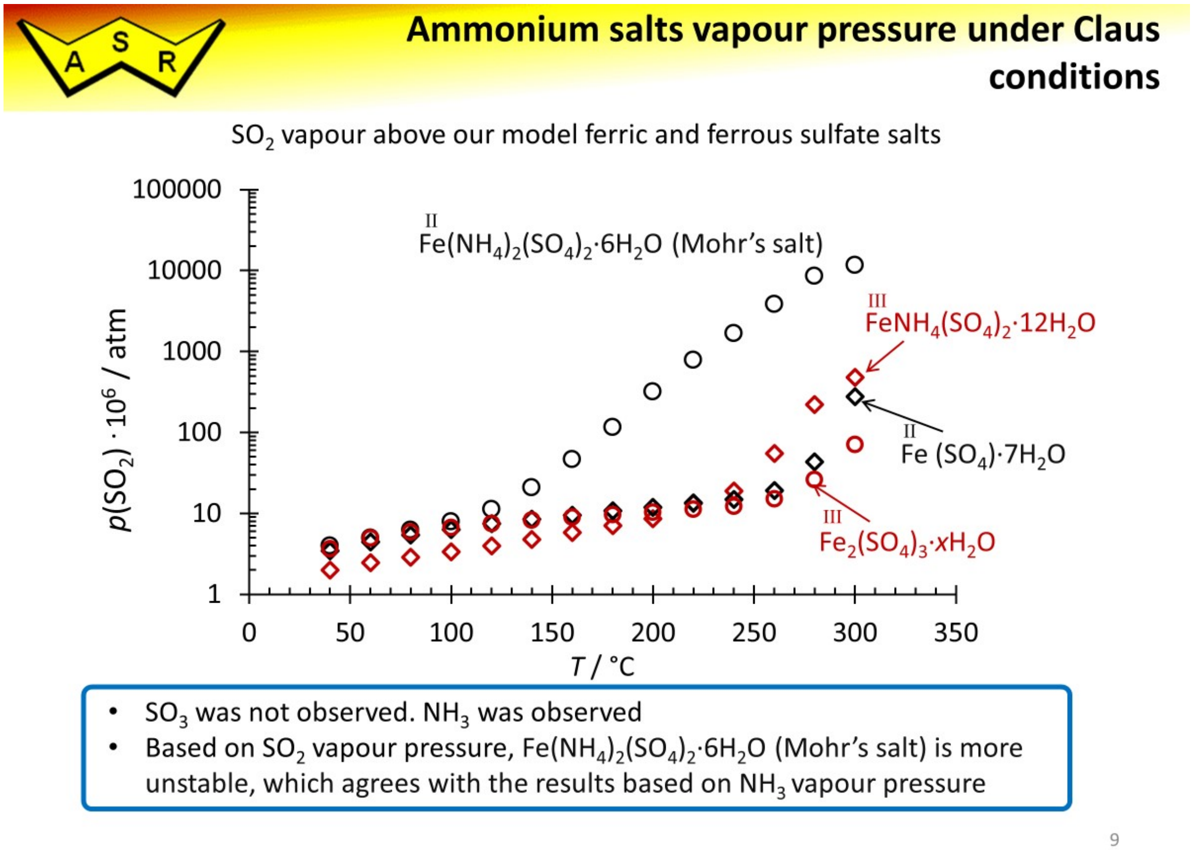
CRP 7. Ammonium salt vapour pressure under Claus conditions

Commercial Objective
To measure the vapour pressure of iron containing ammonium salt that may deposit in the Claus plant

Environmental Benefit
Lowering the risk of emissions through flaring or other mechanical failure due to unexpected salt deposition

Project Description
Predicting the potential deposition of solids in the Claus unit requires the use of accurate vapour pressure data. The measurement of vapour pressure for materials of low volatility requires the development of highly sensitive techniques. The previous research measured the vapour pressure expressions for the three ammonium salts $(NH_4)_2S_2O_3$, $(NH_4)_2SO_3$, and $(NH_4)_2SO_4$ using MS to follow the equilibrium vapour species [ASRL QB, Vol. LVIII(1), 2021]. The results demonstrated that ammonium sulfate could form with virtually any amount of SO_3 and NH_3. Without SO_3, ammonium thiosulfate can form SO_2 and H_2O in the Claus system with T = 80 to 90°C. These temperatures are colder than anticipated/design, but not unprecedented. Finally, the vapour pressure of iron sulfate or Mohr's salt ($Fe(SO_4)(NH_4)_2(SO_4)\cdot 6H_2O$) was also proposed as a potential deposit. The experimental set up used in the previous work was upgraded to allow for measurement at vapour higher temperatures $T > 150$ °C.

Specific Objectives
Following a similar procedure from the 2021 publication, attempt to measure the vapour pressure for Fe_2SO_4, FeS_2O_3, $(NH_4)_2Fe(SO_4)_2\cdot 6(H_2O)$ [Mohr's salt] between 150 to 250°C



Ammonium salts vapour pressure under Claus conditions

SO_2 vapour above our model ferric and ferrous sulfate salts

- SO_3 was not observed. NH_3 was observed
- Based on SO_2 vapour pressure, $Fe(NH_4)_2(SO_4)_2\cdot 6H_2O$ (Mohr's salt) is more unstable, which agrees with the results based on NH_3 vapour pressure

CRP 8. Persistence of SO_3^{2-} and its effect on amine unit operation

Commercial Objective

To investigate SO_3^{2-} persistence in amine units

Environmental Benefit

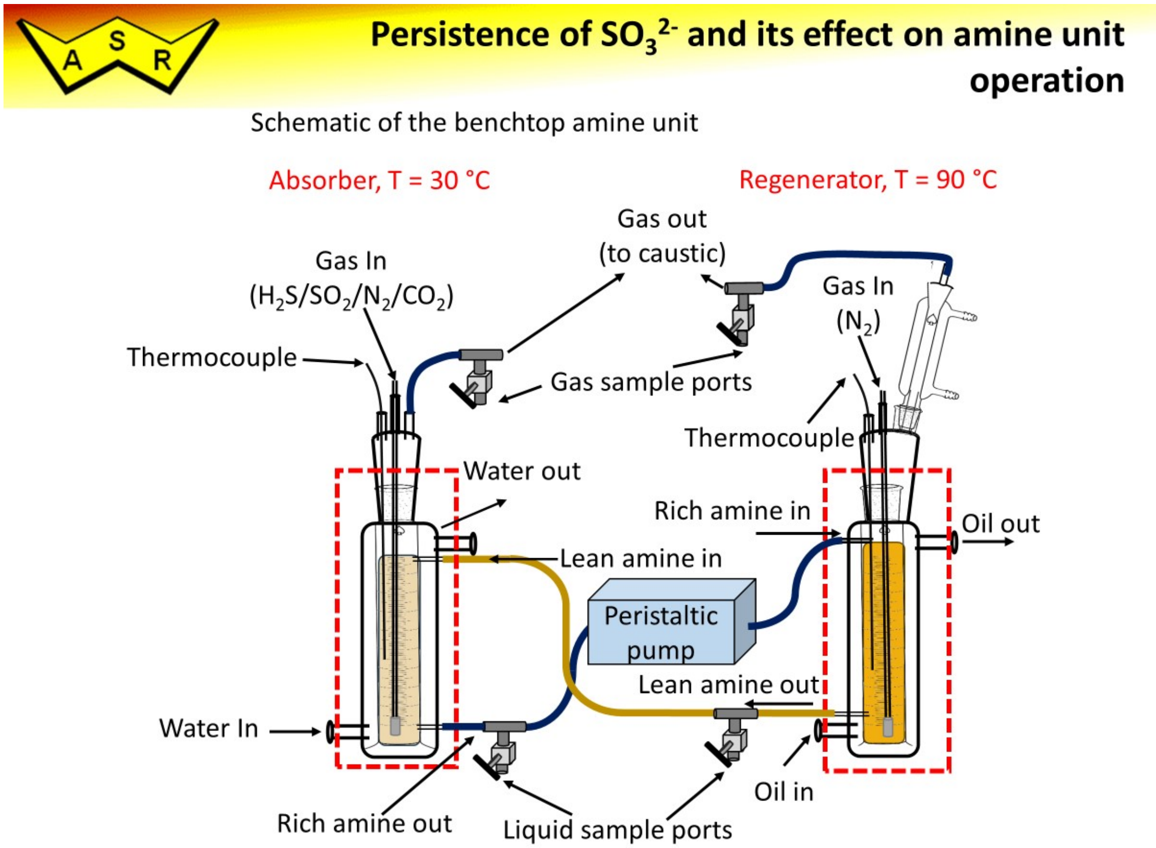
Mitigation of emission risk and corrosion reduction through the potential for amine recovery before excessive formation of heat stable salts. Reduce selective amine waste.

