Minimizing Solvent Oxidation With NO₂ Prescrubbing

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OBJECTIVES
- DOE SBIR FY16 Phase I Release 2: Carbon Capture System Improvements
  - Aerosols, Reclamation, Oxidation
- Amine-based solvents = Ready for Deployment
- Flue gas contaminants oxidize amines († costs)
- Operating costs – amine replacement, waste disposal
- Capital costs – solvent reclaiming
- Integrate NOₓ and SO₂ removal
- No additional capital costs
- Modify chemistry for existing equipment

SOLVENT OXIDATION REACTIONS
R₃NH + NO₂ → HNO₂ + R₃N* 
R₃N* + NO → R₃NNO₂ (nitroamine)

1. Thiosulfate addition inhibits sulfite oxidation
2. Sulfite reacts with inlet NO₂

SULFITE OXIDATION INHIBITION AND REACTION
NO₂ + SO₃²⁻ → NO₃⁻ + SO₄²⁻
SO₃²⁻ + O₂ → SO₄²⁻
SO₃²⁻ + S₂O₃²⁻ → SO₄²⁻ + S₂O₅²⁻
2SO₂⁻ → SO₄²⁻

BENCH SCALE TEST PARAMETERS

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂ Concentration</td>
<td>ppmv</td>
<td>0.5</td>
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<tr>
<td>Temperature</td>
<td>°C</td>
<td>22-55</td>
</tr>
<tr>
<td>Thiosulfate Concentration</td>
<td>mmol/kg</td>
<td>4-50</td>
</tr>
<tr>
<td>Tertiary Amine Concentration</td>
<td>mmol/kg</td>
<td>3-200</td>
</tr>
<tr>
<td>Metal Concentration</td>
<td>mmol/kg</td>
<td>0.1-0.5</td>
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<tr>
<td>EDTA Concentration</td>
<td>mmol/kg</td>
<td>0.02-1</td>
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</tbody>
</table>

EXAMPLE TEST RESULTS

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Concentration (mmol/kg)</th>
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</thead>
<tbody>
<tr>
<td>0</td>
<td>1.5</td>
</tr>
<tr>
<td>5</td>
<td>2.0</td>
</tr>
<tr>
<td>10</td>
<td>2.5</td>
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ESTIMATED ECONOMICS

BASELINE CHEMISTRY

ADVANCED ADDITIVES
- Lower cost
- More effective oxidation inhibitor

TYPICAL PRE-TREATMENT FOR AMINE POST-COMBUSTION CAPTURE SYSTEM

Chemical Additives: Dual Removal of SO₂ / NO₂

SO₂ < 40 ppmv
NO₂ < 5 ppmv

SO₂ ≤ 1 ppmv
NO₂ < 1 ppmv

Flue gas to Atmosphere

CO₂ Lean Solvent

CO₂-Rich Solvent

CO₂ Absorber

Direct Contact Condenser

Gas Phase: NO₂

Liquid Phase: Sulfite Concentration

NCC Pilot Test Results

Additive Concentrations

NO₂ Removal versus pH

NO₂ Removal versus Additive Concentration

SUMMARY
- Validated concept at bench and pilot scales
- Identified novel inhibitors
- Stronger oxidation inhibition
- Lower cost
- No new unit operations required
- Utilizes existing equipment
- Potential net savings > $1/MT CO₂ captured

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