



ALBERTA SULPHUR RESEARCH LTD.
Center for Applied Catalysis and Industrial Sulfur Chemistry
University Research Centre, #6 - 3535 Research Road N.W.
Calgary, Alberta, Canada T2L 2K8
Country Code: 001 Office: 403 - 220 - 5346 Fax: 403 - 284 - 2054
E-mail: asrinfo@ucalgary.ca
Website: www.chem.ucalgary.ca/asr/

ASRL CORE RESEARCH PROGRAM
April 1st, 2012 – March 31st, 2013

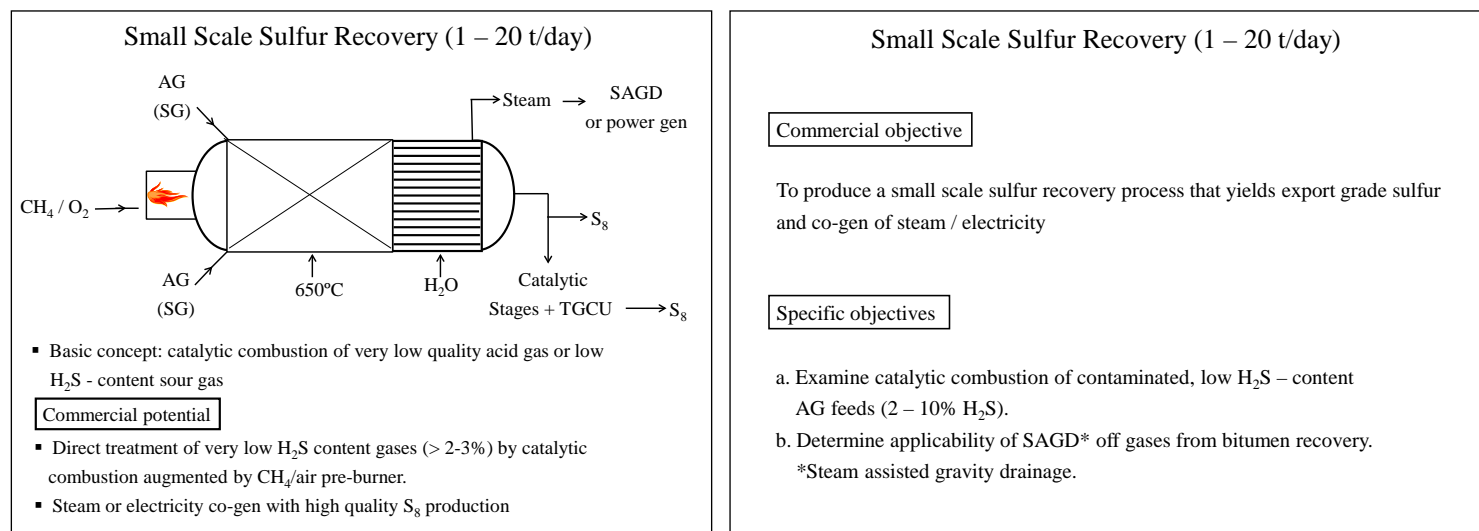
The research program described in the following pages has been compiled with input of the member companies and research staff of ASRL. The research projects were evaluated by the members of the Technical Advisory Committee (TAC) (listed below) and are compiled in the priority as per the TAC evaluation.

MEMBERS OF THE TAC

- Leslie May - BAKER PETROLITE.
- J.K. Chen - CHEVRON ENERGY TECHNOLOGY COMPANY.
- Vincent Wong – FLUOR CORPORATION
- Robert Mann - HAZCO ENVIRONMENTAL AND DECOMMISSIONING SERVICES.
- Jon Gorrie - HUSKY ENERGY INC.
- Sander Kobussen - JACOBS /COMPRIMO SULFUR SOLUTIONS.
- David Stevens - KPS TECHNOLOGY & ENGINEERING LLC.
- Bruce Klint – SULPHUR EXPERTS INC.
- Gavin Proudfoot – SUNCOR ENERGY
- Paul Davis – ALBERTA SULPHUR RESEARCH LTD.
- Peter Clark - ALBERTA SULPHUR RESEARCH LTD.
- Norman Dowling - ALBERTA SULPHUR RESEARCH LTD.
- Robert Marriott - ALBERTA SULPHUR RESEARCH LTD.

LIST OF CORE RESEARCH PROJECTS

1. Small Scale Sulfur Recovery (1 – 20 ton/day)



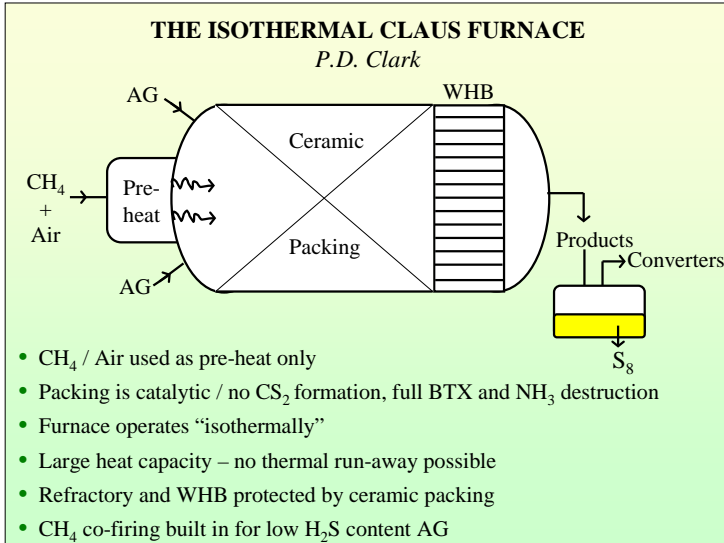
Commercial objective: To produce a small scale sulfur recovery process that yields export grade and co-gen of steam / electricity

Einstein commented that “things should be as simple as possible, but no simpler”. Existing small scale sulfur recovery processes probably do not meet this definition. One of the major difficulties with non-Claus sulfur recovery processes is that they either produce a waste product or impure sulfur, an increasingly important aspect of modern industrial processes. Thus, it is suggested that small scale recovery revert to a Claus type process, but one involving catalytic combustion to overcome the issue of contaminated feeds. This approach incorporates the knowledge gained in the ongoing ASRL research on catalytic combustion of more standard Claus feeds and is different to the Selectox approach in that minimum temperature for the catalytic combustion stage would be 600°C. As is illustrated in the accompanying figure, very low H₂S-content feeds could be accommodated with varying degrees of fuel gas combustion. The important aspect of this approach is that contaminants such as hydrocarbons, including methane and mercaptans would be oxidized in the catalytic stage. Some of the hydrocarbon would end up as CO/H₂ by virtue of the partially oxidizing conditions but these species could be dealt with in the final incineration (catalytic or thermal) stage. As indicated in the Figure, a key aspect of such a process would use heat recovery to produce a co-gen process for steam, electricity and electricity production.

Specific objectives:

- (a) Examine catalytic combustion of contaminated, low H₂S – content AG feeds (2 – 10% H₂S).
- (b) Determine applicability of SAGD (Steam Assisted Gravity Drainage) off gases from bitumen recovery.

2. Catalytic Combustion in a Ceramic-packed Claus Furnace



Catalytic Combustion in Ceramic-Packed Claus Furnaces

Commercial objective:

To develop a simplified process for acid gas combustion and low quality acid gas treatment

Specific Objectives:

- Demonstrate the packed chamber approach for acid gas light off and acid gas conversion (complete)
- Determine catalytic effects for BTX and hydrocarbon conversion (complete).
- Examine ammonia destruction at the adiabatic temperature for this system (complete).
- Conduct long term test to determine catalyst lifetime potential.

