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Fundamentals of Sour Water Stripping

Presented at the
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Outline

- Sources and Characteristics of Sour Water
  - Sour Gas Processing
  - Refining Processes
  - Claus Tail Gas Treating
  - Gasification and Similar Processes
- Processing SWS Offgas in SRU/TGUs
- Alternatives Strategies for Sour Water and Sour Gas

Sources and Characteristics of Sour Water

- Sour Gas Processing
- Oil Refining
- Gasification and Other Thermal Process
- Claus Tail Gas Units

Sour Gas Processing
Sources of Sour Water

- Wellhead Facilities
  - Dry or Wet Pipeline
- Plants
  - Inlet Separators
  - Liquid KO Drums
    - Dehydration Unit
    - Claus Plant
    - Compressor Aftercoolers

Sour Gas Processing
Sources of Sour Water (cont.)

- Plants (cont.)
  - Dehydration Processes
    - Glycol Regen Condensate
    - Solid Bed Absorbent Dehydrator Regen
  - Gas Treating Units – Reflux Purge
  - Tail Gas Units – Quench Water

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Sour Gas Processing Characteristics

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- Two Types of Sour Water
  - Produced Water
    - Water that originates in the reservoir and flows up the tubing with the gas
  - Condensed Water
    - "Salt-free Water" that condenses from the gas after the gas has left the producing reservoir

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Produced Water Characteristics

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- Originates in Reservoir
- Generally Removed in Inlet Separator
- H_2S and CO_2
- Salt-Bearing

Anions	Cations
Chlorides	Potassium
Bromides	Sodium
Sulfates	Magnesium

Produced Water Characteristics (cont.)

- Hydrocarbons
- Methanol/Hydrate Inhibitors
- Corrosion Inhibitors
- Hydrocarbons

Produced Water Processing

- Injection Well with Filtration
  - Local
  - Remote (Trucked)
- Stripping
  - Steam Injection or Steam Reboiler
  - Gas – Avoids Salting Out Potential

Produced Water Processing (cont.)

- Offgas Disposal
  - Flare
  - Low Tonnage Sulfur Recovery
  - Recompression to Pipeline
- Evaporation Ponds
  - Salt Presence

Condensed Water Characteristics

Condensed After Gas has Left Reservoir

"Salt Free"

- H_2S and CO_2
- Hydrocarbons
- Iron Sulfides
- Amines
- Glycols
- Methanol
- Other Hydrate Inhibitors
- Corrosion Inhibitors

Condensed Water Processing

- Stripping
  - Steam Injection or Steam Reboiler
  - Gas
- Disposal of Offgas
  - Flare
  - Claus Plant
  - Integrate with Tail Gas Quench

Condensed Water Processing (cont.)

- Disposal of Stripped Sour Water
  - Injection Well
  - Evaporation Pond
  - Upgrade to BFW

Some Approaches to Sour Water Stripping in Sour Gas Processing Plants

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- Integrate a Sour Water Stripper with a Tail Gas Quench System
- Re-use of Tail Gas Quench Water as Boiler Feed Water

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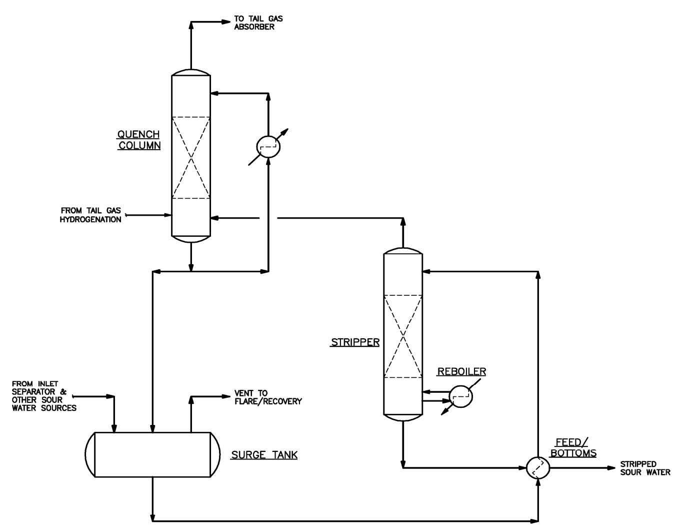
Integrated Sour Water Stripper with Tail Gas Quench



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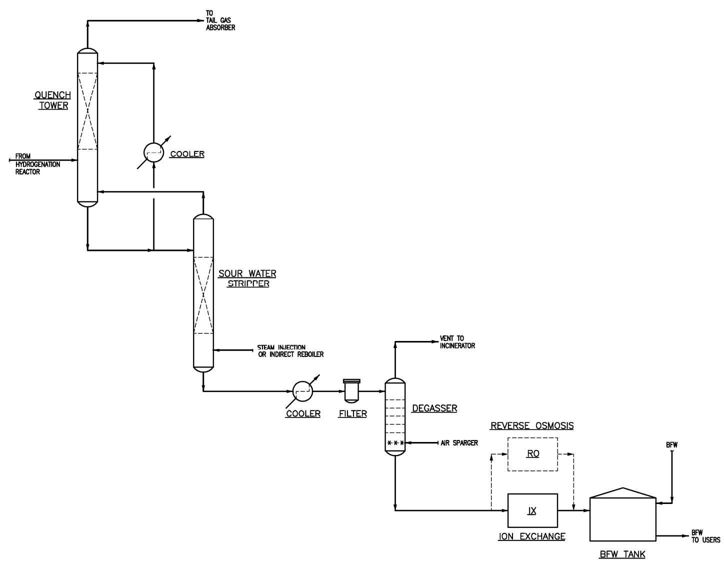
Reuse of Quench Water for BFW



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Oil Refining – Sources of Sour Water

- Desalters
- Crude/Vacuum Units
- Hydrotreaters
- FCCs
- Thermal Cracking
- Hydrocracking
- Amine Treating
- Claus Tail Gas Units

