WSA & SNOX™ technology for the production of sulfuric acid in power plants

Presented by Patrick Polk
January 17, 2013
Agenda

- WSA process
- SNOX™ process
- Economics compared with limestone scrubbing
Wet gas Sulfuric Acid (WSA)

- 95-99.97% of the sulfur content is recovered
- Sulfur is recovered as concentrated sulfuric acid of commercial grade
- No waste products
- Exothermic process
- Simple lay-out
- First reference in 1980
- Over 115 references
WSA configuration

Reaction:
H₂S, H₂SO₄, etc + O₂ → SO₂ + H₂O

Reaction:
SO₂ + 0.5 O₂ → SO₃

Reaction:
SO₃ + H₂O → H₂SO₄ (g)

Reaction:
H₂SO₄ (g) → H₂SO₄ (liq)
WSA applications

- Refineries
  - SAR, Amine off-gas, SWS off-gas, Claus tail gas
- Coal Gasification
  - Rectisol, Selexsol acid gas treatment
- Metallurgical and mineral industry
  - Smelter off-gas
- Power Plant
  - Boiler flue gas
- Coking, Viscose, Petrochemical, etc.
SNOX = WSA + NOx removal

SNOX™ flue gas treatment increases thermal efficiency and reduces CO₂ emission when using high sulfur coal or petcoke for power generation.
Boiler with SNOX™ for high sulfur coal or petcoke

Fuel gases
- H₂S - gas
- SWS - gas

STACK

Steam BFW

Excess air

Cooling air

WSA condenser

Product acid
- 95% H₂SO₄

Boiler

Combustion air

ESP

C.W.

petcoke

RFO

3-6% S

T_d

195-210°

HHB

SO3+H₂O ⇌ H₂SO₄ Vap

190-200°

210-225°

GGH

230-245°

390°

NO+NH₃ → N₂

SO₂ → SO₃

0.2-0.4% SO₂

100°
SNOX™ – bird’s eye view

- SO₂ converter
- SCR reactor
- Gas/gas heat exchanger
- Flue gas blowers
- ESP’s
- WSA condensers
- Stack
- Cooling air blowers
- Hot air return
- Flue gas inlet
Additional heat recovered in SNOX™ plant

Catalytic SO₂ oxidation:

\[ \text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{SO}_3 \quad + 1.34 \text{ BTU/lb S} \]

Gas phase SO₃ hydration:

\[ \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 \text{ (gas)} \quad + 1.31 \text{ BTU/lb S} \]

Acid condensation:

\[ \text{H}_2\text{SO}_4 \text{ (gas)} \rightarrow 95\% \text{ H}_2\text{SO}_4 \text{ (liquid)} \quad + 0.80 \text{ BTU/lb S} \]

Total reaction heat recovered by converting the SO₂ in the flue gas to 95% H₂SO₄ at 200°C is 3.45 BTU per lb sulfur in the fuel or 0.17 BTU per lb fuel with 5% S.

Additional heat recovered by cooling the flue gas from typically 185°C (365°F) with WFGD to 100°C (212°F) with SNOX™ is 0.57 – 0.70 BTU per lb fuel.
With SNOX dirtier is greener

With 5% sulfur in coal or petcoke and SNOX™ as FGD:

- Steam production is 5% higher compared to current alternatives. This corresponds to a 5% reduction of CO₂ emission at the same steam production.

- Replacing limestone FGD (CaCO₃ + SO₂ +½O₂ → CaSO₄ + CO₂) reduces CO₂ emission by 2% compared to wet limestone FGD and by 4 - 5% compared to burning the fuel in a CFB boiler (CaCO₃ → CaO + CO₂).
Cost of flue gas desulfurization

- **SULFUR IN FUEL**: Cost of flue gas desulfurization

**$/kWh**

- Normal coal
- Heavy Residue
- Petcoke

**Limestone scrubber**

**SNOX™**

[Graph showing the cost of desulfurization for different fuels and scrubbing methods]
## Comparison of Operating Costs

