INFRASTRUCTURE
MINING & METALS
NUCLEAR, SECURITY & ENVIRONMENTAL
OIL, GAS & CHEMICALS

Using SWSPlus™ for Sulfur Capacity Addition

By Charles L. Kimtantas and Martin A. Taylor

ckimtant@bechtel.com & mataylo1@bechtel.com

Bechtel Hydrocarbon Technology Solutions. Inc.

3000 Post Oak Blvd, Houston, Texas 77056

REFCOMM® GALVESTON
MAY 7-11 2018

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 (NH_3) and hydrogen sulphide (H_2S)
- Ammonia and H_2S are in equimolar quantities
  - Molecular weight of NH_3 ~ 17
  - Molecular weight of H_2S ~ 34
  - Mass ratio of $H_2S:NH_3$ 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 NH_3, H_2S, 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

$$NH_3 + \frac{3}{4} O_2 \rightarrow 0.5\ N_2 + 1.5\ H_2O$$

If it is not destroyed, ammonia forms salts with H_2S that deposit in the colder parts of the unit – the final sulfur condenser.

$$NH_3 + H_2S \rightarrow NH_4HS$$

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

Effects on Sulfur Plant Design

- $NH_3 + 0.75\ O_2 \rightarrow 0.5\ N_2 + 1.5\ H_2O$
- $H_2S + 0.5\ O_2 \rightarrow S + H_2O$
- 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 NH_3 combustion) helps the Claus reaction because reactants are more concentrated.
- Removing sources of water (SWS AG water, NH_3 combustion water) helps the Claus reaction equilibrium.
- Removing mass allows for expansion or CAPEX reduction.

Effects on Sulfur Plant Design

- $NH_3 + 0.75\ O_2 \rightarrow 0.5\ N_2 + 1.5\ H_2O$
- $H_2S + 0.5\ O_2 \rightarrow S + H_2O$
- 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 NH_3 combustion) helps the Claus reaction because reactants are more concentrated.
- Removing sources of water (SWS AG water, NH_3 combustion water) helps the Claus reaction equilibrium.
- Removing mass allows for expansion or CAPEX reduction.

Effects on Sulfur Plant Design

- $NH_3 + 0.75\ O_2 \rightarrow 0.5\ N_2 + 1.5\ H_2O$
- $H_2S + 0.5\ O_2 \rightarrow S + H_2O$
- Ammonia requires 50% more air/oxygen than sulfur
- Considering nitrogen in air and the water in SWS AG,

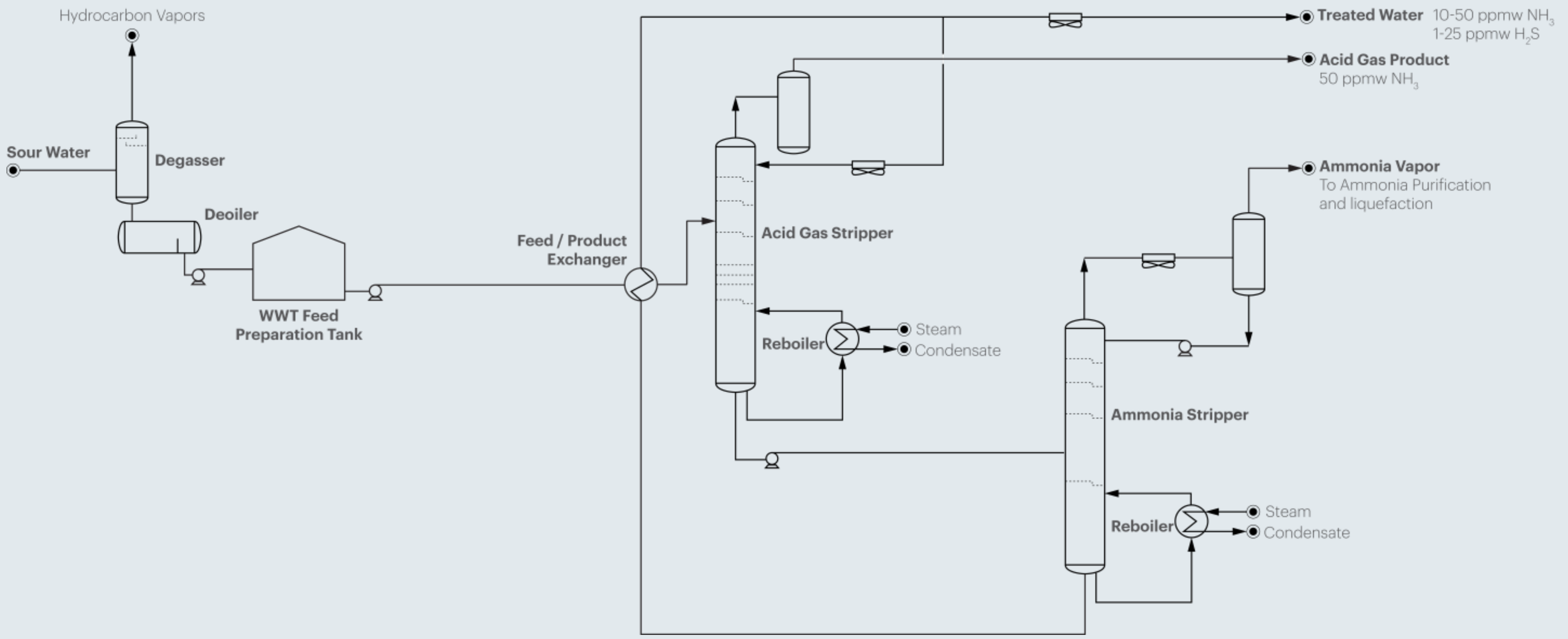
  one ton of ammonia takes up the space of ~**3 tons of sulfur**.
- Removing diluent nitrogen (Air and NH_3 combustion) helps the Claus reaction because reactants are more concentrated.
- Removing sources of water (SWS AG water, NH_3 combustion water) helps the Claus reaction equilibrium.
- Removing mass allows for expansion or CAPEX reduction.