Oil Refining – General Trends

- Higher Sulfur and Nitrogen Content Crudes
- Deeper Levels of Hydroprocessing
- Generate Higher Levels of Sour Water

General Characteristics of Refinery Sour Water

- "Typical" Concentrations
  - H_2S 300 to 12,000 ppm (wt)
  - NH_3 100 to 8,000 ppm (wt)
- Molar Ratio $NH_3:H_2S$
  - Between 1.0 and 2.0
  - Typical 1.1 to 1.4
- Typical pH between 8 and 10
- Sour Water pH dictates $NH_3:H_2S$ Ratio

Refinery Sour Water

- Range of Potential Contaminates

Phenol	Organic Acids	Hydrocarbon
Cyanide	Caustic	Chloride
Selenium	Mineral Acids	Hardness

How the Bad Actors Behave

- Acidic Anions: Chlorides, Sulfates, Formates
  - Depress pH
  - Tie-up Ammonium Ion
- Alkali Cations: Sodium, Potassium
  - Raise pH
  - Tie-up Sulfide Ion
- Phenols – Not readily strippable
- Cyanide – Corrosive; use of polysulfides to form thiocyanate
- Naphthenic and Cresylic Acids

How the Bad Actors Behave (cont.)

- Heavier Hydrocarbons – Multiple problems; Can polymerize
- Carbon Dioxide – Lower pH and tie-up Ammonia
- Calcium – Can precipitate as hardness in stripper
- Oxygen – Egress can form acid which fix Ammonia
- Amine – Can tie-up Ammonia
- Selenium – Can precipitate and foul stripper

The Problem with Phenols

- Phenols are not removed due to solubility characteristics – not tray efficiencies
- Phenolic – Bearing Units (With Other Contaminates such as Cyanides and Colloidal Sulfur)
  - Cokers
  - Crude Units
  - FCCs
  - ARUs and TGU Purge

The Problem with Phenols (cont.)

- Non-Phenol Bearing Units
  - Hydrotreaters
  - Desulfurization Units

Chemistry of Refinery Sour Water

- "Sour Water" forms as Water and Hydrocarbon are in contact and partition the Hydrogen Sulfide and Ammonia in accordance with Henry's Law
- The Ammonia and Hydrogen Sulfide dissolved in the now "Sour Water" ionize to the equilibrium extent according the pH and temperature

Chemistry of Refinery Sour Water (cont.)

- Ammonia and Hydrogen Sulfide can only be stripped if in parent gaseous form, i.e. exerting a partial pressure. The iononized components do not strip
- Presence of ions which raise the pH tie-up Sulfides and aid Ammonia stripping
- Conversely presence of ions which lower the pH tie-up the Ammonia and aid Sulfide stripping

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Approach to Sour Water Management in the Oil Refinery

- Stripped Sour Water Specifications
- Re-use Strategy
- Feed Preparation
- Sour Water Stripper
- Sour Water Offgas Disposal

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Stripped Sour Water Specifications

- Typical WWTP Influent Requirements
  - 25 ppm Ammonia
  - 10 ppm Hydrogen Sulfide
- Lower specs are often observed
- Benzene Waste NESHAPS

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Sour Water Reuse

- Recycle All Stripped Sour Water to Desalter or Coker
- Segregate Phenolic and Non-Phenolic Sour Water
  - Recycle Non-Phenolic to Hydrotreaters/Desulfurizers
    - Hydrotreaters can't tolerate Phenols
    - SWS only removes 10 to 50 % of Phenol
- Recycle Phenolic Sour Water to Desalter were Oil extracts the Phenolic Compounds

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Sour Water Feed Preparation

- Inlet Feed Separation and Hydrocarbon Flash and Skimming
  - Vent to Safe Location
- Sour Water Feed Surge
  - 3-Day Storage Target
  - Oil Skim
  - Design to Prevent Short Circuit

Sour Water Stripper Design

- Non-Refluxed
  - Direct Steam Injection or Reboiler
  - Very High Water Content of Offgas (70+% vol @ 13 psig)
- Refluxed
  - Direct Steam Injection or Reboiler
  - Overhead Condenser or Pump Around
  - Conventional Practice (40+% vol @ 13 psig)

Conventional Sour Water Stripper Practice: Oil Refinery

- Two Main Design Choices – Pros/Cons
  - Pump Around vs. Overhead Condenser
  - Direct Steam Injection vs. Reboiler
- General Trends
  - Steam to Feed Ratio
  - Feed Tray Location
  - Feed Concentration
  - Steam Cost and Number of Trays
  - Caustic Injection and Chlorides

