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ASRL CORE RESEARCH PROGRAM
2022 - 2023

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- Paul Davis – ASRL
- Chris Lavery – ASRL
- Melerin Madekufamba – ASRL

LIST OF CORE RESEARCH PROJECTS

1. Towards a better understanding of sulfiding procedures for CoMo tail gas catalysts
2. Ammonium salt vapour pressure under Claus conditions
3. High-temperature sulfidation of carbon steel and select alloys
4. What happens to SO_3 within the Claus catalyst bed?
5. Sulfuric acid conversion in the Claus thermal reactor
6. COS removal with alkanolamines
7. More on BTX destruction across a TiO_2 catalyst
8. Kinetic studies for the hydrolysis of CS_2 and COS across the Claus catalytic converters
9. Fate of MEA, DEA and DGA in the thermal reactor
10. Sulfur contact corrosion in the presence of aqueous ammonia / ammonium species
11. Persistence of SO_3^{2-} and its effect on amine unit operation
12. Impact of H_2S scavengers and reaction products on fouling of refinery equipment
13. Water entrainment in liquid sulfur
14. Molecular sieve dehydration in sour service [NSERC ASRL IRC Funding]
15. Kinetic modelling of CS_2 destruction in the Claus furnace
16. Trace sulfur sampling from hydrocarbon streams
17. Selective adsorption of sulfur species using activated carbons derived from petroleum coke [NSERC ASRL IRC Funding]
18. Sulfur solubility in rich sour gas fluids
19. The age and friability for different forms of elemental sulfur (modern forms)
20. Phase equilibria of high-pressure sour gas and LPG mixtures at the hydrate phase boundary [NSERC ASRL IRC Funding]
21. Low CO_2 emission technology for manufacture of propylene and butylenes
22. How stable is SLS as a sulfur biocide?

CRP 1. Towards a better understanding of sulfiding procedures for CoMo tail gas catalysts

Commercial Objective

To better understand how various process conditions impact tail gas activity

Environmental Benefit(s)

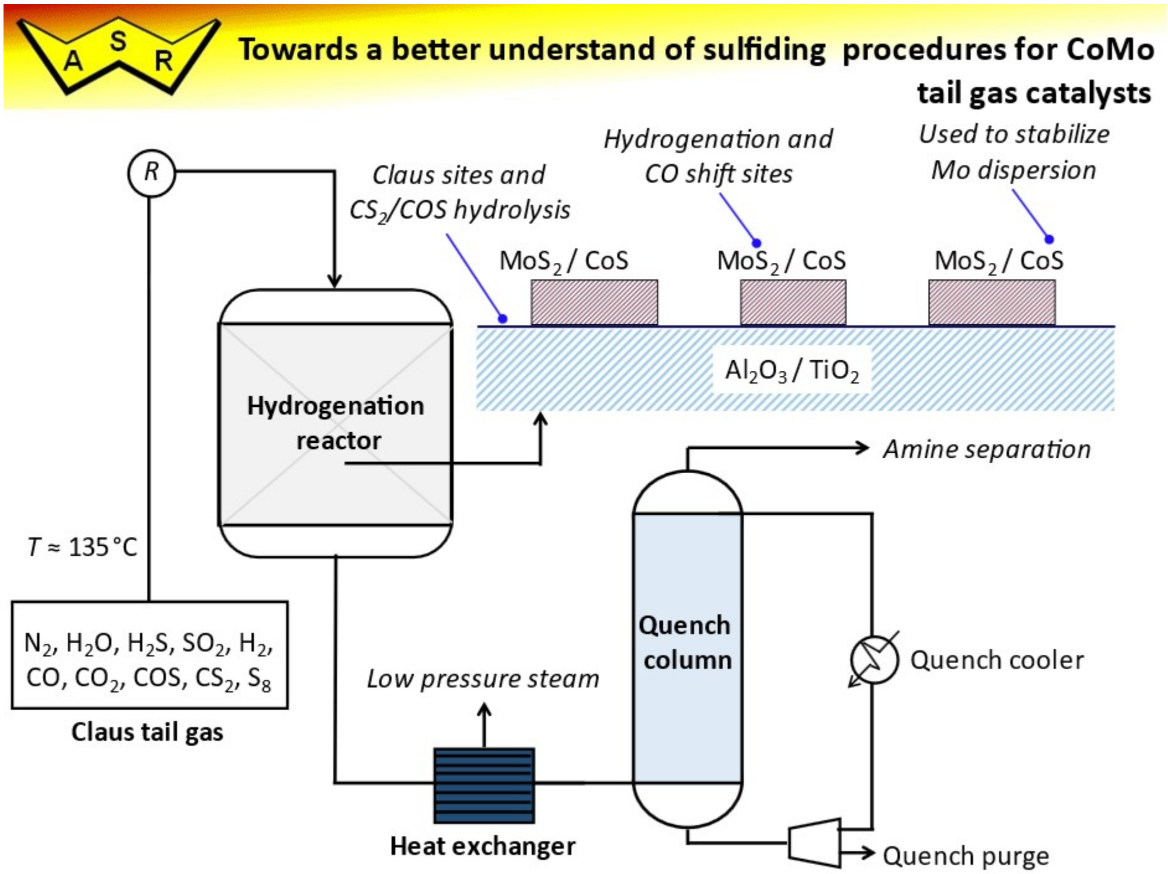
Lowering SO_2 emissions from sulfur recovery units from more efficient operation of reducing / amine-based tail gas cleanup units

Project Description

ASRL has been requested to investigate what role the catalyst support material (*i.e.*, Al_2O_3 versus TiO_2) may have on the resulting reactivity and ease of sulfidation. The ability for further sulfiding to take place under normal operation Claus tail gas conditions may help alleviate concerns of temperature limitations during initial sulfiding procedures. As such, various sulfiding finishing temperatures will be employed here, followed by longer term reactivity studies. The impact of catalyst (sulfide and oxide forms) exposure to hydrogen in the absence of H_2S will also be further probed to establish actual sensitivity of CoMo reduction to elemental form under representative conditions. Finally, the impact of BTX, resulting from use of an impure hydrogen source, on catalyst performance at various temperatures will also be included in the short-term plans for this research project.

Specific Objectives

a) Confirm ASRL prepared materials are representative of commercial catalysts used in the field
b) Determine sulfiding capability of normal operation tail gas conditions
c) Investigate exposure to hydrogen and impact of BTX on long term catalyst activity
d) If time permits in this research year, establish effect of O_2 ingress and ability to recover activity



CRP 2. Ammonium salt vapour pressure under Claus conditions

Commercial Objective

To explore the vapour pressure equilibria for ammonium salts which may deposit in the Claus plant

Environmental Benefit

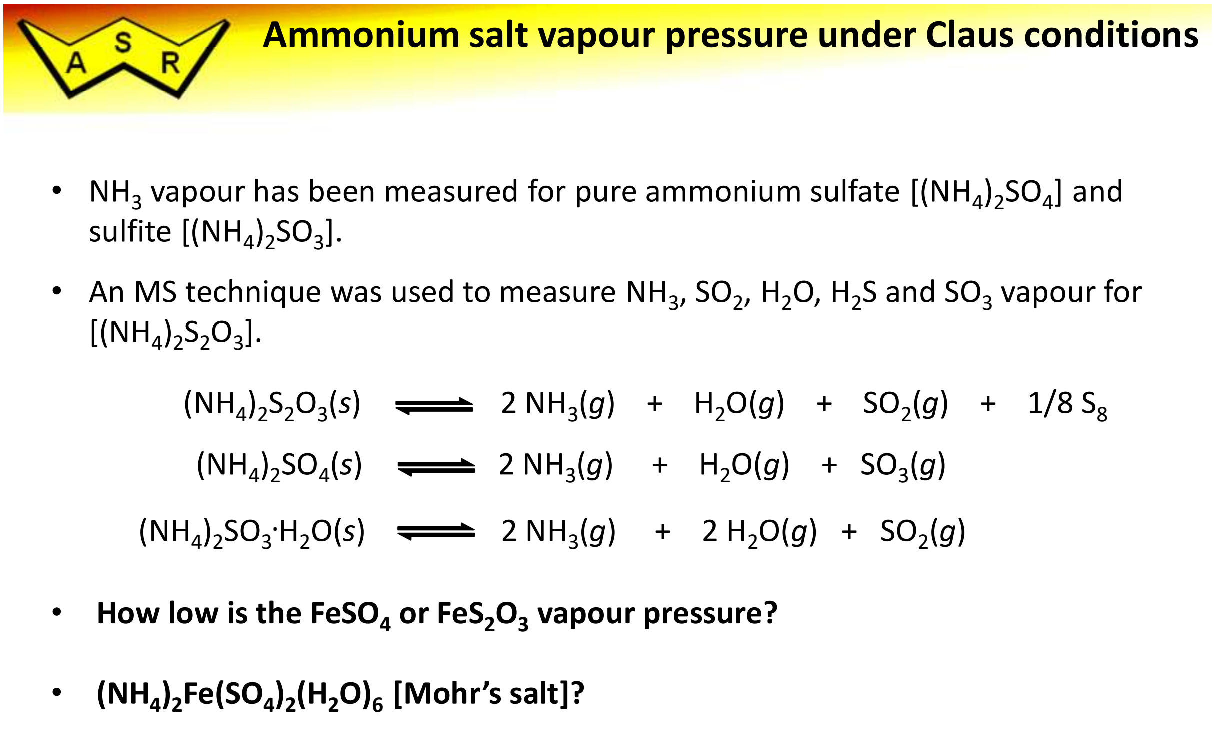
Mitigation of emission risk through flaring or other mechanical failure due to unexpected salt deposition

Project Description

Incomplete ammonia destruction in the furnace or potential ammonia formation can lead to ammonium salt deposition issues in the cold spots; however, these salts require a species to form the anion. With the previous research work in this area, we reported the vapour pressure expressions for 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.