What to Do about the Ammonia

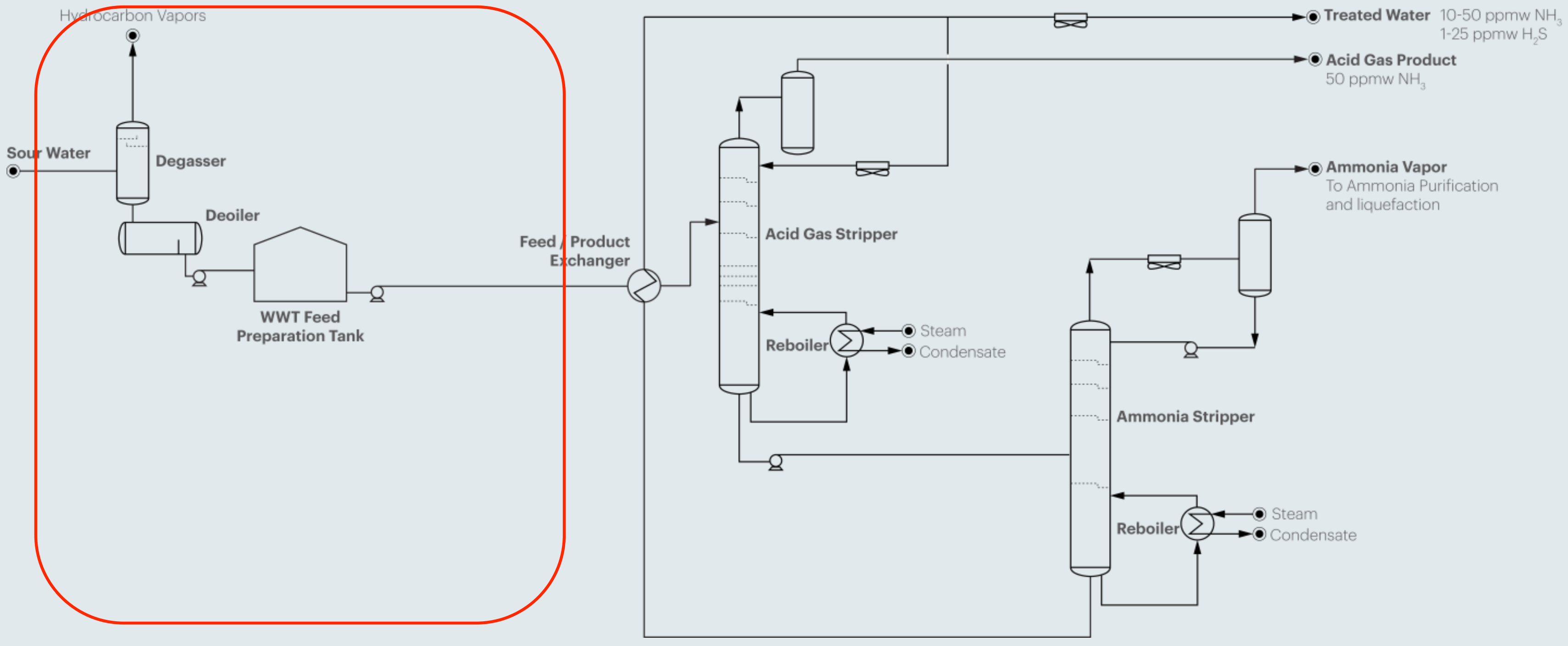
- Ammonia in the feed to an SRU is not desirable.