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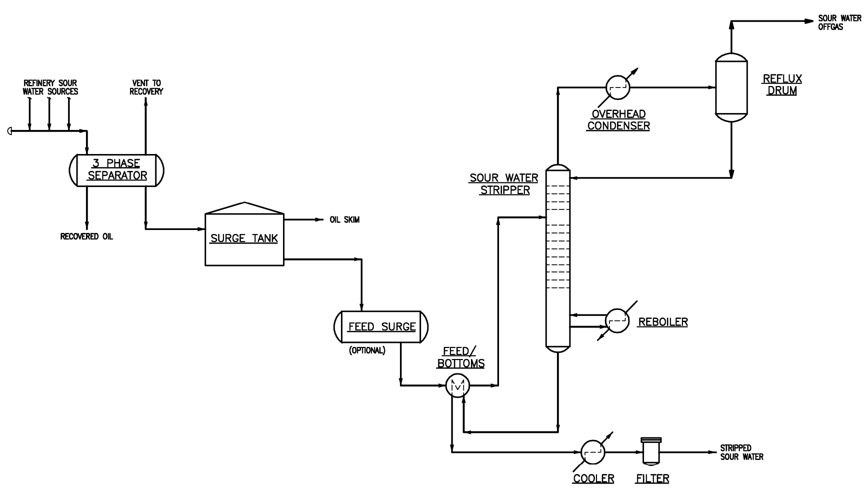
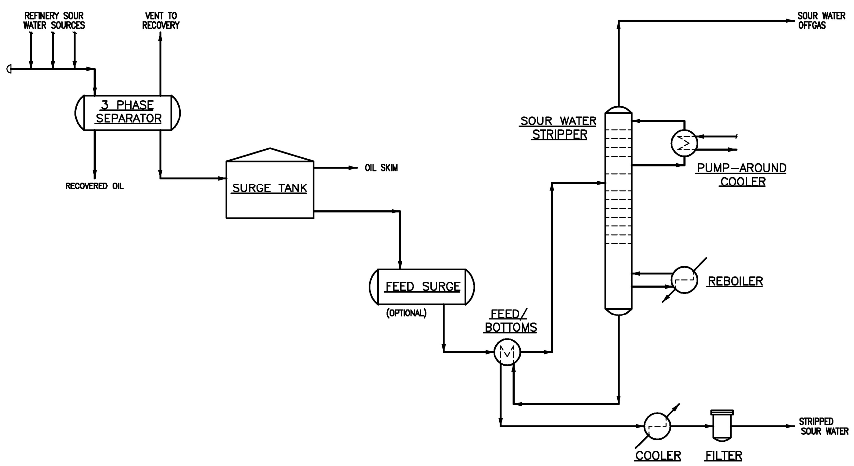
Conventional Overhead Condenser



Pump Around Condenser



Sour Water Stripper Design Approach

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- Materials of Construction
  - CS was predominant choice in the day
  - Overhead Line was most often upgraded
  - Current designs upgrade – especially as function of feed
- Simulation Basis
  - Sour – Pro/II
  - GPA Sour – Pro/II
  - OLI Electrolyte – Pro/II (caustic injection studies)
- Elusive Phenol Removal Process?

Sour Water Stripper Design Approach (cont.)

- Design Basis Issues
  - Don't Over Estimate Feed Sourness
  - Tower Stability and Control Problems
  - MOC Upgrade Creep
  - Design Margin Creep

Sour Water Stripper Design Approach (cont.)

- Nice to Haves
  - Can't have enough hydrocarbon skimming capability
  - Likewise with surge and storage – but be reasonable
  - Dual Reboilers
  - Live Steam Injection
  - Some degree of redundancy/overcapacity for catch-up and addressing the inevitable fouling episode(s)

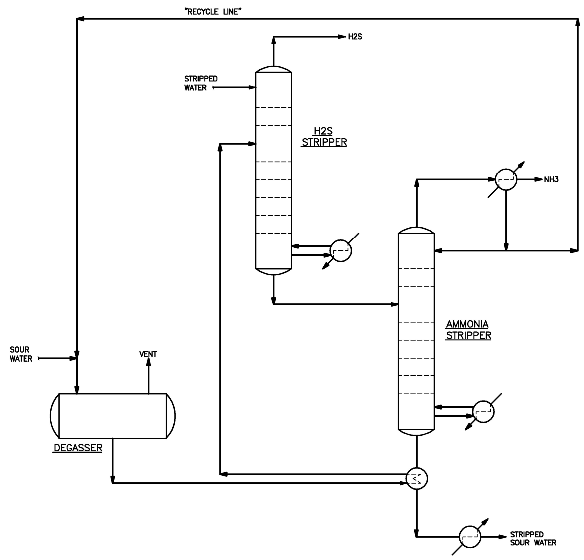
Sour Water Offgas Disposal

- Flare - Back-up and Limited
- Fired Heaters
  - Direct Combustion of SWS Offgas
  - Separate NH_3 from H_2S and Burn Ammonia in Heater
- Claus SRUs
  - The Most Common Approach
  - And the Most Interesting

Separate Ammonia from Hydrogen Sulfide

- Most common approach in refinery application is Chevron WWT
- Two Column Operation
- Ammonia can be recovered
  - Aqueous
  - Anhydrous
- Main Concerns
  - CAPEX (Due to Equipment Count and MOC)
  - Complexity
  - Ammonia Sales

Chevron WWT Process



Sour Water From Claus Tail Gas Treating

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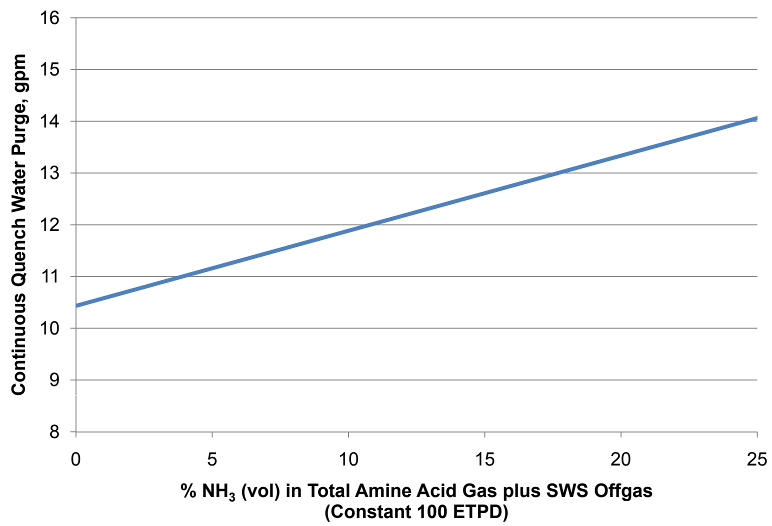
- Sour Water Produced from Quench
- Claus / Tail Gas Feeds
- Components

H_2S	TOC
NH_3	Thiosulfate
CO_2	Sulfide

- Production Characteristics
  - 100 LTPD S Generates 10.5 gpm Sour Water
  - 100 STPD Ammonia Generates 40.5 gpm Sour Water

Calculated Effect of Sour Water Stripper Offgas in Claus SRUs on Quench Water Purge