Specific Objectives

a) Follow-up the 2021 publication with a short study for the vapour pressure of iron ammonium sulfates



Ammonium salt vapour pressure under Claus conditions

- NH_3 vapour has been measured for pure ammonium sulfate [$(NH_4)_2SO_4$] and sulfite [$(NH_4)_2SO_3$].
- An MS technique was used to measure NH_3, SO_2, H_2O, H_2S and SO_3 vapour for [$(NH_4)_2S_2O_3$].

$$(NH_4)_2S_2O_3(s) \rightleftharpoons 2\ NH_3(g) + H_2O(g) + SO_2(g) + 1/8\ S_8$$

$$(NH_4)_2SO_4(s) \rightleftharpoons 2\ NH_3(g) + H_2O(g) + SO_3(g)$$

$$(NH_4)_2SO_3\cdot H_2O(s) \rightleftharpoons 2\ NH_3(g) + 2\ H_2O(g) + SO_2(g)$$

- **How low is the $FeSO_4$ or FeS_2O_3 vapour pressure?**
- **$(NH_4)_2Fe(SO_4)_2(H_2O)_6$ [Mohr's salt]?**

CRP 3. High-temperature sulfidation of carbon steel and select alloys

Commercial Objective
To provide laboratory corrosion rates for carbon steel and select alloys under Claus waste heat boiler / molecular sieve regeneration conditions and compare against existing predictive tools

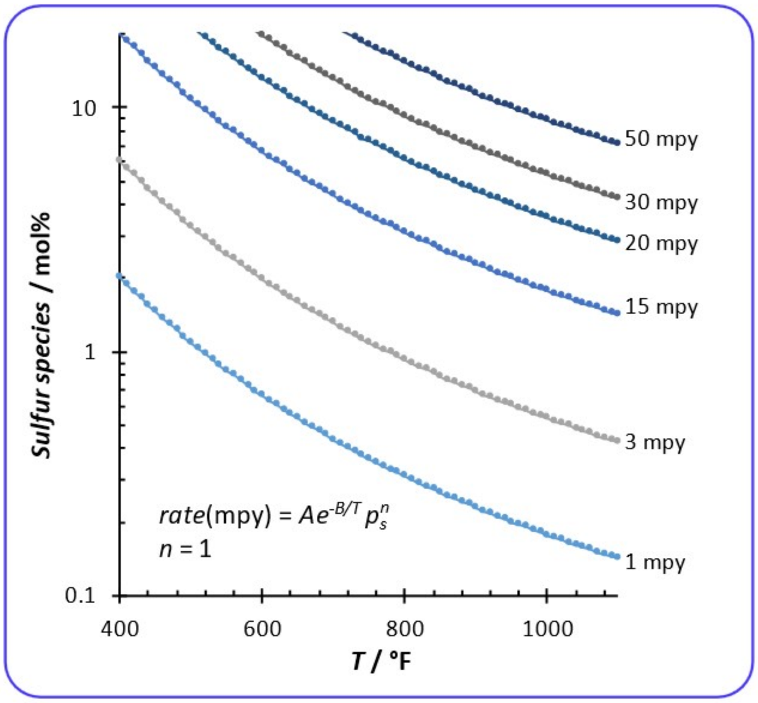
Environmental Benefit(s)
Savings in energy/material and subsequent reduction in CO_2 footprint, through longer service lifetimes

Project Description
Given the current level of interest within the industry, ASRL continues to investigate high-temperature sulfidation of carbon steel and select alloys under simulated Claus WHB conditions and molecular sieve regeneration conditions (direct fired or otherwise). During the last research year, we have corrected our measured rates to account for “onset” versus “steady-state” corrosion rates. While our low-temperature experiments (300-350°C) are in good agreement with the Couper-Gorman curves (naphtha desulfurizers), our research indicates a more significant dependence on total sulfur concentration compared against other existing predictive tools.

Specific Objectives

a) Further probe influence of H_2O and CO_2 on corrosion scale formed which influences the mechanism and corresponding rate order
b) Extend one experiment to 28 days to ensure our rates have indeed stabilized to within the sensitivity of our measurements
c) Given ability for NH_3 to inhibit wet sulphur contact corrosion, asses the impact of adding NH_3 on corrosion rates
d) Conduct representative tests with 310 stainless steel and HR-160 corrosion coupons

High-temperature sulfidation of carbon steel and select alloys



CRP 4. What happens to SO_3 within the Claus catalyst bed?

Commercial Objective

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

Environmental Benefit(s)

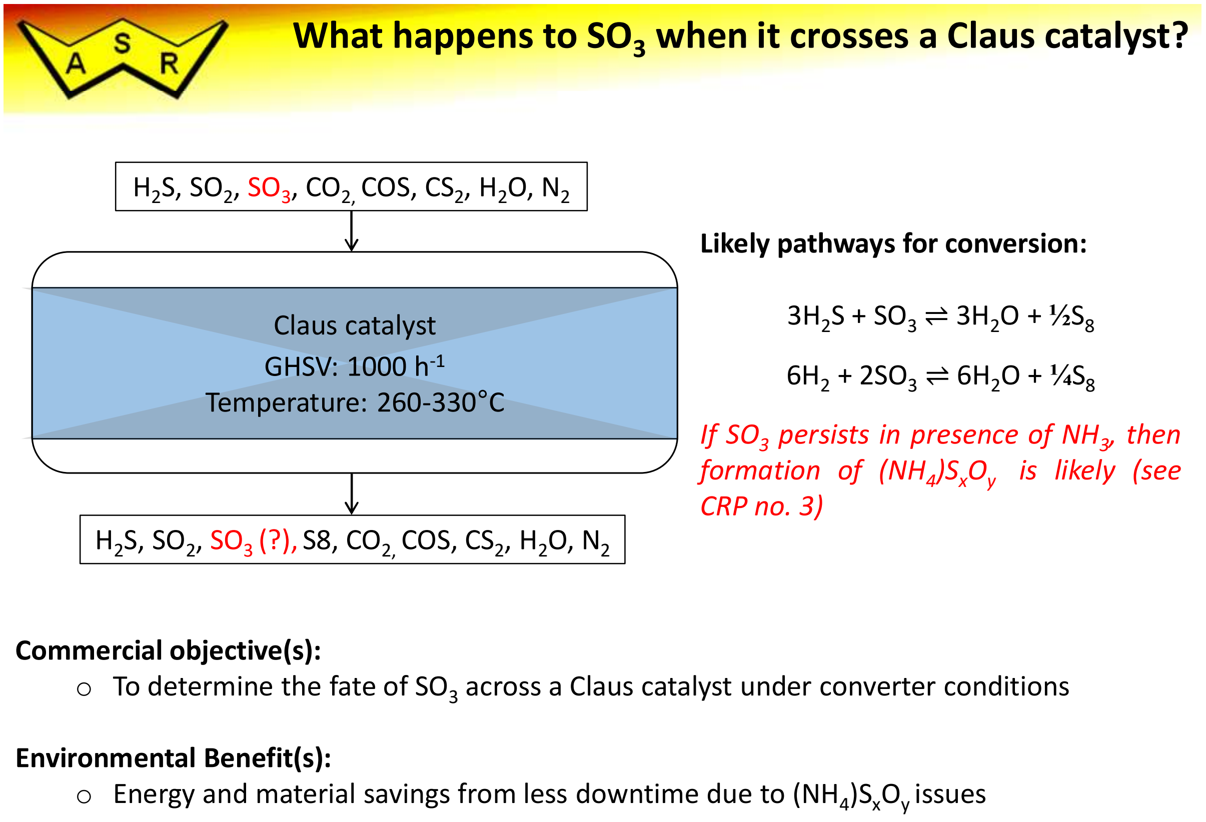
Savings in energy and material by less frequent plant failure / shut down due to corrosion and / or ammonium salt deposition (plant or refinery sustainability)

Project Description

Improperly operated acid gas fired reheaters can lead to the formation of SO_3 which, if able to persist, can lead to unfavourable consequences. In the presence of NH_3, our research has shown the persistence of SO_3 leads to facile formation of $(NH_4)S_xO_y$ salts. Additionally, in the presence of H_2O vapour, persistence of SO_3 can result in condensation of corrosive H_2SO_4. 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 study to investigate the fate of SO_3 across Claus catalysts under first, second, and third converter conditions. The impact of temperature, H_2S concentration, GHSV, 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 under first, second, and third converter conditions
b) Investigate fate of SO_3 across Claus TiO_2 under first, second, and third converter conditions



What happens to SO_3 when it crosses a Claus catalyst?

Likely pathways for conversion:

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

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

If SO_3 persists in presence of NH_3, then formation of $(NH_4)S_xO_y$ is likely (see CRP no. 3)

Commercial objective(s):

- To determine the fate of SO_3 across a Claus catalyst under converter conditions

Environmental Benefit(s):

- Energy and material savings from less downtime due to $(NH_4)S_xO_y$ issues

CRP 5. Sulfuric acid conversion in the Claus thermal reactor

Commercial Objective

To study the decomposition or complications involving the decomposition of sulfuric acid within the Claus thermal reactor

Environmental Benefit(s)

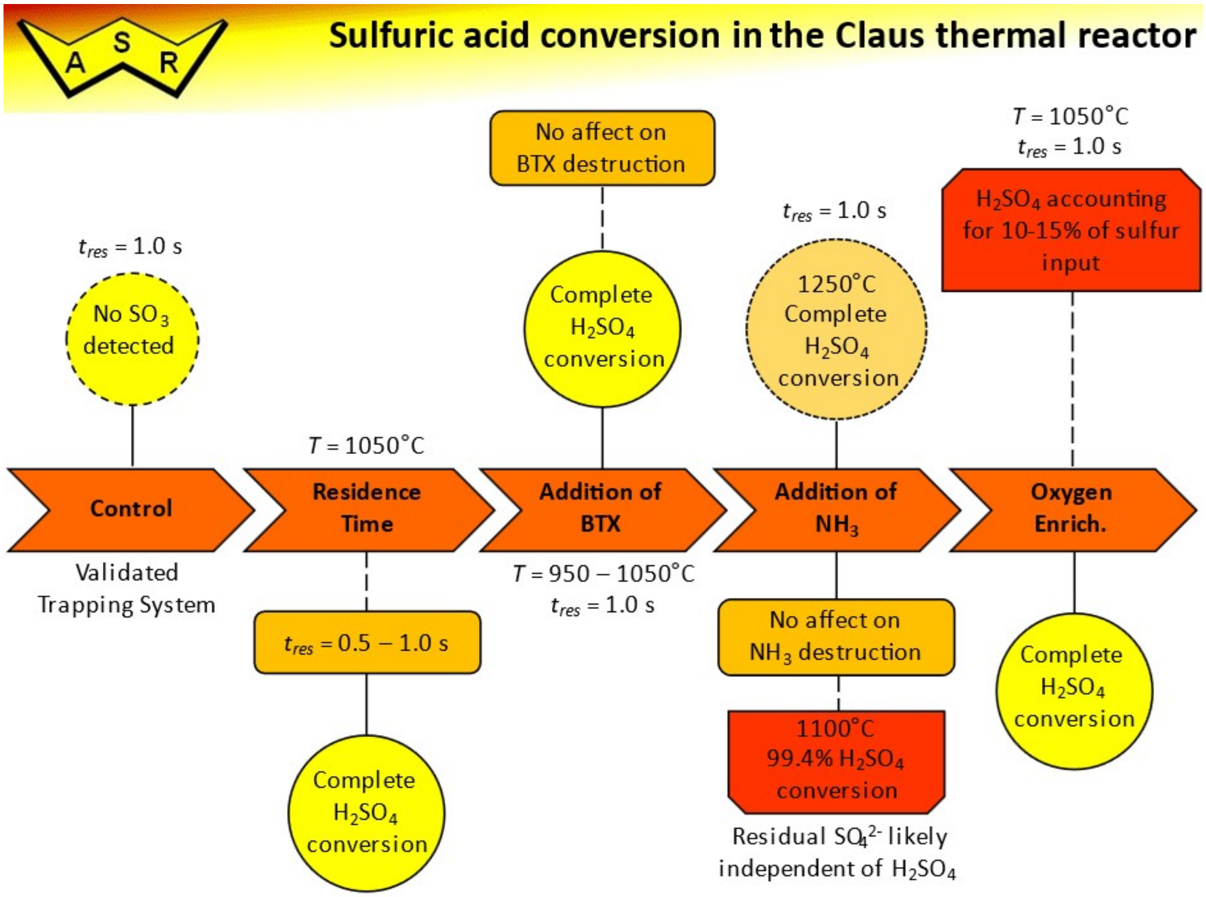
Reduction in CO_2 and SO_2 emissions through higher and more efficient sulfur recoveries; alternative sulfur recovery technologies and/or acid disposal

Project Description

Applications including the disposal of unwanted sulfuric acid and/or emerging tail gas cleanup technologies which destroy H_2SO_4 within the Claus thermal reactor. We previously reported the conversion of H_2SO_4 and its impact on the destruction of contaminants such as CH_4, BTX and NH_3. In all cases, H_2SO_4 addition to the reactor feed did not negatively influence the expected Claus chemistry nor the destruction of the contaminants present. Concentrations of H_2SO_4 as high as 10-15% of the total sulfur input to the thermal reactor were tested and complete H_2SO_4 conversion was still observed. Current studies are probing the kinetic limitations of H_2SO_4 conversion under Claus thermal reactor conditions and revisiting conditions where NH_3 is not fully destroyed.

