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## **ASRL CORE RESEARCH PROGRAM 2023 - 2024**

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## ***LIST OF CORE RESEARCH PROJECTS***

1. What happens to  $\text{SO}_3$  when it crosses a Claus catalyst?
2. Correlating thermal oxidizer operating conditions with  $\text{SO}_3$  formation
3. Towards a better understanding of sulfiding procedures for CoMo tail gas catalysts
4. COS removal with alkanolamines
5. More on BTX destruction across a  $\text{TiO}_2$  catalyst
6. Ammonium salts vapour pressure under Claus conditions
7. High temperature sulfidation of carbon steel and select alloys
8. Persistence of  $\text{SO}_3^{2-}$  and its effect on amine unit operation
9. Kinetic modelling of  $\text{CS}_2$  destruction in the Claus furnace
10. Sulfur contact corrosion in the presence of aqueous ammonia / ammonium species
11. Fate of alkanolamines in the thermal reactor
12. Water entrainment in liquid sulfur
13. Sulfur solubility in rich sour gas fluids
14. Trace sulfur sampling from hydrocarbon streams
15. Remelting sulfur pipelines
16. How stable is SLS as a biocide
17. Phase equilibria of  $\text{CO}_2$  and NGL mixtures at the hydrate phase boundary
18. The age and friability for different forms of elemental sulfur (modern forms)

## CRP 1. What happens to SO<sub>3</sub> when it crosses a Claus catalyst?

### Commercial Objective

To study the fate of SO<sub>3</sub> 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

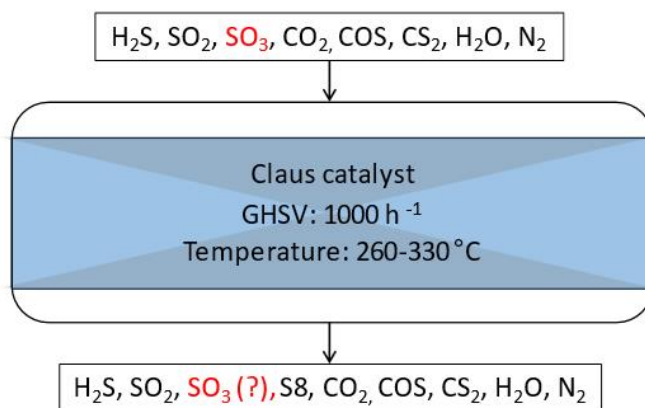
Improperly operated acid gas fired reheaters can lead to the formation of SO<sub>3</sub> which, if able to persist, can lead to unfavourable consequences. In the presence of NH<sub>3</sub>, it has been shown the persistence of SO<sub>3</sub> leads to facile formation of (NH<sub>4</sub>)S<sub>x</sub>O<sub>y</sub> salts. Additionally, in the presence of H<sub>2</sub>O vapour, persistence of SO<sub>3</sub> can result in condensation of corrosive H<sub>2</sub>SO<sub>4</sub>. Laboratory data on the fate of SO<sub>3</sub> 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<sub>3</sub> across Claus catalysts under first, second, and third converter conditions. The impact of temperature, H<sub>2</sub>S concentration, GHSV, and Claus alumina versus titania will be considered. The controlled condensation method will be utilized to trap any residual SO<sub>3</sub> in the reactor effluents as H<sub>2</sub>SO<sub>4</sub> which will be analyzed for using anion chromatography.

### Specific Objectives

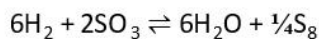
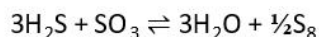
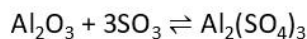
- Investigate fate of SO<sub>3</sub> across Claus Al<sub>2</sub>O<sub>3</sub> under third converter conditions
- Investigate fate of SO<sub>3</sub> across Claus TiO<sub>2</sub> under third converter conditions
- Pending results of (a) and (b), first and second converter conditions may be worth visiting



## What happens to SO<sub>3</sub> when it crosses a Claus catalyst?



Possible pathways for conversion:



*If SO<sub>3</sub> persists, then formation of (NH<sub>4</sub>)S<sub>x</sub>O<sub>y</sub> and / or condensation of H<sub>2</sub>SO<sub>4</sub> is possible*

## CRP 2. Correlating thermal oxidizer operating conditions with SO<sub>3</sub> formation

### Commercial Objective

Describing conditions which lead to excess SO<sub>3</sub> formation in the thermal oxidizer.

### Environmental Benefit(s)

Avoiding harmful environmental release of SO<sub>3</sub> and potential damage to a thermal oxidizer.

### Project Description

Increased SO<sub>3</sub> levels in the thermal oxidizer can lead to sulfuric acid condensation during heat recovery or in the plume. Since 1746 (Roebuck) it has been well known that excess O<sub>2</sub> at very hot temperatures can lead to NO<sub>x</sub> which can catalyse the formation of SO<sub>3</sub> from SO<sub>2</sub> through the lead chamber process. In this study we will investigate flame temperature, excess O<sub>2</sub> (2 to 10%), NO<sub>x</sub> concentrations and SO<sub>3</sub> formation. The experimental work will look at post flame temperatures from 350 to 800°C with fixed NO<sub>x</sub> 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<sub>2</sub> concentrations.

### Specific Objectives

- Provide a review of NO and NO<sub>2</sub> formation kinetics
- Measure SO<sub>3</sub> formation in the presence of predetermined NO concentrations at 500 to 800°C and residence times of 0.5 to 2.0 seconds
- Combine the experimental and literature to describe how excess oxygen and SO<sub>2</sub> can lead to SO<sub>3</sub> formation through the lead chamber process in a thermal oxidiser



### Correlating thermal oxidizer operating conditions with SO<sub>3</sub> formation

In addition to over-combustion, we can also envisage SO<sub>3</sub> formation by the lead chamber process which involves NO<sub>x</sub> formation:



Increased SO<sub>3</sub> leads to higher H<sub>2</sub>SO<sub>4</sub> dew points which will have severe emissions and corrosion implications

#### **Commercial objective(s):**

- Determine NO<sub>x</sub> formation at varying flame temperatures and varying O<sub>2</sub> levels (may need help from CFD colleagues and calculate possible NO<sub>2</sub> concentrations)
- Investigate SO<sub>3</sub> formation in the presence of predetermined NO<sub>x</sub> levels under applicable temperatures (350C-800°C) and residence times (0.5-2.0 sec)

#### **Environmental Benefit(s):**

- Energy and material savings from less downtime related H<sub>2</sub>SO<sub>4</sub> corrosion
- Help optimize treatment for SO<sub>3</sub> coming off of thermal oxidizer
- Understanding of how much SO<sub>2</sub> is converted to SO<sub>3</sub>