- 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

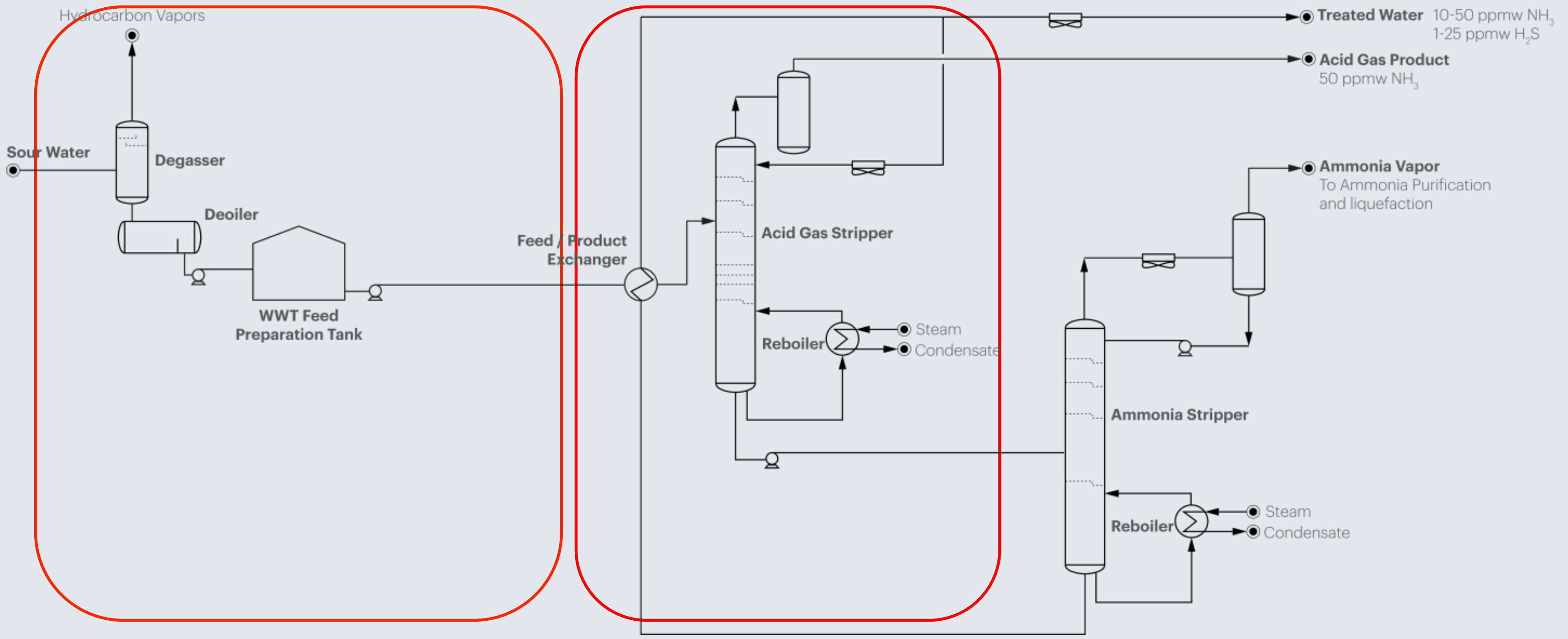
The SWSPlus™ Process



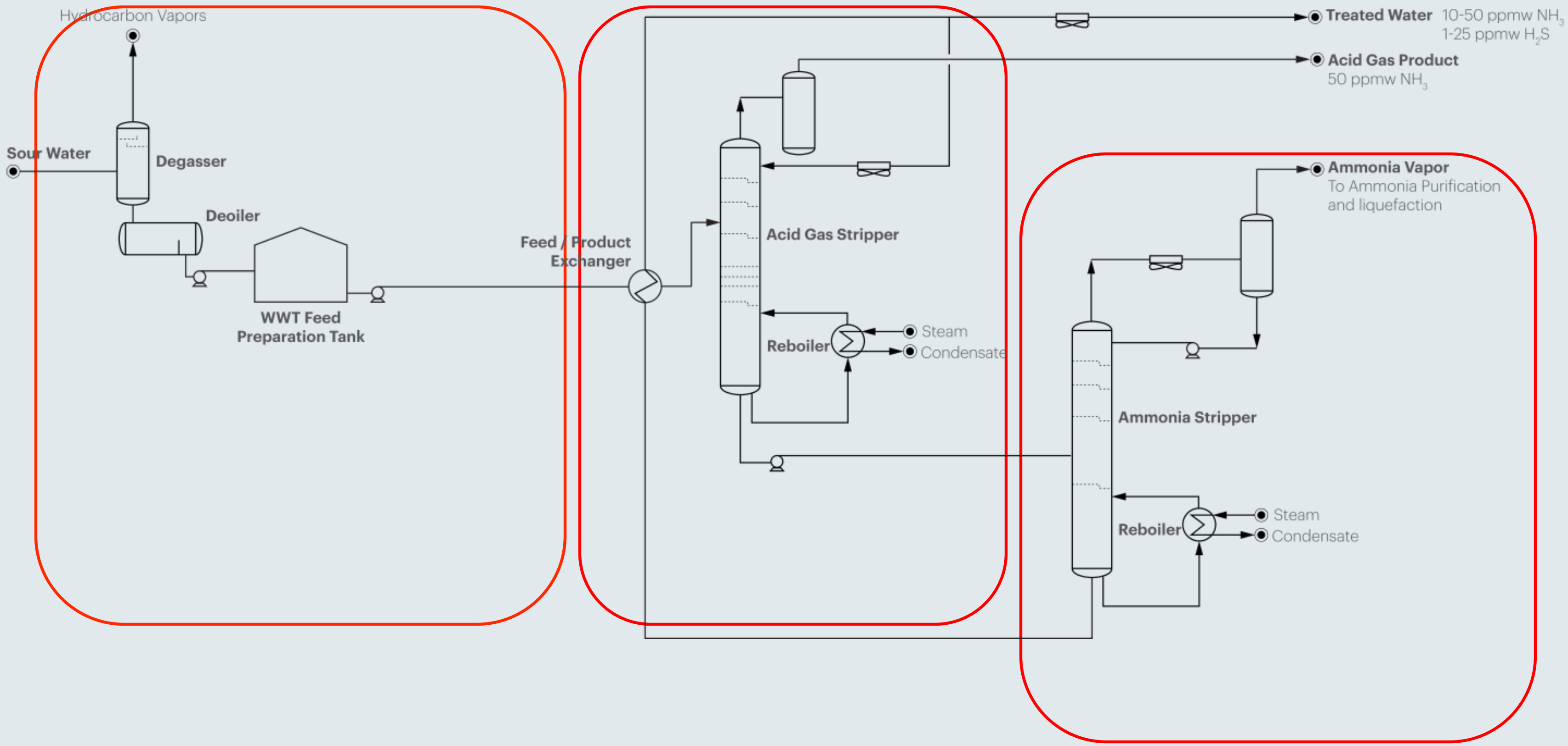
The SWSPlus™ Process



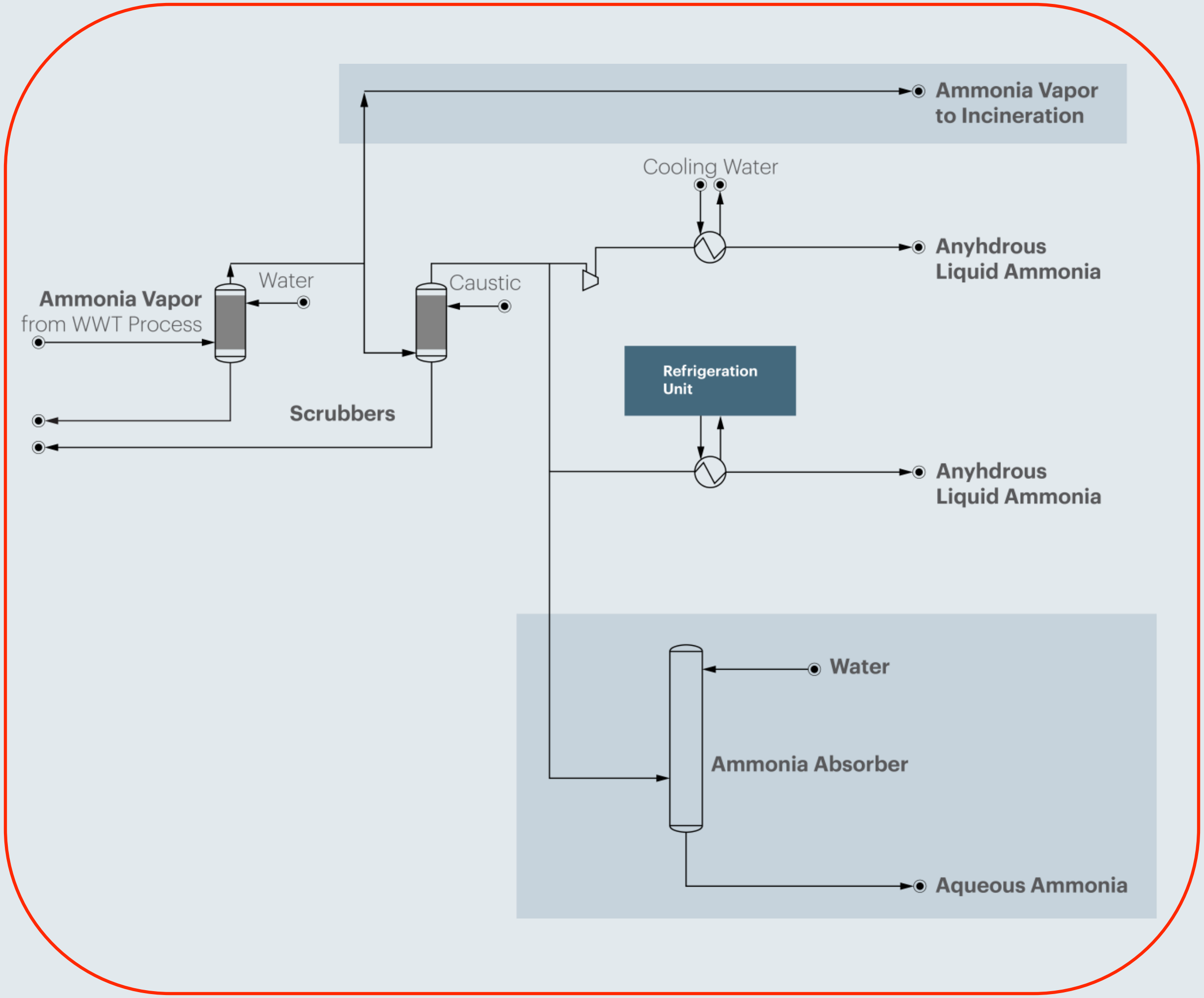
The SWSPlus™ Process



The SWSPlus™ Process



The SWSPlus™ Process



Ammonia Incineration

Anhydrous Ammonia Production

Aqueous Ammonia Production

Benefits of a Licensed Unit

Proprietary simulating tool from Chevron heritage

- Better thermodynamic data covering the entire range of NH_3 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 a 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% H_2S)
  - 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 % NH_3 and 2.4 wt % H_2S in sour water
  - Case 2 – 2.0 wt % NH_3 and 4.0 wt % H_2S in sour water
- Products
  - 50 ppmw NH_3 in stripped water
  - 10 ppmw H_2S in stripped water
  - Anhydrous Ammonia by using compression
  - <5 ppmw H_2S in ammonia product
  - H_2S to Claus unit