Specific Objectives

a) Investigate lower limiting temperatures and/or shorter residence times, to establish if there are any kinetic limitations for H_2SO_4 conversion under Claus thermal reactor conditions
b) Probe the influence of H_2S to SO_3 ratio on kinetic limitations determined above



CRP 6. 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 a raw natural gas.

Environmental Benefit

Lower emission levels through more efficient removal of sulfur species

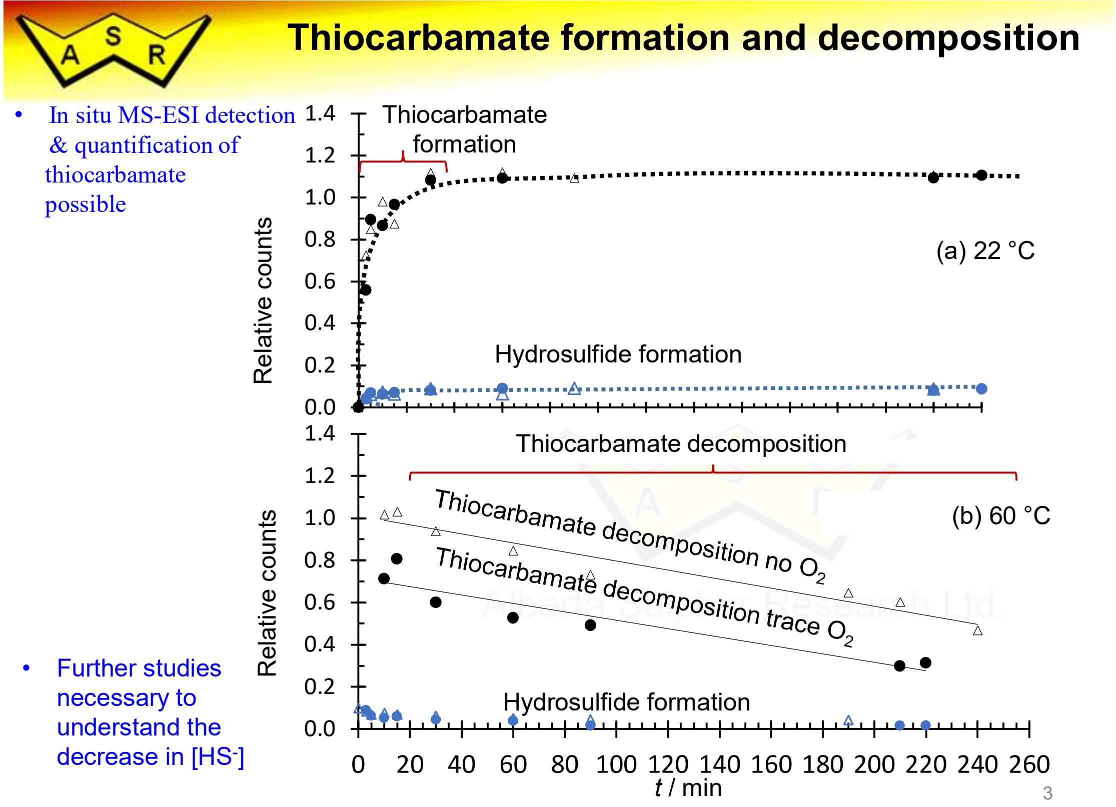
Project Description

The chemistry and kinetics for H_2S and CO_2 removal with alkanolamines are well understood, but COS removal is less certain. Kinetic data for the reaction of carbonyl sulfide (COS) with alkanolamine is important in order to model and optimise treating. For example, it is important to know which kinetic and/or equilibrium parameters are required for simulation during absorption and regeneration. Following the reduction of COS in the gas phase can provide empirical rate information, but gas phase analysis alone do not indicate which reactions are taking place in the aqueous phase. 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 and may lead to thiocarbonate species. This research is designed to look at evolving species in various amine solutions through NMR and ESI-MS. A significant focus of our research has been to develop a method to follow all the relevant anions simultaneously.

Specific Objectives

a) Use mass spectroscopy with electrospray ionisation (MS-ESI) technique to identify and quantify aqueous species *in situ* for COS in amine solvents.

a) Amines of interest include MEA, DEA, TEA, MDEA, DGA, DIPA and piperazine at the temperature range from 25 to 75°C.



Thiocarbamate formation and decomposition

- In situ MS-ESI detection & quantification of thiocarbamate possible
- Further studies necessary to understand the decrease in [HS⁻]

CRP 7. 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)

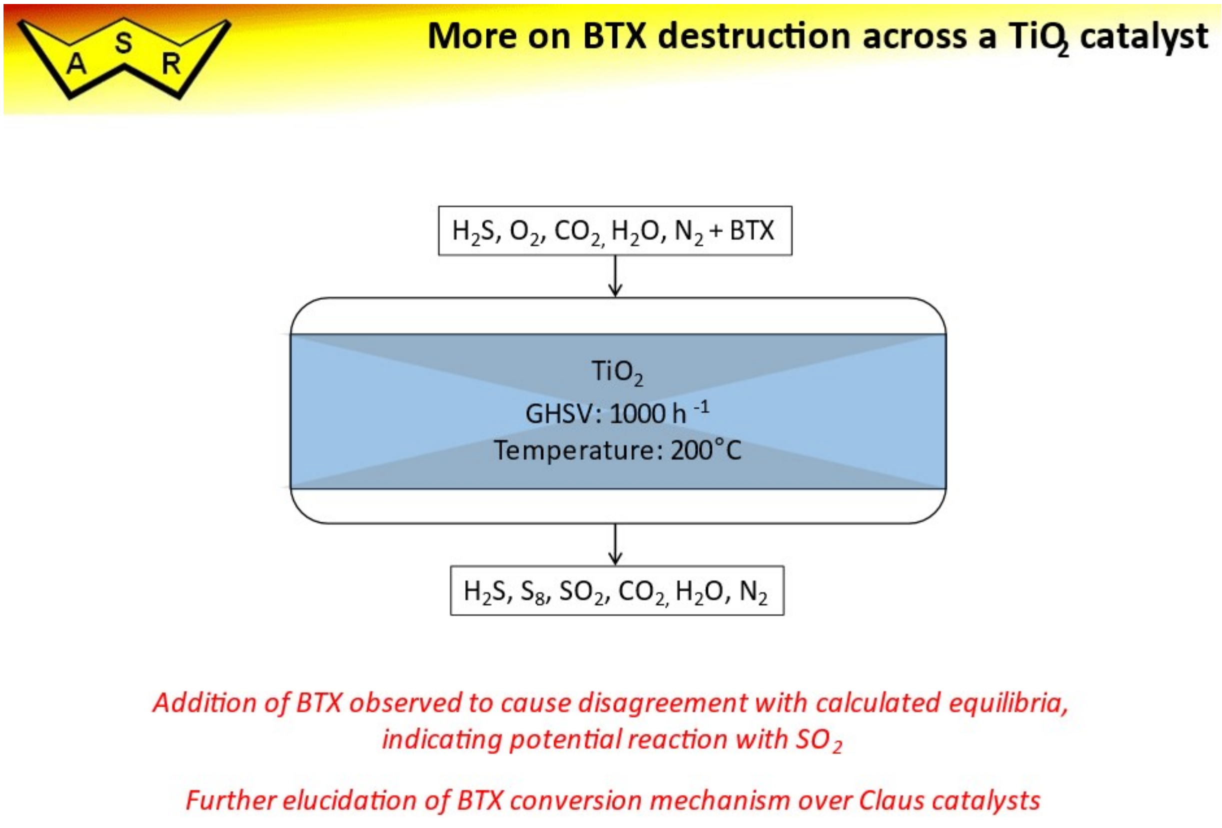
Reduction in SO_2 and CO_2 emissions from higher and more efficient sulfur recoveries

Project Description

Previous research at ASRL 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_2 may also be a viable pathway for BTX destruction. Most noticeable for TiO_2, introduction of BTX to a Claus feed has been observed to correspond with a significant drop in SO_2 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

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) 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_2 catalyst

Addition of BTX observed to cause disagreement with calculated equilibria, indicating potential reaction with SO_2

Further elucidation of BTX conversion mechanism over Claus catalysts

CRP 8. Kinetic studies for the hydrolysis of CS_2 and COS across the Claus catalytic converters

Commercial Objective

To obtain end-of-run kinetic data for CS_2 and COS conversion over Claus catalysts

Environmental Benefit(s)

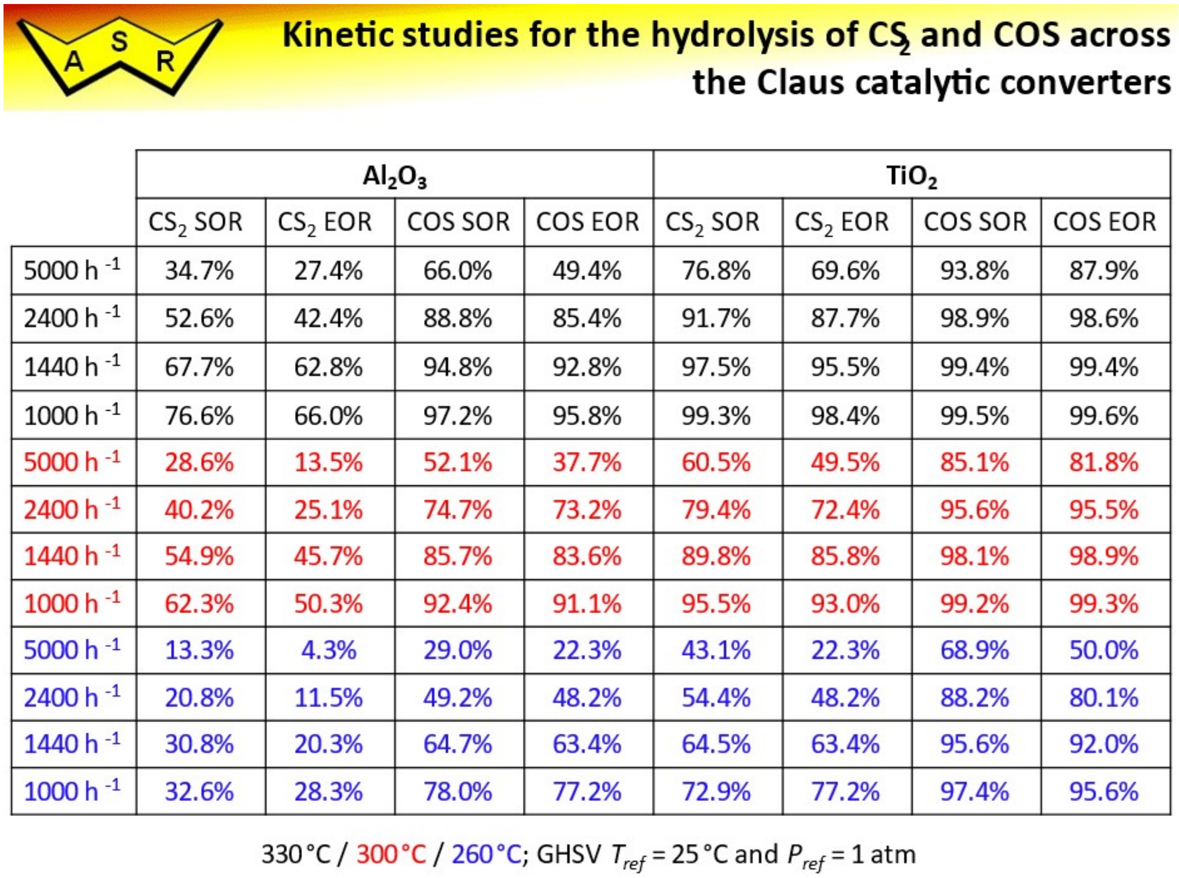
Reduction in SO_2 emissions from more efficient sulfur recovery; less energy required for potentially lower reactor temperatures

Project Description

With a representative first converter feed, we have determined the standard kinetic Arrhenius parameters, E_a and A, for CS_2 and COS hydrolysis over Al_2O_3 and TiO_2 Claus catalysts in start-of-run condition. Current research efforts here involve extending this study to include several commercially available Al_2O_3 and TiO_2 catalysts that have been treated to simulate end-of-run conditions. Initial results indicate our end-of-run experiments potentially cross two different kinetic regions (*i.e.*, diffusional versus chemically limited) while using Al_2O_3 as the catalyst and more data at lower GHSVs may be necessary to confirm this. To date our GHSVs have been reported at $T_{ref} = 25°C$ and $P_{ref} = 1$ atm. During final publication of this research, any kinetic parameters that have been determined will be reported based on GHSVs and residence times at actual conditions.