Project Description

While our previous measurements have shown very rapid formation of elemental sulfur with the ingress of SO_2 into an alkanolamine system, there has been the suggestion that SO_3^{2-} formed from SO_2 persists long enough to be purged from a TGU amine system (before thiosulfate formation). In this context, we intend on reviewing the pH-dependent products and investigate the kinetics of SO_3^{2-} reacting in (i) a buffered solution, (ii) some lean MDEA solutions, (iii) amine solutions containing H_2S and (iv) amine solutions containing CO_2. How long does SO_3 persist or does it disproportionate to other species before we can regenerate the system? In order to study these kinetics is a more reasonable time, we have constructed a small laboratory scale rig for selective amine treatment.

Specific Objectives

a) Review volt-equivalent diagrams for SO_3^{2-} disproportionation as a function of pH
b) Develop a method for following the decay of SO_3^{2-}
c) Provide updated kinetic data for aqueous SO_3^{2-} persistence



Persistence of SO_3^{2-} and its effect on amine unit operation

Schematic of the benchtop amine unit

CRP 9. Kinetic modelling of CS_2 destruction in the Claus furnace

Commercial Objective

To obtain experimental data that can be used to build a simplified kinetic model for CS_2 destruction in the Claus thermal reactor

Environmental Benefit(s)

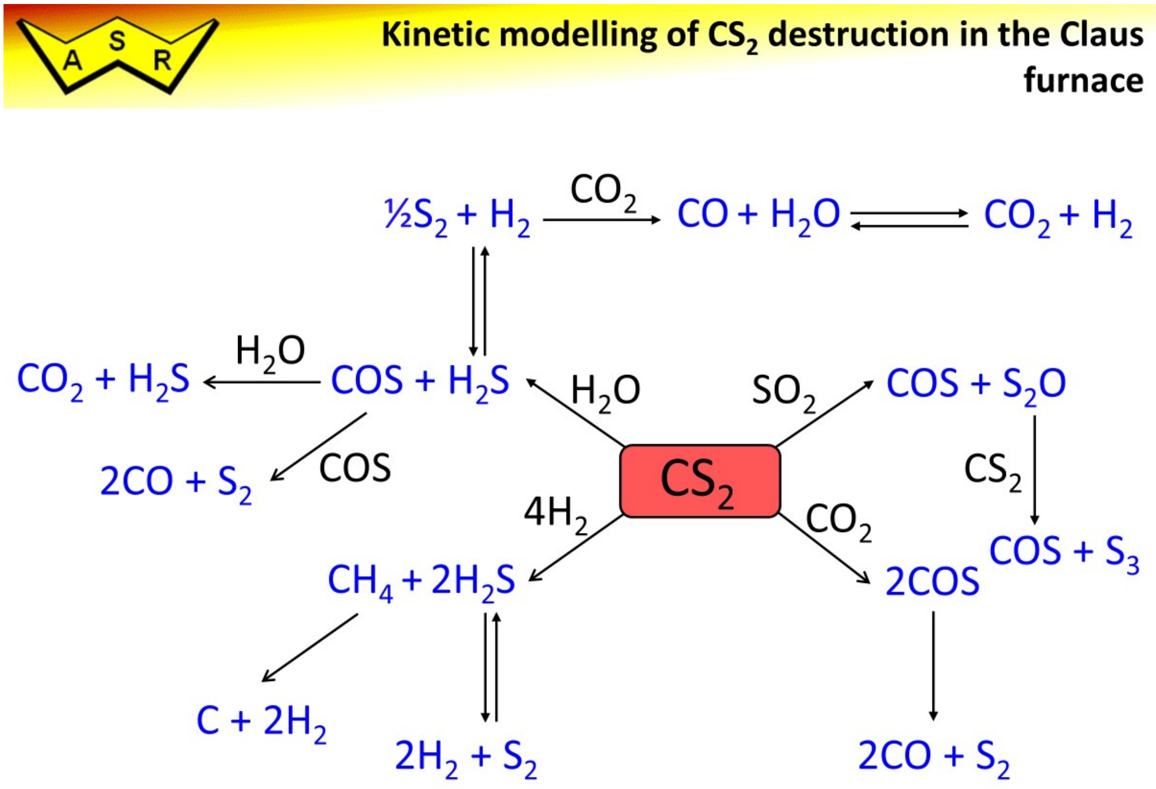
Reduction in SO_2 and CO_2 emissions from higher and more efficient sulfur recoveries

Project Description

To build a comprehensive rate-based model for the Claus thermal reactor, kinetic expressions for formation and conversion of all species are required. Previously, we have analyzed laboratory data for CS_2 conversion under several sets of conditions and deduced rate expressions for these data; however, these experiments used simple binary reactant mixtures ($CS_2 + H_2O$ or $CS_2 + SO_2$) and short residence times. Longer residence time data, especially at temperatures exceeding 1000°C, suggest a more complex mechanism for CS_2 destruction. In these cases, the rate expressions obtained from the simple reaction mixtures will not describe the system accurately. Thus, the overall objective of this research project is to collect kinetic data for CS_2 destruction using full Claus feed acid gas mixtures at typical operating temperatures. Finite analysis, CFD and/or zone residence time may all be used to understand an acceptable mechanism.

