RECOVERY BOILER CHEMICAL PRINCIPLES

Mikko Hupa
Åbo Akademi University
Turku, Finland

RECOVERY BOILER CHEMICAL PRINCIPLES - OUTLINE

• S and Na in recovery boilers
  - an overview
• Lower furnace and char bed
• Flue gases and dust
• Foreign components
## KRAFT BLACK LIQUOR
### ELEMENTARY COMPOSITION
(Sample before the mixing tank)

<table>
<thead>
<tr>
<th>Element</th>
<th>% in BL dry solids</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>38.2</td>
</tr>
<tr>
<td>H</td>
<td>3.4</td>
</tr>
<tr>
<td>O</td>
<td>31.1</td>
</tr>
<tr>
<td>N</td>
<td>0.1</td>
</tr>
<tr>
<td>S</td>
<td>5.2</td>
</tr>
<tr>
<td>Na</td>
<td>19.8</td>
</tr>
<tr>
<td>K</td>
<td>1.9</td>
</tr>
<tr>
<td>Cl</td>
<td>0.1</td>
</tr>
<tr>
<td>Others</td>
<td>0.2</td>
</tr>
<tr>
<td>(Ca, Si, Fe, Mg, Al, Mn)</td>
<td></td>
</tr>
</tbody>
</table>

\[ S/Na_2 = 0.38 \]

## SULPHUR COMPOUNDS IN KRAFT BLACK LIQUORS
(Sample before the mixing tank)

<table>
<thead>
<tr>
<th>Compound</th>
<th>% of total S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphide, ( S^{2-} )</td>
<td>11</td>
</tr>
<tr>
<td>Thiosulphate, ( S_2O_3^{2-} )</td>
<td>36</td>
</tr>
<tr>
<td>Sulphite, ( SO_3^{2-} )</td>
<td>13</td>
</tr>
<tr>
<td>Sulphate, ( SO_4^{2-} )</td>
<td>5</td>
</tr>
<tr>
<td>Organic S (balance)</td>
<td>35</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100 %</strong></td>
</tr>
</tbody>
</table>
Na AND S COMPOUNDS IN RECOVERY FURNACE

<table>
<thead>
<tr>
<th>Solids or liquids</th>
<th>Gases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$S</td>
<td>H$_2$S (g)</td>
</tr>
<tr>
<td>Na$_2$CO$_3$</td>
<td>SO$_2$ (g)</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td></td>
</tr>
<tr>
<td>NaOH</td>
<td>NaOH (g)</td>
</tr>
<tr>
<td>NaHSO$_4$</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solids or liquids</th>
<th>Gases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$S</td>
<td>mp 1180°C/2160 F H$_2$S (g)</td>
</tr>
<tr>
<td>Na$_2$CO$_3$</td>
<td>mp 860°C/1580 F SO$_2$ (g)</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>mp 880°C/1620 F</td>
</tr>
<tr>
<td>NaOH</td>
<td>mp 320°C/610 F NaOH (g)</td>
</tr>
<tr>
<td>NaHSO$_4$</td>
<td>mp 180°C/360 F</td>
</tr>
</tbody>
</table>
**RECOVERY FURNACE CHEMISTRY**
(g sulphur/kg BL solids)

- Na: 200 g/kg BL solids
- \( \text{Na}_2\text{CO}_3 \)
- \( \text{Na}_2\text{S} \)
- S: 45 g/kg BL solids

**SODIUM BALANCE IN A KRAFT RECOVERY BOILER**
(g Na/kg BL solids)

**EMISSIONS**
- 0.04 \( \text{Na}_2\text{SO}_4 \) (50 mg/m³)

**MAKE UP SMELT**
- Na+: 200
- \( \text{Na}_2\text{SO}_4 \)
- 7

**SMELT**
- 137 \( \text{Na}_2\text{CO}_3 \)
- 63.3 \( \text{Na}_2\text{S} \)
- 6.7 \( \text{Na}_2\text{SO}_4 \)
- 18
SULPHUR BALANCE IN A KRAFT RECOVERY BOILER (g sulphur/kg BL solids)

0.03 Na$_2$SO$_4$ (50 mg/m$^3$)
0.25 SO$_2$ (50 ppm)
0.02 H$_2$S (5 ppm)

RECOVERY BOILER CHEMICAL PRINCIPLES - OUTLINE

• S and Na in recovery boilers
  - an overview
• Lower furnace and char bed
• Flue gases and dust
• Foreign components
SODIUM BALANCE IN A KRAFT RECOVERY BOILER (g Na/kg BL solids)