Commercial objective: to develop a simplified process for acid gas combustion and low quality acid gas treatment

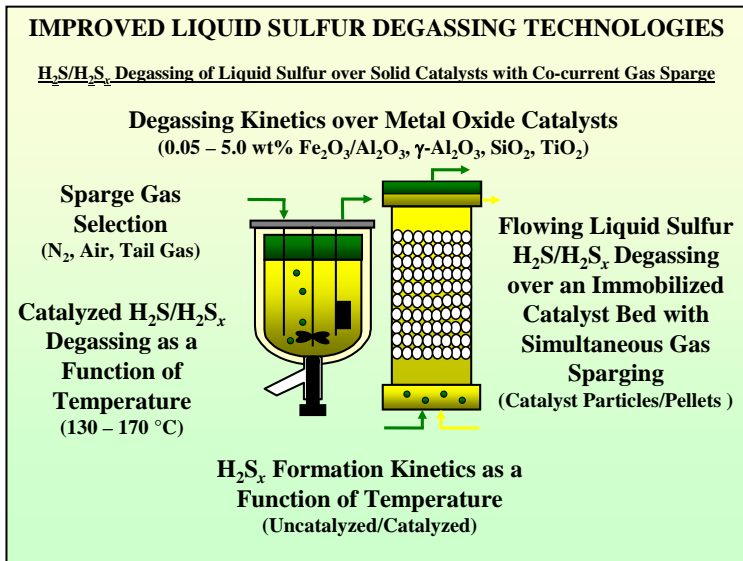
Previously, it has been demonstrated that catalytic combustion of low quality AG containing BTX results in complete conversion of BTX at 900° C along with Claus conversion according to equilibrium expectations. T and X conversion were complete at 700° C and in all experiments trace hydrocarbons were oxidized to CO₂ and water. Also, it was found that catalytic combustion of NH₃-containing AG resulted in complete ammonia destruction at temperatures ca. 200° C below those required for a gas phase combustion.

The catalyst is alumina stabilized by a rare earth oxide deposited on a cordierite monolith. It is believed that this catalyst formulation will be stable at the adiabatic temperatures obtained for both rich and lean acid gas. Studies in the 2012 – 2013 period will focus on long term stability and activity of the catalyst by conducting long term activity tests.

Specific Objectives:

- Demonstrate the packed chamber approach for acid gas light off and acid gas conversion (complete).
- Determine catalytic effects for BTX and hydrocarbon conversion (complete).
- Examine ammonia destruction at the adiabatic temperature for this system (complete).
- Conduct long term test to determine catalyst lifetime potential.

3. Improved Liquid Sulfur Degassing Technologies



Improved Liquid Sulfur Degassing Technologies

Commercial objective:

To examine the technology and chemistry for solid catalyst liquid sulfur degassing

Specific Objectives:

- Complete work simulating formation of H₂S_x during sulfur condensation and degassing of liquid sulfur in the thermal condenser
- Publish the experimental degassing data accumulated during the project.

Commercial objective: To examine the technology and chemistry for solid catalyst liquid sulfur degassing.

Over the last 3 years, the ASRL core research program has investigated the chemical mechanisms of degassing with solid catalysts. One of the major findings has been that solids such as Claus alumina can be used effectively with a variety of sparge gases including Claus tail gas. The degree of degassing obtained with Claus tail gas is a function of the H₂S partial pressure but < 10 ppmw residual total H₂S can be achieved using tail gas typically obtained from the second catalytic converter.

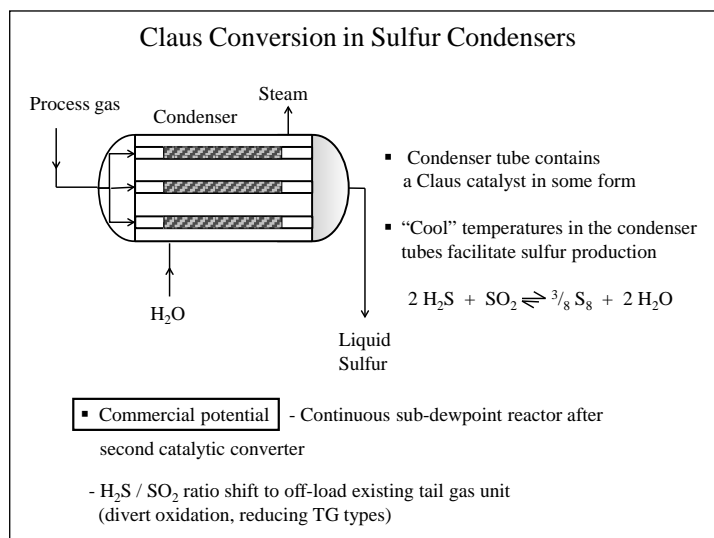
It was concluded that H₂S_x is formed, in large part, during the condensation of liquid sulfur so it was proposed that incorporation of a catalytic phase in the condenser would lead to sulfur degassed to an amount proportional to the partial pressure of H₂S in that condenser. This concept was validated for the condensers downstream of the first and second catalytic units. Work is underway to confirm the behaviour of condensers downstream of the Claus furnace.

2012 - 2013 activities will conclude the condenser investigations and be directed to reporting of all data in the ASRL QB.

Specific Objectives:

- Complete work simulating formation of H₂S_x during sulfur condensation and degassing of liquid sulfur in the thermal condenser
- Publish the experimental degassing data accumulated during the project.

4. Claus Conversion in Sulfur Condensers



Claus Conversion in Sulfur Condensers

Commercial objective

To examine the potential of a catalytic condenser to improve sulfur recoveries in a Claus plant

Specific objectives

- Examine use of the thermal condenser for enhanced CS₂ and Claus conversion.
- Examine the use of 2ND / 3RD converter condensers for on-line continuous sub-dew point operation and ratio shift.

Commercial objective: To examine the potential of a catalytic condenser to improve sulfur recoveries in a Claus plant

During ASRL core research program studies on catalytic degassing, it was noticed that considerable (ca. 40 %) conversion of H₂S and SO₂ to sulfur occurred alongside the degassing reactions. Thus, by incorporating a catalyst in a condenser tube in some way, perhaps as a layer on the inside of a condenser tube, as suggested in the presentation given at the June 2011 Chalk Talks, each sulfur plant condenser could be used to enhance production of sulfur. Taking the thermal condenser as an example, it is expected that rapid conversion to sulfur would occur as the process gas cooled from ca. 600 to 180° C with most conversion occurring when all components are still in the gas phase. Significant conversion of CS₂ might also occur because of the very high temperatures in the initial section of a thermal condenser tube.

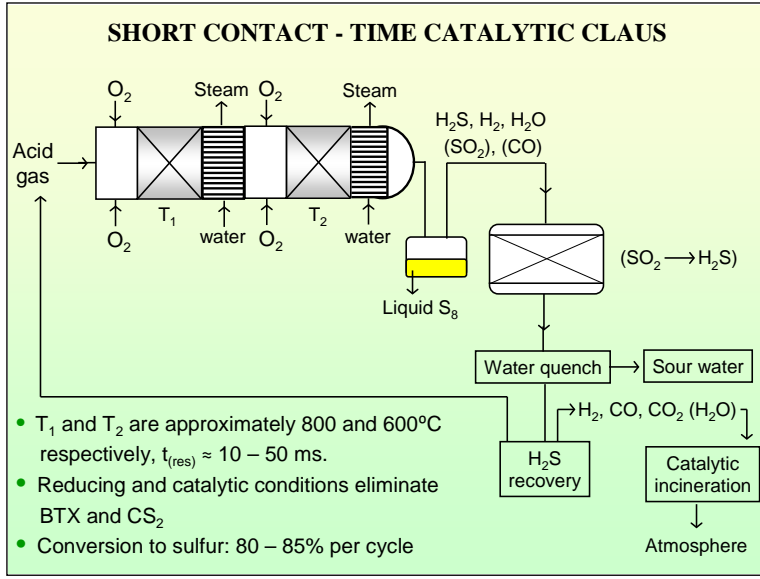
In Claus plants with either 2 or 3 catalytic converters, retro-fit of the downstream condensers to quasi-catalytic units may enable continuous on-line sub-dew point operation with overall plant sulfur recoveries exceeding 99.8% with no formal tail gas unit. Such a scenario would only be possible if the catalyst pore structure did not become completely filled with liquid sulfur. Regardless of whether on-line sub-dew point operation can be achieved, a reasonable degree of Claus conversion in the final condenser would be of great value in a plant using TGPU requiring high ratio operation.

The aim of this new research project would be to investigate the possible application of a dual catalyst-condenser unit to enhance sulfur recovery.

Specific objectives:

- Examine use of the thermal condenser for enhanced CS₂ and Claus conversion.
- Examine the use of 2ND / 3RD converter condensers for on-line continuous sub-dew point operation and ratio shift.