Specific Objectives

a) While using full Claus acid gas feeds (low and high CO_2), determine the kinetics of CS_2 destruction at 900, 1000, 1100 and 1200°C



Kinetic modelling of CS_2 destruction in the Claus furnace

CRP 10. More on BTX destruction across a TiO_2 catalyst

Commercial Objective

To further elucidate the mechanism of BTX destruction over Claus catalysts

Environmental Benefit(s)

Reduction in SO_2 and CO_2 emissions from higher and more efficient sulfur recoveries

Project Description

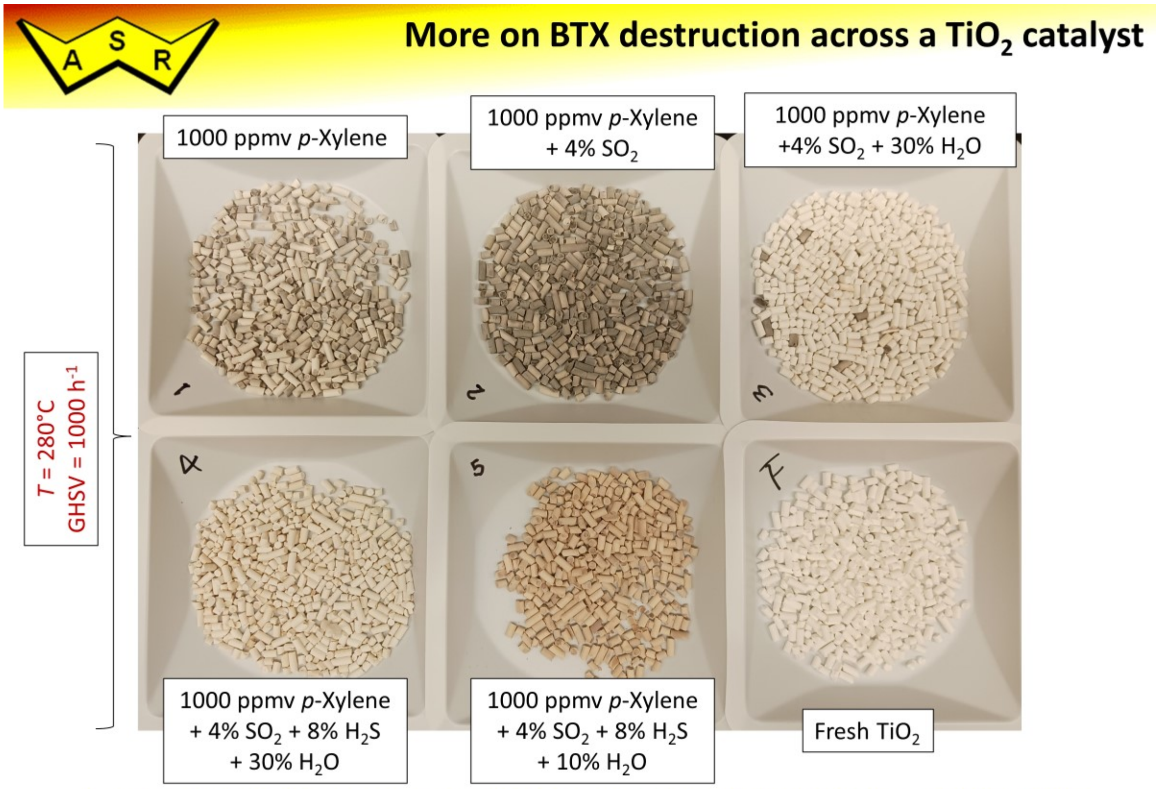
Previous research at ASRL proposed a plausible mechanism for BTX destruction over Claus catalysts involving reaction with catalyst Brønsted acid sites and BTX to ultimately form coke and carsul-like species. Recent laboratory experiments have shown reaction with adsorbed SO_2 as another viable pathway for BTX destruction. As this research unfolds, it seems that while both Brønsted and Lewis acid sites are likely involved in BTX destruction, it is really the H_2O concentration under Claus conditions that governs the extent of catalyst fouling. This work aims to gain a more complete understanding of the mechanism for BTX destruction under Claus conditions and to potentially help better guide operating conditions when BTX is present.

Specific Objectives

a) Introduce reactants to the feed in a stepwise manner to isolate all possible pathways for BTX destruction in a Claus environment with an emphasis on reaction with SO_2

b) Performing experiments at bed inlet and outlet temperatures to ensure trends and findings are consistent across different temperatures

More on BTX destruction across a TiO_2 catalyst



Increased acidity leads to increased BTX decomposition but under Claus conditions it is water concentration that seems to dictate level of coke and / or carsul formation

CRP 11. Water entrainment in liquid sulfur

Commercial Objective

To further understand the evolution of water entrained in condensed liquid sulfur

Environmental Benefit(s)

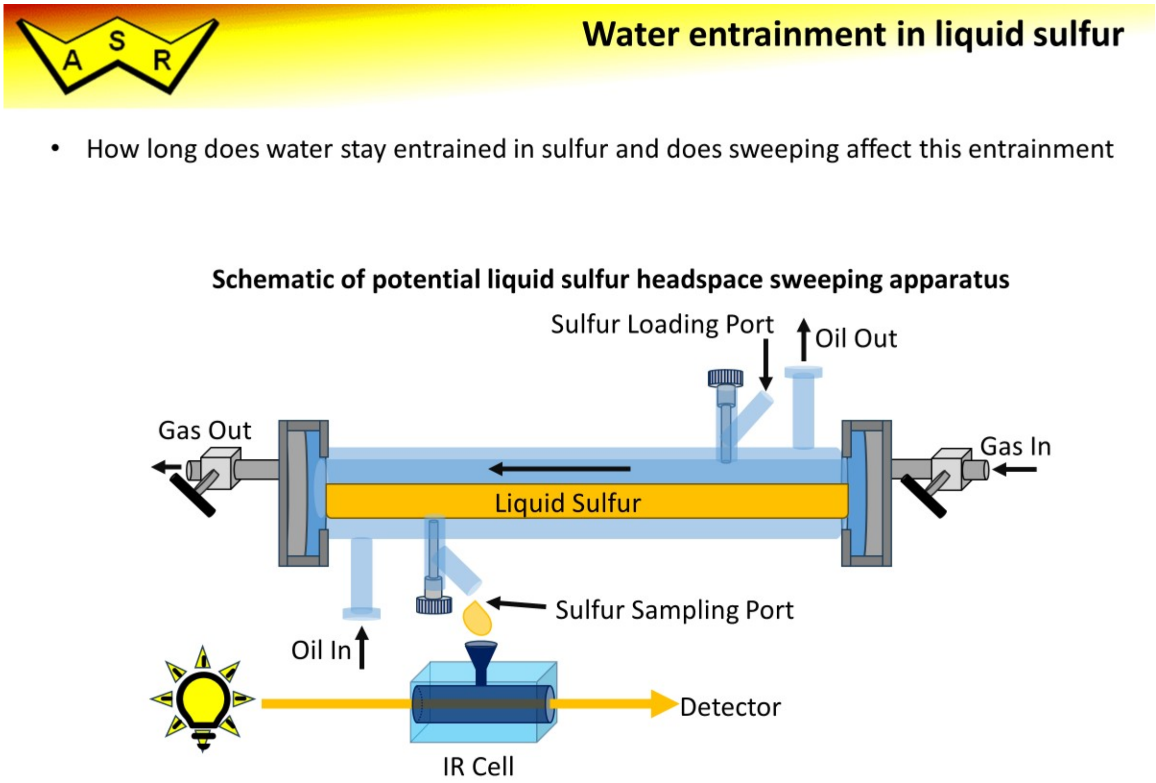
Increased safety and corrosion understanding related to liquid sulfur storage

Project Description

Within the past dozen years, we have re-examined the equilibrium chemical incorporation of H_2S into liquid sulfur, the solubility of SO_2 in liquid sulfur and the evolution of H_2S and SO_2 vapours from a non-swept liquid sulfur tank using IR. All of these metastable sulfur solutes are a consequence of sulfur being condensed within a Claus stream containing N_2, H_2S, SO_2 and H_2O. While H_2O is not soluble in liquid sulfur (more volatile and less polarizable than sulfur), H_2O is also much more concentrated in the condenser. Any dissolved or entrained H_2O will naturally evolve from the liquid sulfur during handling; however, the actual H_2O incorporated and rate of H_2O gas evolution after exiting the condenser is unknown. Our IR spectrometer used for dissolved H_2S, H_2S_x and SO_2 can be used to measure H_2O in the liquid sulfur phase, where we aim to measure both Henry's law solubility in a condenser and the evolution during storage (swept and un-swept).