**Basis:** Petcoke
300 MW electric power
Unit: USD per year

### Income:
- Sales of sulfuric acid at $30/t

### Costs:
- Limestone at $20/t
- Ammonia at $300/t
- Waste disposal at $20/t
- Additional petcoke consumption at $40/t

### Net Operating Income

<table>
<thead>
<tr>
<th></th>
<th>Downshot PC boiler with SNOX™</th>
<th>CFB boiler with SCR DeNOx and limestone FGD</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Basis:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>300 MW electric power</strong></td>
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<tr>
<td><strong>Unit:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>USD per year</strong></td>
<td></td>
<td></td>
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<tr>
<td><strong>Income:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sales of sulfuric acid at $30/t</td>
<td>3,600,000</td>
<td>0</td>
</tr>
<tr>
<td><strong>Costs:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Limestone at $20/t</td>
<td>0</td>
<td>7,500,000</td>
</tr>
<tr>
<td>Ammonia at $300/t</td>
<td>600,000</td>
<td>240,000</td>
</tr>
<tr>
<td>Waste disposal at $20/t</td>
<td>0</td>
<td>12,000,000</td>
</tr>
<tr>
<td>Additional petcoke consumption at $40/t</td>
<td>0</td>
<td>400,000</td>
</tr>
<tr>
<td>Total costs</td>
<td>600,000</td>
<td>20,000,000</td>
</tr>
<tr>
<td><strong>Net operating income</strong></td>
<td>+ 3,000,000</td>
<td>– 20,000,000</td>
</tr>
</tbody>
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WSA/SNOX™ – references (location)

January 2010

- Oil refining
- Coking
- Gasification
- Metallurgical
- Viscose
- Sundry applications
WSA/SNOX™ plants – references

Contracted plants:

- 35 in oil refining (including 4 SNOX™)
- 30 in coking industry
- 24 in gasification
- 13 in metallurgical industry
- 7 in viscose industry
- 8 in other industries (including 2 SNOX™)
## SNOX™ references

<table>
<thead>
<tr>
<th>Plant</th>
<th>Capacity (flue gas)</th>
<th>Start-up</th>
<th>Fuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nordjyllandsværket, Denmark</td>
<td>1,000,000 Nm³/h 900 MM SCFD</td>
<td>1991</td>
<td>Coal</td>
</tr>
<tr>
<td>Raffineria di Gela, Italy</td>
<td>1,200,000 Nm³/h 1,075 MM SCFD</td>
<td>1999</td>
<td>Petcoke + RFO</td>
</tr>
<tr>
<td>OMV Refinery, Austria</td>
<td>820,000 Nm³/h 735 MM SCFD</td>
<td>2007</td>
<td>RFO + sour gas</td>
</tr>
<tr>
<td>Petrobras RNEST, Brazil</td>
<td>2 x 650,000 Nm³/h 2 x 582 MM SCFD</td>
<td>Expected</td>
<td>Petcoke + sour gas</td>
</tr>
<tr>
<td>Ohio Edison, USA (demonstration plant)</td>
<td>135,000 Nm³/h 121 MM SCFD</td>
<td>1991-96</td>
<td>Coal</td>
</tr>
</tbody>
</table>
SNOX™ – Raffineria di Gela, Italy

Raffineria di Gela, Sicily, Italy

Boilers: approx. 250 MW + steam and heat

Fuel: 90% Petroleum coke

Additional fuel: Oil and gas

Total flue gas flow: 1,200,000 Nm³/hr
                  1,075 MM SCFD

H₂SO₄ (95%): 225 t/d

SO₂ removal: 96.5%

Commissioned: 1999

Left stack emits 1,000,000 Nm³/h SNOX™ treated (invisible) flue gas

Right stack emits (hazy) flue gas from the 4th boiler before it was connected to the SNOX™ plant
SNOX™ – OMV, Austria

OMV Refinery, Schwechat, Austria

Boilers: 180 MW<sub>e</sub> + 1,000 t/h steam

Fuel: Visbreaker residue

Additional feed: Claus tail gas

Total flue gas flow: 820,000 Nm<sup>3</sup>/hr
                     735 MM SCFD

H<sub>2</sub>SO<sub>4</sub> (94%): 225 t/d

SO<sub>2</sub> removal: 98%

Commissioned: 2007
Eight good reasons for SNOX™

- Excellent heat recovery
- Reduced CO₂ emissions
- No process chemicals except NH₃ for SCR
- No process water consumption
- No production of waste solids and liquids
- Valuable sulfuric acid product
- Clean, proven and reliable technology
- Low operating & maintenance costs.
Thank you for your attention!