Specific Objectives

a) Continue to work through remaining commercial samples under end-of-run conditions
b) If time permits, testing new hybrid catalyst and investigate what catalyst properties are beneficial for CS_2 and COS conversion (*e.g.*, surface area, pore size, sulfate poisoning, acidity, basicity, hydrophilicity, etc.)



Kinetic studies for the hydrolysis of CS_2 and COS across the Claus catalytic converters

	Al_2O_3				TiO_2			
	CS_2 SOR	CS_2 EOR	COS SOR	COS EOR	CS_2 SOR	CS_2 EOR	COS SOR	COS EOR
5000 h^{-1}	34.7%	27.4%	66.0%	49.4%	76.8%	69.6%	93.8%	87.9%
2400 h^{-1}	52.6%	42.4%	88.8%	85.4%	91.7%	87.7%	98.9%	98.6%
1440 h^{-1}	67.7%	62.8%	94.8%	92.8%	97.5%	95.5%	99.4%	99.4%
1000 h^{-1}	76.6%	66.0%	97.2%	95.8%	99.3%	98.4%	99.5%	99.6%
5000 h^{-1}	28.6%	13.5%	52.1%	37.7%	60.5%	49.5%	85.1%	81.8%
2400 h^{-1}	40.2%	25.1%	74.7%	73.2%	79.4%	72.4%	95.6%	95.5%
1440 h^{-1}	54.9%	45.7%	85.7%	83.6%	89.8%	85.8%	98.1%	98.9%
1000 h^{-1}	62.3%	50.3%	92.4%	91.1%	95.5%	93.0%	99.2%	99.3%
5000 h^{-1}	13.3%	4.3%	29.0%	22.3%	43.1%	22.3%	68.9%	50.0%
2400 h^{-1}	20.8%	11.5%	49.2%	48.2%	54.4%	48.2%	88.2%	80.1%
1440 h^{-1}	30.8%	20.3%	64.7%	63.4%	64.5%	63.4%	95.6%	92.0%
1000 h^{-1}	32.6%	28.3%	78.0%	77.2%	72.9%	77.2%	97.4%	95.6%

330 °C / 300 °C / 260 °C; GHSV $T_{ref} = 25$ °C and $P_{ref} = 1$ atm

CRP 9. Fate of MEA, DEA and DGA in the thermal reactor

Commercial Objective

To describe the conditions necessary to destroy alkanolamine which has been carried over into the thermal reactor [Could amine carryover potentially result in the formation of ammonia (NH_3) intermediates?]

Environmental Benefit(s)

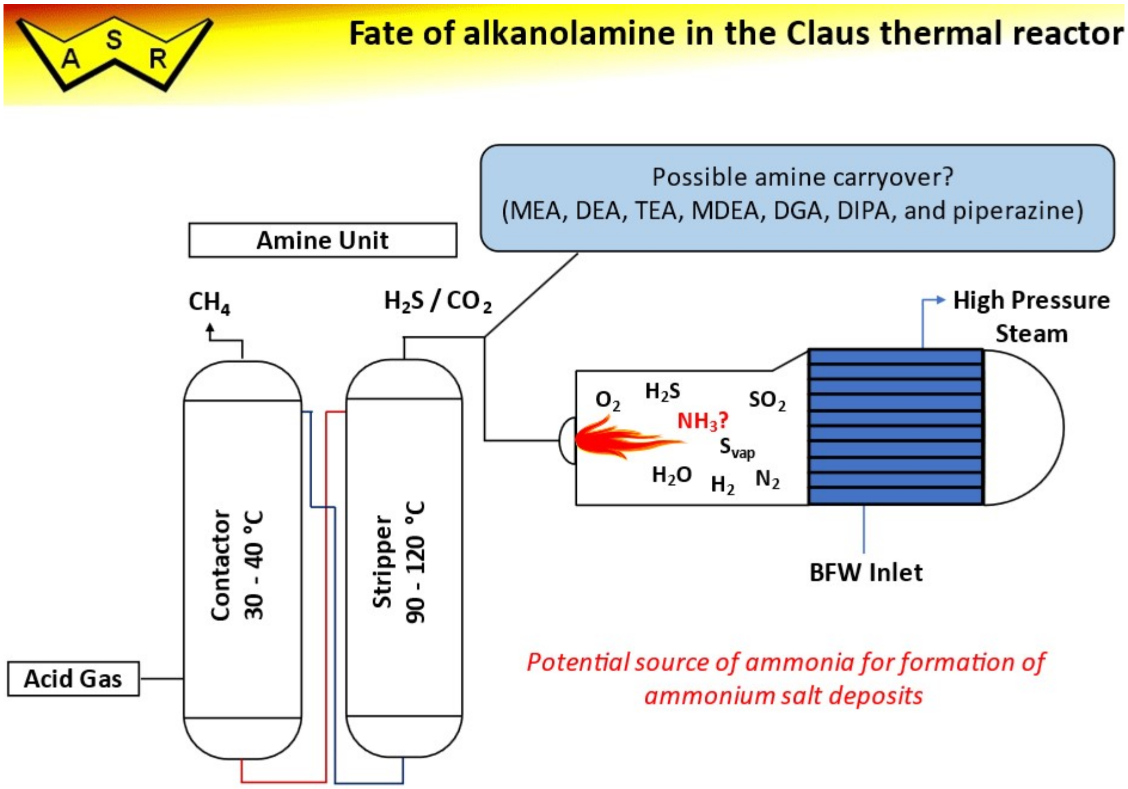
Savings in energy and material by less frequent plant failure / shut down due to ammonium salt deposition (plant or refinery sustainability)

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 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.

Specific Objectives

a) Validate analytical methodology for tracking amine conversion and corresponding destruction intermediates and products
b) By sequentially introducing Claus components to feed, gain mechanistic insight into pathway(s) for conversion
c) Determine kinetic limitations of conversion / destruction



Potential source of ammonia for formation of ammonium salt deposits

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

Commercial Objective

To explore the corrosion inhibition properties for NH_3/ NH_4^+ in different gas processing applications

Environmental Benefit

Reduce potential corrosion issues causing leaks and environmental contamination

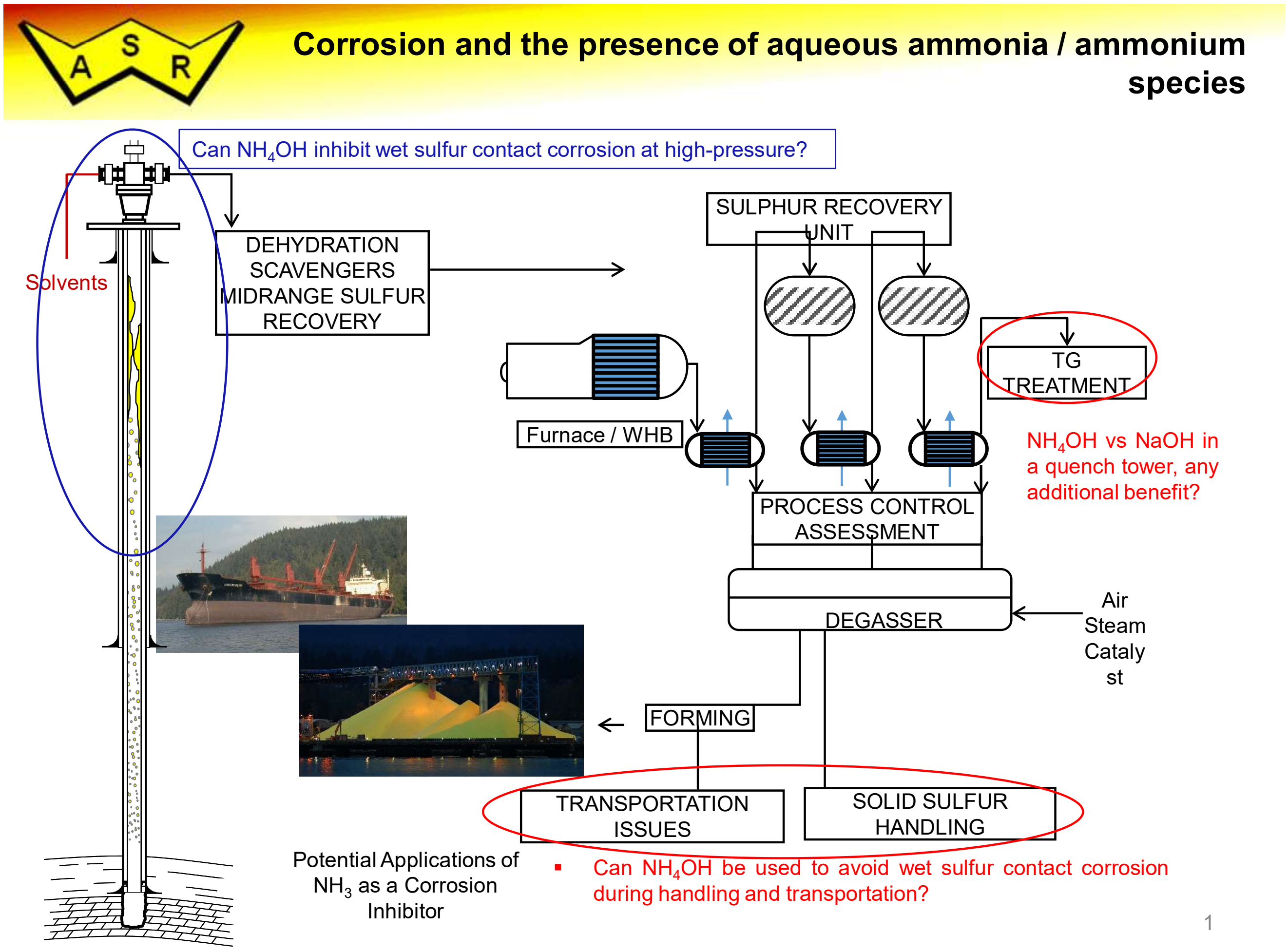
Project Description

Previous research at ASRL has demonstrated the potential benefits of NH_3/NH_4^+ based solvents with respect to wet sulfur contact corrosion inhibition. While previous research covered different applications including sour water stripper operation and some storage applications, the current work seeks to explore high pressure acid gas applications. Questions remain as to whether NH_3/NH_4^+ offer protection from wet sulfur contact corrosion in presence of $CO_2/(NH_4)_2CO_3$? Does pH play a significant role under these conditions?