Specific Objectives

a) Attempt to measure the Henry's law solubility of H_2O in liquid sulfur
b) Measure the evolution of H_2O from liquid sulfur during an active sweep and no sweep



Water entrainment in liquid sulfur

- How long does water stay entrained in sulfur and does sweeping affect this entrainment

Schematic of potential liquid sulfur headspace sweeping apparatus

CRP 12. Sulfur solubility in rich sour gas fluids

Commercial Objective

To update the ASRL sulfur solubility models with new data for condensable or hydrocarbon rich fluids - the models are useful in the areas of gas transportation and compression

Environmental Benefit

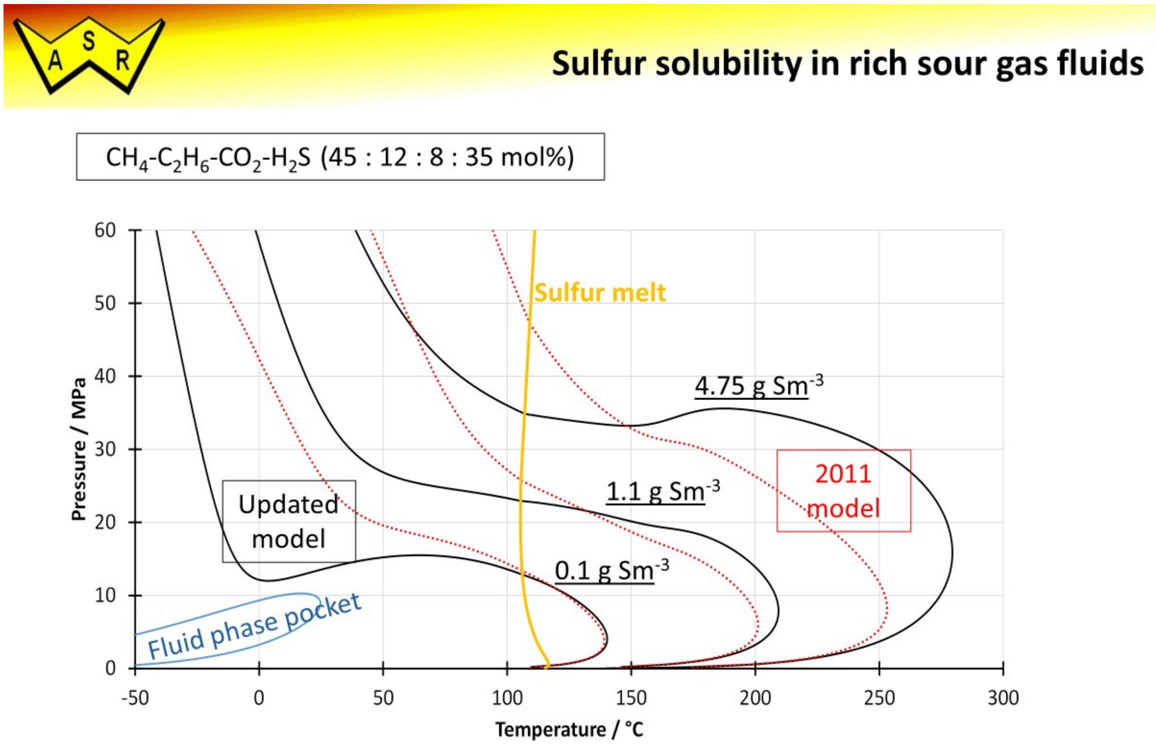
Energy savings resulting in less downtime caused by flow assurance issues. Increased compression and gas lift integrity.

Project Description

Understanding sulfur solubility is important for predicting and mitigating potential deposition at well heads, pipes and regulators if solubility limit is exceeded. ASRL has historically studied elemental sulfur deposition in the context of native reservoir sulfur, which is limited to very lean hydrocarbons. With hydrocarbon rich sour gases, oxygen ingress can lead to elemental sulfur deposition in compression systems; however, the existing data cannot validate the ASRL model for condensable fluids and low temperatures. In order to incorporate the high-density fluids (liquid or supercritical), we intend on updating the model to a more robust correlation. The current work is aimed at measuring solubility data at targeted conditions to update the model. Data has been measured for ethane, propane, butane and CO_2. During model calibration with mixed fluids, it was discovered that the models are influenced by a lack of accurate data for CH_4.

Specific Objectives

a) Remeasure sulfur solubility for CH_4 and select binary mixtures at conditions where literature is suspect or sparse
b) Recalibrate the ASRL sulfur solubility model based on the new data to verify the grouping of virial coefficients.



Sulfur solubility in rich sour gas fluids

CH_4-C_2H_6-CO_2-H_2S (45 : 12 : 8 : 35 mol%)

CRP 13. Remelting sulfur pipelines

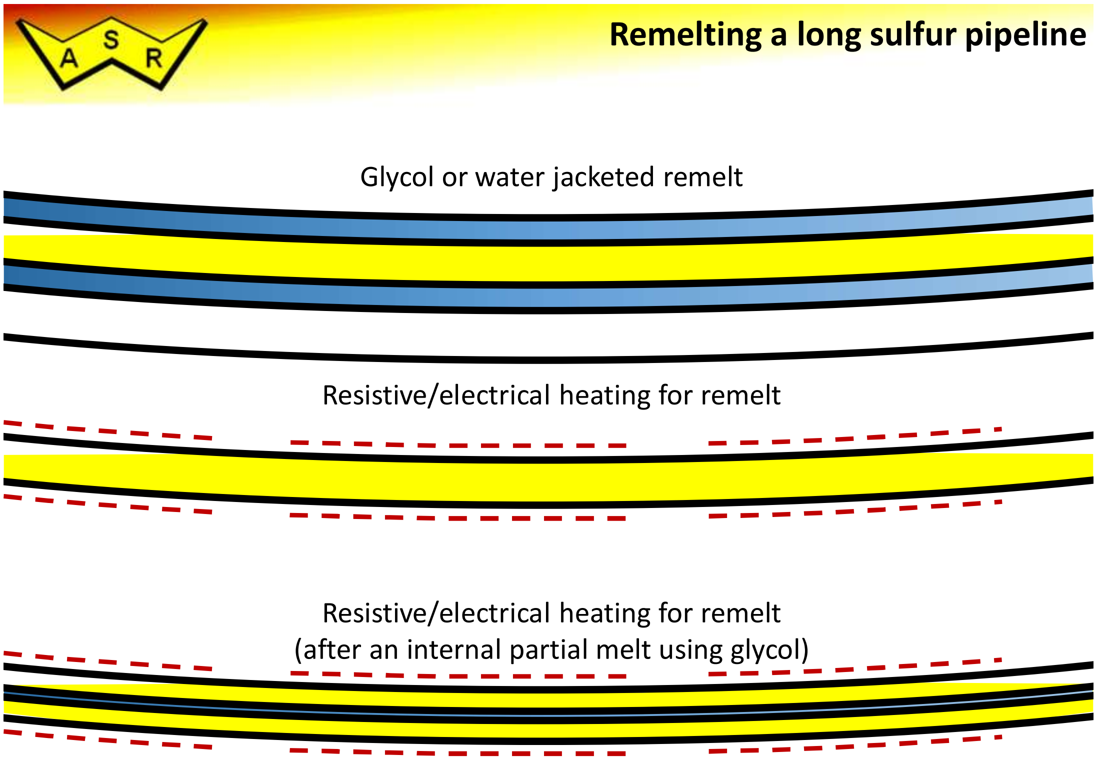
Commercial Objective
To investigate the effectiveness of remelting sulfur pipelines using radial liquid heat exchange versus axial electric heat.

