Using SWSPlus™ for Sulfur Capacity Addition

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Outline

Sour Water Effects on Sulfur Plant Design
SWSPlus™ - Ammonia Recovery Process
Benefits of a licensed unit
Historical uses of Ammonia
Ammonia Markets
Case Studies
Summary
Sour Water

- Sour water is normally found in refineries with 100’s of ppmw to a few % of ammonia (NH₃) and hydrogen sulphide (H₂S)
- Ammonia and H₂S are in equimolar quantities
  - Molecular weight of NH₃ ~ 17
  - Molecular weight of H₂S ~ 34
  - Mass ratio of H₂S:NH₃ in sour water is therefore ~2:1
- Sour Water Strippers boil off contaminants
- Stripped water to either recycling or discharge
  - Phenolic water to a desalter
  - Non-phenolic water to a hydrotreater
- Vapors to SRU
  - Approximately equimolar in NH₃, H₂S, and water
A Sulfur Plant is not an Ammonia Plant

Sulfur Recovery Units do not recover ammonia

We cannot convert ammonia into sulfur, only nitrogen and water

\[ \text{NH}_3 + \frac{3}{4} \text{O}_2 \rightarrow 0.5 \text{N}_2 + 1.5 \text{H}_2\text{O} \]

If it is not destroyed, ammonia forms salts with H\(_2\)S that deposit in the colder parts of the unit – the final sulfur condenser.

\[ \text{NH}_3 + \text{H}_2\text{S} \rightarrow \text{NH}_4\text{HS} \]

This leads to higher pressure losses and an unplanned shut-down.

Avoiding this requires

- A minimum residence time in the Reaction Furnace
- A minimum temperature in the Reaction Furnace, which is difficult to maintain.
- A proprietary burner
- Additional oxygen for the chemical reactions with ammonia
NH₃ + 0.75 O₂ → 0.5 N₂ + 1.5 H₂O
H₂S + 0.5 O₂ → S + H₂O
Ammonia requires 50% more air/oxygen than sulfur
Considering nitrogen in air and the water in SWS AG,

one ton of ammonia takes up the space of ~3 tons of sulfur.

Removing diluent nitrogen (Air and NH₃ combustion) helps the Claus reaction because reactants are more concentrated.

Removing sources of water (SWS AG water, NH₃ combustion water) helps the Claus reaction equilibrium.

Removing mass allows for expansion or CAPEX reduction.
Effects on Sulfur Plant Design

- \( \text{NH}_3 + 0.75 \text{ O}_2 \rightarrow 0.5 \text{ N}_2 + 1.5 \text{ H}_2\text{O} \)
- \( \text{H}_2\text{S} + 0.5 \text{ O}_2 \rightarrow \text{S} + \text{H}_2\text{O} \)
- Ammonia requires 50% more air/oxygen than sulfur
- Considering nitrogen in air and the water in SWS AG, one ton of ammonia takes up the space of ~3 tons of sulfur.
- Removing diluent nitrogen (Air and \( \text{NH}_3 \) combustion) helps the Claus reaction because reactants are more concentrated.
- Removing sources of water (SWS AG water, \( \text{NH}_3 \) combustion water) helps the Claus reaction equilibrium.
- Removing mass allows for expansion or CAPEX reduction.
- \[ \text{NH}_3 + 0.75 \text{O}_2 \rightarrow 0.5 \text{N}_2 + 1.5 \text{H}_2\text{O} \]
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- Ammonia requires 50% more air/oxygen than sulfur
- Considering nitrogen in air and the water in SWS AG, **one ton of ammonia** takes up the space of ~**3 tons of sulfur**.
- Removing diluent nitrogen (Air and \text{NH}_3 combustion) helps the Claus reaction because reactants are more concentrated.
- Removing sources of water (SWS AG water, \text{NH}_3 combustion water) helps the Claus reaction equilibrium.
- Removing mass allows for expansion or CAPEX reduction.
Ammonia in the feed to an SRU is not desirable.

What can we do to handle additional ammonia and/or hydrogen sulfide?

