Low-Temperature Corrosion in Biomass Combustion

Emil Vainio
Total energy consumption by source in Finland

- Biomass based fuels most important renewable source

- Biomass; 28%
- Oil; 25%
- Coal; 9%
- Natural gas; 5%
- Peat; 4%
- Nuclear energy; 18%
- Hydro power; 4%
- Wind power; 1%
- Others; 5%
Biomass Combustion

- Large scale combustion of biomass increases
  - Circulating fluidized beds (CFB)
  - Bubbling fluidized beds (BFB)
- Low grade biomasses of high interest
- Poor fuel quality gives challenges to design and operation

Courtesy of Foster Wheeler and Valmet

Åbo Akademi Databank 2016
Low-temperature corrosion

- Interest of recovering maximum heat without corrosion
- By lowering flue gas temperature 10°C increases the boiler efficiency by 0.5%
- Corrosion of pre-heaters and the flue gas channel
- Cause of corrosion and operational problems not clear
- Acid dew point vs hygroscopic deposits

Flemming et al.
Low-temperature corrosion

- Part 1. Dew point corrosion
  - Sulfuric acid
  - Hydrogen chloride
  - Water dew point and sulfurous acid
- Part 2. Hygroscopic deposits
  - Chlorides
  - Phosphates
  - Carbonates
Low-temperature corrosion – Acid dew point

- A part of the $\text{SO}_2$ that is formed in combustion of sulfur containing fuels is further oxidized to $\text{SO}_3$
- The final $\text{SO}_3$ formation is dependent on many factors, such as:
  - Sulfur content in the fuel
  - Temperature
  - Ash composition ($\text{SO}_3$ is a reactive gas and is partly captured in the ash)
  - Additives
  - Catalysts (e.g. the use of SCR)
- A rule of thumb from fossil fuel combustion is that a few % of $\text{SO}_2$ forms $\text{SO}_3$
Homogeneous SO$_2$ to SO$_3$ conversion

- SO$_2$(g) + O$_2$(g) $\leftrightarrow$ SO$_3$(g)

Example

- Inlet gas with 1000 ppm$_v$ SO$_2$
- 3 and 5 vol% O$_2$
- Residence time: ~5s

Catalytic conversion SO$_2$ to SO$_3$

- Using selective catalytic NOx reduction will lead to catalytic conversion of SO$_2$ to SO$_3$
- Some ash compounds may also lead to catalytic formation of SO$_3$, e.g. iron oxide and vanadium

Unwanted reactions:
- SO$_2$ + 0.5O$_2$ $\leftrightarrow$ SO$_3$
- NH$_3$ + SO$_3$ + H$_2$O $\leftrightarrow$ NH$_4$HSO$_4$

SCR

2NH$_3$ + 2NO + 0.5O$_2$ $\leftrightarrow$ 2N$_2$ + 3H$_2$O

Marier and Dibbs, Thermochimica Acta 8(1-2)
Equilibrium between SO$_3$ and H$_2$SO$_4$

SO$_3$(g) + H$_2$O(g) → H$_2$SO$_4$(g)

SO$_3$ start to form gaseous H$_2$SO$_4$ below 550°C and at 200°C all SO$_3$ converted to H$_2$SO$_4$(g)
Verhoff and Banchero:

\[ T_{\text{dew point}} = \frac{1000}{\{2.276 - 0.0294 \times \ln(p_{H_2O}) - 0.0858 \times \ln(p_{H_2SO_4}) + 0.0062 \times \ln(p_{H_2O}) \times \ln(p_{H_2SO_4})\}} \]

- \( T_{\text{dew point}} \) sulfuric acid dew point [K]
- \( p_{H_2O} \) partial pressure of water vapor [mmHg]
- \( p_{H_2SO_4(g)} \) or \( SO_3 \) partial pressures [mmHg]
Effect of material temperature on sulfuric acid corrosion

If water condenses, SO₂ will absorb in the water, forming sulfurous acid:

\[ \text{H}_2\text{O} + \text{SO}_2 \rightarrow \text{H}_2\text{SO}_3 \]