Specific Objectives

(a) Explore the use of ammonia as a corrosion inhibitor for wellhead and downhole applications. Does NH_4OH inhibit sulfur contact corrosion when CO_2 is present?

(b) Conduct corrosion tests in a Kuentzel vessel (Hastelloy C-276 vessel and coupon holder), for high-pressure applications for low-CO_2 fluids



Corrosion and the presence of aqueous ammonia / ammonium species

Can NH_4OH inhibit wet sulfur contact corrosion at high-pressure?

NH_4OH vs NaOH in a quench tower, any additional benefit?

- Can NH_4OH be used to avoid wet sulfur contact corrosion during handling and transportation?

Potential Applications of NH_3 as a Corrosion Inhibitor

CRP 11. 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

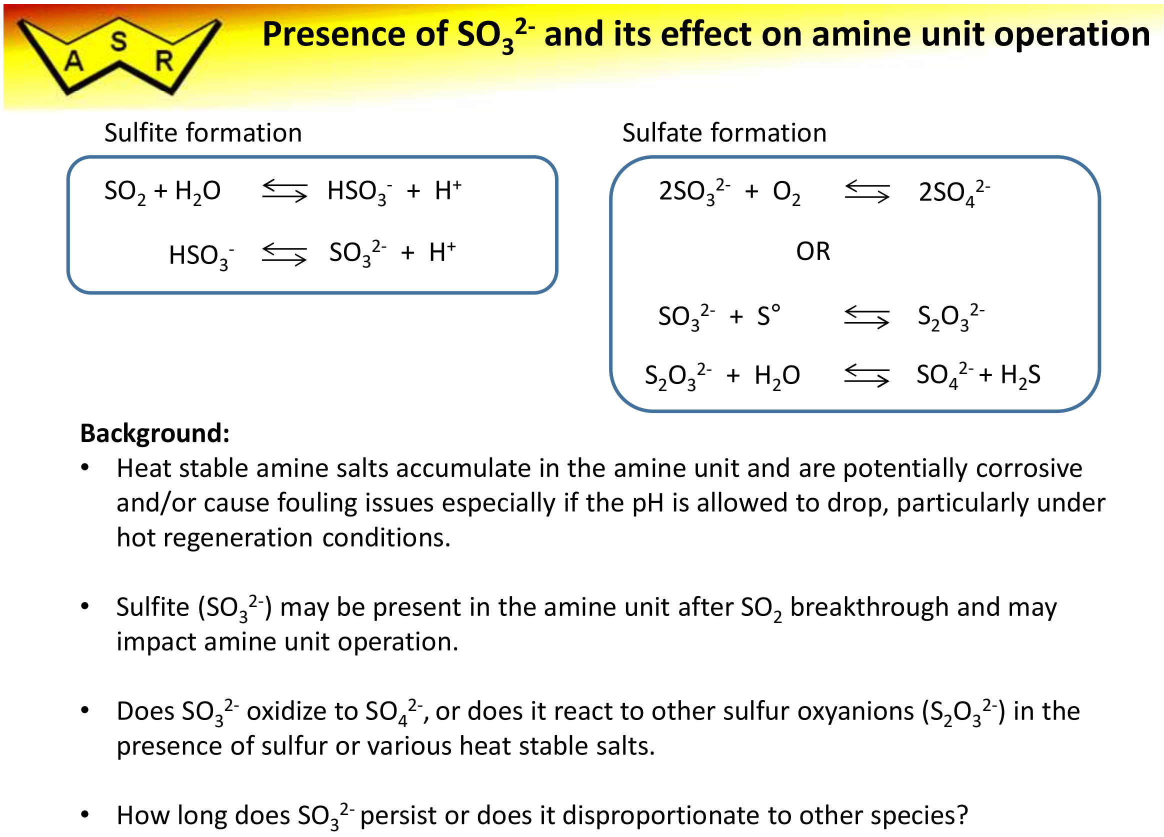
Mitigation of emission risk and corrosion reduction through the potential for amine recovery before excessive formation of heat stable salts

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 is persistent long enough to be purged from an amine system (before thiosulfate). In this context, we intend on reviewing the pH dependant 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.

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



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

Sulfite formation

$$SO_2 + H_2O \leftrightarrows HSO_3^- + H^+$$

$$HSO_3^- \leftrightarrows SO_3^{2-} + H^+$$

Sulfate formation

$$2SO_3^{2-} + O_2 \leftrightarrows 2SO_4^{2-}$$

OR

$$SO_3^{2-} + S° \leftrightarrows S_2O_3^{2-}$$

$$S_2O_3^{2-} + H_2O \leftrightarrows SO_4^{2-} + H_2S$$

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 (SO_3^{2-}) may be present in the amine unit after SO_2 breakthrough and may impact amine unit operation.
- Does SO_3^{2-} oxidize to SO_4^{2-}, or does it react to other sulfur oxyanions ($S_2O_3^{2-}$) in the presence of sulfur or various heat stable salts.
- How long does SO_3^{2-} persist or does it disproportionate to other species?

CRP 12. Impact of H_2S scavengers and reaction products on fouling of refinery equipment

Commercial Objective

To further understand the mechanism and potential mitigation of dithiazine related foulants within refinery equipment

Environmental Benefit(s)

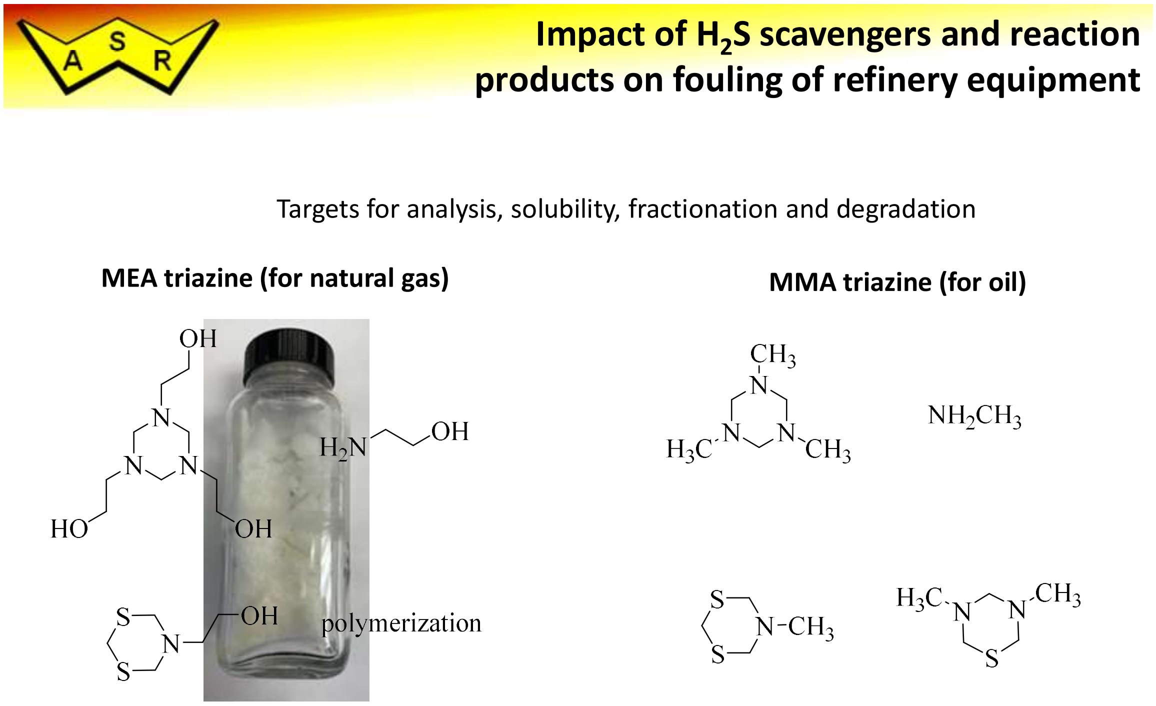
Reduction in free H_2S during transport of crude oil and reduction in refinery fouling

Project Description

With the increase in shale oil production, the transportation of crude oil has undergone a substantial increase in scavenger addition for control of H_2S. Monomethylamine-trianzine (MMA-triazine) is common in treating crude oil, whereas monoethanolamine-triazine (MEA-triazine) is more common in gas treating due to a lower vapour pressure. While the intent is to stop at the dithiazine, MEA-triazine can be susceptible to polymerization (assumed to polymerize in the aqueous phase with high loading of H_2S). Although MEA is water-soluble and expected to be removed with brine in the de-salter (depending on pH), dithiazine can continue into a refinery with the oil phase. Once in the oil preheat train, the thermal degradation of dithiazines or triazines may contribute to potential fouling deposits, for examples see recent publications by Phillips66 and the Canadian Crude Quality Technical Association.

Specific Objectives

a) Investigate/review the partitioning of MEA and MMA-triazine and their respective dithiazine species in aqueous and hydrocarbon phases
b) Determine the distribution and degradation of relevant molecules during fractionation



Impact of H_2S scavengers and reaction products on fouling of refinery equipment

Targets for analysis, solubility, fractionation and degradation

MEA triazine (for natural gas)

MMA triazine (for oil)

CRP 13. Water entrainment in liquid sulfur

Commercial Objective

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

Environmental Benefit(s)

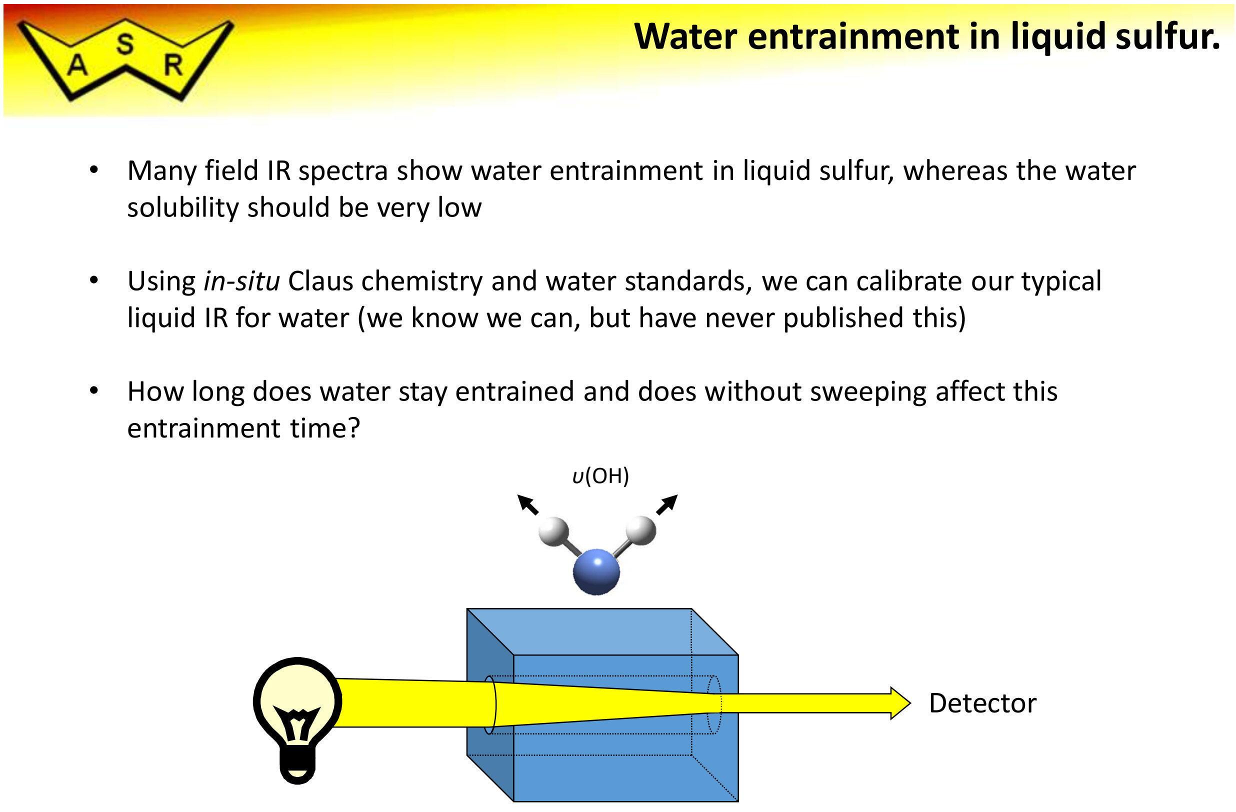
Increased safety and corrosion understanding related to liquid sulfur storage

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 expected to be only slightly soluble in sulfur (more volatile that 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.