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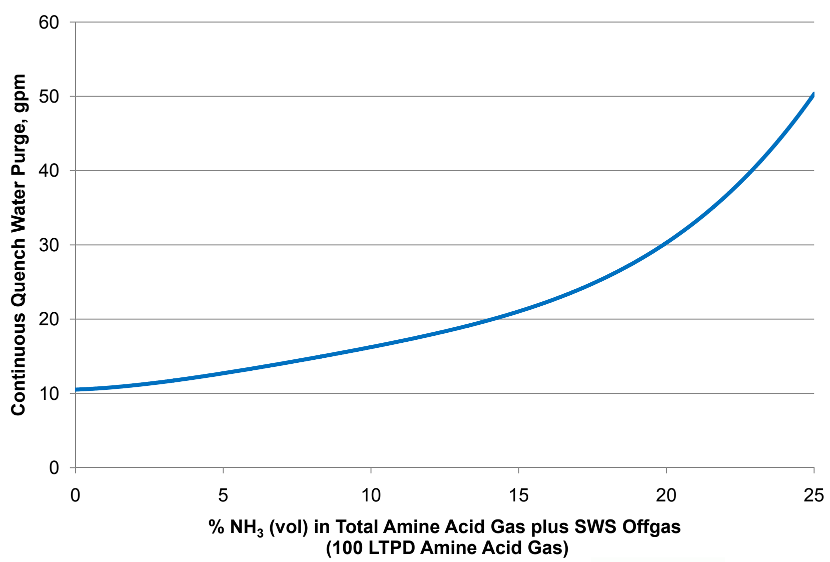
Calculated Effect of Sour Water Stripper Offgas in Claus SRUs on Quench Water Purge



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Gasification and Other Similar Processes

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- Gases derived from Coal
  - Producer Gas
  - Water Gases
- Coke Oven Gas
  - By-product of Coal Coking
- Coal or Pet Coke Gasification
  - Syngas for Power
  - Ammonia
  - Synthetic Natural Gas

Sour Water From Gasification and Other Similar Processes

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- Ammonia and Cyanides Produced During the Thermal Processing are present in the coal-derived gas
  - Up to 1 % vol Ammonia
  - 0.1 to 0.25% vol Hydrogen Cyanide
- Processes Available to Remove the Ammonia directly from the Coal-Derived Gas

Sour Water From Gasification and Other Similar Processes (cont.)

- Typical Thermal Processing involves some form of Water Quench or Scrubber
  - The Sour Water contains all the Ammonia and some of the Hydrogen Sulfide from the coal-derived gas
  - Other water soluble components like organic acids and phenols are present

Some Interesting Processes from the Coal Gas Industry Practices & Experience

- Direct Ammonia Removal Processes
  - React with Strong H_2SO_4 or H_3PO_4 to Produce Ammonium Sulfate or Ammonium Phosphate and Acid Gas
  - Phosam Process to Separate NH_3 and Acid Gases from the Gas Stream

Some Interesting Processes from the Coal Gas Industry Practices & Experience

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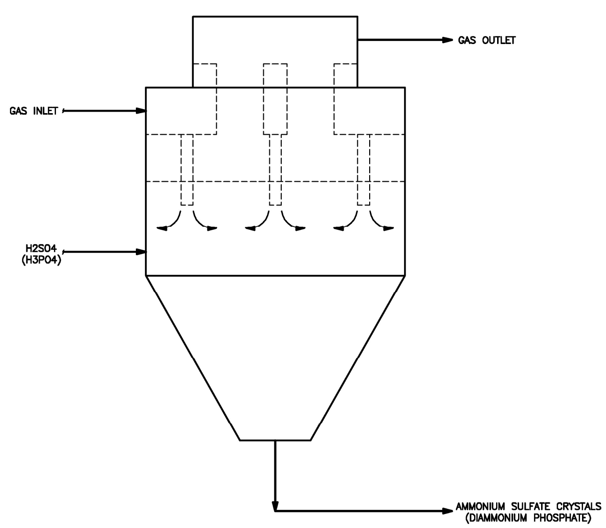
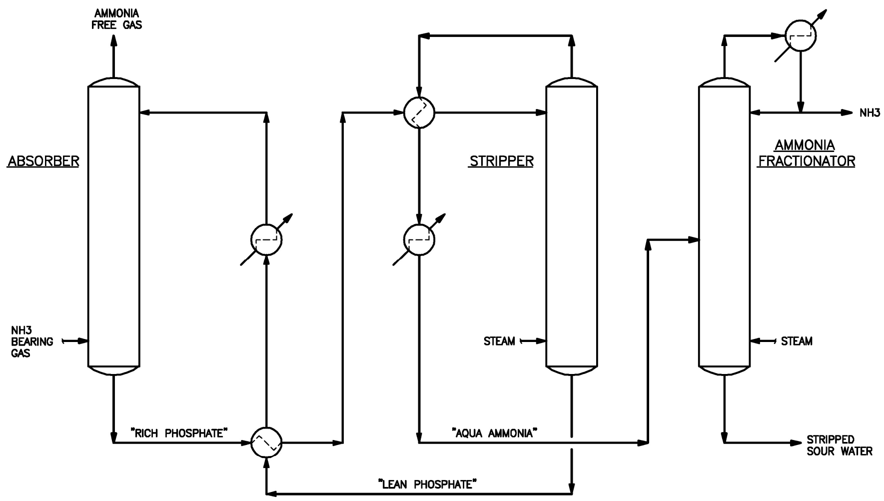
- Ammonia Processing After Water Scrubbing and Sour Water Stripping
  - Catalytic Destruction of NH_3 in Presence of H_2S
  - Oxidation of NH_3 and H_2S in Claus Plant or Incinerator