Maximum corrosion rate caused by sulfuric acid is usually 20-30°C below the dew point temperature.
HCl dew point

\[ T_d = \frac{1000}{3.7368 - 0.1591 \ln(P_{H2O}) - 0.0326 \ln(P_{HCl}) + 0.00269 \ln(P_{H2O}) \ln(P_{HCl})} - 273 \]

- $T_{dew\ point}$: HCl dew point [°C]
- $p_{H2O}$: partial pressure of H$_2$O [mmHg]
- $p_{HCl}$: partial pressure of HCl [mmHg]

1 atm = 760 mmHg
Dew point corrosion

- Dew point corrosion can be prevented by
  - Keeping material temperatures above the dew point
  - Adjusting excess oxygen and peak temperature
  - Using additives, e.g. limestone, that binds $\text{SO}_2$ and $\text{SO}_3$
  - Co-combustion
SO$_3$ capturing potential of biomass ash

- SO$_3$ is very reactive
- Biomass contains alkaline ash
- Can be captured in the furnace by alkali vapors (e.g. KCl, KOH) and ash CaCO$_3$, CaO, KCl, NaCl, K$_2$CO$_3$, Na$_2$CO$_3$
Measurement techniques to assess low-temperature corrosion

1. SO$_3$/H$_2$SO$_4$ measurements to determine dew point
   - Controlled condensation method
   - ÅA KCl salt method
2. Air-cooled corrosion probes
3. Electrochemical measurement techniques
4. Dew point meter
1. SO$_3$/H$_2$SO$_4$(g) measurement techniques: Controlled condensation method

- Flue gas cooled between acid and water dew point temperature
  → Sulfuric acid condenses
- Coil and filter rinsed
- Solution analyzed for sulfate ions with ion chromatography
- Not practical to use in the field
1. \( \text{SO}_3/\text{H}_2\text{SO}_4(g) \) measurement techniques: ÅA KCl salt method

- Selective sulfation of KCl by \( \text{SO}_3 \) or \( \text{H}_2\text{SO}_4 \) can be utilized in measurements. \( 2\text{KCl}(s) + \text{H}_2\text{SO}_4(g) \rightarrow \text{K}_2\text{SO}_4(s) + 2\text{HCl}(g) \)
- Sulfuric acid is captured in the salt and forms sulfate
- \( \text{SO}_2 \) does not react with the salt
- Salt is dissolved in water and analyzed for sulfate ions with IC → \( \text{H}_2\text{SO}_4(g) \) concentration can be calculated

Vainio et al. Energy & Fuels 2013
2. Corrosion probe measurements

• A fresh carbon steel ring is placed in the probe tip
• Short-term exposure: 2h
• After the exposure corrosion products are washed off
• Annual tube wall thickness loss (mm/year) is calculated from weight loss, which is a rough estimation
4. Dew point meter

- Electrodes in the probe tip
- Probe tip temperature slowly decreased
- When condensate is formed on the sensor a current reading can be observed
Case studies

1. Homogeneous $\text{SO}_3/\text{H}_2\text{SO}_4(\text{g})$ formation in air- and oxy-combustion
2. Low-temperature corrosion in fluidized bed combustion of biomass
3. Bark and NCG in a grate fired boiler
Chalmers Oxy-combustion test unit
Test cases

- Fuel: propane doped with SO$_2$
- Fuel input 60kW$_{th}$
- Two cases:
  - Air-fired case
    - SO$_2$ in flue gas: 1000 ppm (on dry basis)
    - $\lambda=1.38$
  - Oxy-fuel case
    - Dry flue gas recirculation
    - SO$_2$ in flue gas: 3000 ppm (on dry basis)
    - 30 vol% O$_2$ in oxidizer
    - $\lambda=1.25$
Results: air-fired case

SO$_3$/SO$_X$ conversion: 2.4-3.4%
Dew point: 148-152°C (calculated)

Vainio et al. Energy & Fuels 2013
Results: oxy-combustion case

OF30

- Salt met. (NaCl)
- Salt met. (KCl)
- Salt met. (K2CO3)
- Temperature (°C)