### 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)

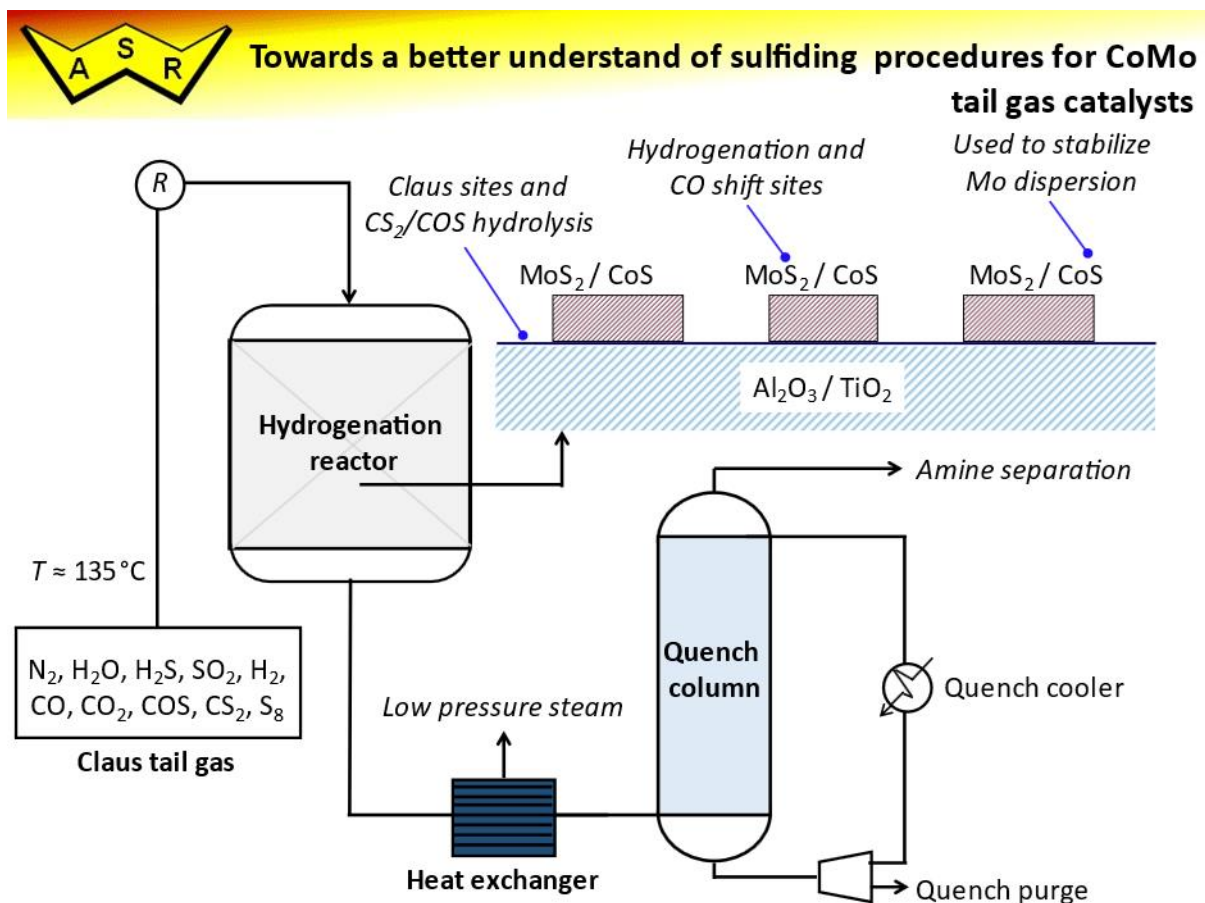
Increased sulfur recoveries / less release of SO<sub>2</sub> to the atmosphere through ensuring optimal performance of tail gas treatment units.

#### Project Description

ASRL has been investigating the influence of various process conditions on tail gas catalyst performance and what impact the catalyst support material (*i.e.*, Al<sub>2</sub>O<sub>3</sub> versus TiO<sub>2</sub>) has on the resulting reactivity. Some key findings so far include: i) excess H<sub>2</sub>S (2.5 versus 1.0 mol%) seems more important for sulfiding Al<sub>2</sub>O<sub>3</sub>-based catalysts compared to TiO<sub>2</sub>-based materials, ii) temperature seems more important than time on stream for further sulfiding, iii) sulfiding with a tail gas itself can provide sufficient performance but, based on catalyst performance, the extent of sulfiding is not as thorough as using N<sub>2</sub> / H<sub>2</sub> / H<sub>2</sub>S stream, iv) exposure of sulfided catalyst (Al<sub>2</sub>O<sub>3</sub>- or TiO<sub>2</sub>-based) to H<sub>2</sub> in absence of H<sub>2</sub>S *did not* negatively impact catalyst performance, and v) exposure of the oxide form of the catalyst to H<sub>2</sub> in the absence of H<sub>2</sub>S *did* negatively impact the performance of an Al<sub>2</sub>O<sub>3</sub>-based catalyst at lower temperatures. There are several ongoing and outstanding longer-term experiments that we would still like to investigate which are outlined in the specific objectives below.

#### Specific Objectives

- Examine the impact of hydrogen exposure to the oxide form of a TiO<sub>2</sub>-based catalyst
- Determine the effect of O<sub>2</sub>-ingress on both Al<sub>2</sub>O<sub>3</sub>- and TiO<sub>2</sub>-based materials
- Adiabatic and TEOM studies to compare sulfiding rates of Al<sub>2</sub>O<sub>3</sub>- and TiO<sub>2</sub>-based catalysts



## CRP 4. COS removal with alkanolamines

### Commercial Objective

Identifying critical parameters necessary for the simulation of COS removal / treatment during amine treating. COS removal with amines contributes to the total sulfur removal from sour natural gas.

### Environmental Benefit

Improving on existing sulfur removal technologies and contributions towards greener processes by reducing SO<sub>2</sub> emissions.

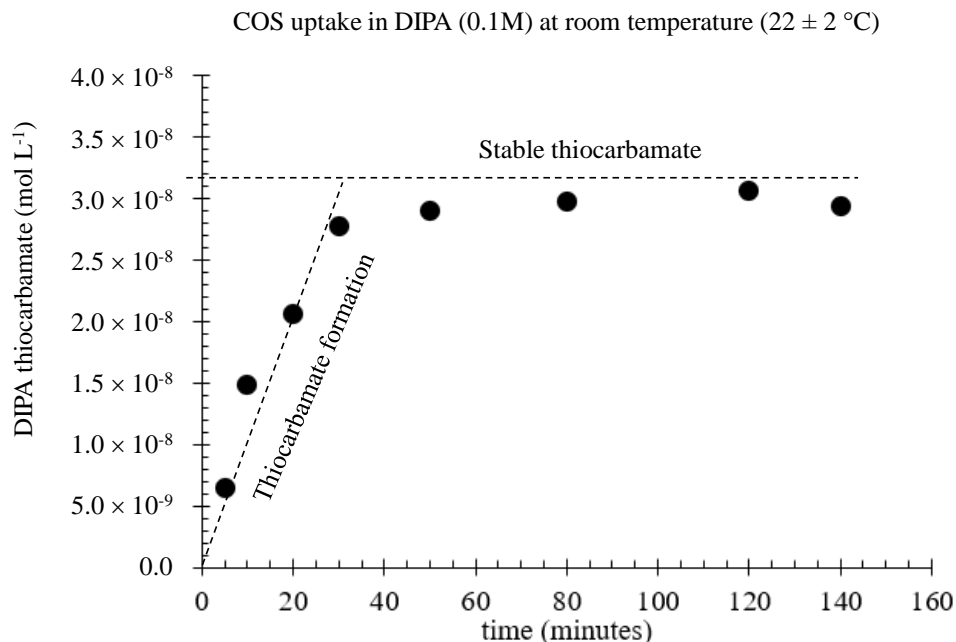
### Project Description

The overall uptake kinetics for COS removal with alkanolamines have been examined in the literature, but speciation data for COS in alkanolamines is less certain. 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. In addition, our early studies show that thiocarbamate does not degrade to hydrosulfide but leads to thiocarbonate species. This research is designed to look at evolving species in various amine solutions through NMR 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

- Use MS-ESI to measure thiocarbamate formation and decomposition rates for TEA, DGA, and piperazine and MDEA/piperazine blends and compare to COS uptake kinetics.
- Explore regeneration species during stripping.
- Use automated ESI-MS to follow hydrosulfide formation during simultaneous COS hydrolysis.