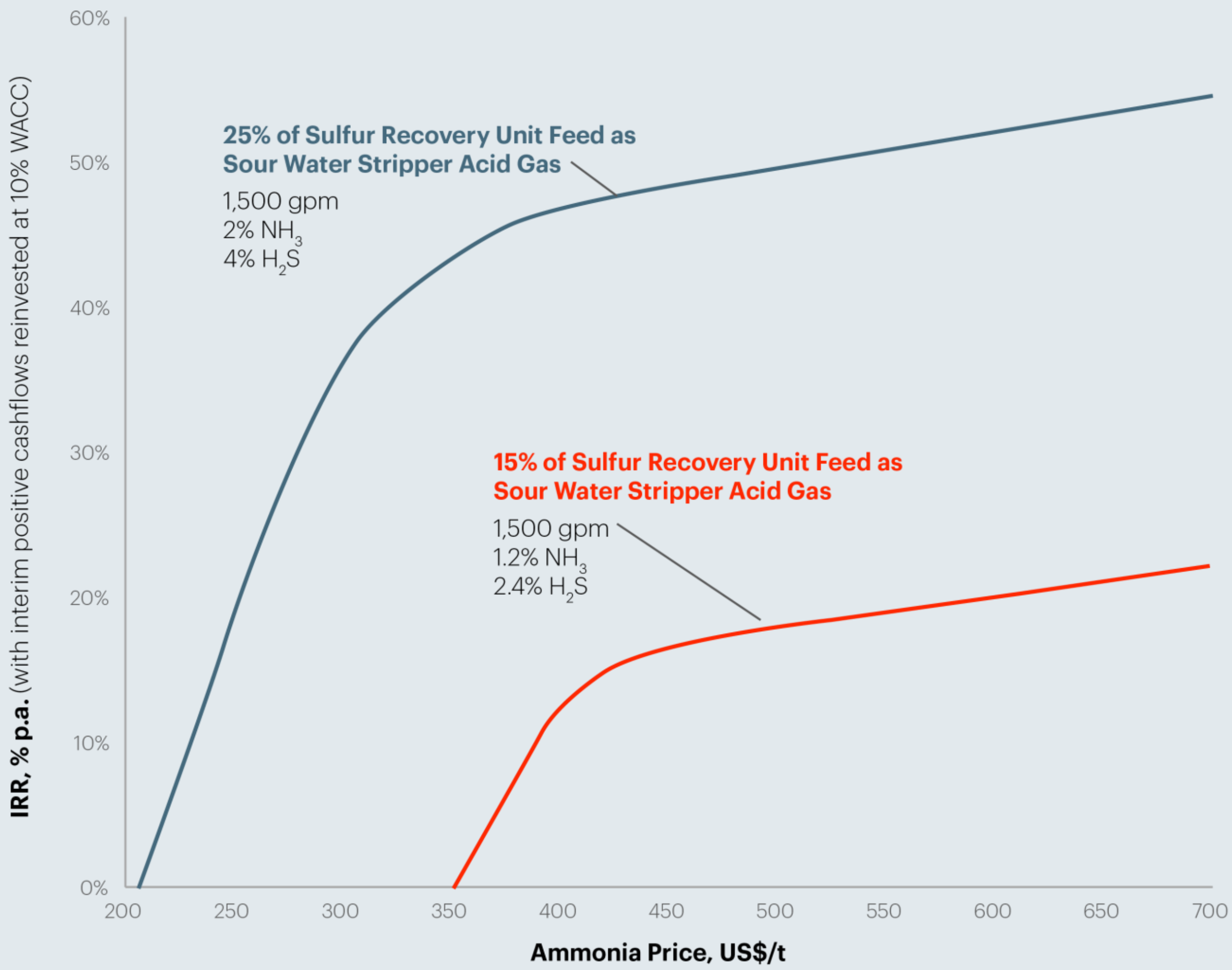
Case Study A – Process Data

- Sulfur Plant
  - Grassroots facility
  - Single 1200 MTPD sulfur capacity
  - Rich acid gas (93% H_2S)
  - 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 % NH_3 and 2.4 wt % H_2S in sour water
  - Case 2 – 2.0 wt % NH_3 and 4.0 wt % H_2S in sour water
- Products
  - 50 ppmw NH_3 in stripped water
  - 10 ppmw H_2S in stripped water
  - Anhydrous Ammonia by using compression
  - <5 ppmw H_2S in ammonia product
  - H_2S to Claus unit

