

# Technical Paper

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## *HCl Control Using Hydrated Lime Dry Sorbent Injection*

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**babcock & wilcox** power generation group

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## Abstract

Babcock & Wilcox Power Generation Group, Inc. (B&W PGG) recently conducted two pilot plant test programs to investigate the use of various hydrated limes for HCl (hydrochloric acid) control. The first program examined the effectiveness of hydrated lime based on B&W PGG’s portable pilot plant testing on a flue gas slipstream extracted from a commercial biomass and biomass/TDF (tire-derived fuel) combustion process. The second program examined the effectiveness of hydrated lime variants of HCl removal from testing conducted on a simulated flue gas from the Small Boiler Simulator-II (SBS-II) at B&W PGG’s Research Center (BWRC) in Barberton, Ohio.<sup>1</sup> Testing included a range of HCl concentrations along with varying amounts of sulfur dioxide (SO<sub>2</sub>). Total removal rates were measured for both in-flight and fabric filter capture of the respective pollutants. The effectiveness of multiple types of hydrated limes was compared to project usage rates required to meet new acid gas emission regulations.

## Introduction

The United States (U.S.) Environmental Protection Agency (EPA) Mercury and Air Toxics Standards (MATS) and the Industrial Boiler MACT rule limit HCl to 0.002 lb/MBtu and 0.022 lb/MBtu, respectively, for existing plants.<sup>2,3</sup> Dry sorbent injection (DSI) is a low capital cost approach for controlling HCl and hydrated lime is a readily available sorbent used in DSI applications. Many utility and industrial operators already use or have a source for hydrated lime, making this sorbent particularly attractive for future use in DSI applications. Hydrated lime injection typically would not detrimentally change flyash properties, although before

any long-term injection, the owner is recommended to study the change in flyash to determine the appropriate management of the waste.

HCl control with hydrated lime has been previously proven, but there is a general lack of published data on the quantification of how well HCl can be controlled with hydrated lime, and how different qualities of hydrates affect HCl control.

In 2009, B&W PGG conducted a pilot plant program on a biomass unit burning TDF and waste sludge to study if DSI with hydrated lime could reduce HCl to levels below 0.0022 lb/MBtu. Additionally, B&W PGG and the Mississippi Lime Company (MLC) co-funded an R&D test program for the control of HCl with DSI using hydrated lime in B&W PGG’s SBS-II pilot plant from August to September 2011 using a simulated flue gas. The goals of this test program were as follows:

- Determine the relationship of dry hydrated lime injection rate vs. HCl removal for both in-flight removal and removal across a pulse jet fabric filter (PJFF). In-flight removal could simulate HCl removal across an electrostatic precipitator (ESP).
- Achieve high HCl removal efficiencies, >95% HCl removal.
- Compare the reactivity/effectiveness of different hydrated limes with HCl removal. The hydrated limes evaluated were based on benchtop screenings by MLC prior to testing in the pilot plant.
- Study competing reactions of HCl and SO<sub>2</sub> by testing at different gas ratios of those compounds to determine whether SO<sub>2</sub> should be considered as a competing reaction.

## Hydrated lime for acid gas control

There are currently over 30 coal-fired utilities mitigating SO<sub>3</sub> through DSI. A majority of these units utilize hydrated lime as their sorbent, specifically a high (>20 m<sup>2</sup>/g) BET surface area hydrated lime. Some units have a short (<1.5 sec) residence time between the injection point and an ESP that limits their capability to use hydrated lime or presents a yield penalty to its use. Additionally, the need to mitigate additional acids such as HCl requires more sorbent. Thus, there is interest in improving the reactivity properties of a hydrated lime sorbent.

MLC is developing higher reactive hydrated limes using benchtop testing. The developmental hydrated limes evaluated were samples targeting improved, faster reactivity for flue gas mitigation. In addition to high surface area and small median particle size, a benchtop screening test indicated that samples HR and MH exhibited improved reactivity versus the standard FGT product. For that reason, the SBS-II pilot plant study was undertaken using these three hydrated limes.

