Hydrated Lime DSI - Solution for Acid Gas Control (SO3, HCl, and HF)

July 19, 2012

MARAMA /ICAC SO2/HCl CONTROL TECHNOLOGIES WEBINAR

HOWARD FITZGERALD - LHOIST NORTH AMERICA
Chemical Lime and Franklin Industrial Minerals merged to form **Lhoist North America**

**Lhoist Group** – Worldwide, 22 countries in Asia, Europe and the Americas

**Lhoist** - Largest lime company in the world

Calcium Focused

Calcium R&D Centers throughout globe
Presentation Objectives

- Provide brief explanation of Calcium Products and Production

- Present a summary of coal-fired boiler test data to show the performance of DSI using hydrated lime as an effective emission control option
  - \( \text{SO}_2 \) – explain the temperature relationship in capture
  - HCl
    - \( \text{SO}_3 \)
    - HF
  - Hg - removal enhancement
  - Trace metals

- Compare the effectiveness of a standard hydrated lime to a high surface area – high porosity optimized hydrate produced specifically for acid gas control applications
I’m a Calcium Missionary

LS Fines \[ \rightarrow \] Heat \[ \rightarrow \] \( \text{CO}_2 \) \[ \rightarrow \] LKD

\( \text{CaCO}_3 \) \[ \text{Limestone} \]

Heat \[ \rightarrow \] \( \text{CO}_2 \) \[ \rightarrow \] Water

\( \text{Ca(OH)}_2 \) \[ \text{Calcium Hydroxide} \]

‘Hydrate’
Hydrated Lime Properties

- Chemically the hydrated limes evaluated are basically the same
- Their difference lies in their physical properties

**Sorbacal®SP and SPS**

- SSA: $>40 \, \text{m}^2/\text{g}$
- Porosity: $\sim 0.23 \, \text{cm}^3/\text{g}$

**Standard Hydrate**

- SSA: $\sim 20 \, \text{m}^2/\text{g}$
- Porosity: $\sim 0.07 \, \text{cm}^3/\text{g}$

Production in Europe and Japan since early 1990s.
Commercially Available in US April 2013
CSAPR – SIP Compliance Strategy
SO₂ Data Summary

Testing at SRI Birmingham – Combustion Research Furnace
High S - ~2000 ppm in flue gas (furnace injection)
Low S - ~600 ppm in flue gas (duct injection)
SO₂ Removal Chemical Reactions

- **WFGD Limestone - SO₂ Removal**
  \[ \text{CaCO}_3 + \text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{CaSO}_4 + \text{CO}_2 \]

- **WFGD Quicklime - SO₂ Removal**
  \[ \text{CaO} + \text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{CaSO}_4 \]

- **SDA/CDA/DSI Hydrated Lime - SO₂ Removal**
  \[ \text{Ca(OH)}_2 + \text{SO}_2 \rightarrow \text{CaSO}_3\cdot\frac{1}{2}\text{H}_2\text{O} + \frac{1}{2}\text{H}_2\text{O} \]
Hydrate FSI – SO$_2$ Control Furnace Injection with ESP
Temperature Impact on SO$_2$ Removal

![Graph showing the impact of hydrate feedrate on SO$_2$ removal. The graph demonstrates the percentage of SO$_2$ removal in relation to the hydrate feedrate (lb/lb SO$_2$). The graph includes data points for two different temperatures: 2100°F and 1700°F. At a hydrate feedrate of 1.5 lb/lb SO$_2$, the SO$_2$ removal is approximately 28%.](image-url)
Hydrate DSI – SO₂ Control Furnace Injection w/ ESP
Comparison of Sorbacal® SPS and Standard Hydrate

% SO₂ Removal

2000 ppm SO₂
ESP Operations
~33%

2100°F

Sorbacal SPS
Std Hydrate

Hydrate Feedrate (lb/lb SO₂)
Hydrate DSI – SO$_2$ Control Air Heater Inlet (670°F) w/ FFBH
Comparison of Sorbacal$^\text{®}$. SPS and Standard Hydrate

![Graph showing SO$_2$ Removal % vs. Hydrate Feedrate (lb/lb SO$_2$)]