Interference from SO₂

SO₃/SOₓ conversion: 1.2-3.1%
Dew point: 157-167°C (calculated)

Vainio et al. Energy & Fuels 2013
2. BFB combustion of biomass

- 107 MW$_{th}$, 118 bar, 535 °C
- Forest residue, sludge, recycled fuels
- Measurements at LUVO area
  - SO$_3$/H$_2$SO$_4$ measurements
  - Corrosion probe
  - Deposit analysis

Objective

- Understand the cause of low-temperature corrosion in biomass combustion
  - Dew point corrosion (sulfuric acid)
  - Hygroscopic deposits
- Role of ash-forming elements on corrosion and impact on boiler operation
Measurement campaign: BFB boiler

- Biomass, sludge and demolition wood
- Limestone addition on and off

Corrosion probe

SO$_2$ (ppm$_v$): 40-200
H$_2$SO$_4$(g) (ppm$_v$): <0.1
HCl (ppm$_v$): <0.1
Low-temperature corrosion in BFB combustion of biomass

- No sulfuric acid detected
- Deposits enriched in Ca and Cl, indicating CaCl₂
- Corrosion when water vapor high ~20 vol%
- Corrosion caused by deliquescence

Deposit analysis

![Deposit analysis chart]

Corrosion rate at 100°C

![Corrosion rate chart]

Vainio et al Fuel 184 (2016)
Low-temperature corrosion in BFB combustion of biomass

SO$_3$ very reactive towards alkaline ash

Low conversion to SO$_3$ due to low furnace temperature and air-staging

CaO(s) + 2HCl(g) $\rightarrow$ CaCl$_2$(s) + H$_2$O(g)
CaCO$_3$(s) + 2HCl(g) $\rightarrow$ CaCl$_2$(s) + H$_2$O(g) + CO$_2$(g)

Vainio et al Fuel 184 (2016)
Grate fired combustor burning bark and NCG

NCG = non-condensable gases from pulping

SO₂ 1200 ppmᵥ
H₂SO₄ <0.1 ppmᵥ
Windward side of the carbon steel ring after washing

- No corrosion at 99°C
- Ca, Cl, K, S, Fe in deposit
- Flue gas temperature during measurements 180-195°C
- More energy could be recovered

<table>
<thead>
<tr>
<th>Ring temperature (°C)</th>
<th>Corrosion rate (mm/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>99</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>86</td>
<td>0.3</td>
</tr>
<tr>
<td>71</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Pure water dew point 57°C
Summary: Part 1. SO$_3$ and dew point corrosion

- A few % of the SO$_2$ may form SO$_3$ in combustion
- Depends on
  - Sulfur content in the fuel
  - Temperature
  - Ash composition
  - Additives
  - Catalysts (e.g. the use of SCR or catalytic compounds in the ash)
- The presence of sulfuric acid in flue gases may cause severe low temperature corrosion, dew point depends on H$_2$SO$_4$(g) and H$_2$O concentrations
- Generally, no acid dew point corrosion in biomass combustion
- Acid dew point corrosion is more a problem in fossil fuel combustion
- In fluidized bed combustion of biomass no H$_2$SO$_4$ due to relatively low furnace temperature leading to low SO$_3$ formation, heavy air-staging (no available oxygen in freeboard) and alkaline fly ash capturing any SO$_3$ formed
Part 2. Hygroscopic and deliquescent salts
Deposit chemistry – formation of hygroscopic salts in FBC

<table>
<thead>
<tr>
<th>Case</th>
<th>Limestone feed</th>
<th>Load</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Limestone off</td>
<td>Full</td>
</tr>
<tr>
<td>2</td>
<td>Limestone off</td>
<td>Low (~55%)</td>
</tr>
<tr>
<td>3</td>
<td>Limestone on</td>
<td>Full</td>
</tr>
</tbody>
</table>

Fuel: bituminous coal with high S and Cl
Case 1 - limestone off, full load

SO$_2$ in the flue gas 900 ppm\textsubscript{v}
No chlorine in deposit
Case 2 – limestone off, 55% load

\[ \text{NH}_3(g) + \text{HCl}(g) \rightarrow \text{NH}_4\text{Cl}(s) \]