## Carbonyl sulfide uptake in DIPA: Quantifying the thiocarbamate species



## CRP 5. More on BTX destruction across a TiO<sub>2</sub> catalyst

### Commercial Objective

To further elucidate the mechanism of BTX destruction over Claus catalysts

### Environmental Benefit(s)

Reduction in SO<sub>2</sub> and CO<sub>2</sub> emissions from higher and more efficient sulfur recoveries

### Project Description

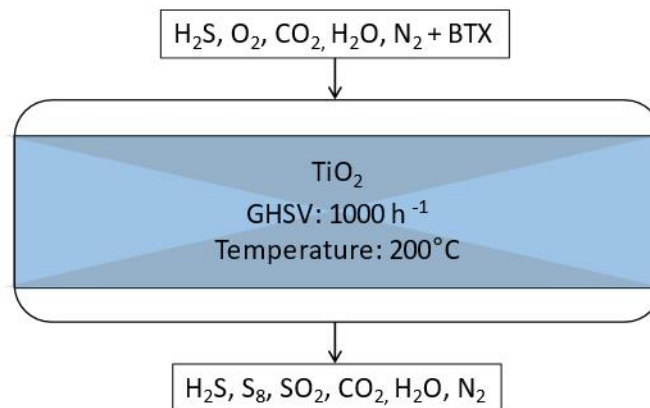
Previous research at ASRL revealed a likely mechanism for BTX destruction over Claus catalysts involving reaction with catalyst Brønsted acid sites and BTX to form coke and carsul-like species. However, recent laboratory observations imply reaction with SO<sub>2</sub> may also be a viable pathway for BTX destruction. Most noticeable for TiO<sub>2</sub>, introduction of BTX to a Claus feed has been observed to correspond with a significant drop in SO<sub>2</sub> within the reactor effluent. This work will aim to gain a more complete understanding of the mechanism for BTX destruction under Claus conditions and potentially facilitate in the design of new generation catalysts more resistant to BTX fouling.

### Specific Objectives

- 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<sub>2</sub>
- In addition to coke formation, determine other possible BTX reaction products that might not be obvious by typical GC analysis



## More on BTX destruction across a TiO<sub>2</sub> catalyst



*Addition of BTX observed to cause disagreement with calculated equilibria, indicating potential reaction with SO<sub>2</sub>*

*Further elucidation of BTX conversion mechanism over Claus catalysts*



## CRP 6. Ammonium salts vapour pressure under Claus conditions

### Commercial Objective

To investigate the vapour pressure of ammonium salt that may deposit in the Claus plant.

### Environmental Benefit

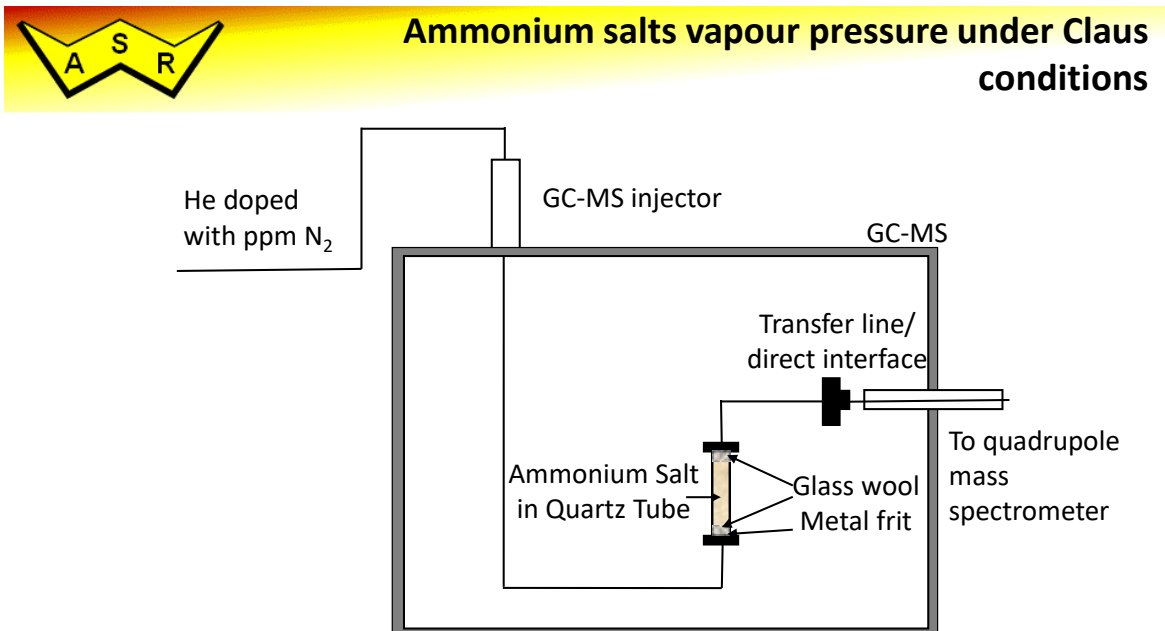
Mitigation of emission risk through flaring or other mechanical failure due to unexpected salt Deposition.

### 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  $(\text{NH}_4)_2\text{S}_2\text{O}_3$ ,  $(\text{NH}_4)_2\text{SO}_3$ , and  $(\text{NH}_4)_2\text{SO}_4$  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  $\text{SO}_3$  and  $\text{NH}_3$ . Without  $\text{SO}_3$ , ammonium thiosulfate can form  $\text{SO}_2$  and  $\text{H}_2\text{O}$  in the Claus system with  $T = 80$  to  $90^\circ\text{C}$ . These temperatures are colder than anticipated/design, but not unprecedented. Finally, the vapour pressure of iron sulfate or Mohr's salt  $(\text{Fe}(\text{SO}_4)(\text{NH}_4)_2(\text{SO}_4)\cdot 6\text{H}_2\text{O})$  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  $T > 150^\circ\text{C}$ .

### Specific Objectives

Following a similar procedure from the 2021 publication, attempt to measure the vapour pressure for  $\text{Fe}_2\text{SO}_4$ ,  $\text{FeS}_2\text{O}_3$ ,  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2\cdot 6(\text{H}_2\text{O})$  [Mohr's salt] between  $150$  to  $250^\circ\text{C}$ .



**How low is the vapour pressure for these iron salt?**

$\text{FeSO}_4$ ,  $\text{FeS}_2\text{O}_3$

$(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2\cdot 6(\text{H}_2\text{O})$  [Mohr's salt],  $(\text{NH}_4)\text{Fe}(\text{SO}_4)_2\cdot 12(\text{H}_2\text{O})$