## Pilot plant descriptions

### Biomass host site and portable pilot plant

The biomass host site is located in the southeast U.S. and uses a bubbling fluidized-bed (BFB) boiler to burn different types of biomass for fuel to power the mill process. The various fuels included TDF, bark, and waste sludge from the paper mill process.

A flue gas slipstream was taken from upstream of the dry ESP to serve as the test gas. The slipstream flue and environmental equipment were located on a flatbed trailer, as shown in Figure 1. Once gas entered the slip stream it passed through a humidification chamber to a fabric filter, and then an induced draft (ID) fan returned it to the site's flue at the same location where it was taken.

The fabric filter captured and removed unreacted sorbent, reaction products, and ash from the flue gas in the slipstream, and had a 3.8:1 air-to-cloth ratio. The collected particulate

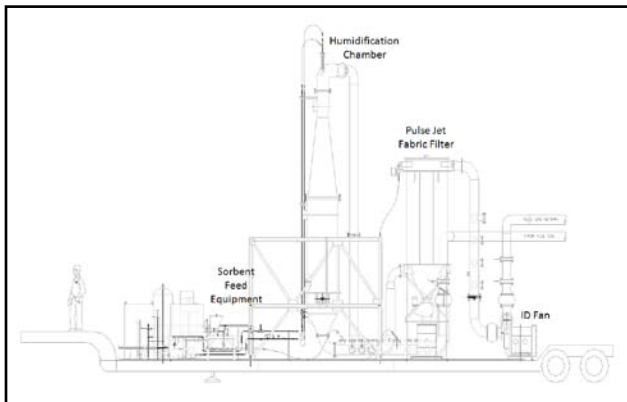


Fig. 1 Side view of the portable pilot plant.

emptied into 55-gallon drums via a rotary feeder and then disposed of by the plant. The humidification chamber was not used during the portion of the testing discussed in this paper. The sorbent feed system included a variable speed gravimetric screw feeder for controlling sorbent injection rate, eductor, convey air blower, and sorbent convey hose. Test taps up and down stream of the sorbent injection point allowed for simultaneous gas sampling to evaluate the sorbent reactivity.

In case the HCl levels were too low to perform adequate testing, an HCl spiking system was provided. The system for spiking the slipstream with HCl consisted of a cylinder of 5% HCl in N<sub>2</sub> with a flow meter and tubing connecting the cylinder to the slipstream. The HCl/N<sub>2</sub> was injected into the slipstream using the pressure in the cylinder and the flow was controlled by rotometers.

### Small boiler simulator II – pilot-scale facility

BWRC's 6 MBtu/hr SBS-II is a totally integrated, state-of-the-art, pilot-scale combustion and emission control facility enabling researchers to conduct performance tests and scale results for utility and commercial use. (See Figure 2.) The SBS-II is designed to accurately represent the time and temperature profile of a utility boiler. The furnace can be operated in either a wall-fired or Cyclone-fired mode, and is equipped to fire natural gas, fuel oil, various coals, and alternative fuels such as biomass and fuel slurries. The SBS-II fuel handling system includes a dryer, crusher, pulverizer, and feed systems for specialized fuel handling requirements and independent studies. The furnace is designed for two levels of overfire air study. Multiple sample ports are located throughout the facility for visual observation, in-furnace and in situ measurements, and extractive sampling. Gas analyzers are located in a number of locations throughout the furnace to collect emissions data. Environmental equipment, including both wet and dry scrubbers, selective catalytic reactors, fabric filters, and a condensing heat exchanger, are integrated in the SBS-II for post-combustion control and study. Flue work is arranged to allow the flue gas to bypass