Ammonium Sulfate or Ammonium Phosphate

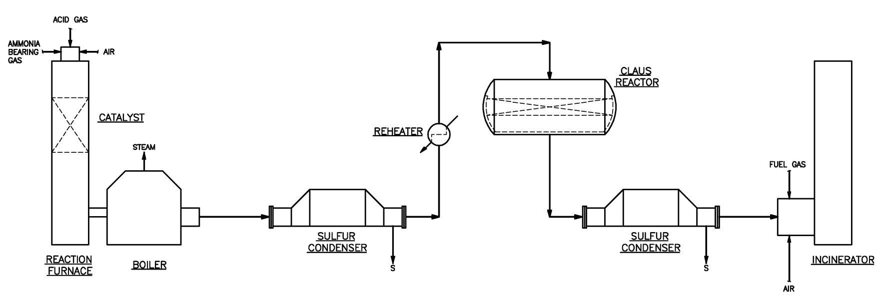


"SATURATOR"

Phosam Process



Catalytie NH_3 Destruction and Sulfur Recovery



Even More Interesting Processes from the Coke-Oven Gas Processing Industry

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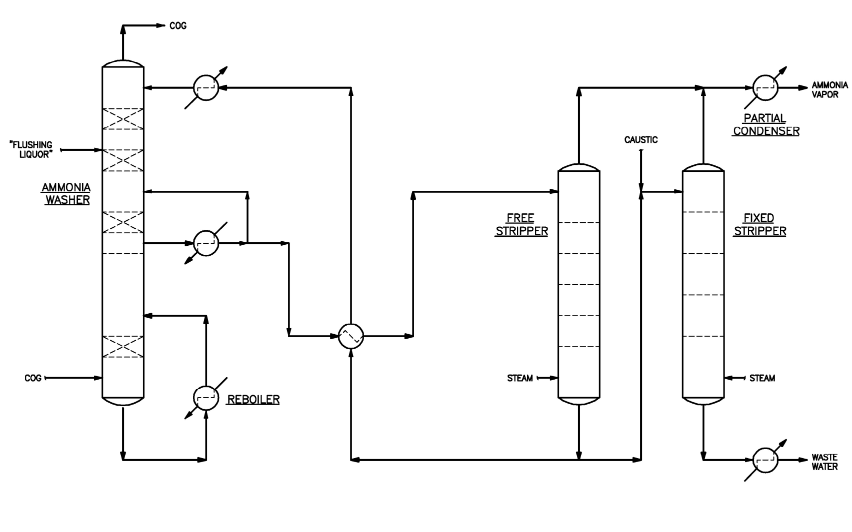
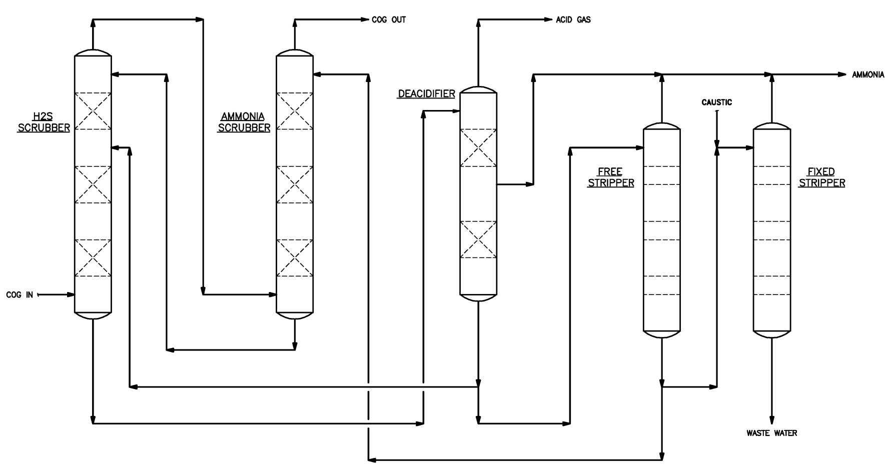
- Process for Ammonia Removal and Recovery from Ammonia Bearing Acid Gas
- Processes for Ammonia and Hydrogen Sulfide Removal Using Ammonia

Ammonia Removal and Recovery



Acid Gas and Ammonia Removal with Ammonia Recovery



Chemistry of Ammonia-Based Processes for H_2S and CO_2 Removal

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- Hydrogen Sulfide

$2\ NH_3\ (g) + H_2S\ (g) \rightarrow (NH_4)_2\ S$

$NH_3\ (g) + H_2S\ (g) \rightarrow (NH_4)\ HS\ (aq)$

- Carbon Dioxide

$2\ NH_3\ (g) + CO_2\ (g) + H_2O\ (l) \rightarrow (NH_4)_2\ CO_3\ (aq)$

$2\ NH_3\ (g) + CO_2\ (g) \rightarrow NH_4\ CO_2\ NH_2\ (aq)$

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Sour Water Offgas to Claus SRUs

- Normally can process up to 2 – 4% (vol) ammonia in Claus SRU without modification to a conventional straight-through design
- Above this level need additional design considerations: preheat, two-zone thermal reactor etc.
- Over 25% (vol) ammonia in total feed gases need to address potential NO_x formation

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Sour Water Offgas to Claus SRUs (cont.)

- Typically like to see Claus thermal reactor effluent ammonia content less than 100 ppmv
- Some reports of Claus thermal reactor effluent ammonia up to 500 to 600 ppmv without difficulty
- Overhead Line Temperature Maintenance
- KO Drum
  - Contains No Demister
  - Multiple Level Devices
  - Fully Traced and Insulated

Sour Water Offgas to Claus SRUs (cont.)

- Instrument Taps
  - Large (2” or 3” on Vessel)
  - All Traced
  - Diaphragm Seals
  - Steam Outs
  - Oversized Venturi Taps
- High Level Trip
  - Isolates Sour Water Offgas Only

Sour Water Offgas to Claus SRUs (cont.)