Environmental Benefit(s)
Mitigation of sulfur release and pipeline damage after inadvertently freezing a sulfur pipeline.

Project Description
Sulfur has been safely transported from 3,000 to 12,000 MT day^{-1} in sulfur pipelines several kilometres long with both resistive skin heating (electric) and hot water (or glycol) jackets. While both these methods allow for liquid sulfur flow, if they fail and sulfur solidifies in the pipeline, remelting the liquid sulfur to re-establish flow can result is very large pressures which can rupture the pipeline. ASRL researchers have used both experiments and thermodynamic modelling to show how the melt process can cause substantial stress, where it was predicted that melting must be controlled from one end of a pipeline to release sulfur liquid and avoid thousands of bars of internal pressure. One potential strategy is to incorporate a supplemental internal flow line, sometime called a gut-line, which could be used to circulate hot glycol/water only after a freezing event. If this strategy were employed, the radial stress could potentially be relieved before re-energizing resistive heating and therefore safely re-establishing flow. In this work, we will simulate low spots in a pipeline using glass tubes to test if this remelting strategy would work.

Specific Objectives

a) Solidify and remelt sulfur in a fragile (glass) pipe with a dead leg using (i) resistive heat only, (ii) resistive heat with a cold spot and (iii) resistive heat after a partial remelt with a radial heat exchanger flowing hot glycol



CRP 14. Trace sulfur sampling from hydrocarbon streams

Commercial Objective

Investigating alternative methods for quantifying low level elemental sulfur in surface natural gas streams

Environmental Benefit

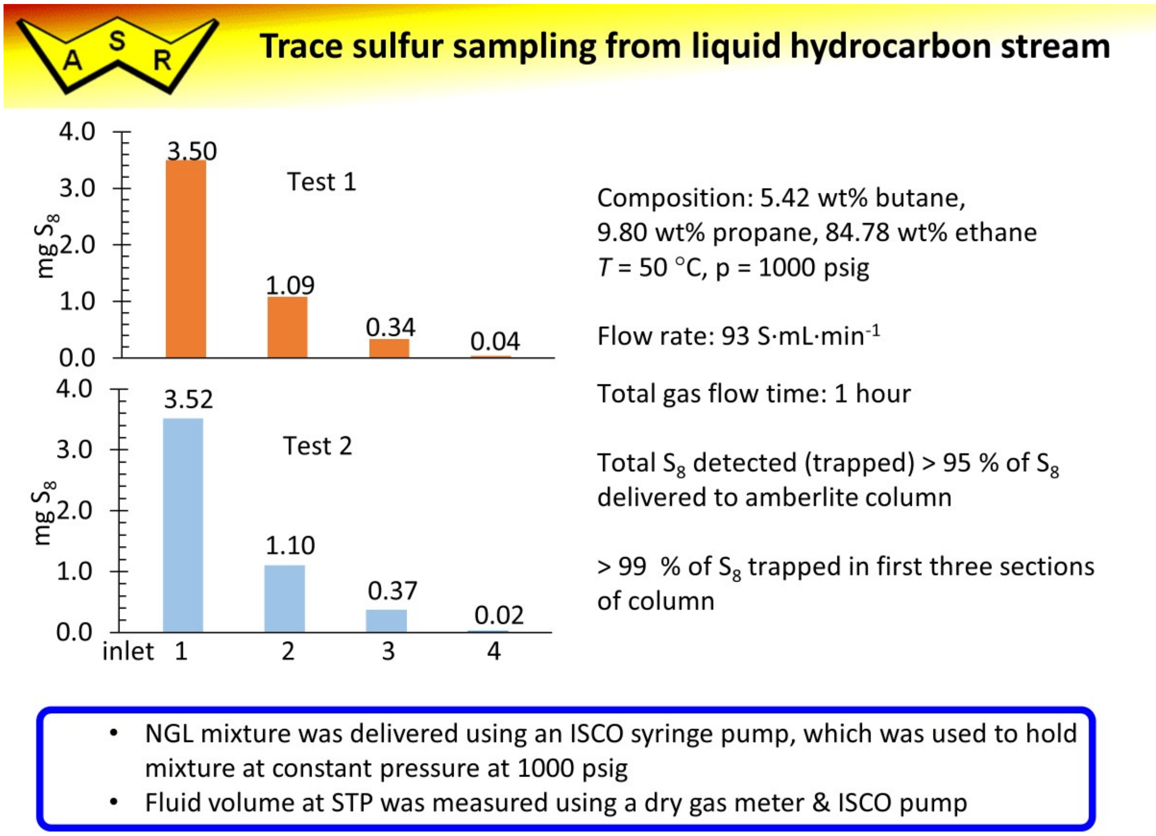
Reducing sulfur deposition failures through more rapid and robust measurement

Project Description

The presence of sulfur in pipeline and compressor fluid leads to adverse effects including flow assurance. The reaction of H_2S with oxygen following oxygen ingress during gas compression can cause failure of both centrifugal and reciprocating compressors, which is both a safety concern and financial loss due to down time. The current method for sampling trace levels of sulfur is the ASTM D7800/D7800M-23 which involves flowing the gas stream through bubblers that are prefilled with triphenyl phosphine solution. With this method, sulfur sensitivity requires longer flowing times (larger gas volume contact). Handling liquid samples can be challenging, requiring long gas flow time and ambient temperature, where low temperatures are required to maintain the liquid solutions. A non-oxidizing adsorbent (amberlite) is being tested as an alternative solid adsorbent bed for sampling trace levels of sulfur. This project seeks to compare a solid adsorbent as an alternative to the ASTM D7800 technique.