EMISSIONS 0.04 Na₂SO₄ (50 mg/m³)

BL

Na⁺

MAKE UP Na₂SO₄

18

Na₂SO₄

Na₂CO₃

Na₂S

SMELT

137 Na₂CO₃

63.3 Na₂S

6.7 Na₂SO₄

SULPHATE REDUCTION IN SMELT

• Either:

  \[ \text{Na}_2\text{SO}_4 \xrightarrow{\text{CO, H}_2} \text{Na}_2\text{S} \]

• Or:

  \[ \text{Na}_2\text{SO}_4 \xrightarrow{\text{C}_{\text{solid}} \text{(char)}} \text{Na}_2\text{S} \]
SULPHATE REDUCTION - SUMMARY

- Sufficient amount of char in the bed
- High enough temperature
  \((T = +50^\circ C \text{ doubles the rate})\)

EQUILIBRIUM COMPOSITION OF LOWER FURNACE GASES VS. TEMPERATURE

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Volume concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>100 %</td>
</tr>
<tr>
<td>800</td>
<td>10 %</td>
</tr>
<tr>
<td>1000</td>
<td>1 %</td>
</tr>
<tr>
<td>1200</td>
<td>1 ppm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Partial pressure, atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>10^0</td>
</tr>
<tr>
<td>10^-1</td>
</tr>
<tr>
<td>10^-2</td>
</tr>
<tr>
<td>10^-3</td>
</tr>
<tr>
<td>10^-4</td>
</tr>
<tr>
<td>10^-5</td>
</tr>
<tr>
<td>10^-6</td>
</tr>
</tbody>
</table>

Graph: Partial pressure vs. temperature, showing various gases and their concentrations.

- Water (H\(_2\)O)
- Carbon dioxide (CO\(_2\))
- Nitrogen (N\(_2\))
- Hydrogen (H\(_2\))
- Carbon monoxide (CO)
- Methane (CH\(_4\))
- Hydrogen sulfide (H\(_2\)S)
- Carbon disulfide (COS)
- Ammonia (NH\(_3\))
- Sodium (Na)
- Sodium hydride (Na\(_2\)H)
- Sulfur dioxide (SO\(_2\))

The graph illustrates the equilibrium composition of these gases at different temperatures.
RECOVERY BOILER CHEMICAL PRINCIPLES - OUTLINE

- S and Na in recovery boilers
  - an overview
- Lower furnace and char bed
- Flue gases and dust
- Foreign components

SODIUM BALANCE IN A KRAFT RECOVERY BOILER (g Na/kg BL solids)

EMISSIONS

0.04 Na₂SO₄ (50 mg/m³)

0.04

18

Na⁺ 200 225 207

MAKE UP

137 Na₂CO₃
63.3 Na₂S
6.7 Na₂SO₄

SMELT
RELEASE OF S AND Na IN LOWER FURNACE

• Mainly H₂S and NaOH

• At increasing temperature:
  S release decreases
  Na release increases

• \((S/Na₂)_{\text{flue gases}} = 0.8 - 1.5\)

RECOVERY FURNACE GASEOUS SULFUR AND SODIUM – TYPICAL DATA

![Graph showing the relationship between temperature and concentration of sulfur and sodium in flue gases.](attachment:graph.png)
REATIONS OF S AND Na IN FLUE GASES
(S/Na₂ = 0.8, hot bed, low sulphidity)

\[ \text{H}_2\text{S}(g) \rightarrow \text{SO}_2(g) \rightarrow \text{Na}_2\text{SO}_4(s) \rightarrow \text{Na}_2\text{CO}_3(s) \]

\[ \text{Na}_2\text{CO}_3(l,s) \]

\[ \text{O}_2(g) \]

\[ \text{CO}_2(g) \]

\[ \text{H}_2\text{S}(g) \]

\[ \text{Na}_2\text{SO}_4(l,s) \]

\[ \text{O}_2(g) \]

\[ 2\text{NaOH}(g) \]

\[ \text{Na}_2\text{CO}_3(l,s) \]

\[ \text{SO}_2(g) \]

\[ \text{O}_2(g) \]

\[ \text{CO}_2(g) \]

\[ \text{Na}_2\text{CO}_3(l,s) \]

\[ \text{Na}_2\text{CO}_3(l,s) \]

\[ \text{2NaHSO}_4(l,s) \]