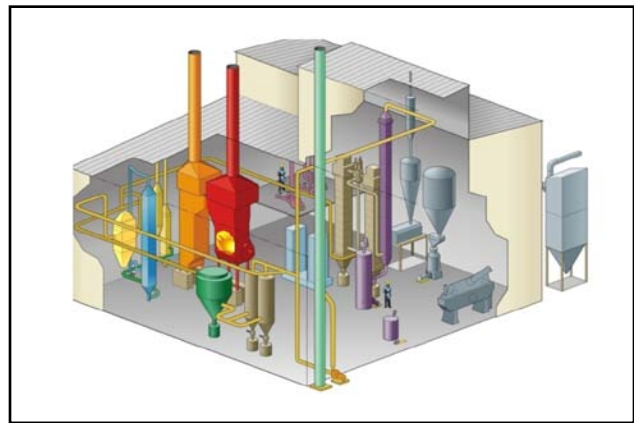


Fig. 2 Small Boiler Simulator-II – combustion and emissions control facility.

any piece of equipment depending on test program objectives. All equipment at the SBS-II can be used for both full facility operation or as an individual piece of test equipment.

A sorbent injection system is in place at the SBS-II that houses various solid/liquid sorbent reservoirs, well-controlled pneumatic injection controls, and flexible hoses that deliver sorbents to numerous locations throughout the facility for nitrogen oxides (NO<sub>x</sub>), SO<sub>2</sub>, SO<sub>3</sub>, HCl, hydrogen fluoride (HF) and mercury emissions reduction studies. A number of different additives have been utilized at the facility including ammonia, urea, limestone, hydrated lime and trona.

Emissions control testing on the SBS-II can be performed using flue gas generated from the combustion of coal, biomass, natural gas or fuel oils. Since different fuel sources provide different SO<sub>2</sub>, SO<sub>3</sub> and HCl concentrations, additional injection of acid gases may be necessary to simulate the range of concentrations in commercial units. Alternately, tests can be carried out with simulated flue gas using heated air humidified and spiked with the desired concentrations of SO<sub>2</sub>, SO<sub>3</sub> or HCl. The acid gas injection (AGI) system consists of compressed cylinders, flow control and delivery equipment, and an SO<sub>3</sub> generator to deliver desired quantities of acid gases to the main unit operations and ducting of the SBS-II.

A simulated flue gas was chosen for this test program rather than fuel burning because one of the main objectives of the program was to study the interaction between SO<sub>2</sub> and HCl at various concentrations and this was not easily accomplished without some type of simulated gas stream. A simulated flue gas eliminates any other interferences with other pollutants that would be difficult to measure, such as SO<sub>3</sub>. The simulated flue gas does not include flyash, so the actual removals in a commercial system may increase with added dust loading, but for practicality, it was not included in the test program.

## Pilot plant testing and results

### Portable pilot plant

#### Test Plan

The test program at the biomass facility used a slipstream of flue gas generated by a BFB boiler burning biomass. The HCl removal was determined by measuring HCl before the hydrated lime injection location and after the PJFF. The level of HCl naturally occurring in the flue gas was very low, already below the EPA limits, so the incoming flue gas was spiked with HCl gas.

Operating conditions during the test:

Nominal Flow Rate:	1700 acfm
Fabric Filter Inlet Temperature:	425 F ± 5 F
Slipstream PJFF DP:	~ 8 in. wc
Humidity:	19 to 24%
Sorbent injection point:	Upstream of PJFF
Range of HCl:	0 to 20 ppm

The HCl gas was injected in the flue at the inlet of the system, upstream of the first sampling location. EPA Method 26 was used to confirm the amount of HCl in the flue gas during the tests. The hydrated lime injection point followed, where the injection nozzle was placed in the middle of the flue. The hydrated lime injection rate was determined by a loss in weight system. From the screw feeder, the hydrated lime was pulled into an eductor which used compressed air to transport the hydrated lime to the injection point.

The overall test program goals were to determine how well hydrated lime would work in removing HCl in a biomass gas condition and, if successful, remove HCl below the Industrial MACT level of 0.0022 lb/MBtu.

The hydrated lime used for this test was provided by Mississippi Lime with the properties shown in Table 1.

#### Results and Discussion

Baseline testing of the unit was carried out before any injection of hydrated lime. The baseline results were already below the Industrial Boiler MACT limit of 0.0022 lb/MBtu for biomass units. Therefore, the flue gas was spiked with HCl gas to 12 to 18 ppmw to carry out the test. For the majority of the test, the SO<sub>2</sub> level was about 22 to 25 ppmv. Results of the test are shown in Table 2.