## CRP 7. 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

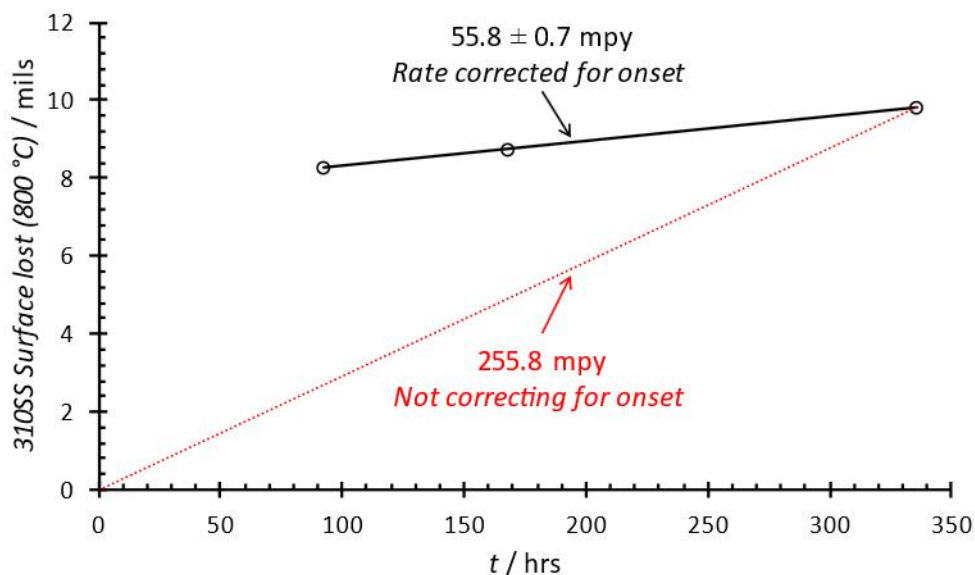
### Project Description

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, particularly at higher temperatures and sulfur concentrations. There are ongoing experiments to hopefully help decipher why this may be the case. Our initial hydrotreating experiments point towards a water partial pressure dependence and less dependence for  $H_2$  partial pressure. In parallel with these experiments probing how each component in a 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

- Continue to probe influence of individual Claus components, particularly water and  $CO_2$
- 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
- 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 8. Persistence of $\text{SO}_3^{2-}$ and its effect on amine unit operation

### Commercial Objective

To investigate  $\text{SO}_3^{2-}$  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.

### Project Description

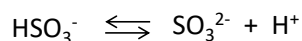
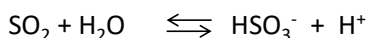
While our previous measurements have shown very rapid formation of elemental sulfur with the ingress of  $\text{SO}_2$  into an alkanolamine system, there has been the suggestion that  $\text{SO}_3^{2-}$  formed from  $\text{SO}_2$  is persistent long enough to be purged from an amine system (before thiosulfate). In this context, we intend on reviewing the pH-dependent products and investigate the kinetics of  $\text{SO}_3^{2-}$  reacting in (i) a buffered solution, (ii) some lean MDEA solutions, (iii) amine solutions containing  $\text{H}_2\text{S}$  and (iv) amine solutions containing  $\text{CO}_2$ .

### Specific Objectives

- Review volt-equivalent diagrams for  $\text{SO}_3^{2-}$  disproportionation as a function of pH
- Develop a method for following the decay of  $\text{SO}_3^{2-}$
- Provide updated kinetic data for aqueous  $\text{SO}_3^{2-}$  persistence

## Presence of $\text{SO}_3^{2-}$ and its effect on amine unit operation

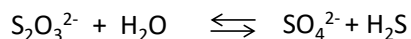
### Sulfite formation



### Sulfate formation



OR



### **Background:**

- Heat stable amine salts accumulate in the amine unit and are potentially corrosive and/or cause fouling issues especially if the pH is allowed to drop, particularly under hot regeneration conditions.
- Sulfite ( $\text{SO}_3^{2-}$ ) may be present in the amine unit after  $\text{SO}_2$  breakthrough and may impact amine unit operation.
- Does  $\text{SO}_3^{2-}$  oxidize to  $\text{SO}_4^{2-}$ , or does it react to other sulfur oxyanions ( $\text{S}_2\text{O}_3^{2-}$ ) in the presence of sulfur or various heat stable salts.
- How long does  $\text{SO}_3^{2-}$  persist or does it disproportionate to other species?

## CRP 9. Kinetic modelling of CS<sub>2</sub> destruction in the Claus furnace

### Commercial Objective

To obtain experimental data that can be used to build a simplified kinetic model for CS<sub>2</sub> destruction in the Claus thermal reactor

### Environmental Benefit(s)

Reduction in SO<sub>2</sub> and CO<sub>2</sub> emissions from higher and more efficient sulfur recoveries

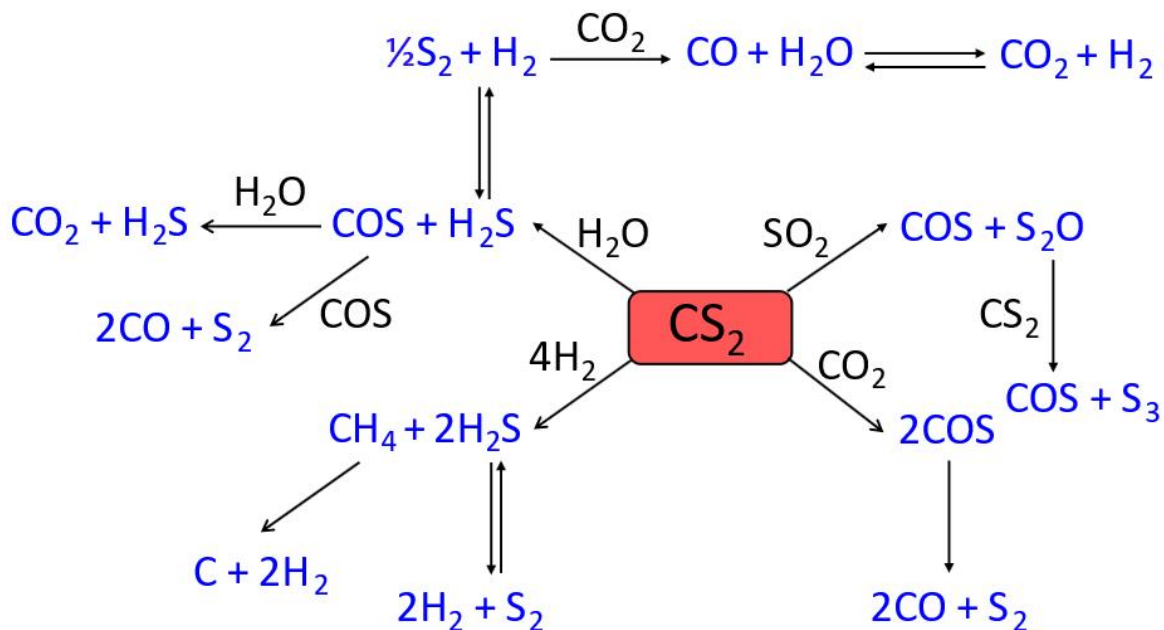
### Project Description

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<sub>2</sub> conversion under several sets of conditions and deduced rate expressions for these data; however, these experiments used simple binary reactant mixtures (CS<sub>2</sub> + H<sub>2</sub>O or CS<sub>2</sub> + SO<sub>2</sub>) and short residence times. Longer residence time data, especially at temperatures exceeding 1000°C, suggest a more complex mechanism for CS<sub>2</sub> 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<sub>2</sub> 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

- While using full Claus acid gas feeds (low and high CO<sub>2</sub>), determine the kinetics of CS<sub>2</sub> destruction at 900, 1000, 1100 and 1200°C

## Kinetic modelling of CS<sub>2</sub> destruction in the Claus furnace



## CRP 10. Sulfur contact corrosion in the presence of aqueous ammonia / ammonium species

### Commercial Objective

To explore the corrosion inhibition properties for  $\text{NH}_3/\text{NH}_4^+$  under well head and down hole conditions

### Environmental Benefit

Environment protection through corrosion management

### Project Description

Ammonia ( $\text{NH}_3/\text{NH}_4^+$ ) based solutions have been shown to 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 acid gas applications. The key questions are whether  $\text{NH}_3/\text{NH}_4^+$  offer protection from wet sulfur contact corrosion in presence of  $\text{CO}_2/(\text{NH}_4)_2\text{CO}_3$  and does pH play a significant role under these conditions?