REATIONS OF S AND Na IN FLUE GASES
(S/Na₂ = 1.5, cool bed, high sulphidity)

\[ \text{H}_2\text{S}(g) \rightarrow \text{SO}_2(g) \rightarrow \text{Na}_2\text{SO}_4(s) \rightarrow \text{Na}_2\text{CO}_3(s) \]

\[ \text{Na}_2\text{CO}_3(l,s) \]

\[ \text{O}_2(g) \]

\[ \text{CO}_2(g) \]

\[ \text{H}_2\text{S}(g) \]

\[ \text{Na}_2\text{SO}_4(l,s) \]

\[ \text{O}_2(g) \]

\[ 2\text{NaOH}(g) \]

\[ \text{Na}_2\text{CO}_3(l,s) \]

\[ \text{SO}_2(g) \]

\[ \text{O}_2(g) \]

\[ \text{CO}_2(g) \]

\[ \text{Na}_2\text{CO}_3(l,s) \]

\[ \text{Na}_2\text{CO}_3(l,s) \]

\[ \text{2NaHSO}_4(l,s) \]

\[ \text{SO}_3(g) \]
**DUST pH vs. DUST COMPOSITION**

![Graph showing pH vs. dust composition with weight fraction in dust from 0% to 20% for NaHSO₄ and Na₂CO₃.](image)

**SO₂ vs CARBONATE IN DUST**

(Courtesy Kvaerner Pulping 2002)

![Graph showing SO₂ emissions vs. carbonate in ash with carbonate content from 0 to 25 wt-% CO₃²⁻.](image)
RECOVERY BOILER CHEMICAL PRINCIPLES - OUTLINE

- S and Na in recovery boilers
  - an overview
- Lower furnace and char bed
- Flue gases and dust
- Foreign components

K AND Cl IN NORTH AMERICAN BLACK LIQUORS

[Graph showing the distribution of K and Cl in different liquors and the average.]
POTASSIUM AND CHLORINE IN LOWER FURNACE

- **Enrichment factors:**

\[
\begin{aligned}
\frac{(\text{Cl/Na}) \text{ in gas}}{(\text{Cl/Na}) \text{ in smelt}} &\quad \left\{ \begin{array}{c}
\frac{(\text{K/Na}) \text{ in gas}}{(\text{K/Na}) \text{ in smelt}} \\
- 2...4
\end{array} \right. \\
\end{aligned}
\]
POTASSIUM AND CHLORINE IN LOWER FURNACE

• Mainly NaCl
  KCl
  KOH

POTASSIUM AND CHLORINE CHANGE MELTING OF Na SALTS

• Smelt freezing point decreases
  (typically 850 C --> 700 C)
• Dust particle sticky temperatures decrease (800 C --> 600 C)
FOREIGN COMPONENTS
SUMMARY (I)

• Cl and K are enriched in gas phase
• Lower furnace: NaCl, KCl, KOH

FOREIGN COMPONENTS
SUMMARY (II)

• K and Cl make dust more "sticky"
• If \((S/Na_2)_{FG}\) high enough:
  \[
  \text{NaCl} \xrightarrow{\text{SO}_2/\text{O}_2} \text{Na}_2\text{SO}_4
  \]
RECOVERY BOILER CHEMICAL PRINCIPLES - OUTLINE

• S and Na in recovery boilers
  - an overview
• Lower furnace and char bed
• Flue gases and dust
• Foreign components
• Conclusions

RB CHEMISTRY - CONCLUSIONS (I)

• Good reduction requires:
  - char in the bed
  - high enough temperature
RB CHEMISTRY - CONCLUSIONS (II)

• Dust/flue gas chemistry controlled by S/Na₂ ratio in flue gas

• Flue gas S/Na₂ ratio decreases when:
  - furnace temperature increases
  - liquor sulphidity decreases

RB CHEMISTRY - CONCLUSIONS (III)

• Low S/Na₂ gives low SO₂ emissions and alkaline dust (Na₂CO₃)

• High S/Na₂ gives high SO₂ emissions and acidic dust (NaHSO₄)

• Dust pH good indicator
• K and Cl are enriched in the flue gases
• K and Cl in the dust lower melting temperature range
• At high S/Na\textsubscript{2} chlorine is released from the dust (NaCl \rightarrow HCl)