- **Sorbacal$^\text{®}$ SPS**
- **Standard Hydrate**

600 ppm SO$_2$

~33% SO$_2$ Removal
SO$_2$ Test Conclusions

- Higher Temperatures are better for SO$_2$ removal
- Sorbacal®SPS performs better than standard hydrate by ~30%
- 70+% removal is achievable with Sorbacal®SPS at a feedrate of ~2 lbs Sorbacal®SPS/lb SO$_2$ with in furnace injection (2100°F) with proper dispersion and an ESP. A baghouse should perform better.
- ~50% removal is achievable with Sorbacal®SPS at the air heater inlet temperatures (700°F to 650°F)
- <20% removal can be expected at the air heater outlet temperature
MATS Compliance Strategy
HCl Data Summary

High Cl Tests
(3300 ppm Cl in Coal, 200 ppm HCl in flue gas)

Moderate Cl Tests
(~800 – 1000 ppm in coal, 63 ppm in flue gas)
Other Acid Gas Chemical Reactions

- **HF Removal**
  - \( \text{Ca(OH)}_2 + 2 \text{HF} \rightarrow \text{CaF}_2 + 2 \text{H}_2\text{O} \)

- **SO₃ Removal**
  - \( \text{Ca(OH)}_2 + \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{CaSO}_4\cdot2\text{H}_2\text{O} \)

- **HCl Removal**
  - \( \text{Ca(OH)}_2 + \text{HCl} \rightarrow \text{CaClOH} + \text{H}_2\text{O} \)
  - \( \text{CaClOH} + \text{HCl} \rightarrow \text{CaCl}_2 + \text{H}_2\text{O} \)

*Note – Lhoist has demonstrated in multiple tests*  
*Hydrated Lime reacts more strongly (or quickly) with HF, then SO₃, then HCl.*
Impact of competing acid gases

% Control

SO₂

SO₃

HCl

HF

Temperature

Low

High
Temperature Impacts on HCl Removal – Sorbacal® SPS

ESP Operations for High Cl Coal
(~3300 ppm in coal – 200 ppm HCl in flue gas)

HCl Removal Better at Low T

Temperature Effects for Sorbacal SPS

Hydrate Feedrate (lb hydrate/lb acid gas)

HCl Removal (%)
ESP Operations for High Cl Coal
(~3300 ppm in coal – 200 ppm HCl in flue gas)

HCl Removal Better at Low T

Temperature Impacts on HCl Removal – Standard Hydrate

Temperature Effect for Sorbacal H

HCl Removal (%)

Hydrate Feedrate (lb hydrate/lb acid gas)
Sorbacal® SPS vs. Standard Hydrate

High Chloride Coal, ESP Operations, DSI @ 350°F

Hydrate Feedrate (lb hydrate/lb acid gas)

HCl Removal (%)

200 ppm HCl in gas
3300 ppm Cl in coal
HCl Removal - Baghouse vs. ESP

HCl Removal vs. lb Hydrate per lb Acid Gas

- Baghouse with SPS
- ESP with SPS

200 ppm HCl in gas
3300 ppm Cl in coal
Sorbacal® SPS performed better than the standard hydrate.

Better performance was shown at the air heater outlet temperature (300 - 350°F) than the inlet temperature (650 - 700°F).

~90% HCl removal was achieved with an ESP and 97% removal with a baghouse.

The utility MATS limit of 0.002 lb/MM Btu was not achieved with this high Cl coal.

DSI can be an effective way to limit Cl corrosion in FGD systems and also reduce waste water treatment costs.
**HCL Removal Across Baghouse**

- **Sorbacal SP**
- **Standard Hydrate**

**Graph Details:**
- **Y-axis:** HCL Removal (%) ranging from 60.0 to 100.0
- **X-axis:** Hydrate Feedrate (lb hydrate/lb acid gas)

- **Legend:**
  - Blue diamonds: Sorbacal SP
  - Red squares: Standard Hydrate

**Graph Notes:**
- 63 ppm HCl in gas
- 800 - 1000 ppm Cl in coal
HCl Removal Across Baghouse

Graph showing HCl removal percentage as a function of hydrate feedrate (lb hydrate/lb acid gas). The graph includes two lines:
- Blue line: Sorbacal SP
- Pink line: Standard Hydrate

Y-axis: HCl Removal (%)
X-axis: Hydrate Feedrate (lb hydrate/lb acid gas)

Key:
- 63 ppm HCl in gas
- 800-1000 ppm in coal
**HCl Removals Across ESP**

![Graph showing HCl removals across ESP.]

