Sulfur Recovery

Chapter 16
Based on presentation by Prof. Art Kidnay

Updated: April 25, 2017
Copyright © 2017 John Jechura (jjechura@mines.edu)

Plant Block Schematic

Updated: April 25, 2017
Copyright © 2017 John Jechura (jjechura@mines.edu)

Topics

- Introduction
- Properties of sulfur
- Sulfur recovery processes
  - Claus Process
  - Claus Tail Gas Cleanup
- Sulfur storage
- Safety and environmental considerations
Sulfur Crystals

Sulfur Crystalites

Wai-o-tapu Hot Springs, North Island, NZ

Sulfur Usage & Prices

Natural gas & petroleum production accounts for the majority of sulfur production.
Primary consumption is agriculture & industry:
- 60% for farm fertilizer:
  - sulfur → sulfuric acid → phosphoric acid → fertilizer
- $50 per ton essentially disposal cost
- Chinese demand caused run-up in 2007-2008

Ref: Smithsonian Museum of Natural History
Updated: April 25, 2017
Copyright © 2017 John Jechura (jjechura@mines.edu)
Properties of sulfur

Sulfur Chemical Structure

Pure sulfur exists as $S_x$ where $X = 1$ to 8

The dominant species are $S_2$, $S_6$, & $S_8$

May be in ring structure or open chain

Species determined by temperature

This composition greatly affects its properties!
Typically a modified Claus process
- H2S-rich stream burned with 1/3 stoichiometric air. Hot gases are then passed over alumina catalyst to produce free sulfur
  - Combustion: \[ \text{H}_2\text{S} + 1.5 \cdot \text{O}_2 \rightarrow \text{H}_2\text{O} + \text{SO}_2 \]
  - Claus Reaction: \[ 2 \cdot \text{H}_2\text{S} + \text{SO}_2 \rightarrow 2 \cdot \text{H}_2\text{O} + 3 \cdot \text{S} \]
- Sulfur formation reaction mildly exothermic
- Sulfur conversion reactors kept above 400°F (sulfur dew point)

The Claus reaction is reversible — therefore, 100% conversion can never be achieved
- Practically, Claus units are limited to about 96% recovery
- Tail gas units are used to provide improved conversion
Modified Claus Process

Temperature Regimes for the Claus Process

THE CLAUSS REACTION

2 H₂S + SO₂ ⇌ 3m S₈ + 2 H₂O

What Limits the Reaction?
- Reaction Products
- Water and sulfur
- Operating Temperature
- Reactant Stoichiometry

Updated: April 25, 2017
Copyright © 2017 John Jechura (jjechura@mines.edu)
Claus Process

Use multiple stages to obtain highest conversion
  - Typically three

Various flow patterns
  - Straight-through – best, used whenever possible
  - Split flow – best at low H₂S feed concentrations (5 to 30 mol% H₂S)
  - Sulfur recycle < 5% H₂S
  - Direct oxidation < 5% H₂S

Claus Process

Claus unit feed usually contains H₂S and CO₂
High concentrations of noncombustible components (CO₂, N₂)
  - Lower flame temperature
  - Difficult to maintain stable combustion furnace flame temperatures below 1700°F

Solutions include
  - Preheating air
  - Preheating acid gas feed
  - Enriching oxygen in air
  - Using split-flow process

Split-flow Claus Process

[Diagram of the split-flow Claus process]
**Typical Claus Configurations**

<table>
<thead>
<tr>
<th>Approximate concentration of H₂S in feed (mol%)</th>
<th>Process variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>55 - 100</td>
<td>Straight-through</td>
</tr>
<tr>
<td>30 - 55</td>
<td>Straight-through + acid gas and/or air preheat</td>
</tr>
<tr>
<td>15 - 30</td>
<td>Split-flow or acid gas and/or air preheat</td>
</tr>
<tr>
<td>10 - 15</td>
<td>Split-flow with acid gas and/or air preheat</td>
</tr>
<tr>
<td>5 - 10</td>
<td>Split-flow with fuel added, O₂ enrichment, or with acid gas and air preheat</td>
</tr>
</tbody>
</table>

**Tail gas Clean Up**

Three process categories:

- Direct oxidation of H₂S to sulfur (Superclaus)
  
  \[ 2 \text{H}_2\text{S} + \text{O}_2 \rightarrow 2 \text{S} + 2 \text{H}_2\text{O} \]

- Sub-dew point Claus processes (Cold Bed Adsorption)

- SO₂ reduction and recovery of H₂S (SCOT)

**Claus Tail Gas Cleanup**

Conventional 3-stage Claus units recover 96 to 97.5% of sulfur
- Remainder was burned to SO₂ and vented
- Adding fourth stage results in 97 to 98.5% recovery

Regulations now require 99.8 to 99.9% recovery

Meeting regulations requires modified technology
Shell Claus Offgas Treating (SCOT)

Four step process:
Mix feed with reducing gas (H₂ and CO)
Convert all sulfur compounds to H₂S
Cool the reactor gas
Strip H₂S using amine

SCOT Process

Mix Claus tail gas with H₂ and CO and heat in inline burner

Catalytically convert all sulfur compounds to H₂S

Some typical reactions:

\[ \text{SO}_2 + 3\text{H}_2 = \text{H}_2\text{S} + 2\text{H}_2\text{O} \]
\[ \text{S}_2 + 2\text{H}_2 = 2\text{H}_2\text{S} \]
\[ \text{COS} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2\text{S} \]
\[ \text{CS}_2 + 2\text{H}_2\text{O} = \text{CO}_2 + \text{H}_2\text{S} \]
Cool reactor gas (exiting at ~570°F [~300°C]) in waste heat exchanger and water wash to complete cooling.

Strip H₂S from gas & recycle to Claus

Typically use MDEA – can get to low H₂S levels in Stack Gas & slip CO₂ so it doesn't build up in the recycle gas

Alternate Conversion & Sulfur Removal Processes

Selector™
- Proprietary catalyst removes need for furnace

CrystaSulf
- Uses modified liquid-phase Claus reaction
- Elemental sulfur removed by filtration
- Mid-range process to handle sulfur amounts between 0.1 and 20 tons per day
Sulfur storage

Sulfur Piles

Sulfur pile at North Vancouver, B.C., Canada, brought by rail from the province of Alberta

Sulfur “Blocking”
Summary

Natural gas & petroleum production accounts for the majority of sulfur production

- Primary consumption is agriculture & industry, 65% for farm fertilizer.
- $50 per ton essentially disposal cost

Sulfur properties depend upon which sulfur species are present

- Dominant species are \( S_2, S_6, \) & \( S_8 \)

Dominant sulfur recovery process is modified Claus

- Extent controlled by chemical equilibrium, so can only get 96% conversion
- Tail Gas Cleanup process required for very low sulfur emissions

Sulfur storage

- Temporary storage as hot liquid
- Shipping in pellets & long-term bulk storage as blocks