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

CaCO₃
Limestone

Heat

CO₂
LKD

Ca(OH)₂
Calcium Hydroxide
‘Hydrate’

LS Fines

Water

CaO
Lime

Heat

CO₂

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 m²/g
- Porosity: ~.23 cm³/g

**Standard Hydrate**

- SSA: ~20 m²/g
- Porosity: ~.07 cm³/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)
SO$_2$ Removal Chemical Reactions

- WFGD Limestone - SO$_2$ Removal
  - $CaCO_3 + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4 + CO_2$

- WFGD Quicklime - SO$_2$ Removal
  - $CaO + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4$

- SDA/CDA/DSI Hydrated Lime - SO$_2$ Removal
  - $Ca(OH)_2 + SO_2 \rightarrow CaSO_3\cdot\frac{1}{2}H_2O + \frac{1}{2}H_2O$
Hydrate FSI – SO$_2$ Control Furnace Injection w/ ESP Temperature Impact on SO$_2$ Removal

- **Sorbacal SPS @ 2100 F**
- **Sorbacal SPS @ 1700 F**

% SO$_2$ Removal vs. Hydrate Feedrate (lb/lb SO$_2$)

- 2000 ppm SO$_2$
- ESP Operations

~28%
Hydrate DSI – SO₂ Control Furnace Injection w/ ESP Comparison of Sorbacal® SPS and Standard Hydrate

2000 ppm SO₂
ESP Operations

~33%

2100°F
Hydrate DSI – SO₂ Control Air Heater Inlet (670°F) w/ FFBH
Comparison of Sorbacal® SPS and Standard Hydrate

![Graph showing SO₂ removal comparison between Sorbacal® SPS and Standard Hydrate with an SO₂ removal of ~33%.]
SO₂ Test Conclusions

- Higher Temperatures are better for SO₂ 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 SO₂ 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**
  - \[ \text{Ca(OH)}_2 + 2 \text{HF} \rightarrow \text{CaF}_2 + 2 \text{H}_2\text{O} \]

- **SO\text{3 Removal}**
  - \[ \text{Ca(OH)}_2 + \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{CaSO}_4\cdot 2\text{H}_2\text{O} \]

- **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 SO\text{3}, then HCl.*
Impact of competing acid gases

- HCl
- HF
- SO₂
- SO₃

% Control vs Temperature

Low → High
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 (%)

- 350 F
- 700 F
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

HCl Removal (%) vs. Hydrate Feedrate (lb hydrate/lb acid gas)

- **Sorbacal SPS**
- **Standard Hydrate**

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

- Baghouse with SPS
- ESP with SPS

200 ppm HCl in gas
3300 ppm Cl in coal
High S, High Cl Test Summary

- 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**

63 ppm HCl in gas
800 - 1000 ppm Cl in coal
HCl Removal Across Baghouse

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

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

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

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 Across ESP

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

63 ppm HCl in gas
800-1000 ppm Cl in coal
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 SO$_3$ removal, without excessive sorbent consumed in SO$_2$ reaction.
Hg Capture Enhancement from Hydrate DSI

- HCl assists in the oxidation of Hg$_E$ to Hg$_O$
- SO$_3$ interferes with PAC to react with Hg
- Hydrated Lime is approximately 1/10$^{th}$ price of PAC
- Tests show Hg removal increased from 40% to >75% with Hydrate DSI removal of SO$_3$ 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

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

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Trace Metal Capture
Selenium and Arsenic Vapor Emissions

- Selenium
- Arsenic

Emissions (ug/dscm)

Baseline

Hydrate Injection
# 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 Hydrate Injection (ppm)</th>
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</thead>
<tbody>
<tr>
<td>Chromium</td>
<td>5</td>
<td>0.1</td>
<td>0.024</td>
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<tr>
<td>Arsenic</td>
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<td>0.05</td>
<td>&lt;0.005</td>
</tr>
<tr>
<td>Selenium</td>
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<td>0.05</td>
<td>0.054</td>
</tr>
<tr>
<td>Silver</td>
<td>5</td>
<td>0.1</td>
<td>&lt;0.005</td>
</tr>
<tr>
<td>Cadmium</td>
<td>1</td>
<td>0.005</td>
<td>&lt;0.005</td>
</tr>
<tr>
<td>Barium</td>
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<td>2</td>
<td>0.477</td>
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<tr>
<td>Mercury</td>
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</tr>
<tr>
<td>Lead</td>
<td>5</td>
<td>0.015</td>
<td>0.07</td>
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</tbody>
</table>
Overall Test Results/Observations

- SO$_2$ removal is better at high temperatures
- HCl/HF/SO$_3$ 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 SO$_3$ 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

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