Catalytic H$_2$S oxidation from coal gasification off-gas

A simple and cost efficient removal of H$_2$S

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Introduction
The H$_2$S pain

- Legislation for emissions
- Odor control
- Risk of explosions
- Obstacle for valorization of other gas components
  - CO$_2$ production
  - Syngas for gas engines
  - Dilute acid production

Geothermal power plant
Sulfur capacities and technologies
Sulfur recovery or treatment?

• Low range <0.2 MTPD
  • Absorbents/Scavengers (consumption of chemicals)

• Mid range 1-50 MTPD (lean gases)
  • Direct Oxidation by SuperClaus
  • *SMC™ Selective Oxidation to SO₂*
  • WSA: Wet Sulfuric Acid

• High range >50 MTPD
  • WSA Wet Sulfuric Acid
  • Claus technology
The lean gas challenges
From ~50 ppm H₂S to ~2 % H₂S

• Too high concentration of H₂S for absorbents

• Too low concentration of H₂S for Claus technologies
  • Even with AGE (Acid Gas Enrichment)

• Wet Sulfuric Acid (WSA) can go lower
  • Below 2-3 % H₂S is still a challenge

• Thermal oxidation w/wo scrubber
  • Requires ~700-850°C → NOₓ formation
  • Low heating value gas → large fuel penalty
**Catalytic H₂S oxidation**

**SMC™ Technology (Sulfur Monolith Catalyst)**

- Low temperature Operation
  - Carbon Steel
  - No NOₓ formation

- Compact

- Handles H₂S, COS, C₂S, CO, H₂ HC, RSH

- Simple to operate
  - No transient switching of valves etc.
  - Low pressure drop

\[
1.5 \, O_2 + H_2S \rightarrow SO_2 + H_2O
\]
**H₂S abatement via catalytic oxidation**
A cost efficient alternative to thermal oxidation

- Targeting lean H₂S gas in:
  - Amine unit off gas
  - Physical solvent unit off gas
  - Membrane separation off gas
  - Claus tail gas catalytic oxidation
  - Geothermal power plants
  - Landfill gases and biogas upgrading
Catalyst pilot testing
Reaction pathways on SMC catalyst
Verified in pilot facility

- **Lean H$_2$S gas: 99,9 % conversion**
  - $\text{H}_2\text{S} + 1.5 \ \text{O}_2 \rightarrow \text{SO}_2 + \text{H}_2\text{O}$

- **Lean CS$_2$ gas: 99 % conversion**
  - $\text{CS}_2 + 2.5 \ \text{O}_2 \rightarrow \text{CO} + 2 \ \text{SO}_2$
  - $\text{CS}_2 + 1.5 \ \text{O}_2 \rightarrow \text{COS} + \text{SO}_2$

- **Lean COS gas: 99 % conversion**
  - $\text{COS} + 1.5 \ \text{O}_2 \rightarrow \text{CO}_2 + \text{SO}_2$

- **H$_2$/CO: < 20 ppm CO slip**
  - $\text{H}_2 + 0.5 \ \text{O}_2 \rightarrow \text{H}_2\text{O}$
  - $\text{CO} + 0.5 \ \text{O}_2 \rightarrow \text{CO}_2$

- **Hydrocarbons: Full oxidation of higher hydrocarbons**
  - $\text{HC} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$
  - $\text{HC} + \text{O}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$
Mapping the operational window

- Low gas temperature or O₂ levels induces S⁰ formation
- High gas temperature or O₂ levels reduces SO₂ selectivity
Efficient conversion of H₂S

- High H₂S conversion
- High selectivity to SO₂
- Low SO₃ formation
Process Layouts
Standard layout

- Oxidation air blower
- Off-gas blower if needed
- Feed effluent heat exchanger
  - Dew Point
- Start-up heat
  - Duct burner
  - Electric heater
- Reactor

\[ \Delta T \text{ per } 0.1 \% \text{ H}_2\text{S} \approx 10^\circ\text{C} \]
Low exothermal
Regenerative SMC Oxidation