5. Short Contact Time Catalytic Claus Process



Short Contact Time Claus Process

Commercial Objective:

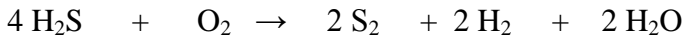
To develop a simplified sulfur recovery process using short contact time catalysis that produces sulfur and hydrogen selectively

Specific Objectives:

- a. Review previous ASRL data (June 2012 Chalk Talk)
- b. Determination of BTX and hydrocarbon conversion in SCT.
- c. Examination of ammonia destruction using SCT and typical sour water stripper gas concentration.
- d. Confirmation of tail gas unit operation with species concentrations produced by SCT

Commercial Objective: To develop a simplified sulfur recovery process using short contact time catalysis that produces sulfur and hydrogen selectively to develop a simplified sulfur recovery process

A thermodynamic analysis of the Claus process suggests that the preferred $H_2S - O_2$ ratio is 4:1 as at this condition sulfur, water and hydrogen are the preferred products.



Previous research in our laboratories has shown that short contact time catalysis (SCT) allows achievement of a product slate close to this ratio when the contact time is around 10 – 50 ms. As depicted in the figure, pure O_2 could be used in two or more stages so limiting the temperature of each stage to $< 1000^\circ C$. The key advantages of this type of process is that all of the “usual” catalytic stages are eliminated in favour of one tail gas stage that uses the standard hydrogenation of any SO_2 and other sulfur species with return of H_2S to the thermal stage. Excess H_2 and any CO would be consumed in a final catalytic incineration stage.

To date, we have not demonstrated destruction of hydrocarbon impurities or ammonia conversion by SCT so it is proposed that these issues be examined in the core research program along with demonstration of the tail gas stage using the high H_2 concentration produced by SCT.

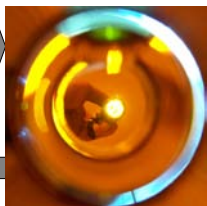
Specific Objectives:

- (a) Review previous ASRL data (June 2012 Chalk Talk)
- (b) Determination of BTX and hydrocarbon conversion in SCT.
- (c) Examination of ammonia destruction using SCT and typical sour water stripper gas concentration.
- (d) Confirmation of tail gas unit operation with species concentrations produced by SCT.

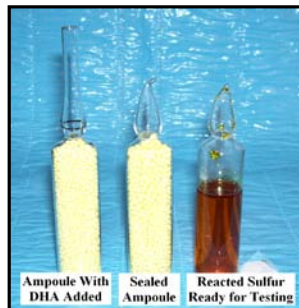
6. FTIR Analysis of Contaminants in Liquid Sulfur

H₂S AND SO₂ SOLUBILITY IN LIQUID SULFUR UPDATING AND CHECKING FTIR CALIBRATIONS

PRELOADED/SEALED CALIBRATION CELLS



AMPOULE CALIBRATION CHECKS



H₂S and SO₂ Solubility in Liquid Sulfur Updating and Checking FTIR Calibrations

Commercial Objective:

Investigation of the uncatalysed Claus reaction in liquid sulfur by FTIR and modified sulfur/H₂S mixtures within hermetically sealed IR cells for remotely checking IR calibrations. Fine tune methods for determination of trace contaminants in liquid sulfur

Specific Objectives:

- Utilize the new absorption coefficient to determine rates of consumption of SO₂ and H₂S in liquid sulfur degassing systems and sulfur storage systems.
- Investigate modified sulfur/H₂S mixtures which could be used to reproducibly melt mixtures in hermetically sealed IR cells for remotely checking IR calibrations.

Commercial Objective: Investigation of the uncatalysed Claus reaction in liquid sulfur by FTIR and modified sulfur/H₂S mixtures within hermetically sealed IR cells for remotely checking IR calibrations.

H₂S dissolved in liquid sulfur often must be degassed before safely transporting or forming. In the past research year the Henry's Law correlation for SO₂ solubility and absorption coefficient for SO₂ was reported relative to H₂S, so that instruments already in service could be modified to measure SO₂ in addition to total dissolved H₂S. While it is known that Claus reaction between SO₂ and H₂S in liquid sulfur is slow, accurate kinetic rates are unknown. The first part of this research will seek to follow the rate of reaction using IR. These rates will be used to understand the non-diffusion limited and uncatalysed rate (chemical rate) which can be used to optimize degassing and/or limit H₂S dissolution.

ASRL has supplied remote IR users with ampoules containing conglomerate mixtures of elemental sulfur and a hydrogen donor. These can be heated to produce a specific quantity of H₂S and H₂S_x in liquid sulfur. While they are not used to calibrate IR instruments, they can be used to check that the initial instrument calibration is correct. Recently, some hermetically sealed IR cells have been investigated for an alternative calibration check; however, more investigations need to be conducted to avoid breaking the cells upon melting the sulfur/H₂S mixture.

Specific Objectives:

- Utilize the new absorption coefficient to determine rates of consumption of SO₂ and H₂S in liquid sulfur degassing systems and sulfur storage systems.
- Investigate modified sulfur/H₂S mixtures which could be used to reproducibly melt mixtures in hermetically sealed IR cells for remotely checking IR calibrations.

7. Development of Enhanced Claus/CS₂ Conversion Catalysts

Development of Enhanced Claus / CS₂ Conversion Catalysts

Commercial objective

To produce low cost, high activity CS₂ conversion – Claus catalysts

Specific objectives

- Prepare and test rare earth (La₂O₃) modified TiO₂ catalysts deposited on high surface area supports (Claus alumina, cordierite monoliths, alumina sponges, etc.)

Commercial potential

- Work reported to date indicates that it may be possible to produce Al₂O₃ – TiO₂ – La₂O₃ composite materials with enhanced Claus / CS₂ conversion activity
- More active Claus catalyst (will be useful in combined Claus condenser – reactor concept).
- More efficient CS₂ conversion catalysts.

Commercial objective: To produce low cost, high activity CS₂ conversion – Claus catalysts

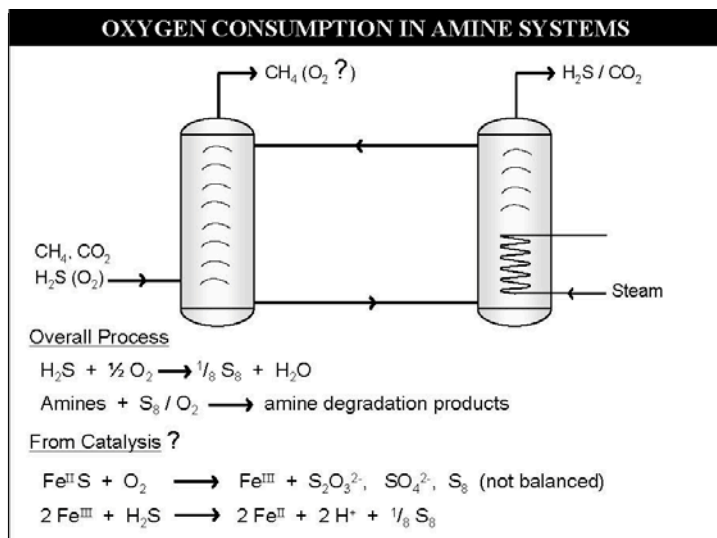
A previous ASRL core research project examined the potential for use of solid SO₂ adsorbents for a high efficiency tail gas process. During this project, several composite oxide materials containing alumina, titania, and magnesium oxide were prepared in which lanthanum oxide was used to create a disordered surface to enhance SO₂ uptake. Since it was known that adsorbed SO₂ can promote CS₂ conversion, some of these materials were tested for this reaction. This initial work showed that some of the titania composites had exceptional CS₂ conversion capacity as well as very high Claus activity. One reason for these high activities is that these catalysts have a high porosity but the associated low packing density could preclude their use in pellet or in extruded form. Consequently, it is proposed that this work be extended to examine preparations in which the modified titania is deposited on an alumina surface with the aim of producing a low cost, high activity CS₂ Claus catalyst.

These catalysts would also be ideal for the catalytic condenser concept as they would provide a catalyst layer with excellent mass transfer properties.

Specific objectives:

- Prepare and test rare earth (La₂O₃) modified TiO₂ catalysts deposited on high surface area supports (Claus alumina, cordierite monoliths, alumina sponges, etc.)