- Mixing SWS Gas with Amine Acid Gas
  - Salt Formation
  - Under Deposit Corrosion
  - All Lines No Pocket and Top Entry
  - Minimum Distance After Mix Point

Sour Water Offgas to Claus SRUs (cont.)

- Amine Acid Gas Preheater
  - Process on Tube Side
  - BEM Axial Flow Configuration to Eliminate Pockets
  - Single Pass to Eliminate Pockets
  - Tube Sheet Material – SA-516-70 w/ 0.1875” (min.) 347 SS Overlay
  - Tube Material – SA-249-TP 321 SS
    - All 321 SS Materials are Stabilized / Annealed
  - Tube to Tubesheet Joint is Rolled and Seal Welded

Ammonia Salts
Solids Deposition Possibilities

- Ammonia Forms a Number Salts That Can Produce Deposits
  - Ammonium Hydrosulfide

    $NH_3 + H_2S \rightarrow NH_4\text{-}HS$
  - Ammonium Carbamate

    $2NH_3 + CO_2 \rightarrow NH_4\text{-}CO_2\text{-}NH_2$
  - Ammonium Bicarbonate

    $NH_3 + CO_2 + H_2O \rightarrow NH_4\text{-}HCO_3$

Ammonia Salts
Solids Deposition Possibilities (cont.)

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- Deposition Temperature Depends on Partial Pressures of NH_3, H_2S, CO_2 and H_2O
- Salts Typically Begin Depositing from 70 - 140F
- Best Practice is Stay at Least 45F Hotter than Calculated Deposition Temperature

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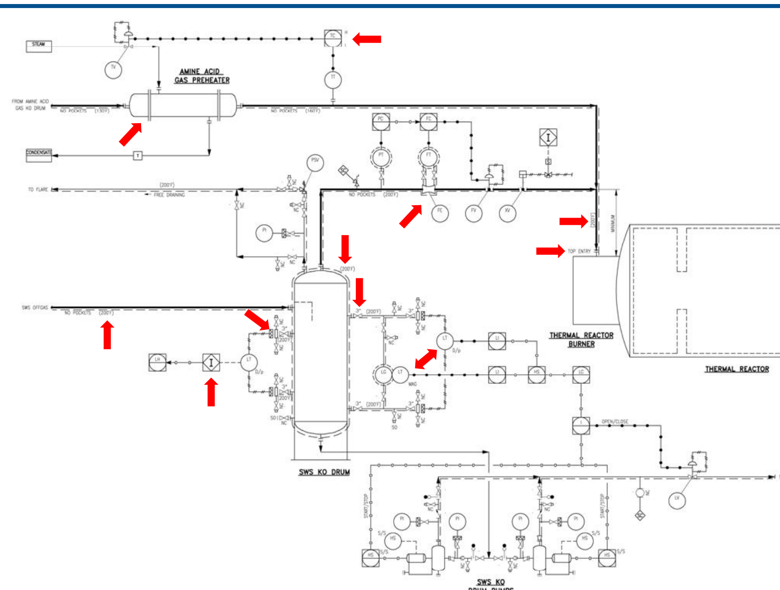

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Theoretical Impact of Processing Sour Water Stripper Offgas on Claus/Tail Gas Unit Capacity

- Claus Reaction

$$H_2S + 3/2\ O_2 \rightarrow SO_2 + H_2O$$
$$2\ H_2S + SO_2 \rightarrow 3S + H_2O$$
$$\overline{3\ H_2S + 3/2\ O_2 \rightarrow 3S + 2\ H_2O}$$

- Ammonia Combustion

$$2NH_3 + 3/2O_2 \rightarrow 2N_2 + 3H_2O$$

- Overall

$$\frac{3/2 \text{ lb mole } O_2}{3 \text{ lb mole S}} \cdot \frac{2 \text{ lb mole } NH_3}{3/2 \text{ lb mole } O_2} \cdot \frac{17 \text{ lb } NH_3}{1 \text{ lb mole } NH_3} \cdot \frac{1 \text{ lb mole S}}{32 \text{ lbs}} \cdot \frac{\text{ST } NH_3}{2000 \text{ lb } NH_3} \cdot \frac{2240 \text{ lbs S}}{\text{LT S}}$$

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Calculated Effect of Processing SWS Offgas on Claus/Tail Gas Unit Capacity

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- "100 tpd Claus/Tail Gas Unit"
- Acid Gas (vol %)
  - 87.5% H_2S
  - 4.5% CO_2
  - 1.9% C_1
  - 6.1% H_2O
- SWS Offgas (vol %)
  - 23.2% H_2S
  - 33.1% NH_3
  - 41.6% H_2O
  - 2.1% C_1

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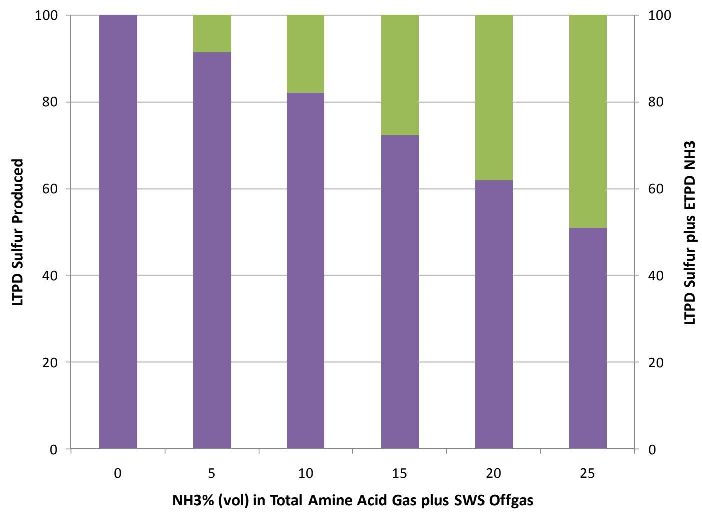
Calculated Effect of Processing SWS Offgas on Claus / Tail Gas Capacity at Constant Air Demand