The results show that hydrated lime in a biomass gas stream with a PJFF effectively removes HCl. Also, the measured HCl emissions for all test runs were well below the 0.0022 lb/MBtu limit. Therefore, it was determined that hydrated lime injection upstream of a PJFF is a viable method to meet the Industrial Boiler MACT limit.

**Table 1**  
Properties of Hydrated Lime

	Type	Specific Surface Area, m <sup>2</sup> /g	MLC Screening Test	D <sub>50</sub> Particle Size, microns	Comments
Hydrated Lime	FGT	22	Good	2	Proven product for DSI industry

**Table 2**  
HCl Removal with Hydrated Lime Injection

Test Run	Injection Rate	HCl Removal	Outlet HCl
Baseline – 7 run avg	0	N/A	0.00084 lb/MBtu
Run 1	4.0 lb/hr	93%	0.00049 lb/MBtu
Run 2	7.5 lb/hr	95%+	0.00014 lb/MBtu
Run 3	2.0 lb/hr	95%+	0.00020 lb/MBtu
Run 4	5.5 lb/hr	95%+	0.00033 lb/MBtu

## Small Boiler Simulator-II

### Test Plan

This test program used heated and humidified air spiked with combinations of HCl and SO<sub>2</sub> gases. The removal efficiency for each gas and for the combinations of each gas was determined for each grade of hydrated lime for an in-flight and post-PJFF condition.

Heated and humidified air operating conditions during the test:

Nominal Flow Rate:	6000 lb/hr (~2000 acfm)
Fabric Filter Inlet Temperature:	320F ± 5F
Humidity:	~5%
Gas injection point:	Trim Heater Outlet
Steam injection point:	Downstream of Gas Injection
Sorbent injection point:	~ 10 ft downstream of steam injection
Range of HCl:	0 to 400 ppm
Range of SO <sub>2</sub> :	0 to 400 ppm

The concentration ranges of HCl used were based as close as possible on typical industrial, biomass and coal plants. The SO<sub>2</sub> range was selected to be as close to HCl as possible to determine if SO<sub>2</sub> competes with HCl at the given operating conditions.

Heated air was drawn through the system as shown in Figure 3. HCl and SO<sub>2</sub> gases were injected immediately downstream of the trim heater, controlled by mass flow controllers. Further downstream, steam was injected to mimic typical flue gas moisture levels, but was limited to ~5% gas moisture due to system constraints. Downstream of the steam injection, FTIR (Fourier Transform Infrared Spectroscopy) measurements confirmed the amount of HCl and SO<sub>2</sub> injected. The hydrated lime injection nozzle was placed in the middle of the flue downstream of the FTIR instrument tap. The hydrated lime injection rate was determined by a weight loss system. A compressed air eductor system transported the hydrated lime from the weight loss feeder system to the injection nozzle.

Three hydrated limes, provided by Mississippi Lime, were evaluated in this test program. Mississippi Lime also provided data on the chemical and physical properties for these sorbents.

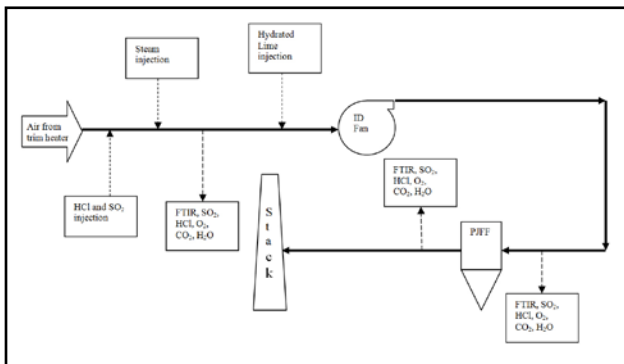


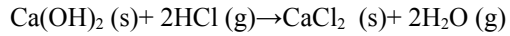
Fig. 3 System schematic.