Specific Objectives

(a) A solid adsorbent bed is being tested for sulfur removal efficiency using methane as carrier gas (T = 50°C and two flow rates), a sour gas as well as a hydrocarbon liquid synthetic mixture



Trace sulfur sampling from liquid hydrocarbon stream

Composition: 5.42 wt% butane, 9.80 wt% propane, 84.78 wt% ethane
T = 50 °C, p = 1000 psig

Flow rate: 93 S·mL·min^{-1}

Total gas flow time: 1 hour

Total S_8 detected (trapped) > 95 % of S_8 delivered to amberlite column

> 99 % of S_8 trapped in first three sections of column

- NGL mixture was delivered using an ISCO syringe pump, which was used to hold mixture at constant pressure at 1000 psig
- Fluid volume at STP was measured using a dry gas meter & ISCO pump

CRP 15. Better understanding of solutes in supercritical CO_2 processes (green solvents)

Commercial Objective

To improve understanding of selective solubility in dense phase CO_2 separation processes

Environmental Benefit

Improved utilization of a green solvent (CO_2) which is non-flammable and non-toxic

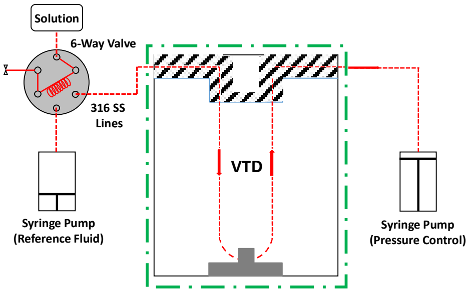
Project Description

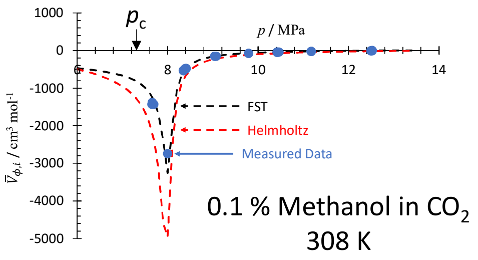
CO_2 is an appealing solvent in industrial applications due to its non-flammable and non-toxic nature. It can be considered a green solvent if it is not emitted as waste and reused in industrial processes as it directly contributes to carbon utilization. CO_2 is already used in the selective extraction of solutes from bulk plant matter, such as caffeine from coffee beans and terpenes from plant waste, where aliphatic alcohols are often used as a cosolvent to increase the solvating power towards more polar solutes. To this end, it is beneficial to understand the thermodynamic properties of dilute CO_2 solutions to better calculate solubility changes in highly compressible systems. This is especially important near the critical point of CO_2. There is a lack of experimental data for thermodynamic properties of these mixtures. This research is the PhD Project of Safeer Nanji and is partially funded through NSERC.

Future Objectives

a) Measure and report partial molar properties for aliphatic alcohols in supercritical CO_2 together with improved binary models
b) Measure and report partial molar properties for two terpenes (d-limonene and isoprene) in supercritical CO_2 to improve solubility models (particularly important for the retrograde region)
c) Provide empirical guidelines for solutes of various polarity and vapour pressure for estimating future solute targets

Better understanding of solutes in supercritical CO_2 processes (green solvents)





Objectives:

A differential flow densimeter upgraded for high-pressure will be used to measure density differences between a binary solution and a pure component fluid. This data will be used to optimize thermodynamic models of binary fluids.

- Limit of detectability of 0.05 $cm^3\ mol^{-1}$
- Small volume requirement (5 mL for liquids)

Target Industrial Mixtures:

Carbon dioxide solution volumes are highly variable near it's critical pressure and temperature (right). Apparent molar volumes of certain solutes in CO_2 will be measured and modelled while varying temperatures and pressures, such as:

- Aliphatic alcohols
- Terpenes
- Caffeine

CRP 16. Sulfur contact corrosion in the presence of aqueous ammonia / ammonium species

Commercial Objective

To explore the corrosion inhibition properties for NH_3 / NH_4^+ under wellhead and downhole conditions

Environmental Benefit

Potential environment protection through extending equipment life

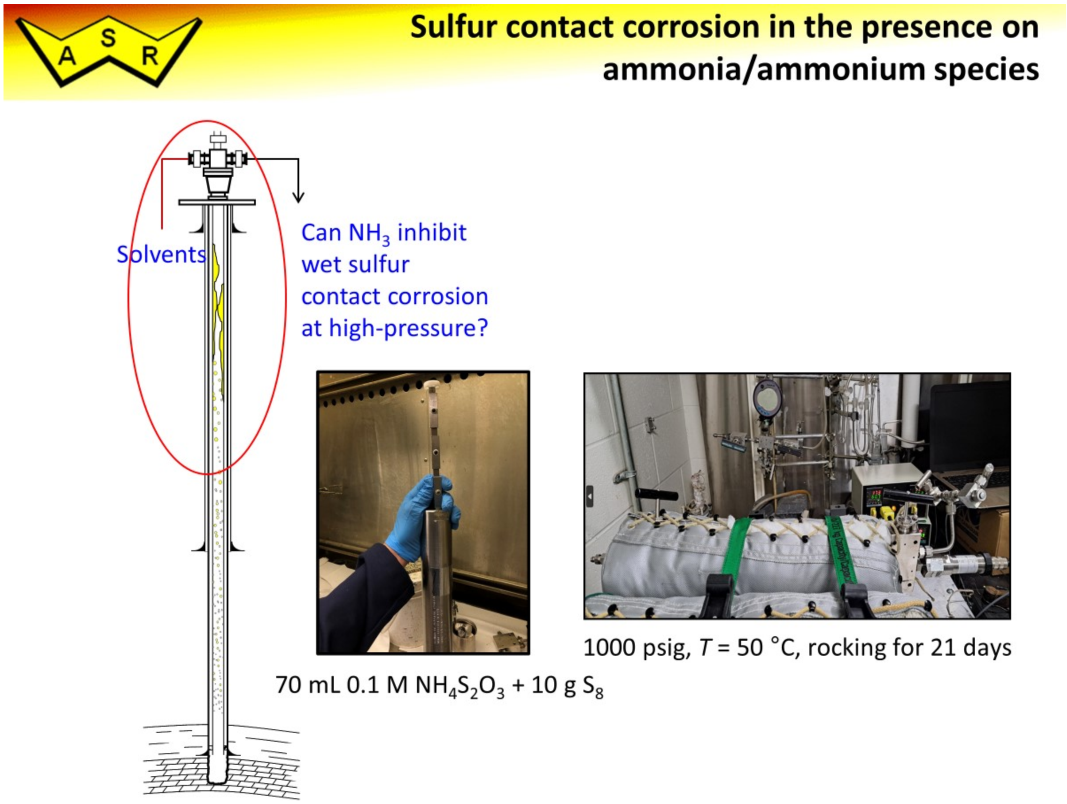
Project Description

Previous research by ASRL has shown that ammonia (NH_3/NH_4^+) based solutions can act as effective inhibitors with respect to wet sulfur contact corrosion under various conditions including, sour water stripper operation and some storage applications. The current work seeks to explore high pressure sour gas applications. The key questions are whether NH_3/NH_4^+ offer protection from wet sulfur contact corrosion in presence of CO_2 and H_2S under high-pressure?

Specific Objectives

(a) Investigate the use of ammonia compounds as corrosion inhibitors for wellhead and downhole applications. Does either $(NH_4)_2S_2O_3$ or NH_4OH inhibit sulfur contact corrosion when CO_2 is present?