8. Oxygen Consumption in Amine Systems



Oxygen Consumption in Amine Systems

Commercial Objective:

To examine the rate of reaction of oxygen with H₂S in an amine contactor

Specific Objectives

- a. Measurement of the rate of O₂ consumption under amine contactor conditions:
 - i. Amines evaluated: MEA, DEA, MDEA
 - ii. Temperature range: 50 to 120°C
 - iii. Effect of H₂S, CO₂, and SO₂ on the rate of O₂ consumption
 - iv. Effect of catalyst (eg. Fe³⁺)
- b. Determine lower level of oxygen required to cause amine degradation under conditions studied in (a).
- c. Attempt to correlate degradation product formation (heat stable salts, bicine, etc.) with conditions studied in (a) by analyzing reactor contents.

Commercial Objective: To examine the rate of reaction of oxygen with H₂S in an amine contactor

Ingress of oxygen into an amine contactor is known to accelerate the degradation of gas sweetening amines, probably through oxidation of H₂S to sulfur and oxy-sulfur anions which then react with the amines. The rate at which oxygen reacts with H₂S in an amine system has not been evaluated and the actual mechanism for amine degradation under contactor conditions has not been reported. The overall aim of this project would be to determine these aspects of oxygen ingress with respect to amine degradation.

Specific Objectives:

- (a) Measurement of the rate of O₂ consumption under amine contactor conditions:
 - i. Amines evaluated: MEA, DEA, MDEA
 - ii. Temperature range: 50 to 120°C
 - iii. Effect of H₂S, CO₂, and SO₂ on the rate of O₂ consumption
 - iv. Effect of catalyst (eg. Fe³⁺)
- (b) Determine lower level of oxygen required to cause amine degradation under conditions studied in (a).
- (c) Attempt to correlate degradation product formation (heat stable salts, bicine, etc.) with conditions studied in (a) by analyzing reactor contents.

9. A Re-examination of Liquid Sulfur Vapour Pressure

VAPOUR PRESSURE OF LIQUID ELEMENTAL SULFUR (THE CALCULATED VAPOUR PRESSURE OF THE LIQUID AT THE MELT HAS BEEN FORCED TO EQUAL THE SOLID)

FIGURE 2. The differences between reported vapor pressures of elemental sulfur and the vapor pressure calculated using Equation (9). ●, experimental data of Baker [1971]; ○, experimental data of Rau *et al.* [1973]; ◊, experimental data of West and Menzies [1929]; —, calculated using the Wagner equation of Peng and Zhao [2001]; - - - - - , calculated from the equation of Rau *et al.* [1973]; ······, calculated using the equations of Shuai and Meison [1995].

A Re-examination of Liquid Sulfur Vapour Pressure

Commercial Objective:

To re-examine the vapour pressure for elemental sulfur at conditions of interest for sulfur deposition in sour gas production systems and in calculating sulfur dew points

Specific Objectives:

- To measure the sulfur vapour pressure of liquid elemental sulfur in the range of 90 – 180 C.
- Improve the calculation for the standard state fugacity of elemental sulfur (vapour pressure equation).
- Recalibrate ASRL's sulfur solubility model.
- Correlate effect of new data on calculation of sulfur dew-points

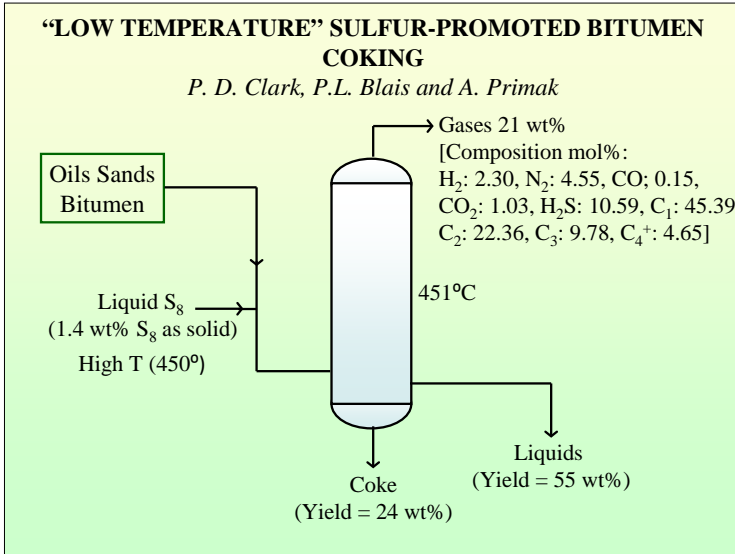
Commercial Objective: To re-examine the vapour pressure for elemental sulfur at temperatures just above the melt to improve models for sulfur deposition and sub-dewpoint catalysis.

By comparison to experimentally-calibrated models developed at ASRL, the sulfur content determination can be used to forecast sulfur deposition during the lifecycle of a well. This information can be used to design and implement sulfur solvent strategies for production of the gas as well as to calculate gas flow rates that will maximize ultimate gas recovery. Through development of those models, it was discovered that there must be a large systematic error in the available sulfur vapour pressure. Because the error likely existed in the liquid data (only one data set available, West and Menzies, 1929), it is proposed that new measurements of the vapour pressure are required. These measurements will be used to improve several sulfur phase behavior models, including those used to estimate sulfur deposition and those used within sub-dewpoint catalysis.

Specific Objectives:

- To measure the sulfur vapour pressure of liquid elemental sulfur
- Improve the calculation for the standard state fugacity of elemental sulfur (vapour pressure equation).
- Recalibrate ASRL's sulfur solubility model.
- Correlate effect of new data on calculation of sulfur dew-points

10. Low Temperature Sulfur Promoted Bitumen Coking



Low Temperature Sulfur-Promoted Bitumen Coking

Commercial Objective:

To examine a low severity bitumen coking process for the production of value-added products

Specific Objectives:

- Examine conditions required to promote sulfur coking.
- Determine product composition of liquid and gaseous products

Commercial Objective: To examine a low severity bitumen coking process for the production of value-added products

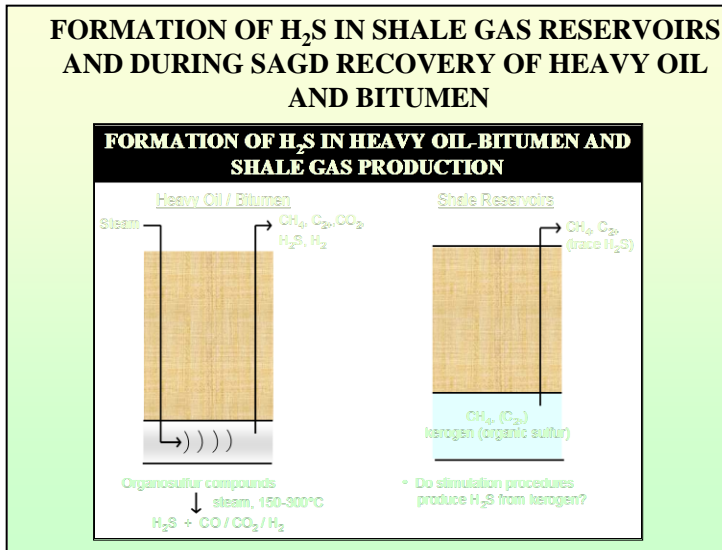
Bitumen upgrading processes include a combination of coking and hydro-treating technologies yielding coke, gases, synthetic crude oil and, in some plants, premium transportation fuels. Recently, we have discovered that addition of elemental sulfur to bitumen accelerates coking chemistry allowing rapid conversion to products at a relatively low temperature (ca. 450°C). In addition, the off-gases of the SAC contained large quantities of ethane, propane and butanes potentially giving this product stream enhanced value. The initial experiment indicates that all of the added sulfur was converted to H₂S.

The accelerating effect of sulfur likely involves formation of sulfur free-radicals which initiate bitumen coking below the standard coking temperature. The objective of this project would be to delineate conditions for SAC and determine the detailed product composition of gaseous and liquid products. One commercial benefit of this process would be a lower energy requirement to conduct the coking step.

Specific Objectives:

- Examine conditions required to promote sulfur coking.
- Determine product composition of liquid and gaseous products

11. Formation of H₂S in Shale Gas Reservoirs



FORMATION OF H₂S FROM SHALE GAS RESERVOIRS

Why do some shale wells produce small amounts of H₂S during the late stages of production?

