CEMS for Measurement of Ammonia, SO$_3$, and Low Level NOx

McIlvaine Company Hot Topic Hour
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Presentation Overview

• Compliance versus process control
• In situ versus extractive
• EPRI monitor evaluation approach
  – Lab assessment
    • Establish monitor accuracy
  – Field demonstration
    • Operability and reliability characteristics
  – Cost benefit application demonstration
• Low level NOx measurement
• Ammonia measurement
  – Issues and approaches taken to address
  – Successful applications
• SO$_3$ measurement
  – SO$_3$ + H$_2$SO$_4$
Compliance vs Process Control

- Compliance Measurements
  - Stack gas application
    - Near particulate free
    - Lower temperature
  - Representative average concentration
  - Daily zero & span checks
  - Span gases meet NIST traceability standards
  - Quarterly and annual QA/QC requirements
  - Availability

- Process Control
  - Economizer exit / air heater inlet applications
    - Ash particles
    - Higher flue gas temperature (i.e. 650 +/- 50 F)
  - Spatial differentiation more important
  - Less rigorous QA/QC required
  - Typically less documentation
In Situ vs. Extractive Measurement

• Issue of getting reactive species to monitor favors *in-situ* methods
  – Typically dealing with trace level concentrations
  – \( \text{SO}_3 / \text{NH}_3 \) reactive with potential reactions including:
    • \( \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 \) Acid dewpoint
    • \( \text{SO}_3 + \text{CaO}_{(s)} \rightarrow \text{CaSO}_4_{(s)} \) < 2000 F
    • \( \text{NH}_3 + \text{SO}_3 + \text{H}_2\text{O} \rightarrow (\text{NH}_4)\text{HSO}_4_{(l)} \) 400–500 F
    • \( 2\text{NH}_3 + \text{SO}_3 + \text{H}_2\text{O} \rightarrow (\text{NH}_4)_2\text{SO}_4_{(s)} \) 400–500 F
  – Sample stream temperature needs to be maintained above highest reaction temperature
  – Potential impacts of sample stream contact with filtration media
• In situ measurements provide potential benefits over extractive approach
  – Limited measurement bias
  – Faster system response
  – Line of sight measurements more representative relative to single point
Three Step General Approach

1. Laboratory Assessment
   - Establish accuracy, detection limits, and possible interferences
     - Test over range of target gas concentrations and cell conditions
     - Vary temperature, moisture, background gas composition

2. Single Path Field Demonstration
   - Establish operability and reliability characteristics
     - Test over range of path lengths with particulate laden flue gas
     - Assess alignment and signal to noise ratio over time and operating conditions
     - Assess maintenance requirements

3. Cost Benefit Application Demonstration
   - Structured test with end use of data stream
     (i.e. process control, operator advisory, etc.)
   - Document implementation specification, capital and installation costs, benefits from end use
CEM Measurement of Low Level NOx

• Important issues identified
  – Instrument Performance
  – NO$_2$ - NO Converter
  – Linearity / Drift Studies
  – Sample Conditioning Systems
  – Sample Lines
## CEM Measurement of Low Level NOx

### NO₂ Converter Efficiency

<table>
<thead>
<tr>
<th>Converter Type</th>
<th>Efficiency</th>
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<tbody>
<tr>
<td>Molybdenum</td>
<td>96.9</td>
</tr>
<tr>
<td>Molybdate-Carbon</td>
<td>94.3</td>
</tr>
<tr>
<td>Molybdate-Carbon (hot &amp; wet)</td>
<td>85.5</td>
</tr>
<tr>
<td>Stainless Steel</td>
<td>97.3</td>
</tr>
<tr>
<td>Vitrous Carbon (hot &amp; wet)</td>
<td>83.3</td>
</tr>
</tbody>
</table>

### Linearity and Drift

<table>
<thead>
<tr>
<th>Converter Type</th>
<th>Linearity</th>
<th>Zero Drift</th>
<th>Calibration Drift</th>
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</thead>
<tbody>
<tr>
<td>Molybdenum</td>
<td>0.9999</td>
<td>0.26</td>
<td>0.24</td>
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<tr>
<td>Stainless Steel</td>
<td>1.0000</td>
<td>0.74</td>
<td>0.13</td>
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<tr>
<td>Moly-Carbon</td>
<td>0.9999</td>
<td>0.29</td>
<td>0.82</td>
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<tr>
<td>Vit.-Carbon h/w</td>
<td>0.9997</td>
<td>NA</td>
<td>NA</td>
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<tr>
<td>Moly-Carbon h/w</td>
<td>0.9985</td>
<td>1.24</td>
<td>6.07</td>
</tr>
</tbody>
</table>
CEM Measurement of Low Level NOx

Sample Conditioning Systems

- Dilution extractive
- Permeation dryer
- Thermoelectric cooler (impinger type)
- Refrigerated (coil type) condenser
- Glass impingers in ice bath
- Duel type (ambient temp. water removal followed by permeation dryer)

Sample Lines

- Stainless Steel 25°C
- Stainless Steel 175°C
- Silcosteel 107°C
- Silcosteel 175°C
- PFA Teflon 107°C
- Dilution extractive sampling probe
- Hot converter & analyzer
- Upfront converter/thermal-electric
Ammonia Measurement Status

- Lab evaluations indicate TDL ammonia monitors tested work well under controlled conditions
- Application to coal-fired boilers introduce complications
  - Optical measurement issues
    - Port installation and alignment
      - Laser signal implications
    - Variable fly ash in flue gas
      - Laser beam attenuation and variable S/N
    - Long path lengths (reduced power and maintenance of alignment)
  - Current uses
    - Non-spatially resolved measurements for data trending
    - Spatially resolved measurements for open loop control
    - Process control and/or optimization
Ammonia Monitor Field Applications

- Successful ammonia monitor field applications
  - SCR process control with NEO monitor
    - 1200 MW unit
    - 15' line of sight cuts corner of reactor
      - Excellent mixing going into SCR
      - Just downstream of expansion joint
  - SNCR process control with Siemens monitor
    - 140 MW unit
    - Hot side ESP eliminates particle effects
    - Nominal 18 foot path length
  - SNCR process control with Unisearch monitor
    - 300 MW unit
    - Partial shielded path
      - Reduces 20’ path to ~14’ path
Continuous $\text{SO}_3$ Measurements

FTIR Measurement Location

- MRC FTIR tests not able to attain target detection limit for $\text{SO}_3$
  - New high power IR source developed
  - Increased signal to be tested for improved $\text{SO}_3$ detection

- FTIR used at MRC for continuous monitoring of $\text{HCl}$, $\text{SO}_2$, $\text{NH}_3$ during SCR testing
  - FTIR results used to vary additive injection rates to compensate for variations in coal used

- System operated completely by MRC personnel
- System maintained alignment over 2 meter path after restarting of SCR