(b) Using reasonable sour gas composition (2:1 ratio H_2S: CO_2) conduct corrosion tests in a Kuentzel vessel (Hastelloy C-276 vessel and coupon holder), for high-pressure applications for low-CO_2 fluids (T = 50° C p = 1000 psig)



Sulfur contact corrosion in the presence on ammonia/ammonium species

Can NH_3 inhibit wet sulfur contact corrosion at high-pressure?

70 mL 0.1 M $NH_4S_2O_3$ + 10 g S_8

1000 psig, T = 50 °C, rocking for 21 days

CRP 17. Carbonyl sulfide stability in sour gas production samples

Commercial Objective

Attempt to estimate the potential change in COS concentration for the time between sampling a production system and analysing the fluid at lab for process design purposes.

Environmental Benefit(s)

Increasing production safety and process design through more robust fluid characterization

Project Description

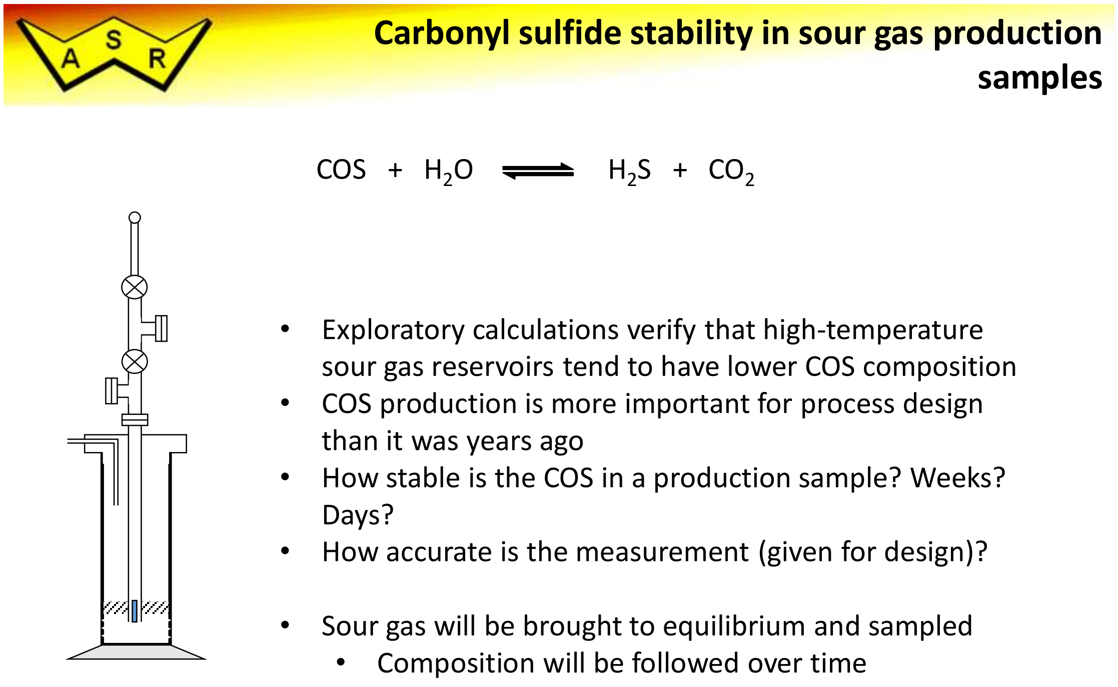
COS can be found in many production fluids and is often removed for total sulfur specifications or potential hydrolysis issues leading to H_2S in associated natural gas liquids, e.g., propane:

$$COS + H_2O \rightleftharpoons H_2S + CO_2$$

Estimating COS in a reservoir is partially successful, because warmer reservoirs with high water vapour seem to have less COS. This estimation is qualitative due to equilibrium shift up the wellbore and/or osmotic changes for different reservoir brines. Nevertheless, samples can be taken in pressurized bombs or downhole tools during early production testing to measure the COS in the fluid. These measurements are important for facility design and understanding. Well fluid samples are cooled and sometimes warmed back to reservoir temperatures before analysing at a laboratory several days or months after sampling. Given that the COS hydrolysis reaction is somewhat slow, errors in COS can arise from cold transportation time or short re-equilibration time. A good estimation of the potential error is not available.

Specific Objectives

a) Study the COS hydrolysis equilibrium shift kinetics from 25 to 125°C in non-passivated stainless steel vessels.



Carbonyl sulfide stability in sour gas production samples

$$COS + H_2O \rightleftharpoons H_2S + CO_2$$

- Exploratory calculations verify that high-temperature sour gas reservoirs tend to have lower COS composition
- COS production is more important for process design than it was years ago
- How stable is the COS in a production sample? Weeks? Days?
- How accurate is the measurement (given for design)?

- Sour gas will be brought to equilibrium and sampled
  - Composition will be followed over time

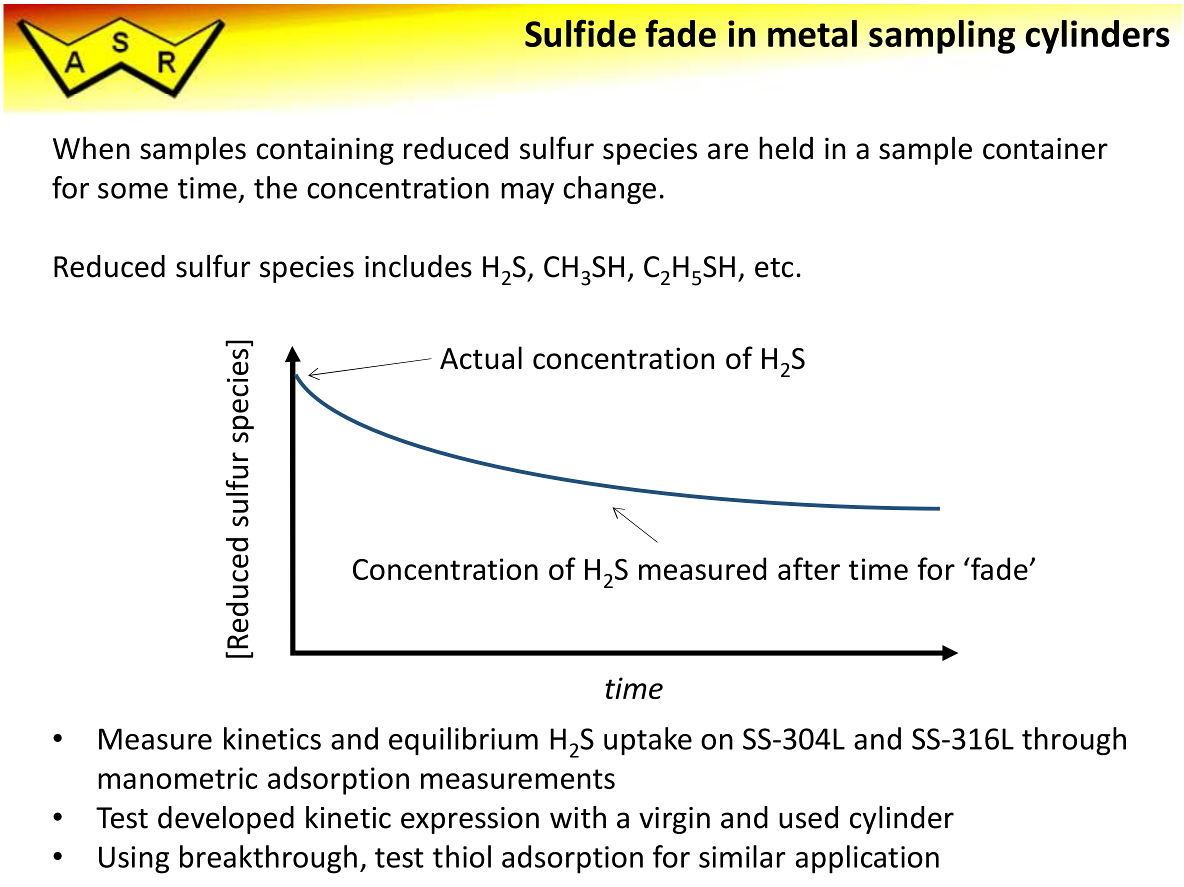
CRP 18. Sulfide fade in metal sampling cylinders