- 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 14. Molecular sieve dehydration in sour service [NSERC ASRL IRC Funding]

Commercial Objectives: To provide reference quality information for simulation / design of molecular sieve dehydration and estimation of material deactivation (lifetime)

Environmental Benefit(s): Safer transportation (lower corrosion), longevity in adsorbent materials and reduced shutdowns / unscheduled service events

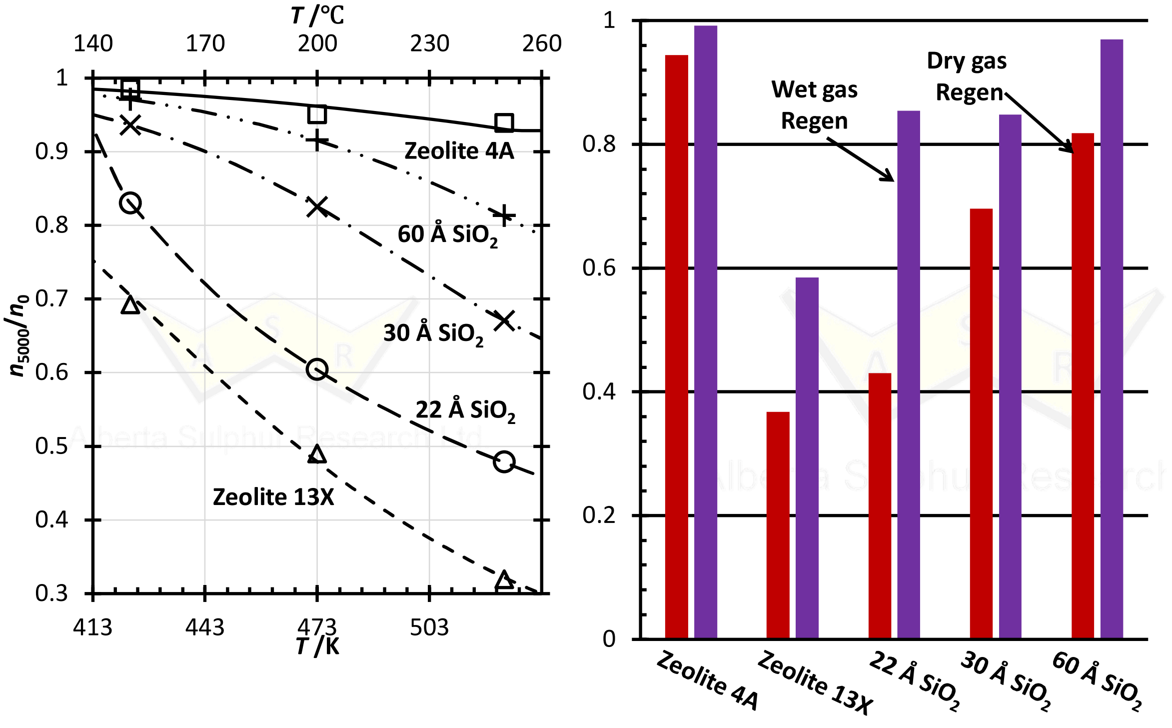
Project Description: Molecular sieves are used for dehydration of sour gas which is produced in remote locations, where gathering and transport lines are protected from corrosion and hydrate issues. In addition, the liquefaction of natural gas requires deep dehydration which is also achieved with molecular sieves. Robust multicomponent adsorption models are required to optimize the thermal regeneration of these processes for several reasons, including adsorbent material degradation and/or deactivation over thousands of cycles. In the past 8 years, our laboratory has built multiple high-pressure adsorption instruments which can handle H_2S, COS, CO_2 and other natural gas contaminants. High-pressure adsorption isotherms for pure and mixed fluids have been measured for calibration of reference quality models which are now being used to simulate bed cycling and optimization under sour gas conditions. New research has turned to material deactivation and extended cycling. This research is funded through NSERC-ASRL IRC grant program.

Specific Objectives

a) Report new measurements/models for pure fluid isotherms on 22 Å and 30 Å pore silica gels
    - Investigate the influence of pore size on silica gel absorption modelling
b) Perform extended cycling tests for adsorbent degradation on zeolite 13X, 4A and silica gels
c) Investigate ZSM5 and DDR degradation to further understand the role of the Si/Al ratio

Molecular sieve dehydration in sour service

Temperature dependence of desiccant degradation after 5000 cycles



CRP 15. 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)

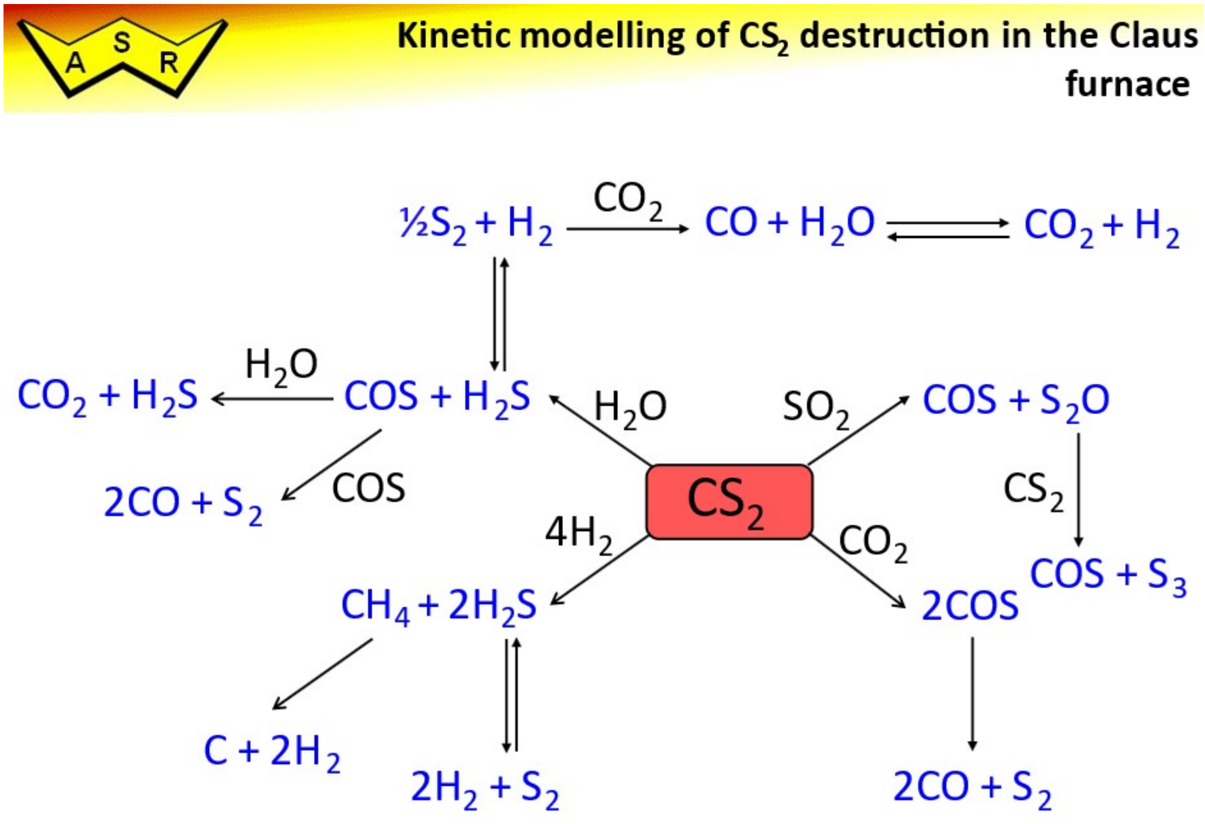
Reduction in SO_2 and CO_2 emissions from higher and more efficient sulfur recoveries

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 time. 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 16. Trace sulfur sampling from hydrocarbon streams

Commercial Objective

Testing alternative methods for quantifying elemental sulfur in surface natural gas streams

Environmental Benefit

Reduced transport and production failure with flow assurance and reduced extraneous corrosion

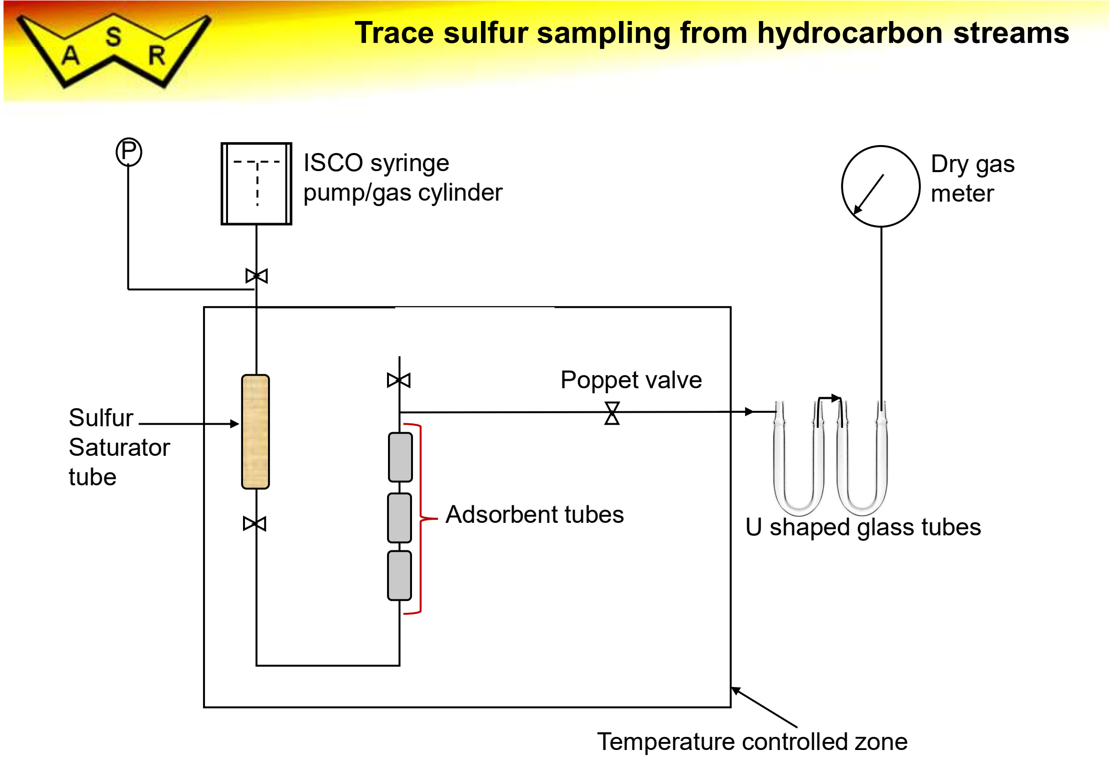
Project Description

Low levels of elemental sulfur in pipeline gas have caused several issues with regulators and metering. Common source of elemental sulfur is reaction of H_2S with oxygen following oxygen ingress during gas compression, which also can cause failure of both centrifugal and reciprocating compressors. One current method for sampling trace levels of sulfur is the ASTM D7800 which involves flowing the gas stream through bubblers that are prefilled with a triphenylphosphine solution. The sulfur reacts with triphenylphosphine to form the sulfur triphenylphosphine sulfide compound (TPPS), which can be analysed using phosphorous specific Gas Chromatography. With this method, lower 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. We are proposing the use of non-oxidizing adsorbents with very small vapour pressure, as an alternative technique 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 will be tested for sulfur removal efficiency using methane gas as carrier gas ($T < 50$°C and various flow rates).