Mineral has been obtained for a cooler reservoir. We'd like to obtain a second sample and our preference is a Horn River mineral sample.

Is the H₂S from aquathermolysis (like SAGD) or preferential desorption of native H₂S?

- Autoclave testing at high-temperature for two shales ($T = 180^\circ\text{C}$)
- High-pressure adsorption isotherms for CH₄, CO₂ and H₂S.

A titanium autoclave and shale sample.
 The sample will be crushed and exposed to water/CH₄/CO₂ at $T = 180^\circ\text{C}$ and $p = 3000$ psia for at least 30 days.

Formation of H₂S in Shale Gas Reservoirs and During SAGD Bitumen Recovery

Commercial objective:

To understand mechanisms for formation of H₂S in shale gas

Specific Objective:

Determine conditions for production of H₂S from shale source rock if it becomes available

Commercial objective: To understand mechanisms for formation of H₂S in shale gas

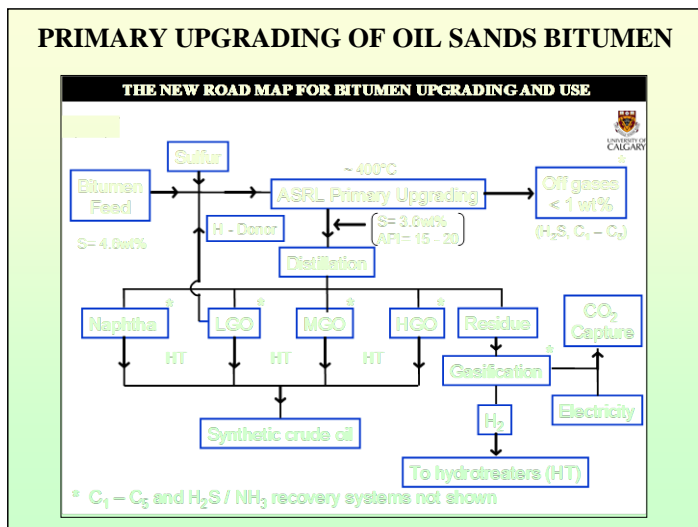
Shale gas has now changed gas production dynamics in North America to the degree that LNG terminals for export of methane from both the USA and Canada are now contemplated. However, several challenges remain for expansion of this resource, including dealing with the small quantities of H₂S found in some shale gas. Research was to have been conducted in last year's program to determine the mechanism for formation of H₂S from shale source materials as it was thought that the H₂S might arise during fracturing of the reservoir. However, no shale material could be accessed for the study.

H₂S production during SAGD recovery of bitumen is also an ongoing problem. This issue has been examined in the ASRL laboratories since the early 1980's and was summarized in the most recent issue of the ASRL Quarterly Bulletin.

Specific Objective:

- (a) Determine conditions for production of H₂S from shale source rock if it becomes available

12. Primary Upgrading of Oil Sands Bitumen



PRIMARY UPGRADING OF OIL SANDS BITUMEN

Primary upgrading of bitumen

- Bitumen samples were heated up to 425°C for ~1h with or without the addition of a hydrogen donor and sulfur
- Upgrading is observed in the samples without sulfur
- It was determined that sulfur promotes coking at these conditions

In-situ upgrading of oil sands

- Samples heated at 200 and 300°C for one month with and without the addition of a hydrogen donor and sulfur
- 300°C showed significant upgrading while 200°C showed no reaction
- Will perform at least one more set of experiments to determine the best way to introduce the additives

Primary Upgrading of Oil Sands Bitumen

Commercial Objective:

To develop efficient and green technology for upgrading bitumen/heavy oil using hydrogen donor solvent chemistry (elimination of coking).

Specific Objectives:

- Delineate process conditions to optimize primary upgrading conditions (H-donor solvent type and quantity, process conditions).
- Characterize upgraded products to ascertain impact on downstream upgrading units.

Commercial Objective: To develop efficient and green technology for upgrading bitumen/heavy oil using donor solvent chemistry.

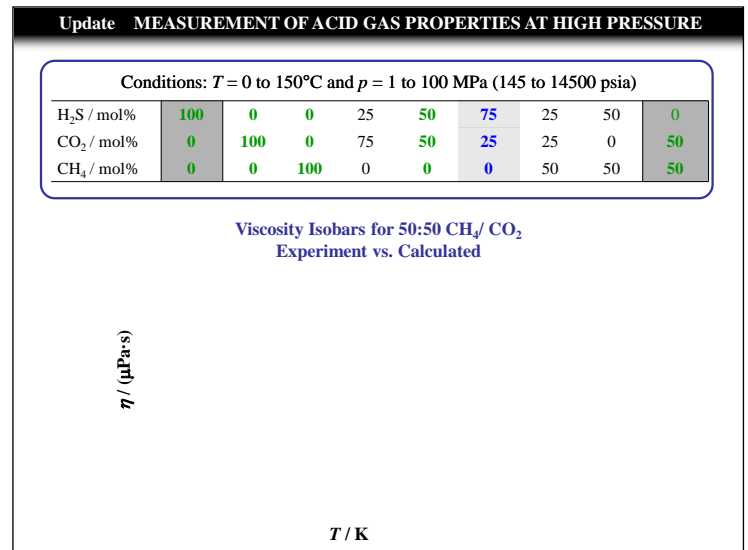
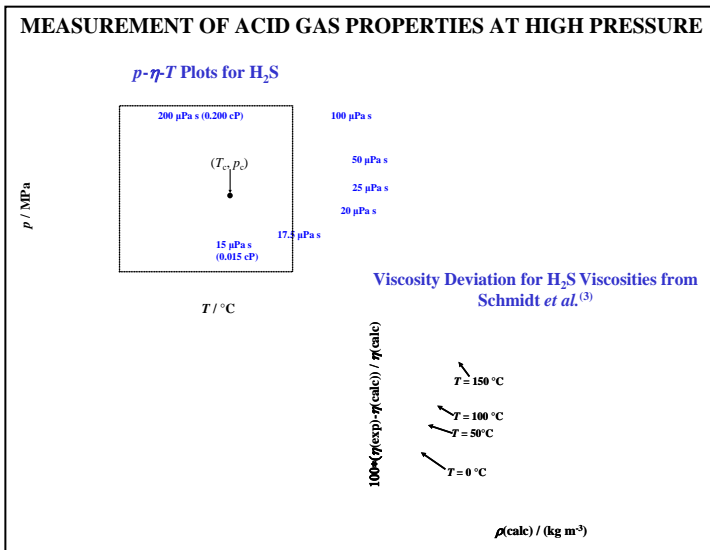
Novel methods for primary upgrading of oil sands bitumen are being sought to produce low viscosity product directly amenable to either hydro-treating to synthetic crude oil or for pipeline transportation without further addition of diluent. In particular, elimination of the coking step from bitumen conversion would greatly alleviate environmental concerns and simplify an upgrading facility. Over the last 2 years, research in our laboratories has demonstrated that sulfur-assisted donor solvent upgrading can accomplish the goal of producing pipeline viscosity oil with approximately 25% reduction in sulfur content. The donor solvent would consist of part of the gas oil fraction produced in the bitumen upgrading facility. The upgraded product should also be suitable for hydro-treatment to synthetic crude oil. The results obtained to date have been published at the January 2009 Chalk Talks and have been published in the ASRL QB.

Research now underway is aimed at optimizing the distillate yield and removal of trace metals from the distillate product by manipulating the process conditions (temperature/sulfur additive quantity). When this work is complete, ASRL will attempt to have an overall process evaluated from engineering/economic viewpoints.

Specific Objectives:

- Delineate process conditions to optimize primary upgrading conditions (H-donor solvent type and quantity, process conditions).
- Characterize upgraded products to ascertain impact on downstream upgrading units.

13. Measurement of Acid Gas Properties at High Pressure



Measurement of Acid Gas Properties at High Pressure

Commercial Objectives:

To provide needed density and viscosity data for designing projects that require handling and injection of high pressure H₂S/CO₂ and CO₂/SO₂ mixtures.

Specific Objectives:

- Complete densities and viscosities for the proposed matrix (see preceding slide).
- Explore semi-empirical correlations for calculating the viscosity of acid gas mixtures
- Write up data for publication in ASRL QB

Commercial Objectives: To provide needed density and viscosity data for designing projects that require handling and injection of high pressure H₂S/CO₂ and CO₂/SO₂ mixtures.