Commercial Objective
To better describe how reduced sulfur species concentrations can change in metal cylinders over time

Environmental Benefit(s)
Increased reliability of fluid characterization for various applications

Project Description
When sampling fluids with hydrogen sulfide or thiols, various sampling vessels and techniques can be appropriate depending on concentration and pressure (partial pressures). For example, Tedlar bags or glass sampling bulbs are appropriate for low pressure tail gas systems or biogas, whereas metal cylinders can be used for high-pressure and high sulfide content (sour gas). If the concentrations are very low, one might choose surface polishing or passivating coatings to reduce any adsorption or reaction with the metal surfaces. Surface treatments aren't always necessary to preserve sample integrity and the kinetics/capacity of sulfide uptake by stainless steel surfaces is variable in the literature. This research focuses measuring slow sulfide fade (chemisorption) on fresh and used SS316 and SS304 surfaces. The measurements will be used to provide guidelines for sample storage time based initial composition and sampling conditions.

Specific Objectives
a) Use dynamic breakthrough, XRD and manometric adsorption to characterise H_2S adsorption kinetics at low partial pressures
b) Compare untreated SS316 and SS304 surfaces to expectations upon storage time and pre-exposure
c) Provide empirical rules for sampling sulfide containing fluids



Sulfide fade in metal sampling cylinders

When samples containing reduced sulfur species are held in a sample container for some time, the concentration may change.

Reduced sulfur species includes H_2S, CH_3SH, C_2H_5SH, etc.

- Measure kinetics and equilibrium H_2S uptake on SS-304L and SS-316L through manometric adsorption measurements
- Test developed kinetic expression with a virgin and used cylinder
- Using breakthrough, test thiol adsorption for similar application

CRP 19. The age and friability for different forms of elemental sulfur (modern forms)

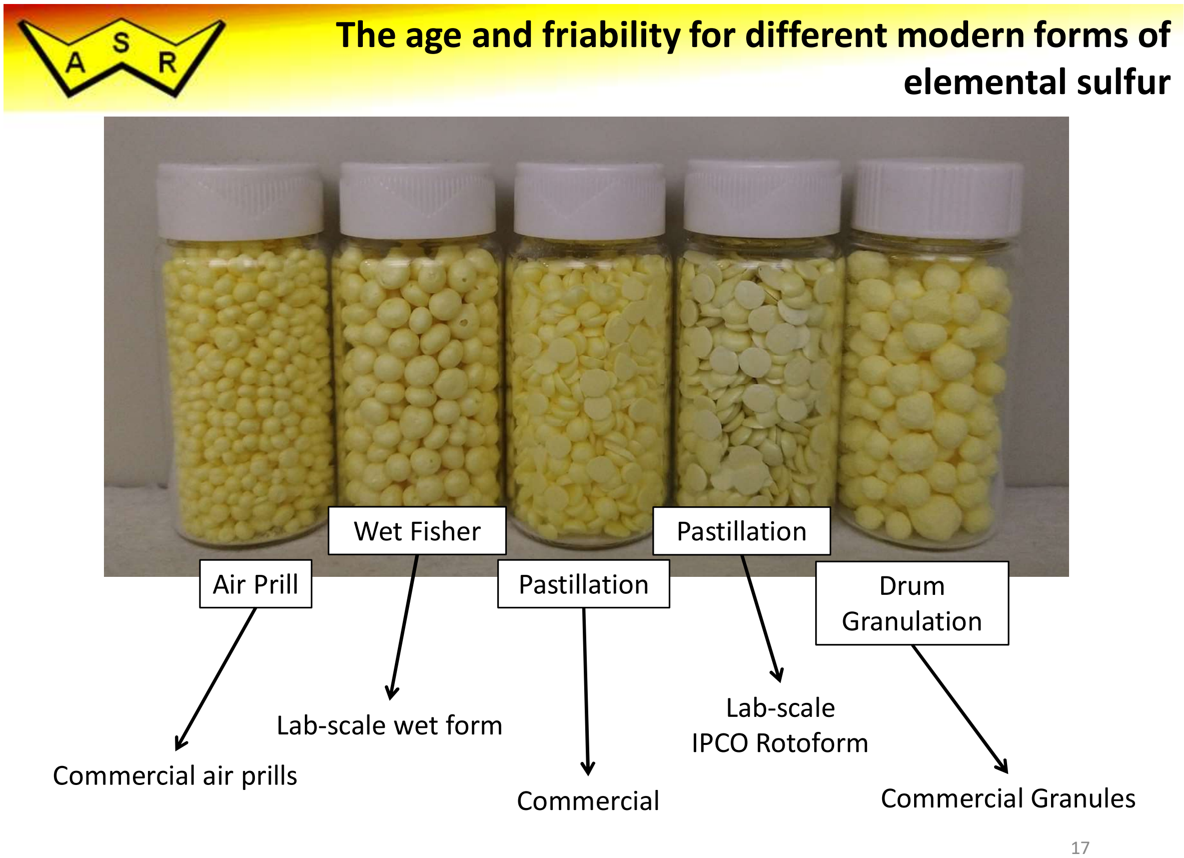
<u>Commercial Objectives</u>: Measure several key properties during the aging of sulfur products which could lead to extraneous dust.

<u>Environmental Benefit(s)</u>: Understanding of factors which lead to dust explosions and / or more aggressive wet sulfur contact corrosion during shipping and transport

<u>Project Description</u>: Both sulfur pastilles and various prills are common commercial products. Several properties are of interest to producers and consumers of these products, such as H_2S content, friability, water capacity, porosity, etc. Many of these properties change during the aging of the products and / or might differ depending on the use of degassed or non-degassed liquid sulfur. Over the past several years, we have followed several properties during thermal aging where any changes might be important for product handling. Polymeric content of solid was studied as a function of liquid sulfur temperature before forming was reported in ASRL QB Vol LVII(3) 2020 and solid ageing studies were reported in ASRL QB Vol LIX(3) 2022. Throughout that work, it became apparent the typical Stress Level II tests or single load tests were not sensitive enough to assess friability differences with modern products. Thus, other methods are being explored.

<u>Specific Objectives</u>

a) A bulk crush strength will be assessed for modern products of various age and polymeric content.



The age and friability for different modern forms of elemental sulfur