(b) A hydrocarbon liquid synthetic mixture also will be tested (to confirm accuracy with rich streams).



CRP 17. Selective adsorption of sulfur species using activated carbons derived from petroleum coke [NSERC ASRL IRC Funding]

Commercial Objectives: To explore the feasibility of selective adsorption of H_2S from a sour gas and/or SO_2 from a flu gas (and tail gas) with a regenerable adsorbent (activated carbon) made from a waste product (petroleum coke)

Environmental Benefit(s): Reduction in SO_2 emissions either by desulfurization of fuel or flue gas in addition to potential increase in sulfur recovery

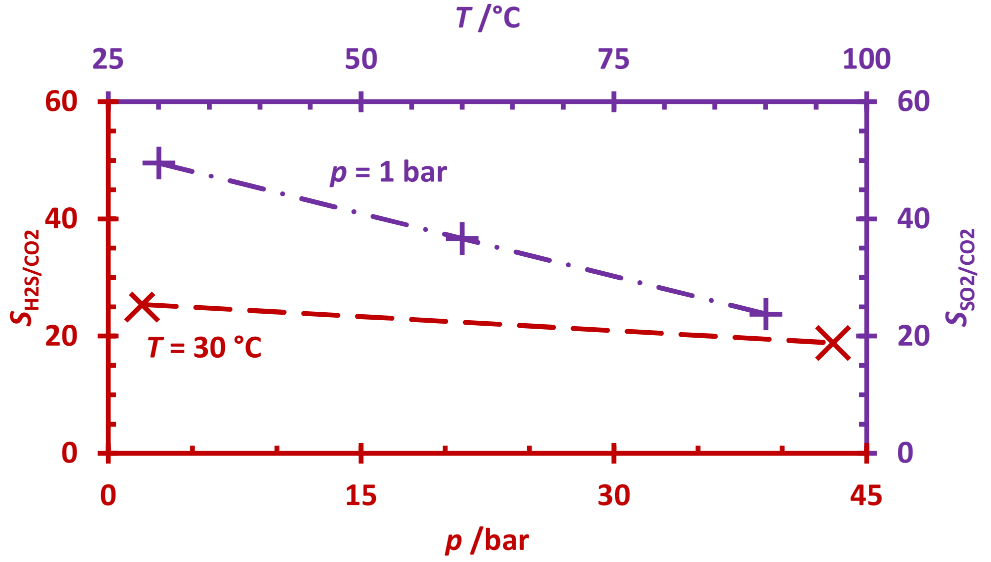
Project Description: Activated carbons are important industrial materials often used for the purification of air, water and industrial emissions. These materials show promise for use in remote/mobile emitters, such as ships, where the use of a large infrastructure to purify emissions is not possible. Activated carbons from waste petroleum coke, when activated, show a high selectivity for H_2S and SO_2 over CO_2, CH_4 and H_2O, making them potential materials for the separation of H_2S and SO_2 from other fluids. Recent work has utilized a custom breakthrough apparatus (MS detection) to rapidly determine gas selectivity on several carbon materials. These measurements will now extend to sour gas at high-pressure (plant inlet), flue gas at low-pressure and tail gas at low-pressure. This research is funded through NSERC-ASRL IRC grant program.

Specific Objectives

a) Screen a variety of petroleum coke activated carbons for comparison to the first batch tested (single component isotherms and dynamic breakthrough)
b) Utilize reference multicomponent modelling to model bed breakthrough and regeneration
c) Investigate empirical correlations for extrapolation to other materials and gases

Selective adsorption of sulfur species using activated carbons derived from petroleum coke

Multicomponent experiments show a high selectivity for H_2S and SO_2 over CO_2.



CRP 18. 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

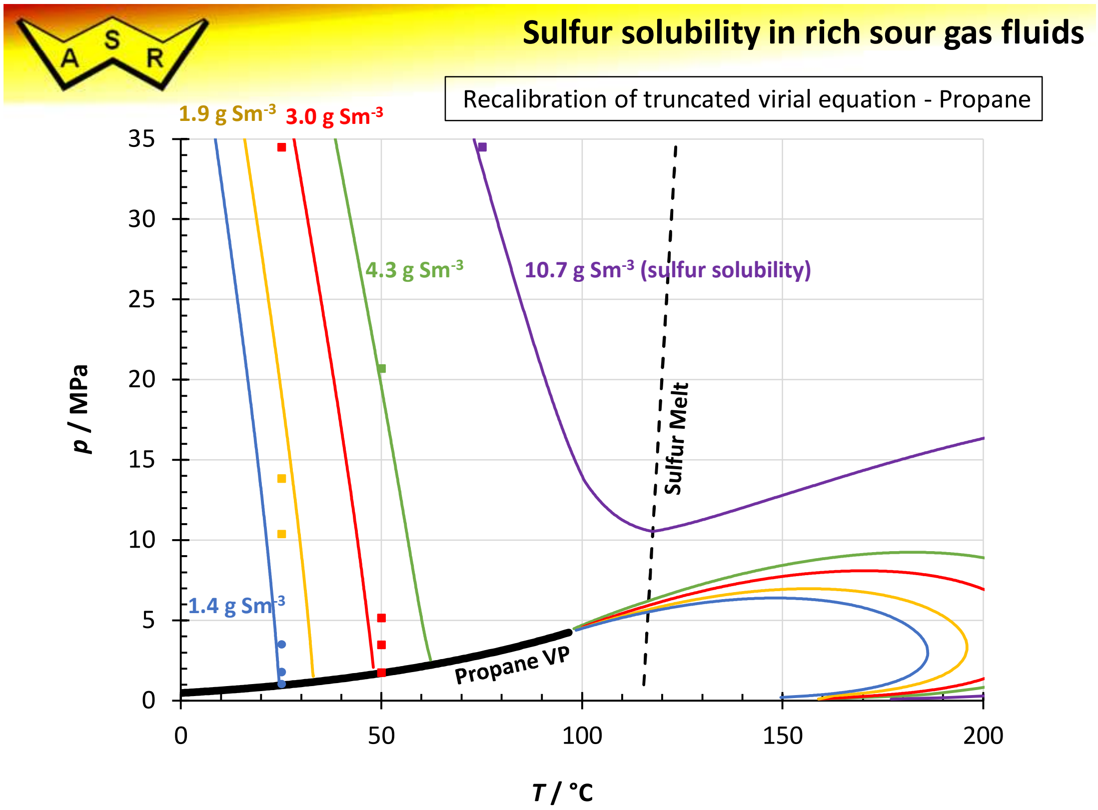
Understanding sulfur solubility is important for predicting and mitigating potential deposition at well heads, pipes and regulators if solubility limit is exceeded. ASRL has historically studied elemental sulfur deposition in the context of native reservoir sulfur, which is limited to very lean hydrocarbons. 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 and butane. Additional ethane, butane and CO_2 data are currently being measured.

Specific Objectives

a) Measure additional sulfur solubility in ethane, butane and CO_2 $T > 25°C$ and $P < 20$ MPa.

b) Recalibrate the ASRL sulfur solubility model based on the new data to verify the grouping of virial coefficients.

c) Test the correlation by measuring the solubility in a synthetic rich sour natural gas.



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

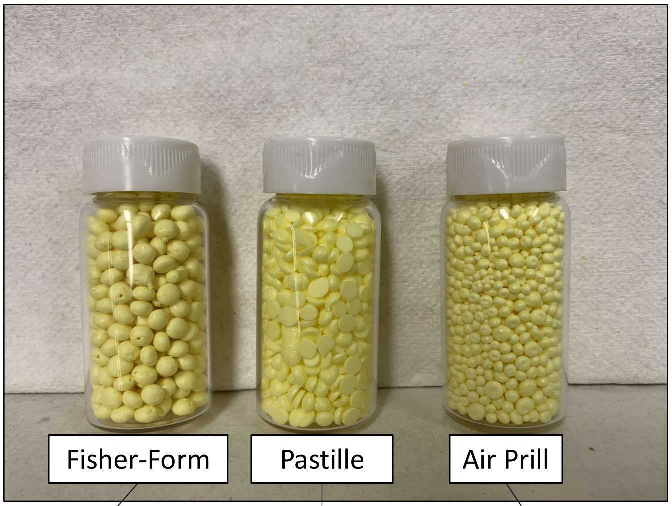
<u>Environmental Benefit(s)</u>: Understanding of factors which lead to dust explosions and / or more aggressive wet sulfur contact corrosion during shipping and transport

<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. With controlled batches of water formed prills, commercial air prills, commercial pastilles and lab formed pastilles (product made within the ASRL labs), we have been following 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.

<u>Specific Objectives</u>

a) Report new polymetric solid annealing rates in QB

The age and friability for different modern forms of elemental sulfur



Lab-scale wet form

Commercial air prills

Lab-scale
IPCO Rotoform

CRP 20. Phase equilibria of high-pressure sour gas and LPG mixtures at the hydrate phase boundary [NSERC ASRL IRC Funding]

Commercial Objectives: Provide reference quality models for water content above acid gas and NGL hydrates

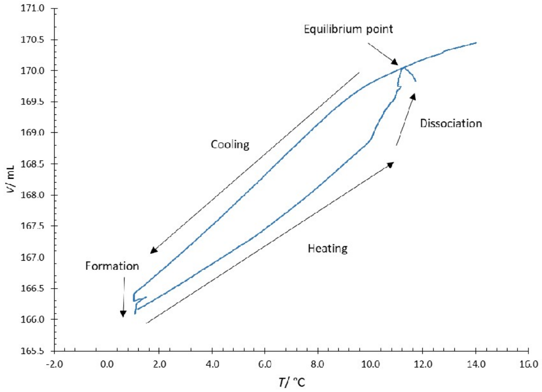
Environmental Benefit(s): Safer transportation

Project Description: With LNG, acid gas injection and cryogenic separation processes, there is the need to understand and simulate how low water streams behave, e.g., how much water is too much? For many of these fluids, gas-hydrate compounds are potential solids being formed and high-pressure liquids will have a different water holding capacity when compared to a high-pressure gas. The H_2S, CO_2 and propane hydrate decomposition conditions in the presence of liquid water have previously been studies by in our labs. In this work the enthalpies for hydrate formation and binary phase boundaries for Type I with Type II formers are being studied. There is an immediate need for high-pressure water contents for mixed fluids, including rich sour gases or LPGs. This research is funded through NSERC-ASRL IRC grant program.