Density and viscosity are two fundamental properties which are required to design compression and injection into a target reservoir. Data for acid gas and sour gas injectate fluids are sparsely available in the open literature due to (i) the difficulty in dealing with H₂S mixtures and (ii) the low range of viscosities for gaseous, liquid and supercritical fluids. ASRL has been using an Anton Paar mPDS Vibrating Tube Density Cell and a VISCO *pVT* High Pressure Viscometer to measure these two properties over a broad range of conditions and concentration:

Composition matrix proposed for investigations at $T = 0, 50, 100 \text{ \& } 150^\circ\text{C}$ and $p = 10, 20, 50, 100, 200, 500 \text{ \& } 1000 \text{ bar}$ (145, 290, 725, 1450, 2900, 7550, 14500 psia)

Mixture	A	B	C	D	E	F	G	H	I
H ₂ S / mol%	100			25	50	75	25	50	0
CO ₂ / mol%		100		75	50	25	25	0	50
CH ₄ / mol%			100				50	50	50

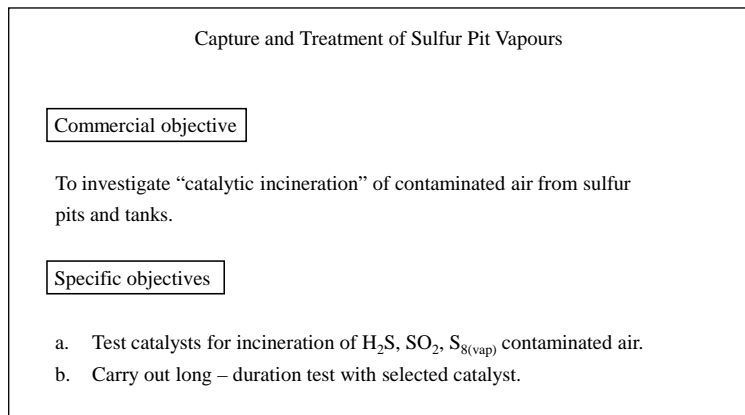
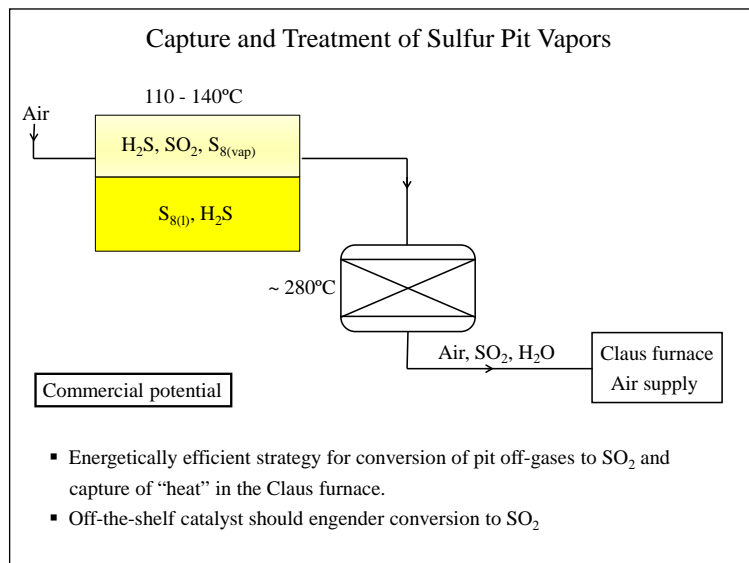
The shaded compositions have been completed.

Over 40% of the target matrix was completed in the first year of the investigation. For the next year, the aim is to complete the matrix and investigate some semi-empirical models which can be used to accurately calculate the viscosity of the mixtures.

Specific Objectives:

- (a) Complete densities and viscosities for the proposed matrix.
- (b) Explore semi-empirical correlations for calculating the viscosity of acid gas mixtures.
- (c) Write up data for publication in ASRL QB.

14. Capture and Treatment of Sulfur Pit Vapours



Commercial objective: To investigate “catalytic incineration” of contaminated air from sulfur pits and tanks.

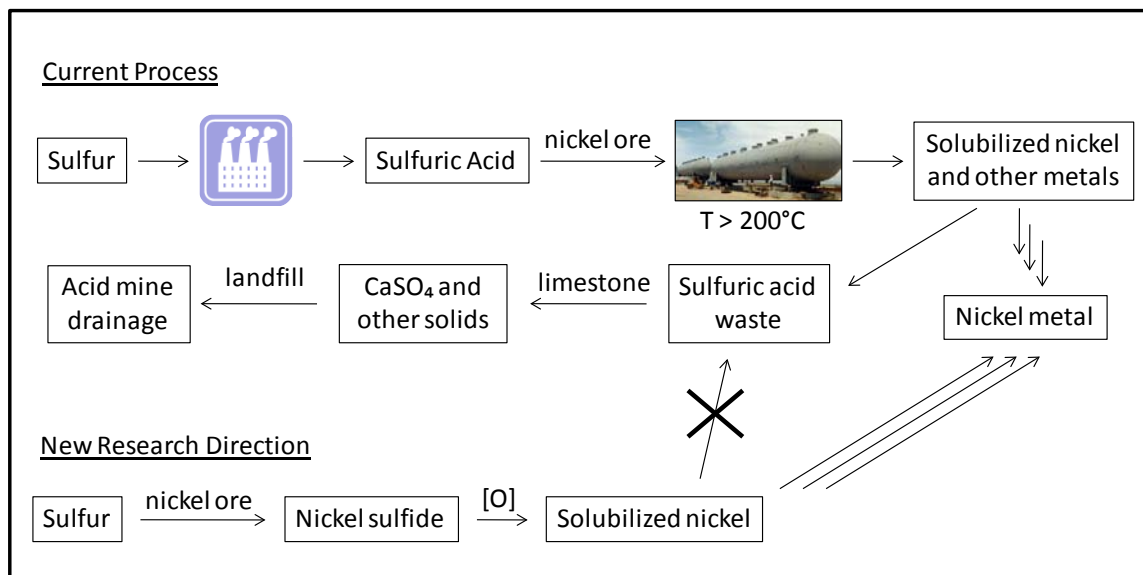
Many sulfur pits and tanks are swept with air to limit H_2S concentrations reaching LEL values. The net result of this action is that significant volumes of air contaminated with H_2S , SO_2 and sulfur vapour must either be sent to the tail gas incinerator or compressed into the main air supply to the furnace. This last option is preferred to prevent sulfur pit off gases contributing to plant emissions but presents operating problems because of sulfur deposition in piping and in the required compression systems.

An alternate pit vapour treatment process may be to oxidize all the sulfur components to SO_2 by a catalytic treatment and then return this stream to the Claus furnace. One benefit of the process is that a homogeneous product gas mixture would be obtained. It is anticipated that off-the-shelf catalysts could be used. An additional benefit of this approach is that the temperature of the treated air stream will be ca. 280°C so engendering an incremental increase in the thermal efficiency of the plant. Several engineering options could be applied to return the hot, SO_2 – air mixture to the Claus furnace. However, metallurgy used in these systems must take into account the potentially corrosive nature of the gas stream.

Specific objectives:

- Test catalysts for incineration of H_2S , SO_2 , $\text{S}_{8(\text{vap})}$ contaminated air.
- Carry out long – duration test with selected catalyst.

15. Use of Elemental Sulfur in Extraction of Nickel from Laterite Ores



Use of Elemental Sulfur in Extraction of Nickel from Laterite Ores

Commercial Objective:

To facilitate use of elemental sulfur in nickel extraction from oxidic ores

Specific Objectives:

- a. Conduct research to improve nickel extraction from oxide ores.
- b. Review the chemistry of acid leaching for production of uranium and thorium

Commercial Objective: To facilitate use of elemental sulfur in commercial applications

At present, sulfur is required in a variety of industrial applications with fertilizer production making up the majority use via consumption of the sulfur as sulfuric acid. In the future, it is expected that the requirements for sulfur will expand considerably through use of sulfuric acid to extract nickel from nickel oxide ores. Such technology has been in use for at least 3 decades in Cuba and new projects are under construction or in operation in several other countries. In some of these projects, due to factors such as the mineral makeup of the local ores and the quality of the process water, the sulfuric acid leaching step has not been very economical and in some cases has failed to meet nickel production expectations.

