RECOVERY BOILER GAS EMISSIONS
AND EMISSION CONTROL

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FLUE GAS EMISSION COMPONENTS

- $\text{CO}_2$ Carbon Dioxide
- CO Carbon Monoxide / $\text{C}_x\text{H}_y$ Hydrocarbons
- $\text{SO}_2$ Sulfur Dioxide / $\text{NO}_x$ Nitrogen Oxides
- PAH Polyaromatic Hydrocarbons
- As, Cr, Ni, V, Pb, Cd, Hg,... Heavy Metals
- Dioxins, Furans
RECOVERY BOILER EMISSIONS - OUTLINE

- Particulates
- Sulfurous Gases
- Nitrogen Oxides
- Conclusion

CARRY OVER PARTICLES

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20 μm
CARRY OVER PARTICLE

TYPICAL PARTICULATE EMISSIONS

50 – 100 mg/m³n  (8 % O₂, dry flue gas)

0.022 – 0.044 gr/DSCF  (8 % O₂, dry gas)
PARTICULATE EMISSIONS - CONCLUSIONS

• Carry-over affects fouling – not emissions
• Particulate emissions mostly fume
• High furnace temperatures increase fume production
• Particulate emissions controlled by dust removal systems (ESP)

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SULFUROUS GASES

- Sulfur Dioxide, SO$_2$
- Reduced Sulfur Compounds, TRS

**REACTIONS OF S AND Na IN FLUE GASES**
(hot bed, low sulphidity)
REATIONS OF S AND Na IN FLUE GASES
(S/Na$_2$ = 1.5, cool bed, high sulphidity)

- $H_2S(g)$, $SO_2(g)$, $Na_2SO_4(s)$, $Na_2CO_3(s)$
- $O_2(g)$, $H_2O(g)$, $SO_3(g)$
- $2NaOH(g)$, $Na_2SO_4(l,s)$, $Na_2CO_3(l,s)$
- $2NaHSO_4(l,s)$, $SO_3(g)$

$S/Na_2 = 0.8$, hot bed, low sulphidity

$S/Na_2 = 1.5$, cool bed, high sulphidity
SULFUROUS GASES

• Sulfur Dioxide, $SO_2$

• Reduced Sulfur Compounds, TRS

TRS: THRESHOLD OF ODOR

- Hydrogen sulfide, $H_2S$: 0.4 to 5 ppb
- Methyl mercaptan, $CH_3SH$: 2 to 3 ppb
- Dimethyl sulfide, $(CH_3)_2S$: 2 ppb

Compare with:
- Sulfur dioxide, $SO_2$: 1 to 5 ppm
## TYPICAL TRS EMISSIONS

<table>
<thead>
<tr>
<th>Source</th>
<th>Emission Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct Contact Evaporator</td>
<td>20 ppm</td>
</tr>
<tr>
<td>&quot;Low Odor&quot; DCE</td>
<td>5 ppm</td>
</tr>
<tr>
<td>No DCE</td>
<td>&lt; 1 ppm</td>
</tr>
</tbody>
</table>

## TRS FORMATION IN DIRECT CONTACT EVAPORATORS

Flue gas CO$_2$ releases the sulfur from black liquor:

$$Na_2S(bl) + CO_2(g) + H_2O(g) \rightarrow H_2S(g) + Na_2CO_3(bl)$$
TRS: LOW ODOR SYSTEMS

• Black liquor sulfide is oxidized to thiosulfate:

  \[
  \text{Na}_2\text{S} \xrightarrow{\text{O}_2} \text{Na}_2\text{S}_2\text{O}_3
  \]

• No release of H\textsubscript{2}S in the DCE of preoxidized liquor

TRS EMISSIONS FROM THE RECOVERY FURNACE

• Minor TRS emissions also from incomplete oxidation of the lower furnace gases

• Can be controlled by improved mixing of the tertiary air
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NITROGEN OXIDES, NO$_x$

\[ \text{NO}_x = \text{NO} + \text{NO}_2 \ ( + \text{N}_2\text{O}) \]
EMISSION UNITS
(Example NO\textsubscript{x})

100 ppm (3 % O\textsubscript{2})

= 72 ppm (8 % O\textsubscript{2})
= 83 ppm (8 % O\textsubscript{2}, dry gas)
= 237 mg NO\textsubscript{2}/m\textsuperscript{3} (3 % O\textsubscript{2}, dry)
= 71 mg NO\textsubscript{2}/MJ (LHV)
= 0.104 gr/DSCF (3 % O\textsubscript{2}, dry)
= 0.00116 gr/BTU (LHV)