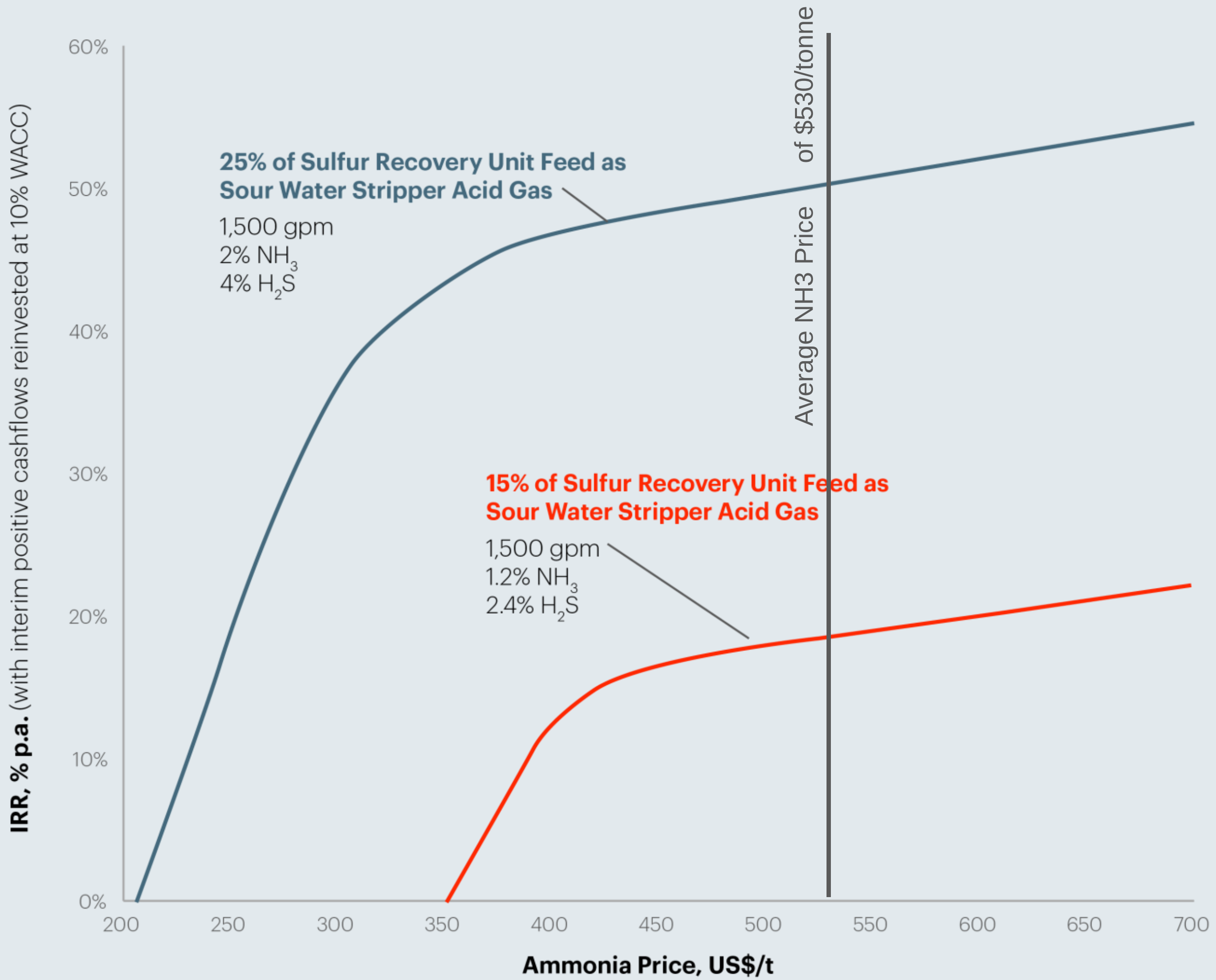
Case Study A – Economic Data

- 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



Case Study A – Results



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

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% H_2S)
- Sour Water Strippers
  - Process processes a fixed percentage of ammonia in SRUs (20.9%)
  - 1/3 H_2S, 1/3 NH_3, 1/3 H_2O
- Variable for the case study is the concentration of ammonia
  - Case 1 is 0.99 wt% NH_3 and 1.98 wt% H_2S (1235 gpm sour water flow)
  - Case 2 is 1.98 wt% NH_3 and 3.96 wt% H_2S (2470 gpm sour water flow)

Case Study B – Process Data

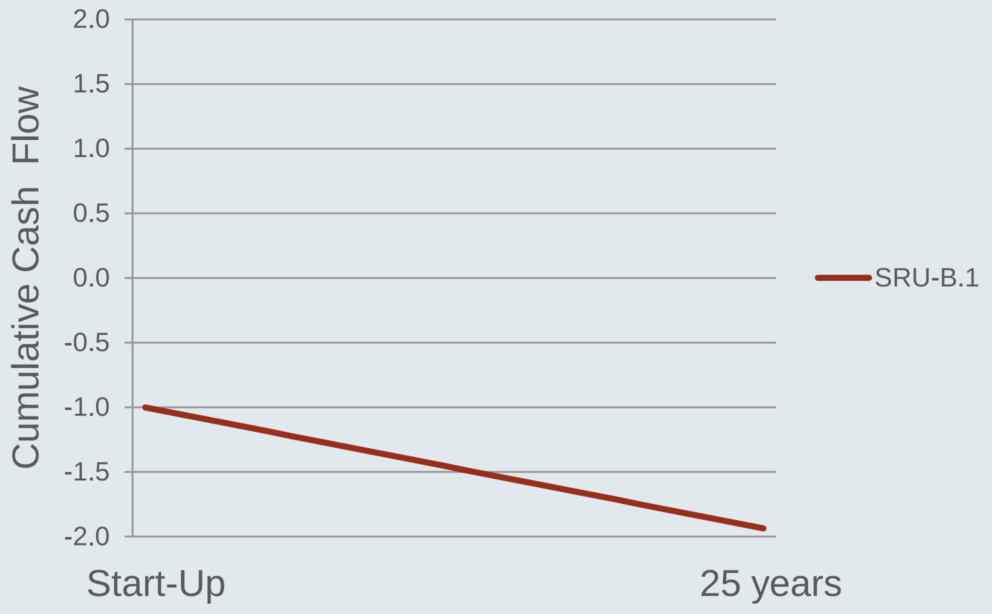
- Scenario: Refinery expansion resulting in
  - 400 MTPD incremental sulfur
  - Ammonia (SWS Gas flow) increases proportionately
    - Same concentration of NH_3 and H_2S in the SRUs as pre-expansion

- Products
  - 50 ppmw NH_3 in stripped water
  - 10 ppmw H_2S in stripped water
  - Anhydrous Ammonia by using compression
  - <5 ppmw H_2S in ammonia product
  - H_2S to Claus unit (no change)