Since nickel oxides represent most of the World's remaining nickel reserves, some kind of improved leaching technology will be required.

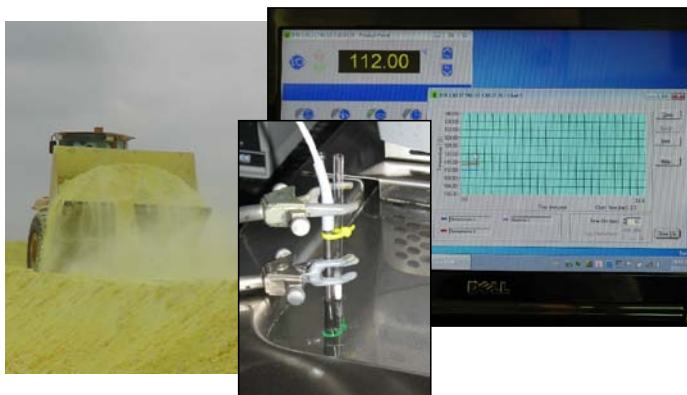
Specific Objectives:

- (a) Conduct research to improve nickel extraction from oxide ores.
- (b) Review the chemistry of acid leaching for production of uranium and thorium

16. Sulfur Dust Properties

SULFUR DUST MELTING POINTS

- Sulfur dust (lab-generated) melting point experiments have been initiated. The objective is to heat the sulfur in a slow manner to obtain the physical melting point which is lower than the observed melting point.



Sulfur Dust Properties

Commercial Objectives:

To determine selected properties of sulfur dust pertaining to handling and transportation of solid sulfur.

Specific Objective:

- a. Characterize the physical properties of sulfur dust by making measurements in the following areas:
 - i. Melting point
 - ii. Surface-adsorbed species, *e.g.*, SO₂, H₂S, H₂S_x
 - iii. Surface absorption capacity
 - iv. Water/other boundary effects on sulfur dust vs. formed sulfur

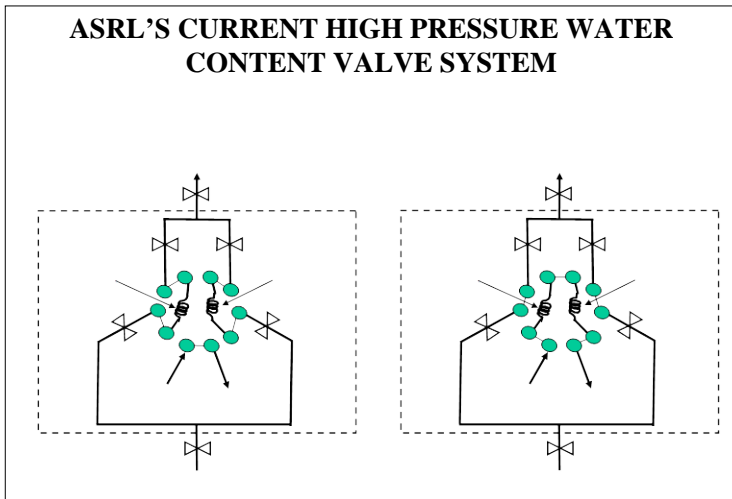
Commercial Objectives: To determine selected properties of sulfur dust pertaining to handling and transportation of solid sulfur.

In the world of sulfur, sulfur dust poses a challenge in that air borne dust tends to remain suspended because of the development of surface charges which cause the particles to repel one another. Critically, air borne dust may spontaneously ignite with explosive force. To support the hypothesis that sulfur dust is kinetically stable, like most aerosols or fogs, thermodynamic changes can be investigated for small particle sizes. This involves showing that the melting temperature is not substantially different for small particles. Finally, for small particles, surface adsorption reduces the charge potential of a surface. CO₂, SO₂ and H₂S surface adsorption isotherms for small particles will be measured for small sulfur particles.

Specific Objective:

- (a) Characterize the physical properties of sulfur dust by making measurements in the following areas:
 - a. Melting point
 - b. Surface-adsorbed species, *e.g.*, SO₂, H₂S, H₂S_x
 - c. Surface absorption capacity
 - d. Water/other boundary effects on sulfur dust vs. formed sulfur

17. Acid Gas Injection: Water Holding Capacity of Acid Gas Mixtures



Acid Gas Injection: Water Holding Capacity for Acid Gas Mixtures

Commercial objective:

To aid acid gas injection design projects by providing data for the water carrying capacity of acid gases at conditions up to reservoir injection.

Specific Objectives:

- a. Measure the water carrying capacity for pure H₂S at $T = 100$ and 150°C .
- b. Time permitting, determine effect of condensable hydrocarbons on water carrying capacity of acid gas and sour gas mixtures.

Commercial objective: To aid acid gas injection design projects by providing data for the water carrying capacity of acid gases at conditions up to reservoir injection.

Accurate prediction of the water carrying capacity of acid gas is needed to engineer and operate acid gas re-injection plants.

Over the past 6 to 7 years ASRL has developed reliable methods for measurement of water dissolved in sour and acid gases. With this capability in-hand, the literature values for water carrying capacity of pure H₂S and CO₂ were surveyed and it was noted that there are very little water content data for pure H₂S in the liquid region and CO₂ at typical reservoir conditions. Experimental data for the pure H₂S species are warranted at conditions that might be experienced for re-injection of acid or sour gas for disposal or enhanced oil recovery schemes.

In the past year, further developments in capabilities have provided the water content of H₂S at $T = 50^{\circ}\text{C}$ and up to $p = 75$ MPa. In the next year H₂S water contents will be measured at $T = 100$ and 150°C .

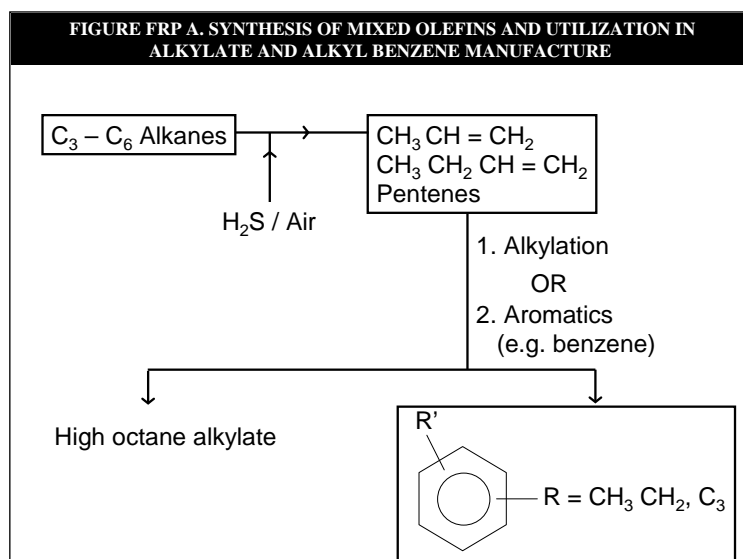
Specific Objectives:

- (a) Measure the water carrying capacity for pure H₂S at $T = 100$ and 150°C .
- (b) Time permitting, determine effect of condensable hydrocarbons on water carrying capacity of acid gas and sour gas mixtures.