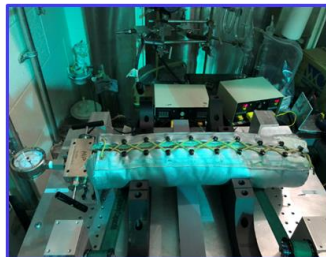
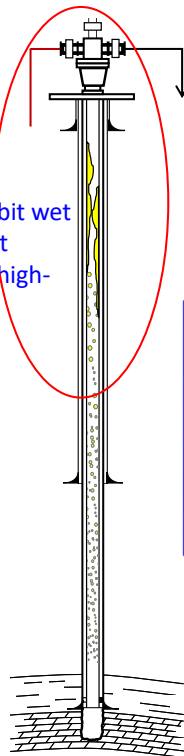
### Specific Objectives

- Investigate the use of ammonia compounds as corrosion inhibitors for well head and down hole applications. Does either  $(\text{NH}_4)_2\text{S}_2\text{O}_3$  or  $\text{NH}_4\text{OH}$  inhibit sulfur contact corrosion when  $\text{CO}_2$  is present.
- Using a fixed acid gas (2:1 ratio  $\text{H}_2\text{S}:\text{CO}_2$ ) conduct corrosion tests in a Kuentzel vessel (Hastelloy C-276 vessel and coupon holder), for high-pressure applications for low- $\text{CO}_2$  fluids ( $T = 50^\circ\text{C}$   $p = 1000$  psig)



## Sulfur contact corrosion in the presence on ammonia/ammonium species

Can  $\text{NH}_3$  inhibit wet sulfur contact corrosion at high-pressure?



## CRP 11. Fate of alkanolamines in the thermal reactor

### Commercial Objective

To describe the conditions necessary to destroy amine which has been carried over into the thermal reactor [Could amine carryover potentially result in the formation of ammonia ( $\text{NH}_3$ ) intermediates?]

### Environmental Benefit(s)

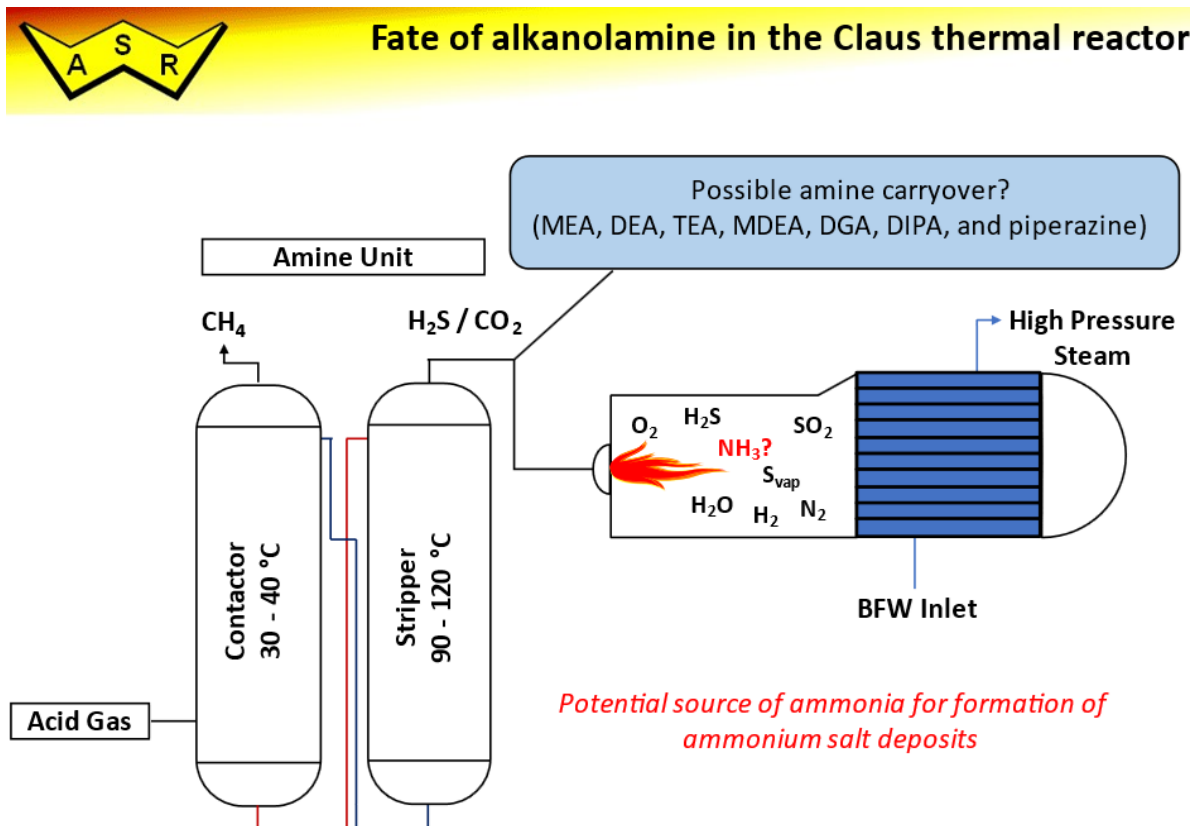
Savings in energy and material by less frequent plant failure / shut down due to ammonium salt deposition (plant or refinery sustainability)

### Project Description

To complement other items in this research program, this study will examine the potential for ammonia generation from incomplete destruction of amine carryover to the Claus thermal reactor, either in the form of a slug or a slow ingress. This research may lead to a better understanding of why ammonium salt depositions can be found in gas plant sulfur recovery units, where no  $\text{NH}_3$  should be present in the process stream. More specifically, the combustion, decomposition, and potentially any long-lived intermediates for MEA, DEA, TEA, MDEA, DGA, DIPA, and piperazine will be studied while employing representative thermal reactor conditions. In our initial experiments, we have confirmed thermal degradation of MEA affords  $\text{NH}_3$  and ethylene intermediates using mass spectrometry.

### Specific Objectives

- Calibrate mass spectrometer to accurately quantify residual  $\text{NH}_3$  levels by cross referencing with gas and ion chromatography results
- By sequentially introducing Claus components to the feed, gain mechanistic insight into pathway(s) for conversion
- Determine kinetic limitations of amine conversion and complete destruction of any long-lived intermediates



## CRP 12. 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<sub>2</sub>S into liquid sulfur, the solubility of SO<sub>2</sub> in liquid sulfur and the evolution of H<sub>2</sub>S and SO<sub>2</sub> 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<sub>2</sub>, H<sub>2</sub>S, SO<sub>2</sub> and H<sub>2</sub>O. While H<sub>2</sub>O is expected to be only slightly soluble in sulfur (more volatile than sulfur), H<sub>2</sub>O is also much more concentrated in the condenser. Any dissolved or entrained H<sub>2</sub>O will naturally evolve from the liquid sulfur during handling; however, the actual H<sub>2</sub>O incorporated and rate of H<sub>2</sub>O gas evolution after exiting the condenser is unknown. Our IR spectrometer used for dissolved H<sub>2</sub>S, H<sub>2</sub>S<sub>x</sub> and SO<sub>2</sub> can be used to measure H<sub>2</sub>O 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).