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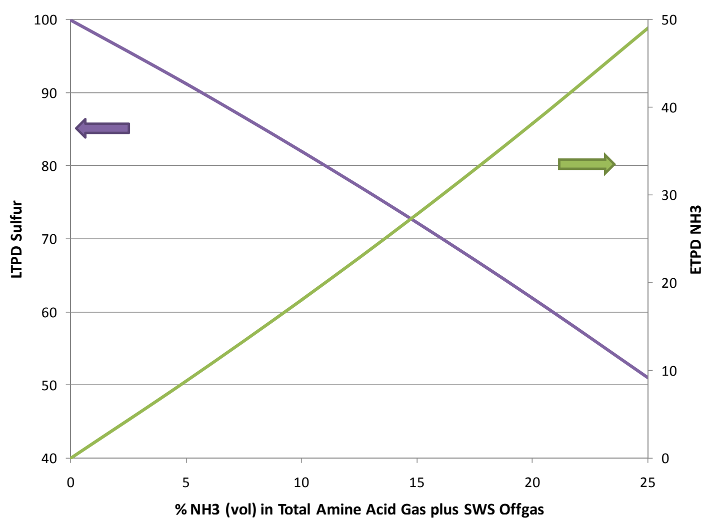
Calculated Effect of Processing SWS Offgas on Claus / Tail Gas Capacity at Constant Air Demand



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Calculated Impact Analysis Based Only on Required Air Demand

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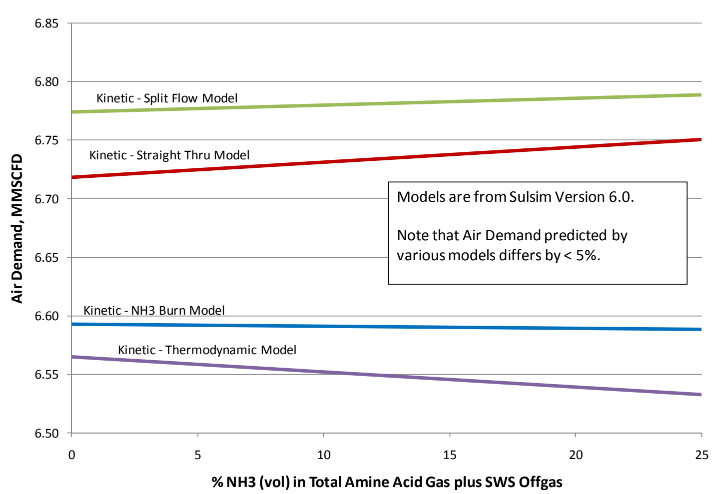
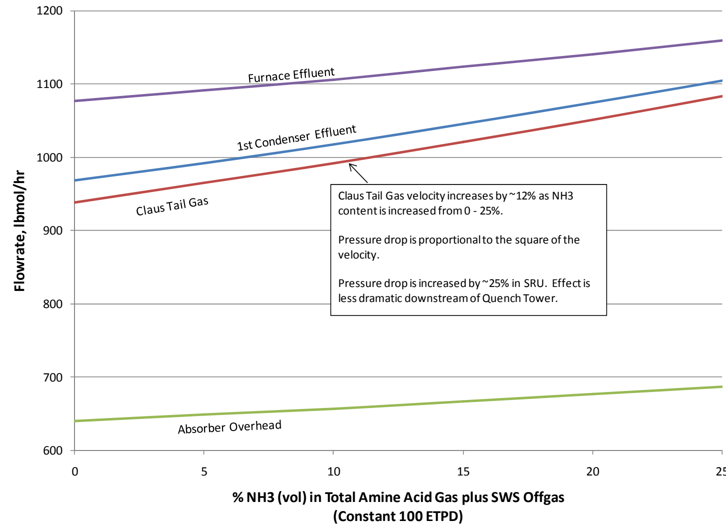
What About Actual Performance Characteristics?

Simulated Effect of Processing Sour Water Stripper Offgas in Claus / Tail Gas Units



Simulated Effect of Sour Water Stripper Offgas in Claus SRUs on Pressure Drop



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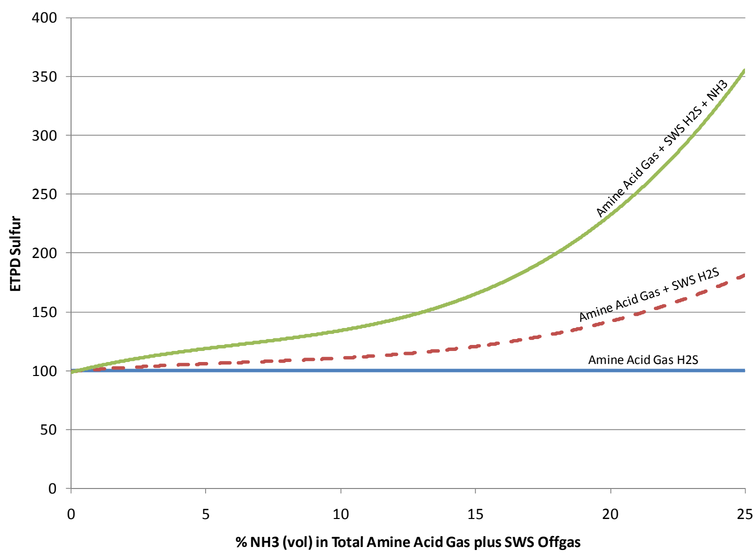
New Plant Construction



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CAPEX Approximation

- Basic "100 tpd" Claus/Tail Gas Unit is US$25MM
  - Typical Two-Bed Claus
  - 20 or 24" Main Gas Line
  - Conventional TGU plus Incinerator

CAPEX Approximation (cont.)