The hydrated lime properties are shown in Table 3. The samples were selected based upon performance on an internal benchtop test aimed at rating the reactivity of hydrated lime. They could be characterized by the properties shown in Table 1.

For each hydrated lime, different combinations of HCl and SO<sub>2</sub> were tested. The test matrix completed is shown in Table 4.

For each test run, HCl and SO<sub>2</sub> measurements were taken before hydrated lime injection, as well as upstream and downstream of the PJFF using an FTIR.

The reaction of hydrated lime with HCl is as follows:



There is one mole of hydrated lime reacting with 2 moles of HCl.

For each test run, the removal efficiency of each acid gas was compared to a calculated normalized stoichiometric ratio (NSR) for either the total acid or for the individual acid gas. The total acid NSR equation is:

$$\text{Total Acid NSR} = \frac{\text{Moles of actual sorbent used}}{\text{Moles of total incoming acids}}$$

where, the total acid NSR is defined as the sorbent flow required to react with 100% of the acid gas, assuming 100% utilization of the sorbent. For hydrated lime, 1 mole of Ca(OH)<sub>2</sub> captures 2 moles of HCl and 1 mole of Ca(OH)<sub>2</sub> captures 1 mole of SO<sub>2</sub>. So the equation can be simplified as:

$$\text{Total Acid NSR} = \frac{\text{Actual Sorbent flow rate} / 74.1}{\text{Incoming HCl flow rate} / (36.5 \times 2) + \text{Incoming SO}_2 \text{ flow rate} / 64}$$

where,

Actual sorbent flow rate is hydrated lime in lb/hr

74.1 is the molecular weight of hydrated lime

Incoming HCl flow rate is the HCl in lb/hr

36.5 is the molecular weight of HCl

2 is the moles of HCl/Ca(OH)<sub>2</sub> for the perfect reaction

Incoming SO<sub>2</sub> flow rate is the SO<sub>2</sub> in lb/hr

64 is the molecular weight of SO<sub>2</sub>

For HCl NSR, the equation is:

$$\text{HCl NSR} = \frac{\text{Moles of actual sorbent used}}{\text{Moles of total incoming HCl}}$$

where,

the theoretical sorbent flow rate is defined as the sorbent flow required to react with 100% of the incoming HCl, assuming 100% utilization of the sorbent. For hydrated lime, 1 mole of Ca(OH)<sub>2</sub> captures 2 moles of HCl. So the equation can be simplified as:

$$\text{HCl NSR} = \frac{\text{Actual Sorbent flow rate} / 74.1}{\text{Incoming HCl flow rate} / (36.5 \times 2)}$$

**Table 3**  
**Properties of Hydrated Limes Tested**

		Type	Specific Surface Area, m <sup>2</sup> /g	MLC Reactivity Screening Test	D <sub>50</sub> Particle Size, microns	Comments
1	Hydrated Lime FGT	FGT	22	Good	2	Proven product for DSI industry
2	HR Hydrated Lime	HR	21	Excellent	2	Developmental product #1
3	MH Hydrated Lime	MH	20	Good	2	Developmental product #2

**Table 4**  
**SBS-II Test Matrix**

	HCl to SO <sub>2</sub> Concentration, ppm <sub>v</sub>			
Hydrated Lime	400:0	300:50	200:100	100:150
FGT	X	X	X	X
HR	X	X	X	X
MH	X	X	X	X

where,

Actual sorbent flow rate is hydrated lime in lb/hr

74.1 is the molecular weight of hydrated lime

Incoming HCl flow rate is the HCl in lb/hr

36.5 is the molecular weight of HCl

2 is the moles of HCl/Ca(OH)<sub>2</sub> for the perfect reaction

***Results and Discussion – HCl Removal at Different Acid Gas Concentrations***

Four different HCl-to-SO<sub>2</sub> gas concentrations (400:0, 300:50, 200:100 and 100:150) were tested with three different hydrated limes. Each HCl-to-SO<sub>2</sub> gas concentration (except 300:50), will be presented with in-flight and overall PJFF system removal based on the total acid NSR. In-flight removal is the amount of acid gas removed from the injection point to the fabric filter inlet; basically an in-flight capture in the fluework. This case may simulate ESP capture. Overall PJFF system removal is the amount of acid gas removed from the injection point at the baghouse exit or stack. The 300:50 gas concentration is not presented graphically in this section because the results are similar to the 400:0 and 200:100 cases. But, some of the 300:50 gas concentration data shown in the competing reaction result section. All of the data will be compared to an mid range NSR and the 400:0 concentration range will also show a high range NSR.