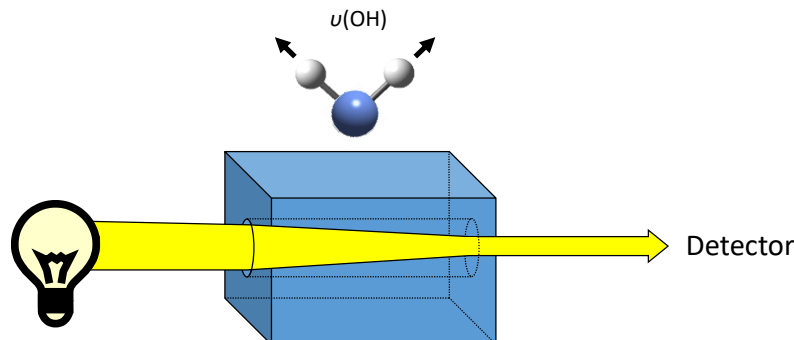
### Specific Objectives

- Attempt to measure the Henry's law solubility of H<sub>2</sub>O in liquid sulfur
- Measure the evolution of H<sub>2</sub>O from liquid sulfur during an active sweep and no sweep



## Water entrainment in liquid sulfur.

- Many field IR spectra show water entrainment in liquid sulfur, whereas the water solubility should be very low
- Using *in-situ* Claus chemistry and water standards, we can calibrate our typical liquid IR for water (we know we can, but have never published this)
- How long does water stay entrained and does without sweeping affect this entrainment time?





### CRP 13. Sulfur solubility in rich sour gas fluids

#### Commercial Objective

To update the ASRL sulfur solubility model with new data for condensable or hydrocarbon rich fluids. The model is useful in the areas of gas transportation and compression.

#### Environmental Benefit

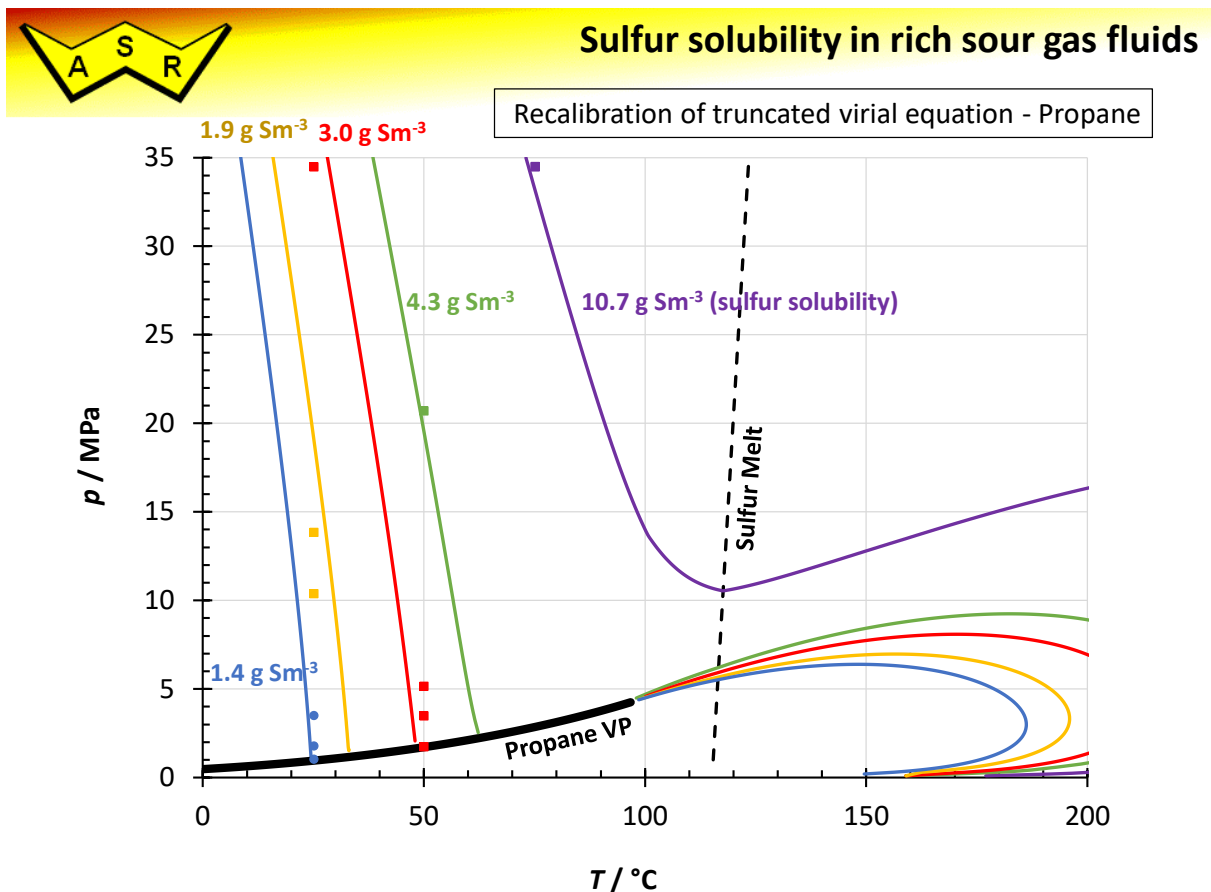
Energy savings resulting in less downtime caused by flow assurance issues. Safe transportation and compression of gases.

#### 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<sub>2</sub>. During model calibration with mixed fluids, it was discovered that the models are influenced by a lack of accurate data for CH<sub>4</sub>.

#### Specific Objectives

- Remeasure sulfur solubility for CH<sub>4</sub> and select binary mixtures at conditions where literature is suspect or sparse
- Recalibrate the ASRL sulfur solubility model based on the new data to verify the grouping of virial coefficients.





## 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

Corrosion and flow assurance issues are some of the side effects of sulfur in pipeline or compressor fluids. 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 which involves flowing the gas stream through bubblers that are prefilled with triphenyl phosphine solution. The sulfur reacts with triphenyl phosphine to form the sulfur triphenyl phosphine compound (TPP-S), which can be analysed using Gas Chromatography. 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 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 ( $T = 50^\circ C$  and two flow rates), a sour gas as well as a hydrocarbon liquid synthetic mixture.



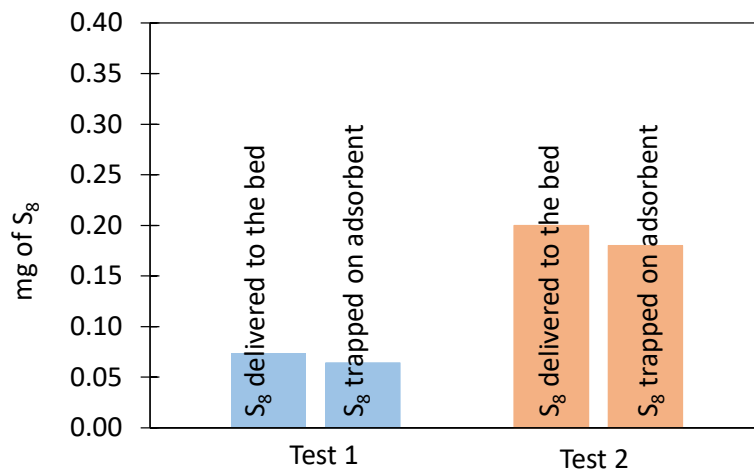
### Efficiency of sulfur adsorption during fluid sampling

Test at  $50^\circ C$  and 1000 psig

Gas composition = 305 ppm  $H_2S$ , 2% CO balance  $CH_4$ ,  $t = 50^\circ C$ ,  $p = 1000$  psig

Standard flow rate =  $500\text{ mL min}^{-1}$

Total flow time was 14 hours (test 1) and 28 hours (test 2)



## CRP 15. Remelting sulfur pipelines

### Commercial Objective

To investigate the effectiveness of remelting sulfur pipelines using radial liquid heat exchange.

