FGD Chemistry: A Review

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SO\textsubscript{2} and IED

- Current position under the LCPD:
  - Monthly ELVs at 400 mg/Nm\textsuperscript{3} or 94% removal efficiency (92% for FGD contracted before 2001)

- Position under IED:
  - ELV of 200 mg/Nm\textsuperscript{3} (existing plant) or 150 mg/Nm\textsuperscript{3} (new plant) monthly
  - Provision for equivalency achieving 96% removal on indigenous coal with detailed justification
  - BAT conclusions will supersede other requirements when finalised (likely to be finalised 2014/15 and implemented in 2019 at earliest). First BREF revision draft still imminent (expected May 2013)
  - Within the TNP period ELV that applies on 31 Dec 2015 must be maintained throughout TNP.
FGD on power plant in the UK

- First power plant FGD in the world were installed at Battersea, Bankside & Fulham Power Stations from 1933 onwards
  - Battersea & Bankside were alkali dosed sea water plant (once through)
  - Fulham was a recirculated lime slurry

- FGD technology was further developed & applied in Germany & Japan in the 1970’s

- The next generation of FGD plant in the UK were constructed in the mid to late 90’s (Drax, Ratcliffe, Uskmouth) in response to the 1988 LCPD

Learning curves

- Development is a good case study for other technologies at utility scale

Rubin, et al. GHGT-8 proceedings, 2006
Technologies applied in the UK power sector

- Dry/Semi-dry NID process
  - Uskmouth
- Sea Water Process
  - Aberthaw
  - Kilroot
  - Longannet
- Limestone Forced Oxidation
  - Cottam
  - Drax
  - Eggborough
  - Ferrybridge
  - Fiddlers
  - Rugeley
  - Ratcliffe
  - West Burton
NID Dry/Semi-dry process

- Two step process:
  - $CaO + H_2O \rightarrow Ca(OH)_2$
  - $SO_2 + Ca(OH)_2 \rightarrow CaSO_3 \cdot 1/2H_2O + 1/2H_2O$

- Water addition provides some gas cooling (max. T of process ~200 °C), content in end product ~5%

- Process efficiency sensitive to other acid gas species (e.g. HF, HCl, etc.)

- Generally lower CAPEX but higher OPEX than wet processes
Sea Water Process

- Applicable for sea water/estuarine cooled power plant only
- A portion (typically 20%) of CW flow routed to absorber and contacted with flue gas over packed column
- Relies on natural alkalinity of seawater (carbonate & biocarbonate)
- Seawater pH typically 7.6 to 8.4 (site specific, with potential for seasonal variation)
- CW flow recombined and aerated to increase pH and reduce COD for discharge
Sea Water Process Chemistry

\[ SO_2 + H_2O \rightarrow HSO_3^- + H^+ \]
\[ HSO_3^- \rightarrow SO_3^{2-} + H^+ \] \{ Absorption & dissociation \}

\[ HSO_3^- + \frac{1}{2} O_2 \rightarrow SO_4^{2-} + H^+ \]
\[ SO_3^{2-} + \frac{1}{2} O_2 \rightarrow SO_4^{2-} \] \{ Oxidation \}

\[ CO_3^{2-} + H^+ \rightarrow HCO_3^- \]
\[ HCO_3^- + H^+ \rightarrow CO_2 + H_2O \] \{ Acid-Base Reaction \}
Sea Water Process Chemistry (2)

- Oxidation may be enhanced by addition of catalysts (e.g. Ferric Chloride/Sulphate), experience seems to be mixed on their efficacy

- Local sea water alkalinity is critical – should be considered in the early stages of technology selection

- Air sparging may cause issues with foaming depending on sea water quality

- Harsh, highly corrosive environment (low pH, high chloride) in absorber – materials selection is important
Limestone Forced Oxidation (LSFO)
LSFO Chemistry

\[ SO_{2(g)} \leftrightarrow SO_{2(aq)} \]
\[ SO_{2(aq)} + H_2O \leftrightarrow H_2SO_{3(aq)} \leftrightarrow 2H_{(aq)}^+ + SO_{3}^{2-} \]
\[ CaCO_{3(s)} \leftrightarrow Ca_{(aq)}^{2+} + CO_{3}^{2-} \]
\[ CO_{3}^{2-}_{(aq)} + H_{(aq)}^+ \leftrightarrow HCO_{3(aq)}^- \]
\[ HCO_{3}^-_{(aq)} + H_{(aq)}^+ \leftrightarrow CO_{2(aq)} \]
\[ CO_{2(aq)} \rightarrow CO_{2(g)} \]
\[ SO_{3}^{2-}_{(aq)} + \frac{1}{2}O_{2(aq)} \rightarrow SO_{4}^{2-} \]
\[ Ca_{(aq)}^{2+} + SO_{4}^{2-} \rightarrow CaSO_{4(s)} \]

