Sulphur and Nitrogen Chemistry in Pressurized Flue Gas Systems

Tobias Pettersson, Fredrik Normann, Klas Andersson, Chalmers University of Technology

Linda Nylen, Marie Anheden*
Vattenfall Research and Development

*Marie Anheden currently works for Aker Clean Carbon
\[
\begin{align*}
\text{NO} & \xrightarrow{O_2 (g)} \text{NO}_2 \\
\text{HNO}_2 & \\
\text{HNO}_3 & + \text{NO} \\
\text{SO}_2 & \\
\text{H}_2\text{SO}_3 & \\
\text{H}_2\text{SO}_4 & \xrightarrow{O_2 (aq)}
\end{align*}
\]
\[
\begin{align*}
N_2O & \quad \xrightarrow{O_2 (g)} \quad NO_2 \\
NO & \quad \xrightarrow{O_2 (g)} \quad NO_2 \\
N_2O & \quad \xrightarrow{O_2 (g)} \quad NO_2 \\
HNNO_2 & \quad \xrightarrow{H_2O} \quad HNO_3 \\
HNNO_2 & \quad \xrightarrow{H_2O} \quad HNO_3 \\
\text{HNO}_3 & \quad \xrightarrow{H_2O} \quad H_2SO_3 \\
\text{SO}_2 & \quad \xrightarrow{O_2 (aq)} \quad H_2SO_3 \\
\text{SO}_2 & \quad \xrightarrow{O_2 (aq)} \quad H_2SO_4 \\
\end{align*}
\]
Aim

• Evaluate possible and probable reaction routes of NOx and SOx in the oxy-fuel flue gas train

As a way to:
• control SOx and NOx emission
• control acid formation and protect process equipment
1 bar, 25-90°C, 95% H₂SO₄ to pH 13

→ N₂O formed in the liquid at pH around 0

→ Complex dependence on the acidity

1 bar, 25°C, Constant pH 0.77-5

- Important $\text{N}_2\text{O}$ formation in the liquid at low pH
- No $\text{N}_2\text{O}$ formation for pH > 4
- No formation of NO in liquid phase

1-15 bar, 25-400°C, pH not controlled

→ SO₂ absorption enhanced by simultaneous NO₂ absorption

→ NO formation in the liquid

→ The pH is of high importance to the process

Method

• Constructed reaction mechanism (Pettersson et al. 2011)
  – 10 gas phase reactions
  – 18 liquid phase reactions
• Mass transfer between gas and liquid phase
  – two-film theory
• Plug-flow reactor
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reference case value</th>
<th>Sensitivity analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_2$</td>
<td>3000ppm</td>
<td>0-3000ppm</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>65ppm</td>
<td>0-650ppm</td>
</tr>
<tr>
<td>NO</td>
<td>585ppm</td>
<td>0-650ppm</td>
</tr>
<tr>
<td>O$_2$</td>
<td>5%</td>
<td>-</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>Saturated</td>
<td>-</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>Ballance</td>
<td>Ballance</td>
</tr>
<tr>
<td>Temperature</td>
<td>298K</td>
<td>298-338K</td>
</tr>
<tr>
<td>Pressure</td>
<td>20bar</td>
<td>1-30bar</td>
</tr>
<tr>
<td>Liquid/gas</td>
<td>0.003m$^3$/m$^3$</td>
<td>0.001-0.3 m$^3$/m$^3$</td>
</tr>
<tr>
<td>Residence time</td>
<td>100s</td>
<td>25-100s</td>
</tr>
</tbody>
</table>
Simulation Results

![Gas Phase Concentration vs Residence Time](image)

- **Total amount of N**
- **5 bar**
- **20 bar**
Simulation Results
Simulation Results

![Graph showing gas phase concentration over residence time for 20bar with lines labeled Total amount of N and 2*N_2O.](image)
Simulation Results
Simulation Results

![Simulation Results](image_url)

- **H₂SO₃**
- **H₂SO₄**

**Liquid Phase Concentration [mole/m³]**

**Residence Time [s]**

- 20bar
- **H₂SO₃ 5bar**
- **H₂SO₄ 5bar**
Comparison to Imperial College Measurements

- The experiments by Imperial College is modelled
- Tank in series
- Assumed gas-liquid contact area, mass transfer coefficients

NO$_x$ Absorption and SO$_x$ Absorption

Inlet concentration

\[ p = 15 \text{ bar}, \quad \bullet = 143 \text{ s} \]

300 mL prefilled water

\[ p = 5 \text{ bar}, \quad \bullet = 143 \text{ s} \]

300 mL prefilled 3M sulfuric acid
Simultaneous NO\textsubscript{x} and SO\textsubscript{x} Absorption

\begin{itemize}
  \item \(p = 5\ \text{bar}, \ \cdot = 372\ \text{s} \quad 10\ \text{mL} \ \text{prefilled water}\)
  \item \(p = 5\ \text{bar}, \ \cdot = 62\ \text{s} \quad 10\ \text{mL} \ \text{prefilled 3M sulfuric acid}\)
\end{itemize}
Conclusion

The interactions between HNO$_2$ and H$_2$SO$_3$ is crucial to the N-S reaction system

- NO$_x$ and SO$_x$ absorption is favoured
- pH controls the chemistry
- N$_2$O may form as a new stable product
Sulphur and Nitrogen Chemistry in Pressurized Flue Gas Systems

Tobias Pettersson, Fredrik Normann, Klas Andersson, Chalmers University of Technology

Linda Nylen, Marie Anheden
Vattenfall Research and Development