- Add a new SRU
- Add oxygen
- Separate the NH3 and H2S
  » SWSPlus™ Ammonia Recovery Process
  » Phosam W
The SWSPlus™ Process
The SWSPlus™ Process

- Sour Water
- Hydrocarbon Vapors
- Degasser
- Deoil

- WWT Feed Preparation Tank
- Feed Product Exchanger
- Acid Gas Stripper
- Reboiler
- Condensate
- Steam

- Ammonia Vapor
  - To Ammonia Purification and liquefaction

- Treated Water
  - 10-50 ppm NH₃
  - 1-25 ppm H₂S

- Acid Gas Product
  - 50 ppm NH₃

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The SWSPlus™ Process
The SWSPlus™ Process
The SWSPlus™ Process

- Ammonia Vapor from WWT Process
  - Ammonia Vapor to Incineration
  - Cooling Water
  - Anyhydrous Liquid Ammonia
  - Refrigeration Unit
  - Anyhydrous Liquid Ammonia

- Scrubbers
  - Water
  - Caustic

- Ammonia Absorber
  - Water
  - Aqueous Ammonia

- Anhydrous Ammonia Production
- Aqueous Ammonia Production

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Benefits of a Licensed Unit

Proprietary simulating tool from Chevron heritage
- Better thermodynamic data covering the entire range of NH3 concentrations
- Used to design over 25 units, 9 Pre-Concentrators, and multiple SWS

Metallurgy
- 50+ years of operating experience
- 25+ refineries

Operating know-how
- Licensor staff
- Licensee experience
Ammonia markets

Anhydrous and aqueous ammonia* are commodities more common than sulfur and may be transported by pipeline, rail, or truck.

*82-86% used for fertilizer in the US

Two main Products

- **Anhydrous Ammonia**
  - 99.5 wt% NH3 minimum
  - 0.5 wt% H2O maximum
  - 0.58 specific gravity at 100 F
  - 5-10 ppmw oil maximum
  - Vapor pressure is approximately 200 psig at 100 F (13.6 bar at 38 C)

- **Aqueous Ammonia**
  - 26 Baumé
  - 28-30 wt% NH3
  - 0.897 specific gravity maximum at 60 F (15.6 C)
  - 0.05 wt% non-volatile matter
  - Atmospheric vapor pressure at ambient temperatures
Historical Uses of Ammonia from SWSPlus™

- SWSPlus™ ammonia may be blended with Haber ammonia
  - Haber ammonia is made from natural gas and air
  - Haber ammonia is the industrial standard
  - Analogous to “Claus quality sulfur”

- Among licensees
  - 47% Anhydrous
  - 23% Aqueous
  - 30% Incinerate

In all cases, the benefit is that the Ammonia never enters the SRU
Case Study A – Process Data

- **Sulfur Plant**
  - Grassroots facility
  - Single 1200 MTPD sulfur capacity
  - Rich acid gas (93% H₂S)
  - Case 1 = 15% of SRU feed sulfur from SWS acid gas (85% from Amine Regenerators)
  - Case 2 = 25% of SRU feed sulfur from SWS acid gas (75% from Amine Regenerators)

- **Sour Water Stripper Feed**
  - 340 NCMH sour water flow
  - Case 1 – 1.2 wt % NH₃ and 2.4 wt % H₂S in sour water
  - Case 2 – 2.0 wt % NH₃ and 4.0 wt % H₂S in sour water

- **Products**
  - 50 ppmw NH₃ in stripped water
  - 10 ppmw H₂S in stripped water
  - Anhydrous Ammonia by using compression
  - <5 ppmw H₂S in ammonia product
  - H₂S to Claus unit
Case Study A – Process Data

▪ Sulfur Plant
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▪ Products
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  – H₂S to Claus unit

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Case Study A – Economic Data

- 3 year construction period (with zero cash flow)
- 2% escalation of TIC (Total Installed Cost)
- Pre-tax basis
- 3% of TIC for maintenance per year
- Catalyst/Chemicals (initial fill & annualized) included
- Utilities considered:
  - 600 psig steam generation
  - SWSPlus™ reboilers MP steam consumption
  - Cooling Water
  - Electrical Power
Case Study A – Results

25% of Sulfur Recovery Unit Feed as Sour Water Stripper Acid Gas
1,500 gpm
2% NH₃
4% H₂S

15% of Sulfur Recovery Unit Feed as Sour Water Stripper Acid Gas
1,500 gpm
1.2% NH₃
2.4% H₂S
Case Study A – Results

IRR=0 is break even NH3 price; $350 for 15% case and $205 for 25%

- 25% of Sulfur Recovery Unit Feed as Sour Water Stripper Acid Gas
  - 1,500 gpm
  - 2% NH₃
  - 4% H₂S

- 15% of Sulfur Recovery Unit Feed as Sour Water Stripper Acid Gas
  - 1,500 gpm
  - 1.2% NH₃
  - 2.4% H₂S

Average NH3 Price of $530/tonne
Case Study B – Process Data

▪ Sulfur Plant
  – Existing facility
  – Three 400 MPTD SRU Trains (1200 MTPD sulfur capacity), each one is:
    » Modified Claus Plant
    » Thermal stage plus 3 Catalytic Stages
    » Hydrogenation-Amine type TGTU
    » Thermal Oxidizer firing natural gas
    » Rich acid gas (93% H₂S)