Also, the native capture in the system was excluded for each condition to evaluate the hydrated limes on a more equal basis. The pilot plant system has a certain amount of native HCl capture as the gas passes through the system. This is similar to a commercial system where flyash can inherently remove some acid gas.

Figures 4 through 9 plot the test results of in-flight and post-PJFF HCl removal at three acid gas concentrations using three sorbents.

HCl:SO<sub>2</sub> Gas Concentration of 400:0 Summary Results:

- HR hydrate was the most reactive for these tests.
- At high NSRs, HCl removal over 90% was attained in-flight
- At high NSRs, HCl removal over 95% was attained across the PJFF
- At mid NSRs, HCl removal over 80% was attained in-flight
- At mid NSRs, HCl removal over 50% was attained across the PJFF
- For this gas concentration, the data points at the far right were at high NSRs, about 3 times higher than what the other gas concentrations were tested at. This was to observe how much HCl could be removed in the system at a high concentration of HCl.

HCl:SO<sub>2</sub> Gas Concentration of 200:100 Summary Results:

- At the higher removal rates, HR hydrate was the most reactive.
- At moderate NSRs, HCl removal over 75% was attained in-flight
- At moderate NSRs, HCl removal over 90% was attained across the PJFF

HCl:SO<sub>2</sub> Gas Concentration of 100:150 Summary Results:

- HR was the most reactive hydrate
- At moderate NSRs, HCl removal over 80% was attained in-flight
- At moderate NSRs, HCl removal over 90% was attained across the PJFF

Table 5 summarizes the test program data for HCl control using HR hydrated lime at various acid gas concentrations. Some observations can be made from Table 5.

- In a PJFF system, very high removals of HCl can be obtained. This pilot plant showed greater than 95%.
- High in-flight capture, greater than 90%, can be obtained with hydrated lime at high HCl concentrations. In-flight capture would simulate an ESP.

**Table 5**

**Comparison of In-Flight and PJFF HCl Removal at Various Acid Gas Ratios with HR Hydrated Lime**

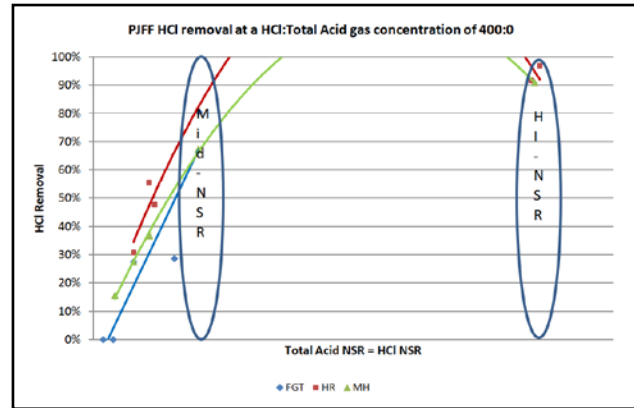
Acid Gas Concentration, HCl:SO <sub>2</sub>	Hydrated Lime Type	NSR, Total Acid	In-flight HCl Removal*	PJFF HCl Removal
400:0	HR	High	90%	95%+
400:0	HR	Mid	50%	80%
200:100	HR	Mid	75%	90%
100:150	HR	Mid	82%	90%

- While keeping the same total acid NSR, the removal efficiency of HCl increases as more SO<sub>2</sub> is introduced in the system. This was expected since there would be more hydrated lime available and less HCl in the system at these conditions.
- These gas concentration ratios tested would, for the most part, simulate industrial gases and indicate that high HCl removals can be achieved.