NO\textsubscript{x} EMISSION FACTORS

Graph showing emission factors for various fuels and processes, including:
- Oil, uncontrolled
- Oil, low-NO\textsubscript{x}
- Coal, uncontrolled
- Coal, low-NO\textsubscript{x}
- SCR
- Wood, grate & FBC
- BLRB
ORIGINS OF NO\textsubscript{x}

- Thermal NO
  Oxidation of N\textsubscript{2} in combustion air
  Only at temperatures $> 1400 \, ^\circ\text{C} / 2500 \, ^\circ\text{F}$

- Fuel NO
  Oxidation of fuel bound nitrogen
  Does not require high temperatures

FUEL NITROGEN CONTENTS

<table>
<thead>
<tr>
<th>Fuel</th>
<th>% in N in DS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coals</td>
<td>1 – 2</td>
</tr>
<tr>
<td>Oil</td>
<td>0.3 – 1</td>
</tr>
<tr>
<td>Bark</td>
<td>0.2 – 0.4</td>
</tr>
<tr>
<td>Wood</td>
<td>0.1 – 0.2</td>
</tr>
<tr>
<td>Black Liquor</td>
<td>0.05 – 0.15</td>
</tr>
</tbody>
</table>
BLACK LIQUOR NITROGEN REACTION ROUTES

DEVOLATILIZATION

BURN-OUT

\[ NBL \leftarrow N_{\text{vol}} \leftarrow N_{\text{char}} \rightarrow N_{\text{smelt}} \rightarrow N_{\text{green liquor}} \]

LIQUOR NITROGEN CONTENTS (Wt %)

- Bagasse/Soda: US-14, Asia-15
- Straw/Soda: Asia-15
- HW/NSSC: Sc-23
NITROGEN DISTRIBUTION BETWEEN FLUE GAS (NO) AND SMELT (NaOCN) (Boiler tests by Andritz, 2006)

NITROGEN CHEMISTRY IN KRAFT RECOVERY
RECOVERY BOILER NO\textsubscript{x} - CONCLUSIONS (I)

- NO\textsubscript{x} emissions 50-100 ppm (8 % O\textsubscript{2})
- Low compared with other combustion systems
- Mostly fuel NO
RECOVERY BOILER NO\textsubscript{x} - CONCLUSIONS (II)

- 20 – 30 % conversion of N\textsubscript{BL} into NO
- N\textsubscript{BL} content varies 0.05 – 0.15 %
- Soft Wood < Hard Wood < Straw

RECOVERY BOILER NO\textsubscript{x} - CONCLUSIONS (III)

- NO can be controlled by operation:
  - air staging systems
  - avoiding droplet burn-out in flight
- NO removal techniques are being tested:
  - ammonia addition (SCR, SNCR)
RECOVERY BOILER NO\textsubscript{x} - CONCLUSIONS (IV)

- Part of the BL nitrogen stays in the smelt in the form of sodium cyanite (NaOCN)
- Smelt cyanite form ammonia in green liquor
- GL ammonia may cause additional emissions

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BL RECOVERY BOILER EMISSIONS

<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>SO₂ (ppm)</td>
<td>1500</td>
<td>500</td>
<td>100</td>
<td>~ 0</td>
</tr>
<tr>
<td>NOₓ (ppm)</td>
<td>70</td>
<td>70</td>
<td>80</td>
<td>50</td>
</tr>
<tr>
<td>TRS (ppm)</td>
<td>300</td>
<td>200</td>
<td>5</td>
<td>~ 0</td>
</tr>
<tr>
<td>Particulate (mg/m³)</td>
<td>500</td>
<td>300</td>
<td>100</td>
<td>30</td>
</tr>
</tbody>
</table>

FLUE GAS EMISSION COMPONENTS

- CO₂, Carbon Dioxide
- CO, Carbon Monoxide / C xH y Hydrocarbons
- SO₂, Sulfur Dioxide / NO x Nitrogen Oxides
- PAH, Polyaromatic Hydrocarbons
- As, Cr, Ni, V, Pb, Cd, Hg..., Heavy Metals
- Dioxins, Furans

Legend:
- 100 %
- 1 %
- 100 ppm
- 0 ppm
- 1 ppb (µg/kg)
- 1 ng/kg
- 1 pg/kg