FUNDAMENTAL RESEARCH PROGRAMS

These projects include ongoing research (Graduate student and PDF) which has partial external funding (University of Calgary and Natural Sciences Engineering Research Council of Canada)

A. Production of C₃ – C₆ Olefins, High Octane Alkylate and Valuable Petrochemicals (ongoing, Ph.D. studies, Z. Premji)



FUNDAMENTAL RESEARCH PROGRAMS

Production of C₃ – C₆ Olefins, High Octane Alkylate and Valuable Petrochemicals (ongoing, Ph.D. studies, Z. Premji)

Specific Objectives:

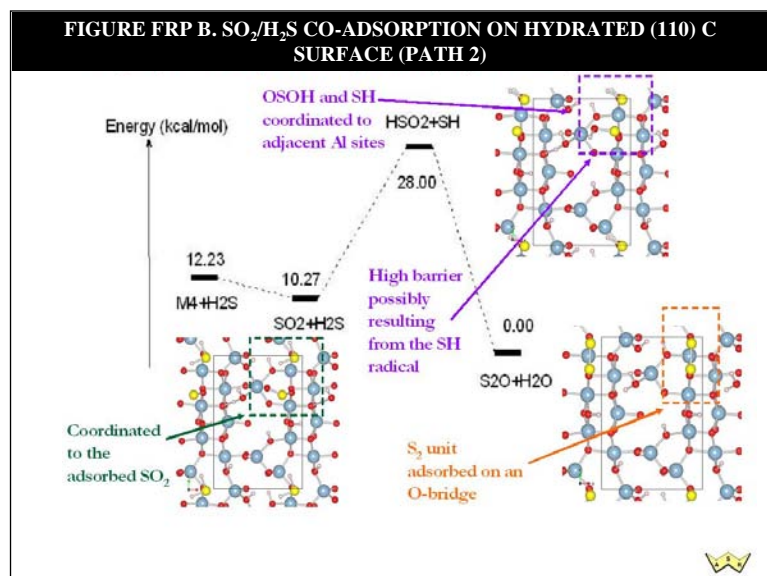
- Determine the feasibility of producing a mixed olefin product from a C₃ – C₆ feed.
- Use the mixed olefins to synthesize high octane alkane mixture so providing a direct route from refinery alkane off-gases to gasoline pool mixtures.
- Use of the olefin mixture to alkylate benzene so providing a direct synthesis of ethyl, iso-propyl and butylbenzenes.

Previous research in our laboratories has identified new, high efficiency technologies for production of ethylene and propylene. The chemical principle behind these technologies is partial oxidation of a hydrocarbon feed using sulfur as an oxygen transfer agent, a strategy that promotes very selective oxidation and very high yields of the olefins (Figure FRP A). Assessments of this work by ASRL members suggest that sulfur assisted olefin manufacture would be more efficient than current technology and, in the case of propylene, represents the highest yield (60%) yet reported. This work will be expanded as part of the Ph.D. program studies of Zahra Premji.

Specific Objectives :

- Determine the feasibility of producing a mixed olefin product from a C₃ – C₆ feed.
- Use the mixed olefins to synthesize high octane alkane mixture so providing a direct route from refinery alkane off-gases to gasoline pool mixtures.
- Use of the olefin mixture to alkylate benzene so providing a direct synthesis of ethyl, iso-propyl and butylbenzenes.

B. Computational Modeling of Catalytic Systems (Dr. John Lo)



FUNDAMENTAL RESEARCH PROGRAMS

Computational Modeling of Catalytic Systems (Dr. John Lo)

Commercial Objectives:

Use of computational techniques to develop enhanced understanding of catalytic processes for sulfur recovery.

Specific Objectives:

- Determine the mechanism of SO₂ and H₂S adsorption at catalytic surfaces, defining the most suitable materials for SO₂ adsorption.
- Examination of the Claus catalytic mechanism.
- Investigation of the mechanism of H₂S assisted oxidation of alkanes to olefins.

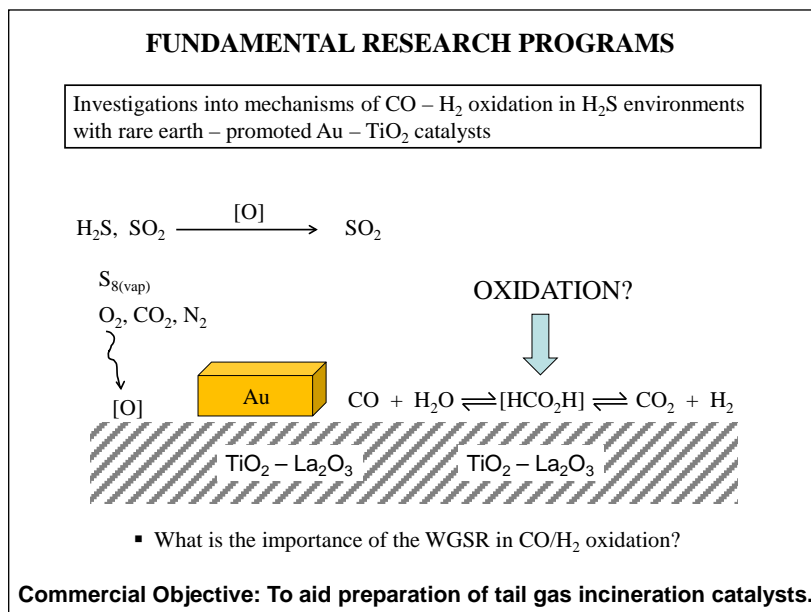
Commercial Objectives: Use of computational techniques to develop enhanced understanding of catalytic processes for sulfur recovery.

Recently, density functional theory (DFT) has allowed calculation of more precise models for surface catalyzed reactions. Much of the theoretical development has been conducted by Dr. T. Zeigler and colleagues in the Chemistry Department of the University of Calgary. Recently, extra funding was obtained through the ASRL-University connection to fund a 2 year position to examine Claus catalysis at the mechanistic level using DFT. This research will also aid the development of the research in projects # 1 and FRP A (Figure FRP B).

Specific Objectives:

- Determine the mechanism of SO₂ and H₂S adsorption at catalytic surfaces, defining the most suitable materials for SO₂ adsorption.
- Examination of the Claus catalytic mechanism.
- Investigation of the mechanism of H₂S assisted oxidation of alkanes to olefins.

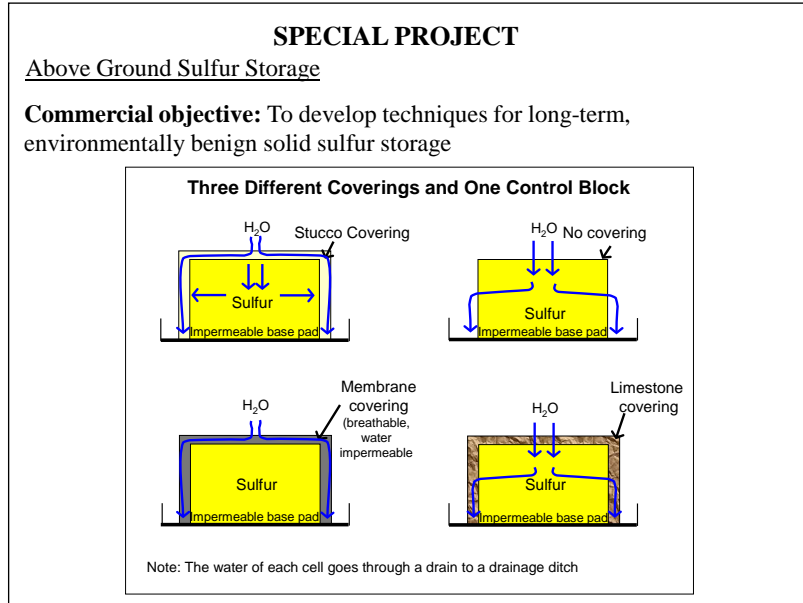
C. Investigations into Mechanisms of CO – H₂ Oxidation in H₂S Environments with Rare Earth – Promoted Au – TiO₂ Catalysts.



SPECIAL PROJECTS

Special projects are research efforts which aim to take ASRL core research work to the commercial demonstration phase. There is currently one such project within the ASRL research portfolio.

1. Above Ground Sulfur Storage



Commercial objective: To develop techniques for long-term, environmentally benign solid sulfur storage

Sulfur supply/demand cycles over the last 50 years have resulted in the need for temporary block storage of many millions of tons worldwide. The most recent cycle produced prices of up to \$850/ton but “business as usual” was resumed with prices dropping to < \$50/ton during the 2009 recession. “Post recession” pricing is showing some recovery. Potentially, new sour gas fields in the Middle East and Central Asia, new production in China and oil sands-derived sulfur could over-whelm the market requiring long term (50+ years) block storage. During the last two years, ASRL has been working with its members to identify strategies for long term storage and to design field pilot projects. In one case, laboratory work has been conducted to examine the viability of spray-on coatings based on construction stucco. This work was reported at the January 2008 and 2009 Chalk Talks.

This project was established in the Fall of 2009, fully founded by four industrial sponsors. The test blocks have been poured at the Shell Burnt Timber gas plant and instrumentation is being put in place. Three types of protective coating were applied in the Spring of 2010.