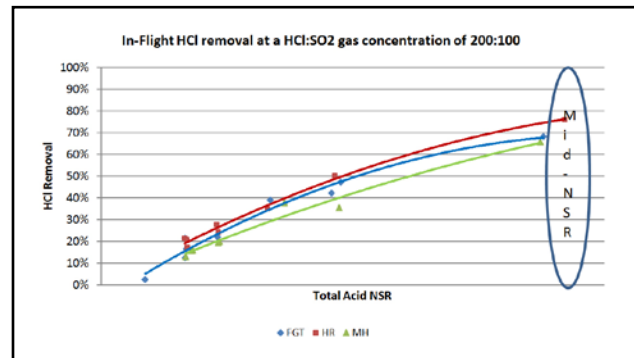
**Results and Discussion – HCl and SO<sub>2</sub> Competing Reactions**

Another part of this study was to determine if there was a competing reaction between HCl and SO<sub>2</sub>. At a temperature of 325F, very little reaction of hydrated lime with SO<sub>2</sub> is expected. This has been proven in past experience. Figure 10 shows tests of the injection rate of FGT hydrate and HCl removal for different acid gas concentrations. These series of curves were developed from previous tests on acid gas concentrations and could be made for any of the hydrated limes. FGT hydrate is being depicted here because this hydrate has the most number of data points.

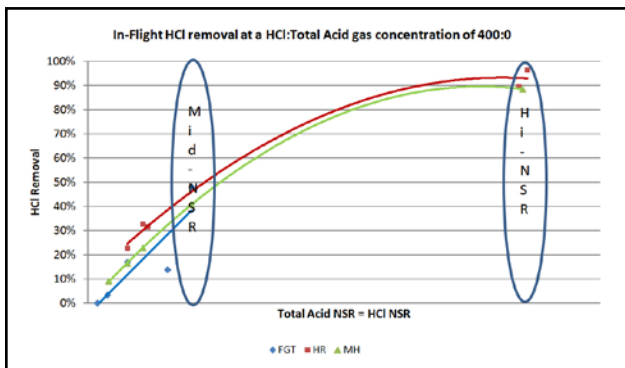
When HCl comprised the majority of the acid gas, there appeared to be no interference or competition with SO<sub>2</sub>, and in these cases, HCl was readily removed. As the SO<sub>2</sub> dominated the acid gas stream, there appeared to be some competition, even though SO<sub>2</sub> was only moderately removed (10 to 15%) in all cases. HCl was readily removed, but the competition required more hydrated lime to achieve the same removal rates. This result was common for all three of the hydrated limes. This result was a little surprising given the fact that hydrated lime typically does not react much with SO<sub>2</sub> at this temperature and humidity range. A field trial to study this is warranted.



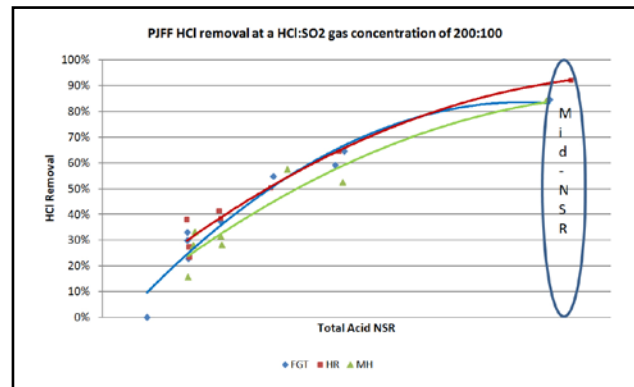
**Fig. 5** HCl removal across a PJFF at HCl:SO<sub>2</sub> gas concentration of 400:0.



