

Hydrated Lime for HCl Mitigation Benefits of High Reactivity Hydrate



Discovering what's possible with calcium

July 18, 2013



Utility Focus - Support of Technical Advancement

- Support of key industry events
 - WPCA member

- Sponsor of 2013 APC Conference in St. Louis
- Dry Hydrate Users Group
- Continued funding of test programs
 - $-SO_3 \& HCl mitigation$
 - 2015 MACT/MATS requirements
- Technical Service and R&D organization
 - Equipment for field tests
 - Additional personnel
 - Focus on new product development









Hydrated Lime DSI (SO₃, HCI, SO₂)

Known

Works well for acid gases
 Good quality hydrate

- Works with hot or cold side injection
- On-site treatment unnecessary – ready to use as delivered
- Simple feed systems
- Ash-friendly

Challenges, new and old

- Tighter regulations for acid gases
- More in-flight capture
- Very marginal ESPs





Factors Affecting Removal Rate

- Hydrated lime quality
 - Purity & reactivity

- Injection system efficiency
 - Feed system
 - Flow splitting
 - Flue gas coverage
- Residence time
- Levels of HCl











Market Needs for Higher Reactivity Hydrate





Performance Improvement





Qualify High Reactive Hydrate

- Lab data
 - Internal reactivity test

- HR Hydrate >> FGT Hydrate >> Industrial Hydrate
- TGA
- Pilot Studies
 - Southern Research Institute
 - B&W
- Full Scale Field Results
 - HCl removal chart
 - Other testing





General Properties – FGT Hydrate

Property	Guaranteed	Comment		
Available Ca(OH) ₂	<u>></u> 94% wt	High purity improves utilization, minimizes byproduct.		
- 325 mesh	<u>></u> 92% wt	Fine power product		
Moisture	<u><</u> 1.0% wt	As shipped, good for handling		
BET	<u>></u> 20.0 m²/g	High surface area improves acid gas capture.		
Surface Area		Major hydrate DSI systems use material with >20 BET material		
SiO ₂	<u><</u> 2.0% wt	Low quantity of inert material		
		Reduced wear on equipment		



Reactivity Test Comparison

Identified potential laboratory screening method for hydrated lime reactivity

	Reactivity	Surface Area	Pore Volume
Construction Hydrate	50+ sec	15	0.050
High SA/PV Hydrate	42 sec	31.5	0.206
Hydrated Lime FGT	27 sec	21.5	0.089
High Reactivity Hydrate	4 sec	21.3	0.097

Determined that HR Hydrate was worthy of additional evaluation at pilot and full scale



Reactivity & Removal

Thermodynamic

• $SO_3 > SO_2 > HF > HCl$

Kinetic

- Maximize collisions
- Hydrate $D_{50} \sim 2-4 \ \mu m$
- Gas particles $\sim 0.0003 \ \mu m$

100 Ca(OH)2(s) + SO3(g) <---> CaSO4(s) + H2O(g) 90 ----> Ca(OH)2(s) + SO2(g) <---> CaSO3(s) + H2O(g) 80 \rightarrow Ca(OH)2(s) + 2HF(g) <---> CaF2(s) + 2H2O(g) 70 Ca(OH)2(s) + 2HCl(g) <---> CaCl2(s) + 2H2O(g) 60 **8** 50 40 30 20 10 0 200 400 600 800 1000 0 1200 1400 1600 deg F

Competing Reactions with Ca(OH)2

Benson, 2012 DHUG







Pilot Scale Testing Hydrate for HCI – In-flight

Hydrate Comparison In-flight HCI removal (before baghouse)







Pilot Scale Testing Hydrate for HCI – Baghouse Outlet

Overall (Baghouse outlet) HCI removal





4 lances/duct – MATS achieved





Test Site 2 – HCI Reduction for MATS

- Smaller (<200 MW) Unit with Baghouse
- Higher SO₂ (~500 ppm) and HCl (~90 ppm) levels
- MATS achieved with >99% HCl reduction
- Also some SO₂ reduction (40-50%)
 Relatively high Hydrate: Total Acid ratio (>3.0)





Test Site 3 – HCI and Hg Reduction for MATS

- Smaller (<200 MW) Unit with ESP
- Lower SO₂ (<400 ppm) and HCl (<10 ppm)
- MATS achieved for HCl
- Selenium emissions also reduced by ~80% when injecting hydrate
- Issues:
 - -Opacity increase, but below limits
 - -pH increase in wet ash pond



Test Site 4 – CFB for HCI

HCI Removal With MLC Hydrate - CFB Application



Mississippi Lime – Confidential Information

Test Site 5 – Cement Plant for HCI

HCI - Cement Plant Reductions

MISSISSIPPI



Highlights of Full Scale Testing for HCI Control

HCI Removal

- MATS Limits met in 6 out of 7 trials in 2012
 - Baghouse
 - ESP
 - Marginal ESP

- Industrial Waste Incinerator
- One trial not meeting MATS (dosage? Repeating test in Aug '13)
 - 96% HCl reduction
- Very marginal ESP and short residence time
 - HCl reduction of ~90% at 0.7 NSR (hydrate:total acid)
 - High chloride coal



Benefits of Using Less Hydrate







- Lower annual freight costs
- Fewer trucks ordered per year
 - Fewer transactions
 - Less local and plant traffic
 - Safety incident potential is reduced
 - Less hookups and disconnects
 - CO₂ reduction from reduced truck shipments
- Less tons of ash to landfill
 - Freight, traffic, transactional, and CO₂
 benefits here also
 - Lower CaOH₂ levels in fly ash



Summary

- Mississippi Lime is an industry leader in Hydrated Lime DSI
- Hydrated Lime FGT is proven for SO₃ and HCl
- High Reactivity Hydrate presents a solution to improved in-flight capture of SO₃ and HCl
- Mississippi Lime has testing equipment and R&D personnel focused on conveying optimization and next generation products



Questions

Pat Mongoven Business Development Manager – FGT pgmongoven@mississippilime.com

Curt Biehn Manager, Marketing and Technical Services crbiehn@mississippilime.com

Mark DeGenova Chief Chemist mgdegenova@mississippilime.com

Eric Van Rens Vice President, Sales & Marketing ecvanrens@mississippilime.com Mississippi Lime Company 3870 S. Lindbergh Blvd. Suite 200 St. Louis, MO 63127 www.mississippilime.com



