NNF Coke Oven Gas Desulfurization Technology

NNF (abbreviation of New Nippon Steel Engineering Fumax)

September, 2012

Nippon Steel Eng. Co., Ltd.
COG : Coke Oven Gas

COG is used mainly as a fuel for steel making or power generation. **But!**

**COG Environmental Problems**

- \( H_2S \) \( \Rightarrow \) \( SO_x \) [Acid Rain]
- \( HCN, NH_3 \) \( \Rightarrow \) \( NO_x \) [Urban Ozone]

Serious influences to human health
COG Treatment Process

Crude COG → Primary Cooling → Desulfurization & Decyanization → NH₃ Removal → BTX Scrubbing → Purified COG

<table>
<thead>
<tr>
<th>Crude COG</th>
<th>Purified COG</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂S</td>
<td>&lt;200mg/Nm³</td>
</tr>
<tr>
<td>NH₃</td>
<td>&lt;100mg/Nm³</td>
</tr>
<tr>
<td>HCN</td>
<td>&lt;100mg/Nm³</td>
</tr>
</tbody>
</table>

H₂S: 4~7g/Nm³, NH₃: 7~10g/Nm³, HCN: 2~4g/Nm³

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Desulfurization process for COG

Desulfurization process

- Dry type (small scale)
- Wet type (large scale)

Non-sulfur recovery (ex. Oxide box)
- Sulfur recovery (ex. Gastechnik process)
- Wet oxidation (ex. HPF, NNF)
- Absorption/Stripping (ex. VASC)

Actual results of COG desulfurization process in China and Japan

80 ~ 90% (Wet oxidation)

10 ~ 20% (Absorption/Stripping)

Why Wet Oxidation?

Desulfurization Efficiency

Wet Oxidation Process > Absorption/Stripping Process

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NNF Desulfurization Process

- The absorbent liquid and the COG contact directly in absorber.
- The absorption of \( \text{H}_2\text{S} \) & HCN is performed by using \( \text{NH}_3 \), which is included in the COG inlet gas.

\[
\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{OH} \\
\text{NH}_4\text{OH} + \text{H}_2\text{S} \rightarrow \text{NH}_4\text{HS} + \text{H}_2\text{O} \\
\text{NH}_4\text{OH} + \text{HCN} \rightarrow \text{NH}_4\text{CN} + \text{H}_2\text{O} \\
\]
The oxidation occurs in the presence of picric acid & air.
H₂S and HCN are removed as the sulfur, salt of NH₄SCN.
Absorber

Regenerator

NNF main equipments
(steelmaking company in Japan)

- COG: 50,000 Nm3/h
- Inlet H₂S: 6g/Nm³
Advantages of NNF (New NSEN Fumax)

1. The high desulfurization efficiency over 99% and decyanization efficiency over 98%
   - No need secondary desulfurization plant

2. NNF process can produce the sulfuric acid from the waste water
   - No contaminated waste water

3. We can use carbon steel for main equipments (absorber and regenerator) and sell sulfuric acid
   - Low life cycle costs
NNF advantage 1: High desulfurization efficiency

Hydrogen sulfide concentration in COG measured by steelmaking company in Japan which has been operating NNF from 2006

![Graph showing hydrogen sulfide concentration over time]](image)

- Operation start
- Under 20mg/Nm³-COG

**IN [g/Nm³]**
- H₂S IN
- H₂S OUT

**OUT [mg/Nm³]**
NNF consist of 3 units.
① Main facilities of desulfurization
② WW condensation & liquid combustion unit
③ Sulfuric acid unit

NNF advantage 2: No contaminated waste water

Crude COG → Absorber → Regenerator → Desulfurized COG

Waste water → Waste water condensation & liquid combustion unit

WW condensation → Furnace → Boiler

SO₂ gas → Sulfuric acid unit

No waste water!!
NNF advantage 3: Can use carbon steel materials

We can use carbon steel for main equipments by controlling the adequate concentration of ammonium salts in the absorbent liquid!
## Comparison of annual operating costs (in case of COG 60kNm³/h)