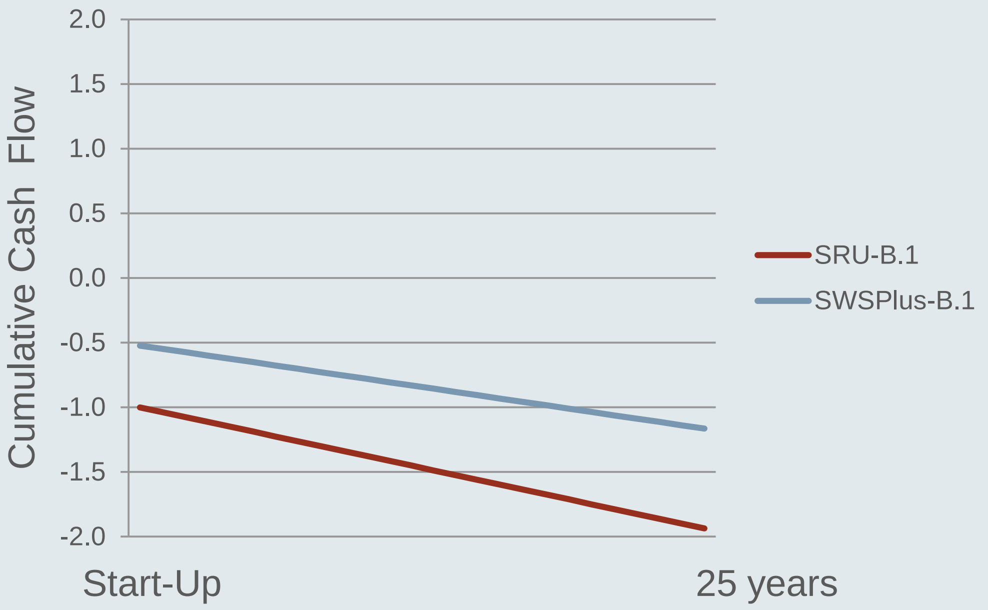
Case Study B – Economic Data

- 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

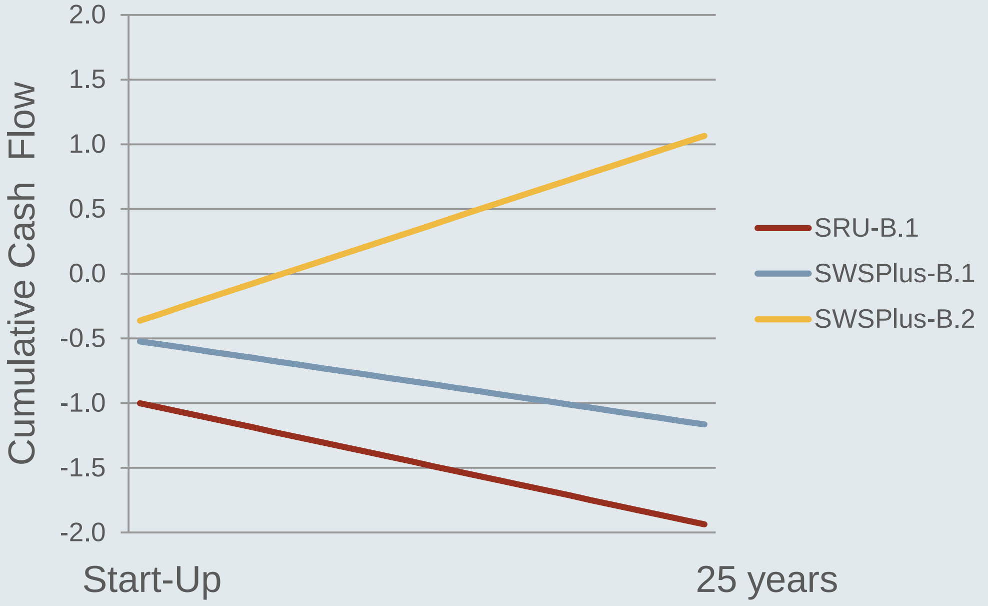
Case Study B – Results



Case Study B.1 – Results



Case Study B.2 – Results



Case Study B – Combined Results

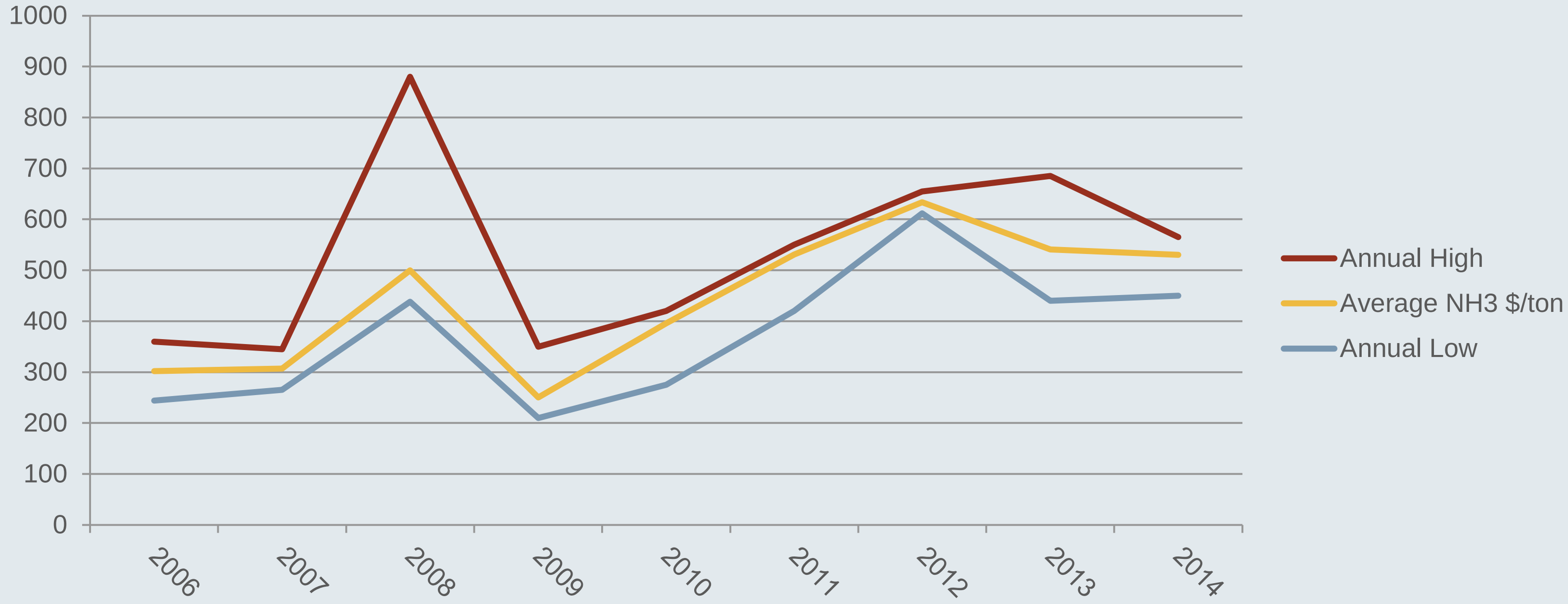
- SRU Train (400 MTPD, no SWSPlus™)
  - Claus Unit plus Tail Gas Treating Unit plus Thermal Oxidizer (Incinerator)
  - Basis of cash flow comparison with value = 1.0
  - Negative cash flow (sulfur sales do not exceed operating costs)
  - Cumulative value is -1.6 times SRU train capex during the project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