- Adding Ammonia Processing
  - 5% - 115 ETPD is US$28MM (105 LTPD S & 4 STPD NH3)
  - 10% - 140 ETPD is US$31MM (115 LTPD S & 10 STPD NH3)
  - 15% - 165 ETPD is US$35MM (125 LTPD S & 16 STPD NH3)
  - 20% - 240 ETPD is US$44MM (145 LTPD S & 38 STPD NH3)
  - 25% - 350 ETPD is US$54MM (180 LTPD S & 68 STPD NH3)

What's it Worth?

- 10% Ammonia Feed
  - Additional US$6MM CAPEX
  - OPEX?
  - Ammonia – Nearly US$3MM/Year
- 20% Ammonia Feed
  - Additional US$19MM CAPEX
  - OPEX?
  - Ammonia – Nearly Over US$11MM/Year

Alternative Sour Water Management Processes

- Ammonia Separation from Sour Water
  - Processes
    - Chevron WWT Process
    - US Steel Phosam Process
  - Uses for Recovered Ammonia
    - Recover as Anhydrous Ammonia
    - Ammonia Sulfate
    - Ammonium Thiosulphate
    - Hydrogen

Alternative Sour Water Stripper Offgas Processes

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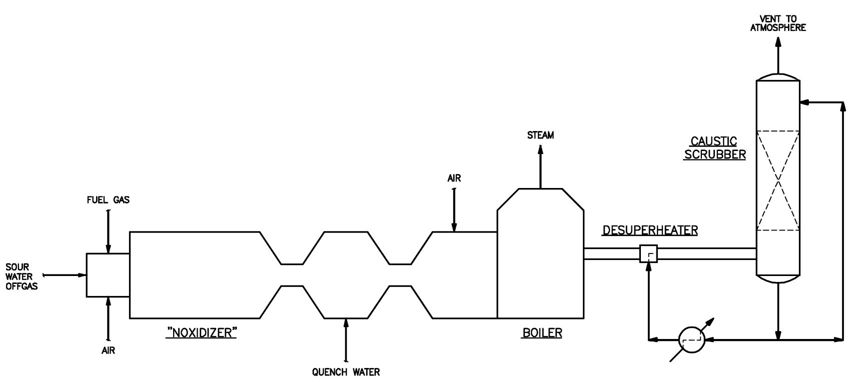
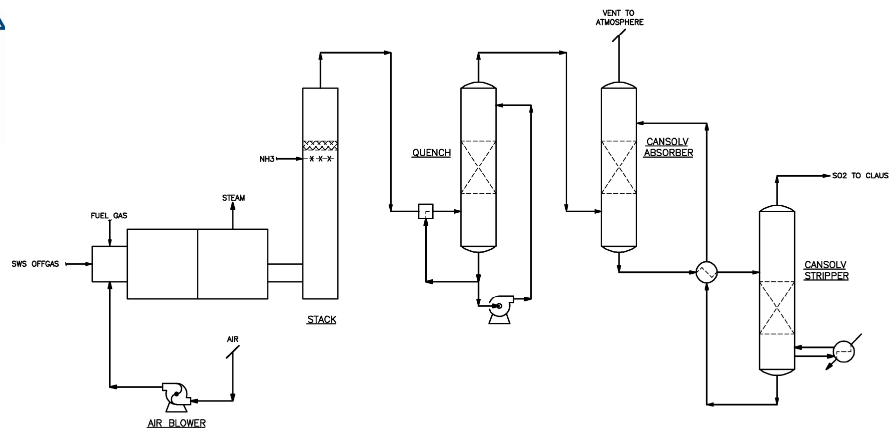
- Direct Sour Water Stripper Offgas Combustion with SO_2 Scrubbing
  - NO_x Production?
    - John Zink "Noxidizer"
    - SCR or SNCR?
  - SO_2 Scrubbing
    - Cansolv (SO_2 Recycle)
    - Caustic
    - Ammonia (Ammonia Sulfate or Ammonia Thiosulphate)
  - Hydrogen – Can be produced from Ammonia (No Joke)

"Noxidizer" with Caustic Scrubber



SCR Combustion with SCR and Cansolv Scrubber



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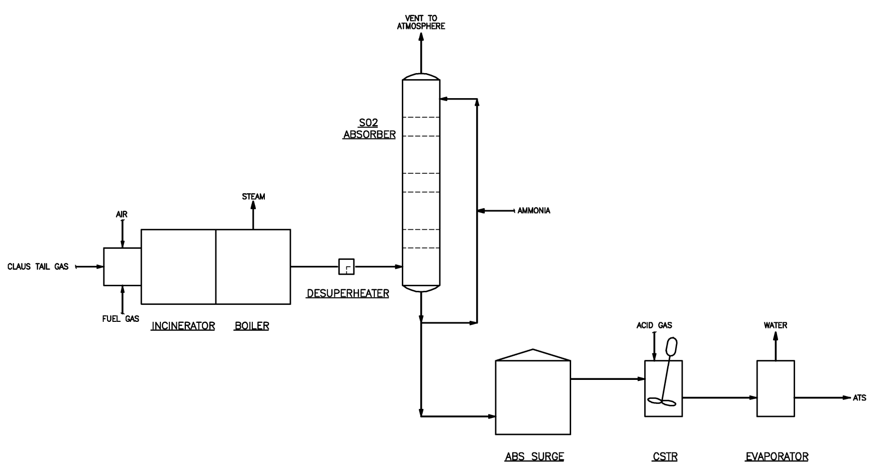
Ammonia Thiosulphate Production



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Some Reflections on Sour Water

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- There are many different approaches to managing sour water – most successful, some not with a few mysteries remaining

Some Reflections on Sour Water (cont.)

TECHNOLOGY ENGINEERING

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- What is the Refiner's Break Point to Look at Alternatives?
  - Removing Load from Claus – Options?
  - Typical Water Cost and Upgrade Complexity to BFW
    - City / Potable
    - Well
    - Surface
    - Sour Water
  - Is Ammonia Recovery a Better Way – Re-look at Economics given Energy Costs and Green Solutions???