### Environmental Benefit(s)

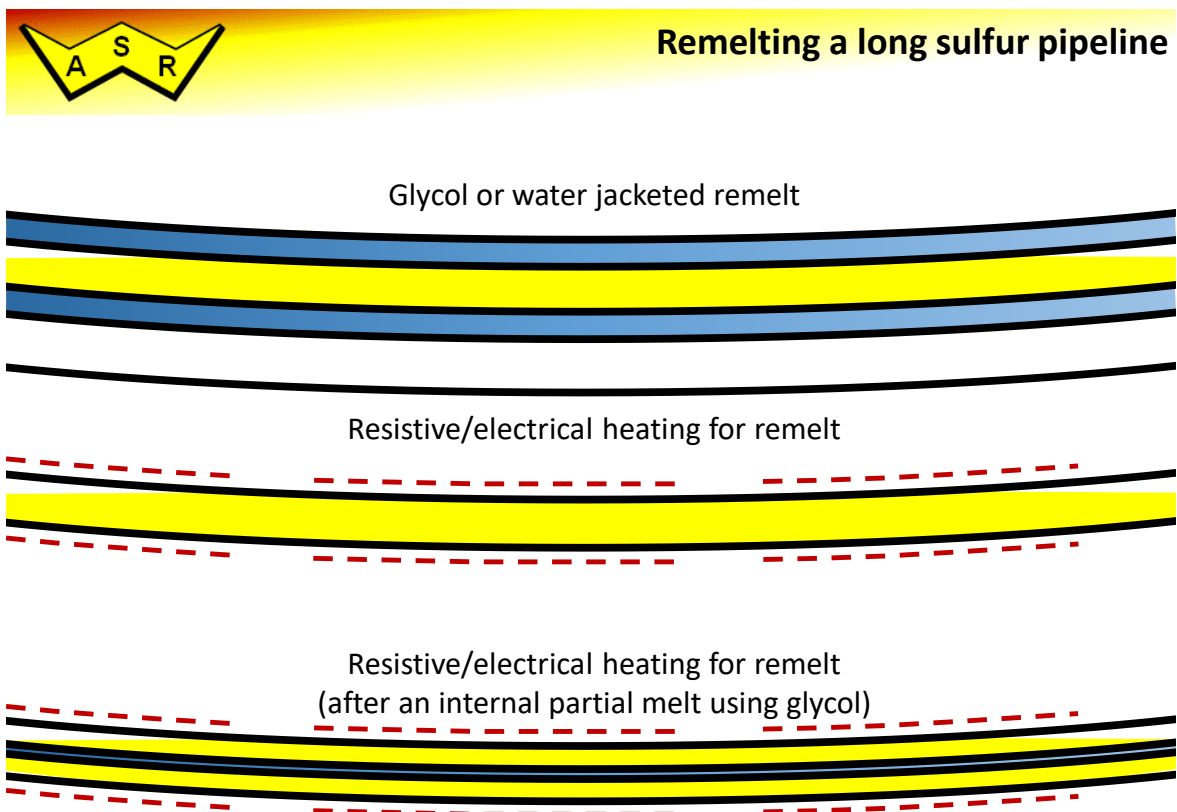
Mitigation of sulfur release and pipeline damage after inadvertently freezing a sulfur pipeline.

### Project Description

Sulfur has been safely transported from 3,000 to 12,000 MT day<sup>-1</sup> in sulfur pipelines several kilometres long with both resistive skin heating (electric) and hot water (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 in 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 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 sulfur dead-legs in glass tubes to test if this remelting strategy would work.

### Specific Objectives

- 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 16. How stable is SLS as a biocide

### Commercial Objective

To determine if the application of extraneous SLS can lead to excess sulfate / corrosion through hydrolysis and to demonstrate that SLS must be applied to product before acid formation.

### Environmental Benefit

Reduction in sulfur contact corrosion (leading to H<sub>2</sub>S release) and acid contamination.

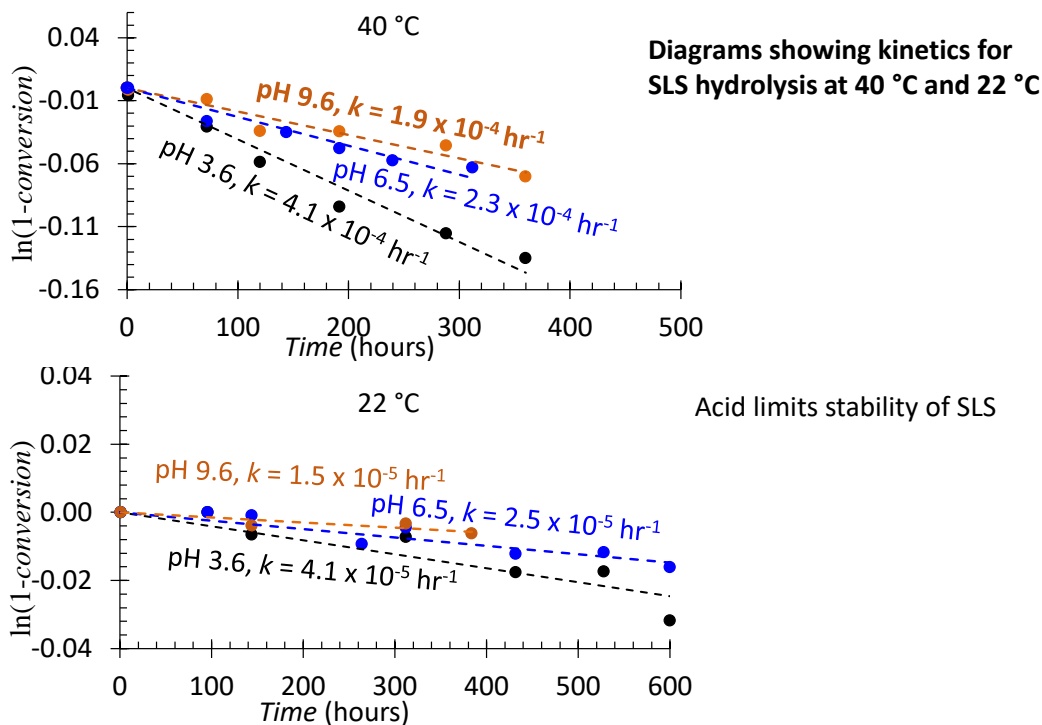
### Project Description

Sodium Lauryl sulfate (SLS) is applied to sulfur as a biocide prior to sulfur transportation. Over a decade ago research at ASRL investigated the effectiveness of SLS for mitigating acidity caused by the bacterial action. Since these studies, transportation has shifted from regional to more continental focus lengthening duration of transport. SLS is known to hydrolyse back to dodecanol and bisulfate. This project is aimed at addressing the how significant SLS hydrolysis is under certain initial pH conditions and in contact with elemental sulfur. Because sulfates are known to enhance sulfur contact corrosion, both hydrolysis and initial acidity could be an issue. If SLS is applied to a product that is (i) not neutralized or (ii) has already undergone significant bacterial acidification, how effective will SLS be in protecting from sulfur contact corrosion and for how long.