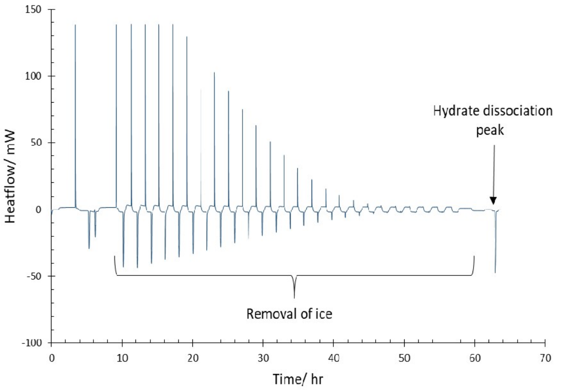
Specific Objectives

a) Investigated H_2S and CO_2 formation enthalpies in the liquid-liquid region using DSC
b) Produce phase boundary information to test how much propane is necessary for type II Hydrate structures
c) Investigate hydrate enthalpies and boundaries for LPG mixtures (Type II)

Phase equilibria of high-pressure sour gas and LPG mixtures above the hydrate phase



CO_2 hydrate Isobaric-Volume search at 13.7MPa using an autoclave coupled to an ISCO pump



An example thermogram obtained from a micro-differential scanning calorimeter. The thermogram is used to obtain a hydrates dissociation enthalpy

CRP 21. Low CO_2 emission technology for manufacture of propylene and butylenes

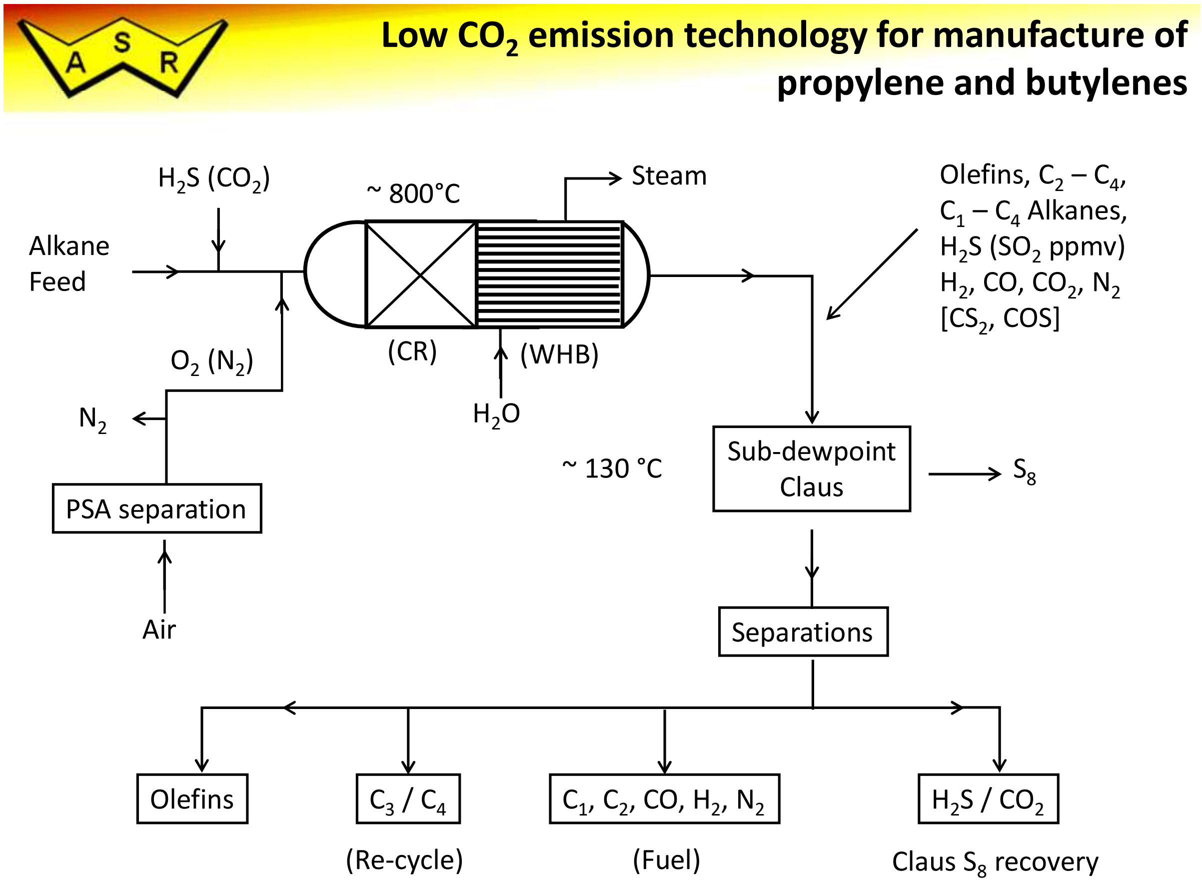
Commercial Objective: To improve the potential technology for selective conversion of propane and butane to propylene and related olefins

Environmental Benefit(s): Reduction of environmental footprint of CO_2 associated with olefin production.

Project Description: Previously ASRL has examined production of ethylene, propylene and butylene by partial oxidation of small hydrocarbons with sulfur. The sulfur may be added directly to the feed hydrocarbons or formed in situ by reaction of H_2S with O_2. The advantage of the latter process is that olefins can be formed selectively, and the process is nearly autothermal. Recently, member companies have expressed renewed interest in this potential technology because of increased amounts of propane and butane produced with shale gas and because the technology is a low CO_2 emissions process. Although ASRL has already conducted a large amount of work in this area, there are still improvements to be explored for coke reduction and product clean-up. A catalyst system is being explored to lower the temperature for conversion (lower coke), an acid gas feed containing CO_2 will be tested, and a SWSG feed will be tested. The key drivers are (i) to lower H_2S and/or SO_2 in the product to reduce clean-up costs, (ii) to lower the temperature to reduce coke formation and (iii) to potentially explore a larger pressure for higher thermal efficiency.

Specific Objectives

a) Further explore using V_2O_5/SiO_2 at longer residence times / lower temperatures
b) SWSG feeds, where NH_3 may allow for clean-up of H_2S and SO_2 upon quench



Low CO_2 emission technology for manufacture of propylene and butylenes

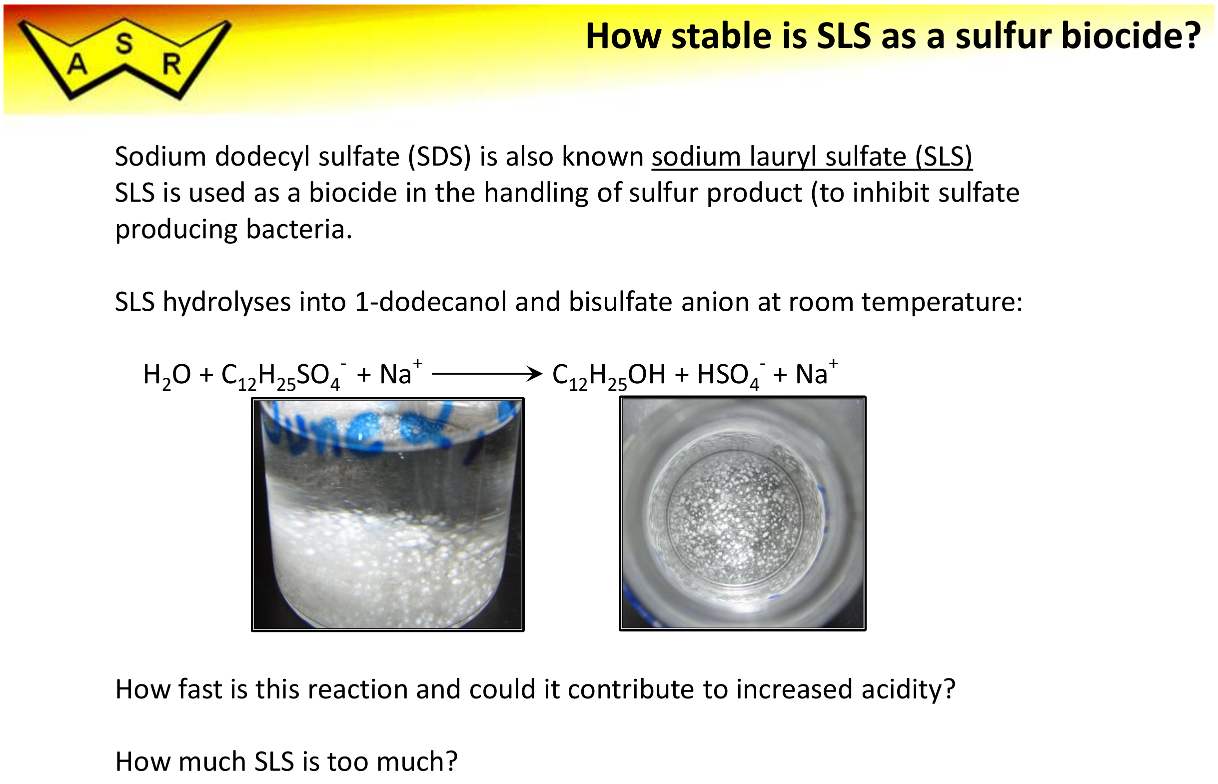
CRP 22. How stable is SLS as a sulfur biocide?

Commercial Objective
To determine if the application of extraneous SLS can lead to excess sulfate / corrosion through hydrolysis

Environmental Benefit(s)
Reduction in sulfur related contact corrosion and acidic contamination

Project Description
Sodium lauryl sulfate (SLS) is commonly applied to sulfur as a biocide which inhibits sulfate producing bacteria. While SLS is not the only biocide on the market, it is cost effective and applied at many handling locations. We investigated SLS in 2014 when researching the stability of fracture fluid additives and found that SLS underwent hydrolysis to product bisulfate. Based on earlier ASRL research, significant amounts of bisulfate would be expected to enhance sulfur contact corrosion. While this sulfate production reaction is slow at room temperature, we have yet to measure the hydrolysis rates on elemental sulfur. Would excess SLS lead to corrosion or acid formation, despite the objective of reducing acid forming bacteria and / or how fast is any SLS degradation. This research may lead to suggestions regarding limits in overall SLS application and or alternative biocides.

Specific Objectives
a) Measure the hydrolysis rate of SLS with and without the presence of elemental sulfur
b) Attempt to quantify pH and / or any changes to sulfur contact corrosion



How stable is SLS as a sulfur biocide?

Sodium dodecyl sulfate (SDS) is also known sodium lauryl sulfate (SLS)
SLS is used as a biocide in the handling of sulfur product (to inhibit sulfate producing bacteria.

SLS hydrolyses into 1-dodecanol and bisulfate anion at room temperature:

$$H_2O + C_{12}H_{25}SO_4^- + Na^+ \longrightarrow C_{12}H_{25}OH + HSO_4^- + Na^+$$

How fast is this reaction and could it contribute to increased acidity?

How much SLS is too much?