Amine Aerosol Characterization by FTIR and PDI in Pilot Plant Testing

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Outline

Introduction
• Amine scrubbing
• Aerosol emissions

Analytical Methods
• Fourier Transform Infrared Spectrometry
• Phase Doppler Interferometry

Results
• Baghouse Pretreatment at NCCC
• SO$_3$ Generation at UT-SRP
• SO$_3$ Concentration Effect on Aerosol Emissions
• WW Temp and Flows
• Generalized Aerosol Emission Correlations
Introduction: Amine-Based CO$_2$ Capture

1. Vapor
2. Aerosol
   - Fly ash
   - $SO_3 \leftrightarrow H_2SO_4$
Analytical Methods

**FTIR**

- Gasmet DX-4000
- Concentrations of H$_2$O, CO$_2$, NH$_3$, SO$_2$, Amines
- No differentiating between vapor and aerosol phases

**PDI**

- Artium Technologies
- Drop sizes 0.1 to 12 $\mu$m
- Concentrations up to $10^7$ per cm$^3$
Results

- Baghouse Pretreatment at NCCC
- $\text{SO}_3$ Generation at UT-SRP
- $\text{SO}_3$ Concentration Effect on Aerosol Emissions
- WW Effect on Aerosol Emissions
- Generalized Aerosol Emission Correlations
Upstream Baghouse Flue Gas Treatment

- NO\textsubscript{X} (Nitrogen Oxides)
- Fly Ash
- SO\textsubscript{3} (Sulfur Trioxide)
- SO\textsubscript{2} (Sulfur Dioxide)
- CO\textsubscript{2} (Carbon Dioxide)

- Selective Catalytic Reduction
- Electro-Static Precipitator
- Bag House (2016)
- Flue Gas Desulfurization
- Pre-Scrubber
- CO\textsubscript{2} Capture

Activated Carbon

Coal Combustion

Baghouse reduces SO\textsubscript{3} concentration from 9-3 ppm down to ~0.5 ppm.
Upstream Baghouse Flue Gas Treatment

NCCC SSTU: 0.05 MWe
500 lb/hr

Pretreatment
Removing fly ash and SO₃ from flue gas

Absorber
Amine Solvent Inlet
Amine Solvent Outlet

Water Wash
FTIR and PDI Sampling Location
Water Wash Inlet

Flue Gas
Pretreatment Outlet

Pretreatment Outlet

Water Wash Outlet
FTIR Sampling of MEA Emissions

Baghouse upstream filtration significantly reduced MEA emissions under identical operating conditions.
Upstream Baghouse Flue Gas Treatment

PDI measurements on SSTU outlet:

Unable to detect aerosol at water wash outlet (<0.1 μm diameter & low concentration)

Bright lasers indicate high aerosol concentration

Faint lasers indicate low aerosol concentration

December 2015

October 2016
SO$_3$ Generation at UT-SRP

Baghouse is effective at aerosol mitigation

- Expensive solution
- Will not be constructed at every facility
- Still need to improve understanding of how amine scrubbing process conditions impact aerosol emissions.
Results

• Baghouse Pretreatment at NCCC
• $\text{SO}_3$ Generation at UT-SRP
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• WW Effect on Aerosol Emissions
• Generalized Aerosol Emission Correlations
SO₃ Generation at UT-SRP

$$\text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{SO}_3$$

Produced 1.7 grams/minute SO₃ during UT-SRP tests

- 8% SO₂/Air
- N₂ Purge
- Two catalyst beds ($V_2O_5$)
- Two-pass tube furnace
- Rotameter for flow control
UT-SRP Pilot Plant: 0.1 MWe

Amine Solvent Inlet

Water Wash

Chiller and Knockout Drum

Intercooling

Flue Gas

SO₃Injection

Amine Solvent Outlet

5 Point FTIR Sampling system:
(1) Inlet
(2) 1/2 Stage
(3) 2/3 Stage
(4) Outlet
(5) KO Outlet
SO$_3$ Generation and PZ Emissions

SO$_3$ Generation, 0.5 g/min, 20 ppm

Increase in WW PZ emissions from 50 to 120 ppm

Time (hh:mm)