▪ Sour Water Strippers
  – Process processes a fixed percentage of ammonia in SRUs (20.9%)
  – 1/3 H₂S, 1/3 NH₃, 1/3 H₂O

▪ Variable for the case study is the concentration of ammonia
  – Case 1 is 0.99 wt% NH₃ and 1.98 wt% H₂S (1235 gpm sour water flow)
  – Case 2 is 1.98 wt% NH₃ and 3.96 wt% H₂S (2470 gpm sour water flow)
Case Study B – Process Data

- Scenario: Refinery expansion resulting in
  - 400 MTPD incremental sulfur
  - Ammonia (SWS Gas flow) increases proportionately
    » Same concentration of NH₃ and H₂S in the SRUs as pre-expansion

- Products
  - 50 ppmw NH₃ in stripped water
  - 10 ppmw H₂S in stripped water
  - Anhydrous Ammonia by using compression
  - <5 ppmw H₂S in ammonia product
  - H₂S to Claus unit (no change)
Case Study B – Economic Data

- 3 year construction period (with zero cash flow)
- 2% escalation of TIC (Total Installed Cost)
- Pre-tax basis
- 3% of TIC for maintenance per year
- Catalyst/Chemicals (initial fill & annualized) included
- Utilities considered:
  - 600 psig steam generation
  - SWSPlus™ reboilers MP steam consumption
  - Natural gas consumption in TOU
  - Cooling Water
  - Electrical Power
Case Study B – Results

![Cumulative Cash Flow Chart](#)
Case Study B.1 – Results

Cumulative Cash Flow

Start-Up  25 years

SRU-B.1
SWSPlus-B.1
Case Study B.2 – Results

The graph shows the cumulative cash flow over a 25-year period for SRU-B.1, SWSPlus-B.1, and SWSPlus-B.2. The cash flow is measured in units from -2.0 to 2.0 on the y-axis, with the x-axis representing time from Start-Up to 25 years.
Case Study B – Combined Results

- SRU Train (400 MTPD, no SWSPlus™)
  - Claus Unit plus Tail Gas Treating Unit plus Thermal Oxidizer (Incinerator)
  - Basis of cash flow comparison with value = 1.0
  - Negative cash flow (sulfur sales do not exceed operating costs)
  - Cumulative value is -1.6 times SRU train capex during the project life
  - Cost of doing business

- Case B.1 (2470 gpm sour water, no SRU train)
  - Smaller CAPEX than an SRU train
  - Positive cash flow (ammonia revenue exceeded operating costs)
  - Did not recoup all capex over the project life
  - Did save 1.3 times the value of an SRU train during the project life
  - Financially attractive

- Case B.2 (1235 gpm sour water, no SRU train)
  - Smaller CAPEX than an SRU train or Case B.1 due to smaller water flow rate
  - Positive cash flow (ammonia revenue exceeded operating costs)
  - Able to recoup capex over the project life and more than 1.5 times capex of SRU train
  - Net increment compared to SRU is 3.1 times SRU train capex
  - Financially attractive
Ammonia pricing

- Main trading hubs are in Tampa, Yuzhny, and the Caribbean
- Peak in September 2008 at $880/metric ton of ammonia
- $530 average for the calendar year 2014
- Supported by corn derived ethanol mandates in the US, increased Chinese/Indian demand, etc.

Source: U.S. Geological Survey
Effects on Worldwide Production?

- Case A produces ~58,700 metric tons NH₃ / year
- Case B produces ~48,667 metric tons NH₃ / year
- 144 million metric tons produced worldwide in 2014
- Each case study is <0.04% of the worldwide total ammonia produced
- Worldwide consumption projected to 167 million metric tons/year in 2018

**World Ammonia Production, million tons/year (2015-2018 est.)**

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Source: U.S. Geological Survey
## Proven Experience

<table>
<thead>
<tr>
<th>Company</th>
<th>Location</th>
<th>Capacity</th>
<th>Startup Year</th>
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<tr>
<td>Flint Hills</td>
<td>St. Paul, Minnesota, USA</td>
<td>500</td>
<td>TBD</td>
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<tr>
<td>Chevron</td>
<td>(Revamp)</td>
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Summary

- Given a sulfur expansion, SWSPlus™ provides superior economics to a traditional SRU train.
- 1 ton of ammonia = 3 tons of sulfur processing capacity
- Allows easy SRU and SWS expansion to higher nitrogen crudes
- Converts a waste stream into a salable product
- SWSPlus™ is Proven Technology in 25+ refineries over 50+ years
  - Configurations
  - Operating philosophies
  - Crude slates
  - Climates
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