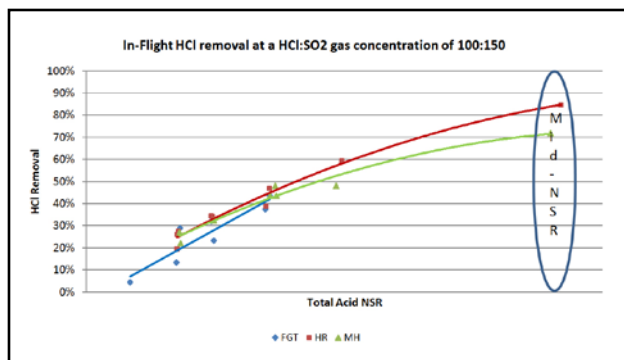
**Fig. 6** In-flight HCl removal at HCl:SO<sub>2</sub> gas ratio of 200:100.



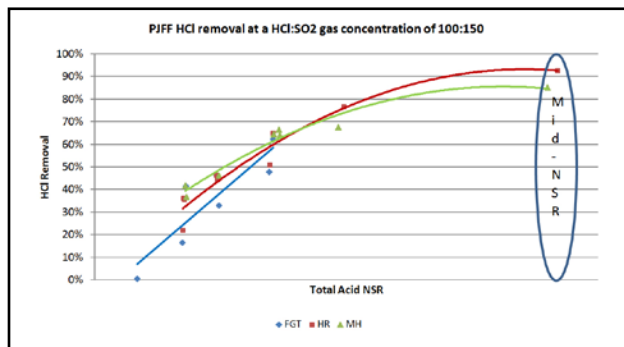
**Fig. 4** In-flight HCl removal at HCl:SO<sub>2</sub> gas concentration of 400:0.



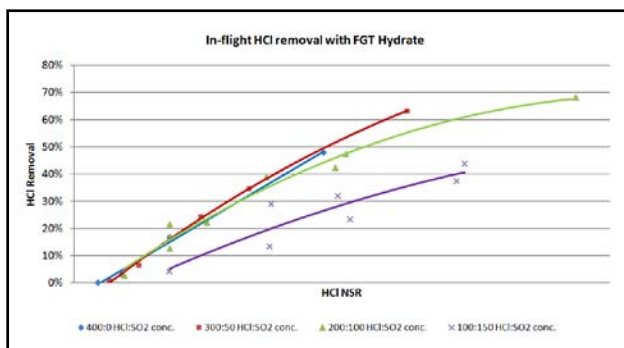
**Fig. 7** HCl removal across a PJFF at HCl:SO<sub>2</sub> gas ratio of 200:100.



**Fig. 8** In-flight HCl removal at HCl:SO<sub>2</sub> gas concentration of 100:150.



**Fig. 9** HCl removal across a PJFF at HCl:SO<sub>2</sub> gas concentration of 100:150.



**Fig. 10** In-flight HCl removal with FGT hydrate with varying HCl:SO<sub>2</sub> gas concentrations.

## Conclusions

At a biomass unit, the portable pilot plant testing proved that high levels of HCl could be removed using hydrated lime and a PJFF at biomass flue gas conditions (425F and 24% flue gas moisture).

Testing at the SBS-II, using a simulated flue gas, proved different grades of hydrated lime can remove HCl at high levels. HR hydrate was expected to be the most reactive, and testing verified this theory. The improved reactivity of the HR hydrate was more noticeable at the high removal rates. HR removed a higher rate of HCl than FGT and MH in all cases. FGT and MH hydrates performed similarly and could attain high levels of HCl removal.

Other observations made:

- The overall removal across the PJFF was between 8 to 30% higher than the in-flight removal at a common mid-level total acid NSR.
- Up to 90% HCl removal, excluding native capture, was attained in-flight.
- Up to 95% HCl removal, excluding native capture, was attained across the PJFF.
- Improved HCl removal may be attained in a commercial system since native capture will occur. Flyash and the equipment arrangement will remove some pollutants naturally.

Some competition between SO<sub>2</sub> and HCl will occur as the SO<sub>2</sub> dominates the acid gas concentration even though only moderate levels of SO<sub>2</sub> removal occur. This is best studied in a field trial.

Hydrated lime is an effective sorbent to remove HCl, but each case must be evaluated individually to confirm the most effective sorbent for each plant.

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## Key words

HCl, Hydrated Lime, SO<sub>2</sub>, Biomass



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