- Absorption & acidification
- Dissolution
- Acid-base reaction
- Oxidation
- Crystallisation
Oxidation

- Oxidation is critical to LSFO FGD performance
- Proceeds via free radical mechanism

<table>
<thead>
<tr>
<th>Chain initiation</th>
<th>$M^{3+} + HSO_3^-$</th>
<th>$\rightarrow \bullet SO_3^- + M^{2+} + H^+$</th>
<th>$\text{Ri}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\bullet SO_3^- + O_2$</td>
<td>$\rightarrow \bullet SO_5^-$</td>
<td>$\text{Rii}$</td>
<td></td>
</tr>
<tr>
<td>Propagation</td>
<td>$\bullet SO_5^- + HSO_3^-$</td>
<td>$\rightarrow \bullet SO_3^- + HSO_5^-$</td>
<td>$\text{Riii}$</td>
</tr>
<tr>
<td></td>
<td>$HSO_5^- + 2M^{2+} + H^+$</td>
<td>$\rightarrow SO_4^{2-} + 2M^{3+} + H_2O$</td>
<td>$\text{Riv}$</td>
</tr>
<tr>
<td></td>
<td>$2M^{3+} + 2HSO_3^-$</td>
<td>$\rightarrow 2\bullet SO_3^- + 2M^{2+} + 2H^+$</td>
<td>$\text{Rv}$</td>
</tr>
<tr>
<td>Termination</td>
<td>$\bullet SO_3^- + \bullet SO_3^-$</td>
<td>$\rightarrow S_2O_6^{2-}$ (dithionate)</td>
<td>$\text{Rvi}$</td>
</tr>
<tr>
<td></td>
<td>$\bullet SO_3^- + \bullet SO_5^-$</td>
<td>$\rightarrow S_2O_6^{2-}$ (peroxodisulphate)</td>
<td>$\text{Rvii}$</td>
</tr>
</tbody>
</table>

Where $M = \text{e.g. Co, Fe, Mn, Ni}$
Non-ideality in LSFO chemistry

- **Absorption** – series of equilibria linked to oxidation of sulphite to sulphate. Inhibited oxidation can affect SO$_2$ removal

- **H$_2$SO$_3$ dissociation** – reduced by presence of stronger acids (e.g. HCl, H$_2$SO$_4$)

- **Limestone dissolution** – High levels of CaCl$_2$ can inhibit, also Al & F can cause blinding

- **Limestone overdosing** - high residual limestone levels in slurry possibly leading to demister fouling and gypsum quality issues

- **Gypsum crystallisation** – low solids concentrations can inhibit nucleation within the slurry – this can lead to poor crystal growth (difficult dewatering) & scaling
Oxidation inhibition

• Radical ‘killers’ can enter the FGD from upstream

<table>
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<tr>
<th>Inhibitors ( (X^n) )</th>
<th>( \bullet \text{SO}_3^- + X^n )</th>
<th>( \rightarrow \text{SO}_3^{2-} + X^{n+1} )</th>
<th>Ra</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \bullet \text{SO}_5^- + 3X^n + 2H^+ )</td>
<td>( \rightarrow \text{SO}_4^{2-} + 3X^{n+1} + \text{H}_2\text{O} )</td>
<td>Rb</td>
<td></td>
</tr>
<tr>
<td>( \text{M}^{3+} + X^n )</td>
<td>( \rightarrow \text{M}^{2+} + X^{n+1} )</td>
<td>Rc</td>
<td></td>
</tr>
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• Iodide can act as a strong inhibitor and is reduced to iodine.

• SN compounds (formed by reaction of NOx with sulphite) can also act as inhibitors (e.g. HADS = HON(SO\(_3\)H)\(_2\))

• **Indicators** – Reduced performance, low redox potential (<300 meV), presence of significant levels of sulphite or iodide, halogen odour, presence of SN compounds
Conclusions

• FGD is a technology with a well-established history in the UK

• A range of FGD techniques are currently applied by the UK power sector with varying degrees of complexity of chemistry

• Understanding process chemistry is key to optimising performance and diagnosing operational issues

• IED compliance is likely require better control of chemistry as well as potential engineering modifications
Thanks for listening

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