Online measurement of siloxanes using FTIR spectroscopy

Ewan McAdam
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www.cranfield.ac.uk
Siloxanes are ubiquitous in commercial products
Fate of siloxanes during wastewater treatment

1. TSS 54% removal
94% of siloxanes within TSS reach digester

2. 1ry Sed.
TSS 46% removal
5% of siloxanes in 2ry reach digester

3. 2ry Sed.

4. Sludge thickening

5. Biogas
17-36% WWTW inlet in biogas;
32-50% digester feed in biogas

6. Boiler
3.3 mm thick deposit; boiler eff. reduced by 30-40%
11-15% of inlet mass recovered from boiler (1.2kg/d)
(36% mass based on boiler inlet)

7. Anaerobic digestion
50% VS destroyed

8. Digestate

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14. Digestate
Siloxanes oxidise in the CHP engine forming quartz

Increased oil changing frequency @ 500 h (21 d) versus 1500 h - £1.5 K per engine
Current practice for managing siloxane carbon filters
Motivation for online FTIR spectroscopy

- Dynamic on-line monitoring
- Response time in seconds
- Unlimited sample number
- Low OPEX
- Multi-ports for across-site cover
- Expensive (capex £35-50 K)

Grab sampling provides high cost data production with limited resolution
Establishing how we can derive value from online analysis

### Analysis

**On-line versus Ex-situ**

- **Value**
- **Usability**
- **Now**

On-line provides greater data density with different cost characteristic: High capex but low opex

| Complexity | ? |
| Performance | ? |
| Cost | ? |
| Energy | ? |
| Carbon intensity | ? |
| Maintenance | ? |
| Compatibility | ? |

### Carbon management

**Better filter resilience**

- **Value**
- **Usability**
- **Now**

Enabling carbon changes closer to breakthrough to limit siloxane load onto the CHP engine

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### Carbon filter diagnostics

**Filter characterisation**

- **Value**
- **Usability**
- **Retrofit**

Using online analysis to characterise and diagnose full scale filter design to better enhance filter capacity for siloxanes

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Case study site
Production of reference gases
Production of reference gases

CH$_3$Si-(CH$_3$)$_2$Si-O

Absorbance peak height

Expected reference gas D5 concentration (mg m$^{-3}$)
Using partial least squares to resolve interference

<table>
<thead>
<tr>
<th>Gas</th>
<th>Total Siloxanes (mg m(^{-3}))</th>
<th>On-line analysis</th>
<th>Calibration</th>
<th>Error</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Digester biogas</td>
<td>87.7(^{b,e}) 13.4(^{c,e})</td>
<td>FTIR</td>
<td>3.2 mg m(^{-3}) (LOD)</td>
<td>RMSE = 9.8 mg m(^{-3}) (Upstream)</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>RMSE = 1.5 mg m(^{-3}) (Downstream)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Primary reference gas (110 mg D5 m(^{-3}) CH(_4)) 4% error.</td>
<td></td>
</tr>
</tbody>
</table>

|                 | 6 mg m\(^{-3}\)                  |                  |                 | Deutz                                       |                 |
|                 | 12 mg m\(^{-3}\)                 |                  |                 | Jenbacher                                   |                 |
|                 | 30 mg m\(^{-3}\)                 |                  |                 | Waukesha                                    |                 |

Analysis
Daily sampling downstream of carbon filters using grab sampling/GC-MS £36,500 p.a.; Payback, 1.37 years – plus greater sampling intensity
Using FTIR for process diagnostics

- Siloxane concentration (mg m$^{-3}$) vs Biogas volume treated (Bed volumes, Bv)
- Modified Reynolds number ($Re_p$) vs Bed volumes to breakthrough at 30 mg m$^{-3}$ (Bv, x10$^3$)

- Breakthrough points for GAC1, GAC2, GAC3, GAC4, GAC5
Using FTIR for process diagnostics

Using on-line FTIR to characterise and diagnose existing assets can help identify OPEX savings through identifying best design practice.

### Carbon Filter Diagnostics

Using FTIR for process diagnostics

Using on-line FTIR to characterise and diagnose existing assets can help identify OPEX savings through identifying best design practice.

### Table: Carbon beds operated using either:

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Cost</th>
<th>Existing unit</th>
<th>New unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capital cost for new asset</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>180 kg Vessel; 170 m³/h gas flow</td>
<td>£3000</td>
<td>-</td>
<td>£3000</td>
</tr>
<tr>
<td>Pipework and ancillaries</td>
<td>£4000</td>
<td>-</td>
<td>£4000</td>
</tr>
<tr>
<td>Operating Costs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Replace GAC (180 kg virgin GAC)</td>
<td>-</td>
<td>72 hours</td>
<td>247 hours</td>
</tr>
<tr>
<td>Number of changes per annum</td>
<td>-</td>
<td>122</td>
<td>36</td>
</tr>
<tr>
<td>Exchange cost</td>
<td>£792</td>
<td>£96,624</td>
<td>£27,432</td>
</tr>
<tr>
<td>Annual OPEX saving (compared to existing unit)</td>
<td></td>
<td></td>
<td>£69192</td>
</tr>
<tr>
<td>Payback for vessel installation</td>
<td>£7000</td>
<td></td>
<td>1.2 months</td>
</tr>
<tr>
<td>Payback period for FTIR spectrometer + vessel outlay</td>
<td>£50,000</td>
<td></td>
<td>9.9 months</td>
</tr>
</tbody>
</table>
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