- **Sorbacal SP**
- **Standard Hydrate**

- **HCl Removal (%):**
  - 63 ppm HCl in gas
  - 800-1000 ppm Cl in coal
HCl Emissions Across Baghouse

- **Sorbacal SP**
- **Standard Hydrate**

63 ppm HCl in gas
800-1000 ppm Cl in coal

HCl Emissions (lb/MM Btu)

Hydrate Feedrate (lb hydrate/lb acid gas)
**HCl Emissions Across ESP**

- **Sorbacal SP**
- **Standard Hydrate**

63 ppm HCl in gas
800-1000 ppm Cl in coal

**Graph Details:**
- **Y-axis:** HCl Emissions (lb/MM Btu)
- **X-axis:** Hydrate Feedrate (lb hydrate/lb acid gas)
HCl Test Summary

- Sorbacal® SP performed better than the standard hydrate.
- Utility MATS emission level (0.002 lb/MM Btu) was achieved with Sorbacal® SP and a baghouse with 800 - 1000 ppm Cl in coal.
- Utility MATS emission level was not achieved with an ESP particulate collection device.
- Utility MATS emission level was not achieved with the standard hydrate with either collection device.
- The coal Cl level vastly impacts the ability to achieve the MATS emission level.
- Hydrate dispersion in the gas is imperative with ESP.
- Hydrated Lime is selective – High levels of HCl and SO₃ removal, without excessive sorbent consumed in SO₂ reaction.
Hg Capture Enhancement from Hydrate DSI

- HCl assists in the oxidation of Hg\textsubscript{E} to Hg\textsubscript{O}
- SO\textsubscript{3} interferes with PAC to react with Hg
- Hydrated Lime is approximately 1/10\textsuperscript{th} price of PAC
- Tests show Hg removal increased from 40\% to >75\% with Hydrate DSI removal of SO\textsubscript{3} to <3ppm
- Some tests have shown removal of Hg at MATS level with Hydrate DSI only through Carbon in Fly Ash
- Hydrate dispersion in the gas is imperative with short residence times in duct
Delta Wing
Static gas mixer

SGM for mixing of gas:
- concentrations
- temperatures
- volume flows

Section A - A
Vortices generated on plate edges

Working principle:
leading edge vortices created by gas flows arriving at shaped plates under an angle of attack generate turbulences for mixing purposes

Tony Licata
508-854-3853
Tlicata@babcockpower.com
Trace Metal Capture
Selenium and Arsenic Vapor Emissions

- **Baseline**
- **Hydrate Injection**

Emissions (ug/dscm):
- Selenium
- Arsenic
# Leaching Tests

<table>
<thead>
<tr>
<th>Leached Metal</th>
<th>TCLP Haz Waste Reg. Limit (ppm)</th>
<th>Primary Drinking Water (ppm)</th>
<th>Baseline (ppm)</th>
<th>Hydrate Injection (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium</td>
<td>5</td>
<td>0.1</td>
<td>0.024</td>
<td>&lt;0.005</td>
</tr>
<tr>
<td>Arsenic</td>
<td>5</td>
<td>0.05</td>
<td>&lt;0.005</td>
<td>0.008</td>
</tr>
<tr>
<td>Selenium</td>
<td>1</td>
<td>0.05</td>
<td>0.054</td>
<td>0.096</td>
</tr>
<tr>
<td>Silver</td>
<td>5</td>
<td>0.1</td>
<td>&lt;0.005</td>
<td>&lt;0.005</td>
</tr>
<tr>
<td>Cadmium</td>
<td>1</td>
<td>0.005</td>
<td>&lt;0.005</td>
<td>&lt;0.005</td>
</tr>
<tr>
<td>Barium</td>
<td>100</td>
<td>2</td>
<td>0.477</td>
<td>0.225</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.2</td>
<td>0.002</td>
<td>0.011</td>
<td>0.013</td>
</tr>
<tr>
<td>Lead</td>
<td>5</td>
<td>0.015</td>
<td>0.07</td>
<td>&lt;0.005</td>
</tr>
</tbody>
</table>
Overall Test Results/Observations