H$_2$O and CO$_2$ (vol %)

PZ, NH$_3$, and SO$_3$ (ppm)

1-2 stage
2-3 stage
WW outlet
KO outlet

12:39 13:08 13:37 14:06
SO$_3$ Generation and PZ Emissions
### SO$_3$ Generation and PZ Emissions

<table>
<thead>
<tr>
<th></th>
<th>Average</th>
<th>Min</th>
<th>Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_3$ Concentration (ppm)</td>
<td>41</td>
<td>9</td>
<td>112</td>
</tr>
<tr>
<td>SO$_3$ Generated (g/min)</td>
<td>0.84</td>
<td>0.23</td>
<td>1.68</td>
</tr>
<tr>
<td>SO$_3$ Conversion Rate (%)</td>
<td>93.5</td>
<td>81.3</td>
<td>98.1</td>
</tr>
</tbody>
</table>

| WW PZ Emissions with SO$_3$ Injection | 90 | 9 | 189 |

| ppm PZ emitted per ppm SO$_3$ injected | 1.50 | 0.00 | 7.56 |

- 224 ppm for NCCC SSTU (0.05 MWe)
- 112 ppm for UT-SRP (0.1 MWe)
- 22 ppm for NCCC PSTU (0.5 MWe)
Results

- Baghouse Pretreatment at NCCC
- $\text{SO}_3$ Generation at UT-SRP
- $\text{SO}_3$ Concentration Effect on Aerosol Emissions
- WW Effect on Aerosol Emissions
- Generalized Aerosol Emission Correlations
Water Wash Effect on PZ Emissions

SO$_3$ Generation, 0.5 → 1.4 g/min, 31 → 92 ppm

Increase in SO$_3$ injection rate increases PZ emissions from 50 to 160 ppm.
Results

- Baghouse Pretreatment at NCCC
- $\text{SO}_3$ Generation at UT-SRP
- $\text{SO}_3$ Concentration Effect on Aerosol Emissions
- WW Effect on Aerosol Emissions
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Water Wash Effect on PZ Emissions

SO₃ Generation, 1.4 g/min, 53 ppm

Increase in WW flow rate slightly increases PZ emissions.
Water Wash Effect on PZ Emissions

SO$_3$ Generation, 1.4 g/min, 53 ppm

Stopping WW flow slightly decreases PZ emissions.
Water Wash Effect on PZ Emissions

SO$_3$ Generation, 1.4 g/min, 53 ppm

Resuming WW flow with cooling significantly increases PZ emissions
Results

- Baghouse Pretreatment at NCCC
- $SO_3$ Generation at UT-SRP
- $SO_3$ Concentration Effect on Aerosol Emissions
- WW Effect on Aerosol Emissions
- Generalized Aerosol Emission Correlations
Aerosol Emission Correlations

• Analysis of process properties to observe how each impacts aerosol emissions:
  • Temperatures
  • Flow Rates
  • Gas Phase Concentrations
Aerosol Emission Correlations

<table>
<thead>
<tr>
<th>Temperatures:</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Outlet T</td>
<td>0.564</td>
</tr>
<tr>
<td>Top Solvent/WW T</td>
<td>0.493</td>
</tr>
<tr>
<td>IC Solvent T</td>
<td>0.118</td>
</tr>
<tr>
<td>Top Bed T</td>
<td>0.510</td>
</tr>
<tr>
<td>Middle Bed T</td>
<td>0.172</td>
</tr>
<tr>
<td>Bottom Bed T</td>
<td>0.107</td>
</tr>
</tbody>
</table>

- Temperatures at top bed have greater correlation with amine emissions than lower bed temperatures.
- Amine emissions depend on gas temperatures more than solvent temperatures.
Aerosol Emission Correlations

Higher temperatures correlate to reduced PZ emissions.
### Aerosol Emission Correlations

<table>
<thead>
<tr>
<th>Flow Rates</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water Wash Flow</td>
<td>0.397</td>
</tr>
<tr>
<td>Intercooling Flow</td>
<td>0.206</td>
</tr>
<tr>
<td>L/G</td>
<td>0.162</td>
</tr>
</tbody>
</table>