<table>
<thead>
<tr>
<th>Category</th>
<th>NNF</th>
<th>Vacuum Carbonate</th>
<th>HPF</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Materials &amp; Consumables</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catalyst (desulfurization)</td>
<td>t/year</td>
<td>91</td>
<td>N/A</td>
</tr>
<tr>
<td>Liq.-NH₃</td>
<td>t/year</td>
<td>N/A</td>
<td>113</td>
</tr>
<tr>
<td>KOH</td>
<td>t/year</td>
<td>N/A</td>
<td>186</td>
</tr>
<tr>
<td>NaOH</td>
<td>t/year</td>
<td>N/A</td>
<td>Necessary</td>
</tr>
<tr>
<td><strong>Cooling Water</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cooling water</td>
<td>kt/year</td>
<td>9,198</td>
<td>3,396</td>
</tr>
<tr>
<td>Chilled water</td>
<td>kt/year</td>
<td>0</td>
<td>2,305</td>
</tr>
<tr>
<td><strong>Steam</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Produced steam</td>
<td>kt/year</td>
<td>61</td>
<td>32</td>
</tr>
<tr>
<td>Consumed steam</td>
<td>kt/year</td>
<td>32</td>
<td>20</td>
</tr>
<tr>
<td><strong>Electrical Power</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MWh/year</td>
<td></td>
<td>9,290</td>
<td>9,840</td>
</tr>
<tr>
<td><strong>By product</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfur</td>
<td>t/year</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Sulfuric Acid</td>
<td>t/year</td>
<td>9,502</td>
<td>9,390</td>
</tr>
<tr>
<td><strong>Operating cost (</strong>)**</td>
<td>US$/kNm³</td>
<td><strong>1.1</strong></td>
<td><strong>1.3</strong></td>
</tr>
</tbody>
</table>

( * ) Considering the product sales income & produced steam revenue
Conclusion

1. High desulfurization efficiency
   • The desulfurization efficiency over 99% (≤20mg/Nm3-COG)
   • The decyanization efficiency over 98%
   • You can operate the plant for a long time stably

2. Not produce contaminated waste water
   • NNF process can produce the sulfuric acid from the waste water

3. Low life cycle costs
   • Carbon steel can be used for main part of desulfurization equipment
   • We can sell steam and sulfuric acid which are produced in the process

NNF is good choice for COG desulfurization plant!
Thank you very much!
## Comparison of desulfurization process

<table>
<thead>
<tr>
<th></th>
<th>NNF</th>
<th>Vacuum Carbonate</th>
<th>HPF</th>
</tr>
</thead>
<tbody>
<tr>
<td>De-H2S efficiency</td>
<td>Excellent</td>
<td>good</td>
<td>good</td>
</tr>
<tr>
<td>Waste water treatment</td>
<td>Not required</td>
<td>Required</td>
<td>Required</td>
</tr>
<tr>
<td>Q’ty of equipment</td>
<td>Many</td>
<td>Many</td>
<td>Few</td>
</tr>
<tr>
<td>Plant operability</td>
<td>Easy</td>
<td>Very difficult</td>
<td>Difficult</td>
</tr>
<tr>
<td>Flow plugging</td>
<td>Nothing</td>
<td>Frequently</td>
<td>Frequently</td>
</tr>
<tr>
<td>Chemicals</td>
<td>Not required</td>
<td>2 kinds</td>
<td>Not required</td>
</tr>
<tr>
<td>Catalyst for desulfurization</td>
<td>Required</td>
<td>Not required</td>
<td>Required</td>
</tr>
<tr>
<td>By-product quality</td>
<td>Good</td>
<td>Good</td>
<td>Low</td>
</tr>
<tr>
<td>Environmental protection</td>
<td>Excellent</td>
<td>Good</td>
<td>Not good</td>
</tr>
</tbody>
</table>
Elemental sulfur and ammonium salt with sulfur are accumulated in the circulating absorption liquid, then should be purged a certain amount continuously. After condensation of the filtrate separated from centrifuge, S slurry is mixed and introduced to combustion furnace to produce the conc. SA.
After having passed the 2nd stage of Converter and Absorption Tower, the process gas is discharged to the ambient as tail gas without additional chemical treatment for waste gas due to the highest conversion efficiency, from $\text{SO}_2$ to $\text{SO}_3$. This process producing the conc. SA is the conventional technology in current.
Major issue for Desulfurization

Common problems
(Wet oxidation, Absorption/Stripping)

- Equipment corrosion
- Contaminated waste water
- Un-Stable operation
- Low quality Sulfur
- Sulfuric acid

To establish the adequate technology to produce the valuable by-product with high performance is important, for instance SA, from desulfurization.
Picric acid
(Oxidation/Reduction)