### Specific Objectives

- Measure kinetics of SLS hydrolysis from 20 to 40 °C with and without sulfur
- Measure the pH changes associated with hydrolysis
- Investigate contribution from SLS hydrolysis products to wet sulfur contact corrosion of carbon steel

### Kinetics of SLS hydrolysis by following dodecanol at low temperature



## CRP 17. Phase equilibria of CO<sub>2</sub> and NGL mixtures at the hydrate phase boundary

Commercial Objectives: Provide reference quality hydrate formation models for CO<sub>2</sub> and NGL mixtures

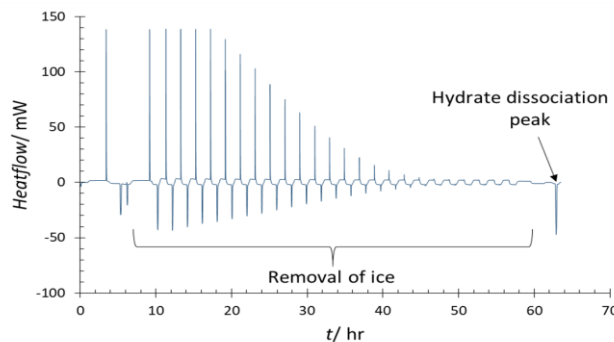
Environmental Benefit(s): Safer transportation if important industrial fluids

Project Description: With CO<sub>2</sub>, NGLs, acid gas injection and cryogenic separation processes, there is the need to understand and simulate the formation conditions for hydrates, *e.g.*, how cold is too cold? For many of these fluids, the gas-hydrate compounds can be either a Type I or a Type II. H<sub>2</sub>S, CO<sub>2</sub> and CH<sub>4</sub> form Type I hydrates; however, with some amount of C<sub>2+</sub>, the hydrate type will change. Upon moving to a Type II hydrate in a mixed system, the formation temperature (at the same pressure) increases due to stabilization from both formers. While hydrate formation temperatures for mixed formers are well studied in the gas phase, there is very little information regarding mixed liquid formers. For an example of application, one might need to know much ethane or propane would cause issues while transporting liquid CO<sub>2</sub>? In this work the enthalpies for hydrate formation and binary phase boundaries for Type I with Type II formers are being studied. There is a future need for high-pressure water contents for other mixed fluids, including acid gases and LPGs. This research is funded through the NSERC Discovery Grant program.

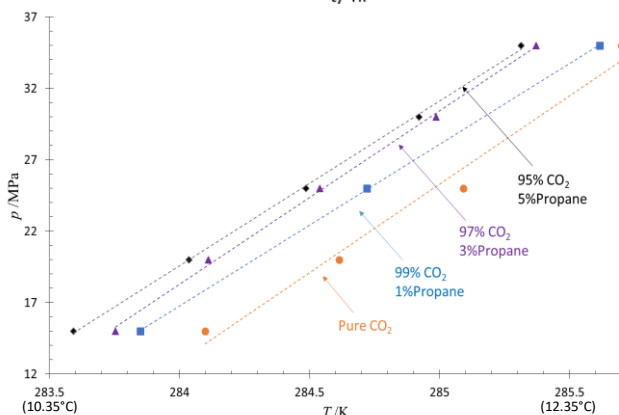
### Specific Objectives

- Investigated CO<sub>2</sub> + C<sub>3</sub>H<sub>8</sub> formation enthalpies in the liquid-liquid region using Differential Scanning Calorimetry
- Produce phase boundary information to test how much propane is necessary for type II Hydrate structures
- Investigate hydrate enthalpies and boundaries for LPG and acid gas mixtures

### Phase equilibria of high-pressure sour gas and LPG mixtures at the hydrate phase boundary



- Conversion of ice to hydrate through repeated heating/cooling cycles



- CO<sub>2</sub>-Propane phase boundary diagram at different compositions
- Increasing propane concentration lowers temperature
- No phase transition observed from type 1 to type 2 hydrate at 5% propane

## CRP 18. The age and friability for different forms of elemental sulfur (modern forms)

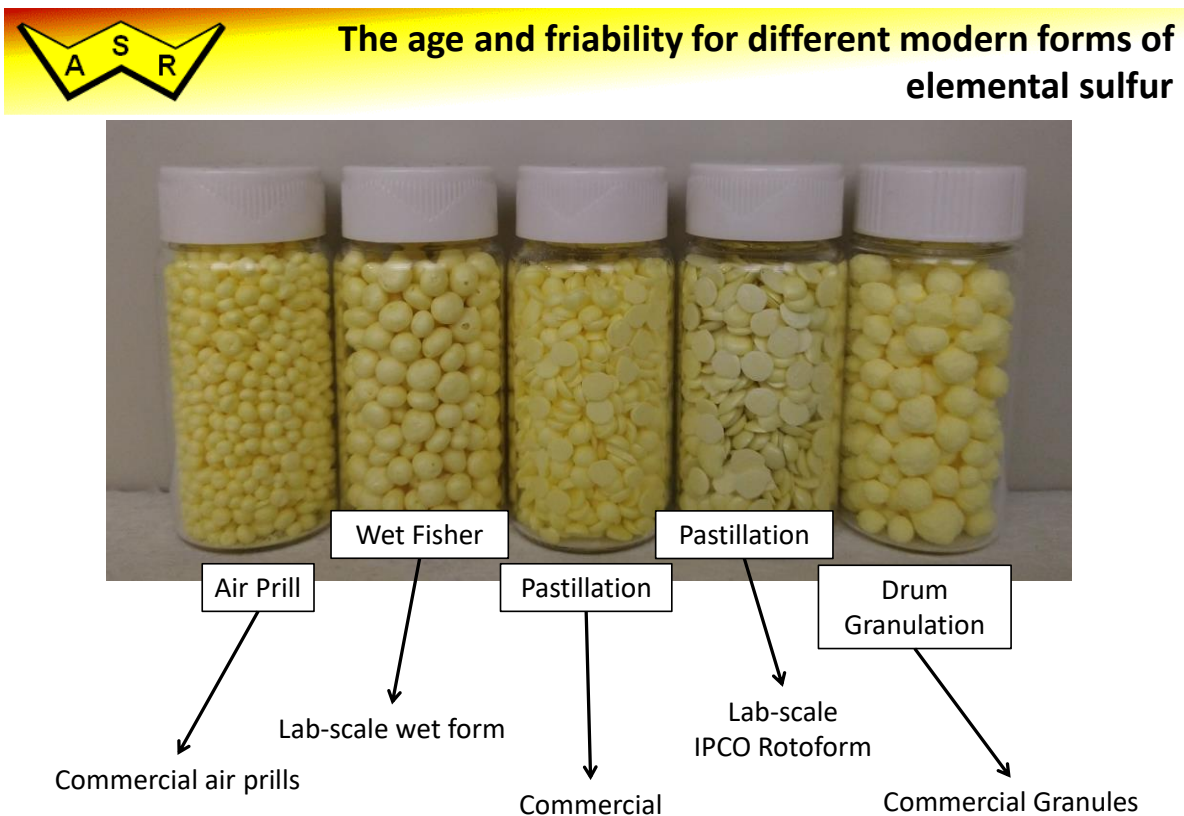
Commercial Objectives: Measure several key properties during the aging of sulfur products which could lead to extraneous dust.

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

Project Description: 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<sub>2</sub>S 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. With controlled batches of water formed prills, commercial air prills, commercial pastilles and lab formed pastilles (product made within the ASRL labs), we have followed several properties during thermal aging where any changes might be important for product handling. In order to develop pastilles made in the ASRL labs, an IPCO Rotoform MI is being installed to develop the needed batches of pastilles for the project. Polymeric content of solid was studied as a function of liquid sulfur temperature before forming was published in ASRL QB Vol LVII(3) 2020. The remaining solids results have been presented at the Chalk Talks and are to be summarized in an upcoming QB.

### Specific Objectives

- a) Report new polymetric solid annealing rates in QB



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