- Solvent flow rates at top beds have a greater impact on amine emissions than flow rates through lower beds.
Aerosol Emission Correlations

<table>
<thead>
<tr>
<th>Gas Phase Concentrations</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CO}_2 \text{ In}$</td>
<td>0.143</td>
</tr>
<tr>
<td>$\text{CO}_2 \text{ Out}$</td>
<td>0.270</td>
</tr>
</tbody>
</table>

- $\text{CO}_2$ concentration at absorber outlet has greater correlation with amine emissions than $\text{CO}_2$ concentration at inlet.
Conclusions

• Baghouse pretreatment mitigates amine aerosol at NCCC.
• Increasing SO$_3$ concentrations increases amine emissions.
• Process temperatures most significant in determining aerosol emissions.
  • Gas temperatures matter more than solvent temperatures.
  • Temperatures at absorber outlet more significant than temperatures at the inlet.
• Solvent emissions more dependent on water wash flow rates than intercooling/lower bed flow rates.
• Increasing CO$_2$ concentration at absorber outlet decreases amine aerosol emissions.
Acknowledgements

Thank you

- Rochelle Lab
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- Dr. Eric Chen
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- NCCC SSTU operations crew
- UT-SRP operations crew
References


Photodetectors quantify drop size via phase shift
- Reduces window attenuation

Droplet movement causes Doppler shift in phases
- Determines droplet velocity

Velocity + number count used to determine particle concentration

Size Range:
0.1 – 12.0 μm

Concentration Limit:
$10^7$ per cm$^3$
Upstream Baghouse Flue Gas Treatment

PDI measurements on SSTU outlet:

- **December 2015**: Doppler Burst
- **October 2016**: No aerosol detected

Lack of aerosol confirmed with oscilloscope
SO$_3$ Generation, 1.4 g/min, 93 ppm

Temperature increases for absorber middle bed correlate to increased PZ emissions.
Aerosol Emission Correlations

Temperatures

- Gas Outlet: 0.564
- Top Solvent/WW: 0.493
- IC Solvent: 0.1181
- Top Bed: 0.5102
- Middle Bed: 0.1722
- Bottom Bed: 0.1074

Temperatures at top bed have greater correlation with amine emissions than temperatures in lower beds.
Aerosol Emission Correlations

Flow Rates

Increasing water wash flow rate correlates with decreased amine emissions

Flow Rate (lb/hr); L/G x 1000 (m/m)

IC Flow Rate (lb/hr)
WW Flow Rate (lb/hr)
L/G x 1000 (m/m)
Aerosol Emission Correlations

Rich and Lean Loading (mol/kg solvent)

Solvent Loadings

Rich loading influences amine emissions more than lean loading.
### Aerosol Emission Correlations

<table>
<thead>
<tr>
<th>Solvent Loadings</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rich Loading</td>
<td>0.367</td>
</tr>
<tr>
<td>Lean Loading</td>
<td>0.005</td>
</tr>
</tbody>
</table>

- Rich loading has greater influence on amine emissions than lean loading
Aerosol Emission Correlations

Inlet and Outlet CO\textsubscript{2} Concentrations

Increasing CO\textsubscript{2} concentration at absorber outlet decreases amine emissions.

PZ emitted per ppm SO\textsubscript{3} injected vs. CO\textsubscript{2} Concentration (vol %)
NCCC SSTU

Absorber Column

Gas Outlet

Lean Solvent Inlet

Flue Gas Inlet

PSTU Blower

Rich Solvent Outlet

SSTU Blower

Water Wash Column

Blower and VSD

PDI and Test Cell

FTIR Probe

To BDU

Wash inlet

Wash outlet

~55’ of 4” piping
FTIR and PDI Field Sampling
FTIR and PDI Field Sampling

- Heated FTIR Sample Probe
- Heated FTIR Sample Line
- PDI and Test Cell
- FTIR CPU and User Interface
- FTIR Heated Element Controls
- FTIR Heated Sample Pump and Filter