• For lower consumption of support fuel

• 350 + references for CATOX and REGENOX plants
Installation and reactor design
Topsoe SMC™ catalysts: Compact and modular

• Catalyst volume:
  • 100,000 Nm³/h → ~15 - 30 m³
  • 10,000 Nm³/h → ~2 - 5 m³

• Reactor footprint
  • For 100,000 Nm³/h → 12 - 16 m²
  • For 10,000 Nm³/h → 4 - 6 m²
Application Examples
SMC™ Performance example
Claus Tail Gas Oxidation

- 100 MTPD SCOT-like plant
  - Fuel saving 14-16 GJ/h
- 100 MTPD Sulfreen-like plant
  - Fuel saving ~16 GJ/h

- Catalyst volume 2-3 m³

- Low pressure and above acid dew point
- Carbon steel hardware
- Less steam production

Air
1.5 \text{O}_2 + \text{H}_2 \text{S} \rightarrow \text{SO}_2 + \text{H}_2\text{O} + \text{H}_2\text{O}
250 \degree \text{C}
400 \degree \text{C}
40 \text{bar g}
280 \degree \text{C}
SRU gas
Heater
Catalytic Reactor
Stack Flue Gas
Fuel
Haldor Topsoe
Thermal vs. Catalytic Oxidation
50,000 Nm³/h, 150 ppm H₂S, 600 ppm HC

- Both solutions require SO₂ handling
- Numbers verified by TO vendor and independent sulfur consultant
- Business case is dependent on local gas prices and legislation
- The SMC catalyst may also operate in regenerative mode

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<thead>
<tr>
<th></th>
<th>RTO Technology</th>
<th>SMC™ technology</th>
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<tbody>
<tr>
<td><strong>Consumption</strong></td>
<td></td>
<td></td>
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<tr>
<td>El. Power</td>
<td>350 kW (3-4 % O₂)</td>
<td>110 kW (1 % O₂)</td>
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<tr>
<td>Fuel penalty</td>
<td>21 Gj/h (97% eff.)</td>
<td>none</td>
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<td><strong>CAPEX</strong></td>
<td>Comparable</td>
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<tr>
<td><strong>Emissions</strong></td>
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<tr>
<td>H₂S</td>
<td>&lt;3 ppm</td>
<td>&lt;3 ppm</td>
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<tr>
<td>CO</td>
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<tr>
<td>HC</td>
<td>~4 ppm</td>
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<tr>
<td>NOₓ</td>
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<tr>
<td>H₂SO₄</td>
<td>~15-20 ppm</td>
<td>&lt;1 ppm</td>
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**Geothermal CO₂**
Valorization of tail gas

- Valorization of CO₂
- Green houses and food grade CO₂

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**Diagram:**

- Geothermal Well
- Steam Turbine
- Off-Gas
- Condensate
- Air
- SMC
- SO₂ scrubber
- Gas Polisher
- CO₂

**SMC:**
- 1% H₂S
- 0.5% SO₂
- 0.5% H₂
- 88% CO₂
- 10% H₂O

**Byproduct:**
Landfill- and Biogas Valorization of tail gas

- Gas conditioning for gas engines

![Diagram showing the process of gas conditioning for gas engines](image-url)

- Landfill / Digester
- Gas conditioning: 1.5% H₂S, 40% CH₄, 0.5% H₂, 40% CO₂, 8% H₂O, 10% N₂
- SMC w. Siloxane guard
- Removal of CO₂, O₂, N₂
- SO₂ Scrubber + dryer
- CH₄ for natural gas grid
Summary of SMC technology
Topsoe SMC™ catalysts: Compact and modular

• Ideal for lean H₂S gas:
• Low/no fuel penalty
• Conversion >99.9%
• Selectivity to SO₂ >99.5%
• Low Pressure drop <10 mbar
• Handles H₂S, COS, CO, H₂, HC +…
• No NOₓ formation
• Simple installation  
  • Compact low temperature installation
• Simple operations  
  • No transient switching of valves etc.
Thank You