Vainio et al. 23rd FBC conference
Stability of NH$_4$Cl

The diagram illustrates the stability of NH$_4$Cl as a function of temperature and ammonia concentration (NH$_3$ ppm). The graph shows three curves for different HCl ppm concentrations: 1 ppm, 10 ppm, and 100 ppm. As the temperature increases, the concentration of NH$_3$ required for NH$_4$Cl to remain stable decreases.
Case 3 – limestone on, full load

Formation of CaCl₂

Vainio et al. 23rd FBC conference
Stability of CaCl$_2$

- CaO(s) + 2HCl(g) $\leftrightarrow$ CaCl$_2$(s) + H$_2$O(g) \hspace{1cm} (1)
- Ca(OH)$_2$(s) + 2HCl(g) $\leftrightarrow$ CaCl$_2$(s) + 2H$_2$O(g) \hspace{1cm} (2)
- CaCO$_3$(s) + 2HCl(g) $\leftrightarrow$ CaCl$_2$(s) + H$_2$O(g) + CO$_2$(g) \hspace{1cm} (3)
Deliquescence: process by which a salt absorbs enough water from the flue gas to fully dissolve.
Hygroscopic and deliquescent salts/deposits

Deposit build-up

Corrosion of heat exchangers

Corrosion during down time

PM removal

Plugging and corrosion

Stack
Deliquescence

- Process by which a salt absorbs enough water from the flue gas to fully dissolve
- DRH = deliquescence relative humidity, relative humidity at which a salt takes on water to fully dissolve
- For a mixture the DRH is usually lower than for the individual salts
- CRH = crystallization relative humidity
- DRH ≠ CRH
- Deliquescence temperature = temperature at which deliquescence occurs at a certain vol% H₂O

<table>
<thead>
<tr>
<th>Salt</th>
<th>DRH</th>
<th>CRH</th>
</tr>
</thead>
<tbody>
<tr>
<td>KH₂PO₄</td>
<td>96.6</td>
<td></td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>87</td>
<td></td>
</tr>
<tr>
<td>KCl</td>
<td>85</td>
<td>62</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>84</td>
<td></td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>77</td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>75</td>
<td>47</td>
</tr>
<tr>
<td>K₂CO₃</td>
<td>43</td>
<td></td>
</tr>
<tr>
<td>NH₄HSO₄</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>CaCl₂·6H₂O</td>
<td>31</td>
<td></td>
</tr>
</tbody>
</table>

DRH at 25°C for some salts

Albayrak et al., Colloid and Interface Science 2014
Deliquescence and recrystallization

- Example: Measurement of DRH and CRH of NaCl aerosol particles
  - DRH = 75%
  - CRH = 47%

Pinterich T., Atmos measurement Technique. 2017
RH and DRH

Above the red line in the figure NaCl will absorb moisture and may cause corrosion.

Above the blue line in the figure CaCl₂ will absorb moisture and may cause corrosion.

RH = \frac{p_{\text{H}_2\text{O}}}{p^{*}_{\text{H}_2\text{O}}}

p_{\text{H}_2\text{O}} = \text{partial pressure of water vapor}

p^{*}_{\text{H}_2\text{O}} = \text{equilibrium vapor pressure of water}
Mutual Deliquescence Relative Humidity (MDRH) for NaCl+KCl

Mixtures of salts can be more hygroscopic than the individual salts.

Li et al. Atmospheric Environment 82 (2014)
Study of hygroscopic properties of salts at ÅA

- Deliquescence and recrystallization properties of
  - Chlorides: \( \text{CaCl}_2 \), \( \text{NH}_4\text{Cl} \), \( \text{PbCl}_2 \), \( \text{ZnCl}_2 \), \( \text{KCl} \), \( \text{NaCl} \)...
  - Phosphates: \( \text{K}_3\text{PO}_4 \), \( \text{KH}_2\text{PO}_4 \)...
  - Carbonates: \( \text{K}_2\text{CO}_3 \), \( \text{CaCO}_3 \)
  - Sulfates: \( (\text{NH}_4)_2\text{SO}_4 \), \( \text{NH}_4\text{HSO}_4 \), \( \text{K}_2\text{SO}_4 \), \( \text{CaSO}_4 \)...