- SO₂ removal is better at high temperatures
- HCl/HF/SO₃ removal is better at lower temperatures
- HCl MATS emission level can be achieved with Sorbacal® SP and a baghouse at a moderate Cl coal
- HCl performance significantly impacted by coal Cl content
- Removal of SO₃ enhances performance of PAC for Hg removal – Hydrate DSI is an efficient method
- DSI can be an effective means of limiting HCl corrosion and waste water impacts
- DSI with hydrated lime reduced vapor phase trace metals – particularly Se and As
- Metals from DSI flyash leached at an order of magnitude lower than the TCLP hazardous waste limits
DSI with hydrated lime can be a viable low capital incremental emission control option for coal-fired boilers
Questions ??

please contact

Howard B. Fitzgerald
FGT Applications Specialist
Lhoist North America
8840 Waterside Drive
Ball Ground, GA 30107
Office: 770-889-3111
Mobile: 817-995-3011
Email: howard.fitzgerald@lhoist.com
# DSI System Suppliers and Engineers

<table>
<thead>
<tr>
<th>Company</th>
<th>Main Contact</th>
<th>email</th>
<th>Phone</th>
<th>website</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADA ES</td>
<td>Greg Fillipelli</td>
<td><a href="mailto:gregf@adaes.com">gregf@adaes.com</a></td>
<td>443-860-9213</td>
<td><a href="http://www.adaes.com">www.adaes.com</a></td>
</tr>
<tr>
<td>BCSI</td>
<td>Bill Caputo</td>
<td><a href="mailto:bill@bulkcsi.com">bill@bulkcsi.com</a></td>
<td>412-675-0420</td>
<td><a href="http://www.bulkcsi.com">www.bulkcsi.com</a></td>
</tr>
<tr>
<td>Breen ES</td>
<td>Cal Lockert</td>
<td><a href="mailto:clockert@breenes.com">clockert@breenes.com</a></td>
<td>440-840-0137</td>
<td><a href="http://www.breenes.com">www.breenes.com</a></td>
</tr>
<tr>
<td>Clyde Bergmann</td>
<td>James Fisher</td>
<td><a href="mailto:james.fisher@us.cbpg.com">james.fisher@us.cbpg.com</a></td>
<td>610-695-9710</td>
<td><a href="http://www.cbpg.com">www.cbpg.com</a></td>
</tr>
<tr>
<td>FL Smidth</td>
<td>Dave Escott</td>
<td><a href="mailto:david.escott@flsmidth.com">david.escott@flsmidth.com</a></td>
<td>610-360-1964</td>
<td><a href="http://www.flsmidth.com">www.flsmidth.com</a></td>
</tr>
<tr>
<td>McGill Air Clean</td>
<td>Gerald Childress</td>
<td><a href="mailto:jchildress@mcgillairclean.com">jchildress@mcgillairclean.com</a></td>
<td>614-829-1350</td>
<td><a href="http://www.mcgillairclean.com">www.mcgillairclean.com</a></td>
</tr>
<tr>
<td>Nol-Tec Systems</td>
<td>Jerry Vanderwerff</td>
<td><a href="mailto:jerryvanderwerff@nol-tec.com">jerryvanderwerff@nol-tec.com</a></td>
<td>651-780-8600</td>
<td><a href="http://www.nol-tec.com">www.nol-tec.com</a></td>
</tr>
<tr>
<td>SEI Group</td>
<td>Wes McKenzie</td>
<td><a href="mailto:wmckenzie@seigroup.com">wmckenzie@seigroup.com</a></td>
<td>614-259-6505</td>
<td><a href="http://www.seigroup.com">www.seigroup.com</a></td>
</tr>
<tr>
<td>United Conveyor</td>
<td>Jon Norman</td>
<td><a href="mailto:JonNorman@unitedconveyor.com">JonNorman@unitedconveyor.com</a></td>
<td>315-440-3244</td>
<td><a href="http://www.unitedconveyor.com">www.unitedconveyor.com</a></td>
</tr>
</tbody>
</table>