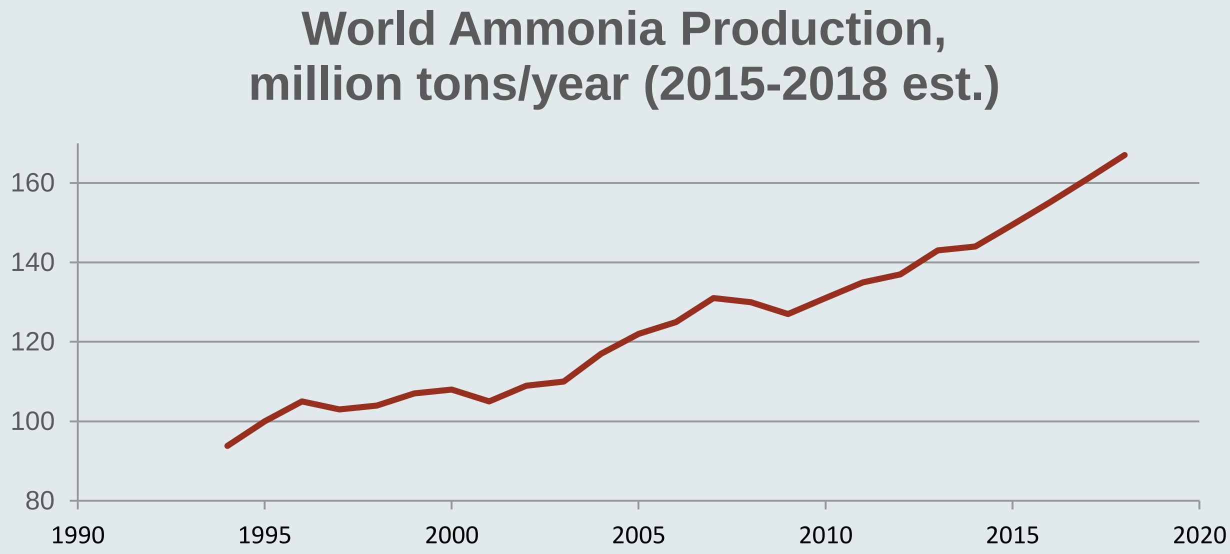
- Main trading hubs are in Tampa, Yuzhny, and the Caribbean
- Peak in September 2008 at $880/metric ton of ammonia
- $530 average for the calendar year 2014
- Supported by corn derived ethanol mandates in the US, increased Chinese/Indian demand, etc.



Source: U.S. Geological Survey

Effects on Worldwide Production?

- Case A produces ~58,700 metric tons NH_3 / year
- Case B produces ~48,667 metric tons NH_3 / 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



Source: U.S. Geological Survey

Proven Experience

Company	Location	Capacity gpm	Startup Year
Flint Hills	St. Paul, Minnesota, USA	500	TBD
Chevron	(Revamp)	500	2010
SynCrude Canada	Fort McMurray, Alberta, Canada	1,565	2006
Shell	Colorado, USA	2-100	2005
Shell	Martinez, California, USA	320	1995
Chinese Petroleum Corporation	Kaohsiung, Taiwan	70	1992
Statoil	Mongstad, Norway	295	1989
Taiyo Oil Company	Kikuma, Japan	140	1988
Syncrude Canada	Fort McMurray, Alberta, Canada	200	1987
Chevron	Richmond, California, USA	160	1985
Tesoro Petroleum Corporation	Martinez, California, USA	280	1983
Chevron	Pascagoula, Mississippi, USA	285	1983
Delaware City Refining	Delaware City, Delaware, USA	94	1979
Suncor Energy	Montreal, Quebec, Canada	250	1978
Syncrude Canada	Fort McMurray, Alberta, Canada	250	1978
Fuji Oil Company	Sodegaura, Japan	70	1976
ExxonMobil	Beaumont, Texas, USA	630	1975
Idemitsu Kosan Company	Himeji, Japan	125	1970
Chevron	El Segundo, California, USA	260	1970
Nippon Petroleum Refining	Negishi, Japan	93	1969
Fuji Oil Company	Sodegaura, Japan	23	1968
Kuwait National Petroleum	Shuaiba, Kuwait	140	1968
Chevron	Richmond, California, USA	230	1966

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

INFRASTRUCTURE
MINING & METALS
NUCLEAR, SECURITY & ENVIRONMENTAL
OIL, GAS & CHEMICALS

Using SWSPlus™ for Sulfur Capacity Addition

By Charles L. Kimtantas and Martin A. Taylor

ckimtant@bechtel.com & mataylo1@bechtel.com

Bechtel Hydrocarbon Technology Solutions. Inc.

3000 Post Oak Blvd, Houston, Texas 77056

REFCOMM GALVESTON
MAY 7-11 2018