![Images of deliquescent salts changing between solid and liquid states.](image-url)
Methods

- Hygroscopic properties
  - Visual analysis
  - Thermogravimetric analysis
- Electrochemical methods, chronoamperometry
- Corrosion studies
TGA of CaCl\(_2\) at 25 vol\% H\(_2\)O

\[ \text{CaCl}_2 \rightarrow \text{CaCl}_2 \cdot 0.3\text{H}_2\text{O} \rightarrow \text{CaCl}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{CaCl}_2(\text{aq}) \]

At 160°C back to anhydrous CaCl\(_2\)

Deliquescence 108°C

CaCl\(_2\) → CaCl\(_2\)·0.3H\(_2\)O → CaCl\(_2\)·2H\(_2\)O → CaCl\(_2\)(aq)
Chronamperometry

- Deliquescence and recrystallization
- 5-35 vol% H₂O, rest nitrogen
- Heating and cooling rate: 0.4 °C/min

**Diagram Description:**
- Steam Generator
- Heated line
- Tube Furnace
- Potentiostat
- Vent Gases (dry)
- Condenser Unit

**Measurement cell:**
- Electrode
- Thermocouple 1: above salt
- Teflon coated electrodes
- Thermocouple 2: beneath the sample holder
- Crucible
- Teflon probe

Vainio E., Hupa E., Engbolm M., Lehmusto J., Lindberg D. 23rd FBC conference: A Novel Method to Detect Hydrate formation and Deliquescence of Salts and Deposits Related to Low-Temperature Corrosion in FBC
Chronoamperometry
CaCl$_2$ at 35 vol% H$_2$O

Hydrate formation at 150°C

Deliquescence at 119°C
Hysteresis of CaCl$_2$ – 25 vol% H$_2$O

Corrosive Deliquescence

- Temperature (°C)
- Current (µA)

Key Points:
- Deliquescence at 118°C
- 130°C
- 140°C
- 150°C

Time (h)
- Current (µA)
Corrosivness of CaCl$_2$ summary

Temperature (°C) vs. Water vapor (vol%) graph showing the deliquescence and recrystallization of CaCl$_2$.

- Deliquescence of CaCl$_2$ measured with TGA.
- Recrystallization of CaCl$_2$ measured with SI.

The shaded area indicates the corrosive range.
Example. Material temperature 110°C and fluctuating H₂O due to sootblowing (15→35 vol% H₂O)

Salt will not recrystallize
2. Corrosion tests

- 100 mg of CaCl$_2$ placed on carbon steel coupons
- Various H$_2$O concentrations:
  - Temperature
    - 100-160°C
- Exposure time: 4h
- Corrosion rate (mm/year) determined from weight loss
Corrosion tests

- 10 vol% H₂O
- 25 vol% H₂O
- 50 vol% H₂O
- 0.5h 50 vol% H₂O + 3.5h 25 vol% H₂O

<table>
<thead>
<tr>
<th>25vol% H₂O</th>
<th>100°C</th>
<th>110°C</th>
<th>120°C</th>
<th>130°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>After exposure</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
</tbody>
</table>
Summary: Part 2. Hygroscopic and deliquescent deposits

- Ash composition, additives, boiler load has an effect on the ash composition in the cold end
- Small changes in the combustion process may have a significant effect on deposit composition
- Deposits contain hygroscopic and deliquescent salts. Examples of highly deliquescent salts are: CaCl$_2$, K$_2$CO$_3$, ZnCl$_2$
- Deliquescence is the process by which a salt absorbs enough water from the gas to fully dissolve. This leads to a highly corrosive environment
- Deliquescent deposit in biomass conversion the main cause of low-temperature corrosion
- May also lead to filter plugging, deposit build-up and down-time corrosion
- Knowledge on ash chemistry and hygroscopic properties of salts leads to more efficient and reliable power production