



## **Results of Dry Sorbent Injection Testing to Reduce HCl**

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### **ABSTRACT**

Power plants currently having no flue gas treatment beyond particulate removal and possibly SCR for NO<sub>x</sub> control are facing the need to comply with pending new regulations. The EPA Mercury and Air Toxics Standards (MATS), formerly referred to as the Utility MACT, require among other HAPS control of HCl emissions in plants that do not already treat acid gases. The Cross State Air Pollution Rule (CSAPR) requires control of SO<sub>2</sub> to within allotted emission credits. Carmeuse Lime participated in dry sorbent injection tests using hydrated lime at several plants. Hydrated lime was injected at two different flue gas temperatures and successfully met the objective of reducing HCl emissions of the plant to under 0.002-lb. HCl/million BTU. SO<sub>2</sub> emissions were also tracked.

### **INTRODUCTION**

The U.S. EPA is in the midst of implementing several sets of regulations that will dramatically affect not only the electric power industry but operators of industrial boilers located predominantly east of the Mississippi River. These regulations will require operators of affected plants to either invest in environmental controls or retire units altogether.<sup>1</sup> Compliance with these new regulations is to be accomplished within a short period requiring utility and small boiler operators to learn about their options quickly.

Older smaller (< 300 MWe) coal-fired power plants including fluidized bed and PC boilers that have little space for FGD equipment and/or a limited or uncertain life span can extend operation and meet new emission requirements for HCl, particulate matter (PM), Hg and possibly dioxin/furans by employing dry sorbent injection (DSI) followed by either an electrostatic precipitator (ESP) or a fabric filter for PM control. There are also additional compliance costs associated with new regulations other than the Utility MACT (MATS) including Criteria Pollutants (NO<sub>x</sub>, SO<sub>2</sub>, ozone and PM), Coal Combustion By-products, water and GHG to be considered. Calcium and sodium-based reagent injection systems provide the

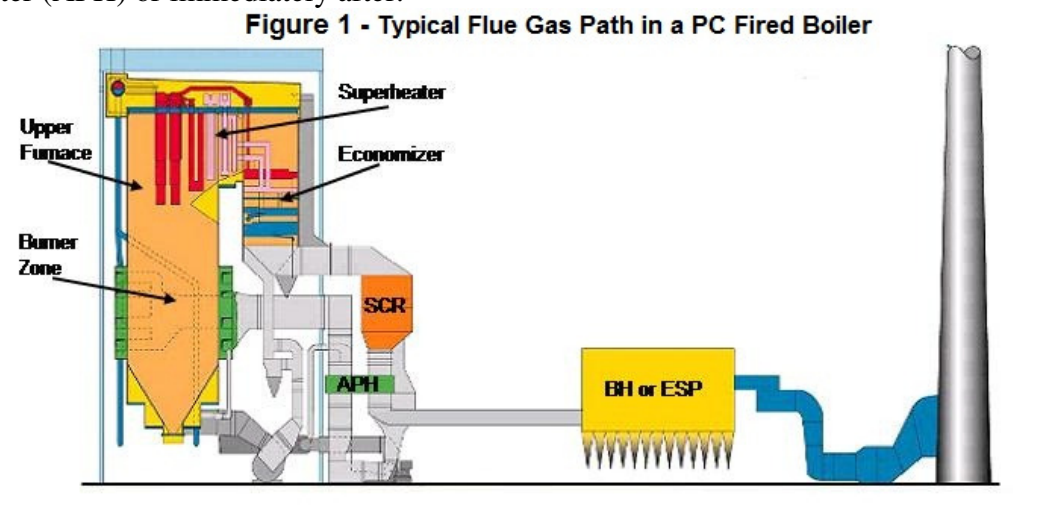
best means to accomplish this but each requires different flue gas conditions to be optimally used.

What Carmeuse has seen with their current and potential hydrated lime customers is that for plants currently operated with only particulate removal; they will concentrate on HCl emission reduction to comply with MATS and use SO<sub>2</sub> emission credit trading with sister plants who over-scrub SO<sub>2</sub>, to comply with CSAPR. This strategy will require burning a low sulfur eastern bituminous coal and maybe also include blending with a PRB or similar fuel.

Carmeuse has been fortunate to participate in full scale DSI tests at several different power plants that have burned a variety of low sulfur fuels; employing either ESP's or bag houses for particulate control. The hydrated lime used in all tests is what would be considered standard in the industry, meaning that no particular effort was made to increase specific surface area or pore volume for the FGT market over what is typically produced. Typical BET surface area and pore volume for the hydrates used in these tests range from 20 to 23-m<sup>2</sup>/g and 0.08 to 0.15-cm<sup>3</sup>/g.

## DRY SORBENT INJECTION

Injection of dry alkaline reagents can occur anywhere in flue gas path from the boiler to the stack but the optimum location depends on the reagent and target pollutant. Regardless of the type of acid gas sorbent used, maximum removal efficiency will be achieved if the time sorbent is entrained in flue gas is as long as possible and the sorbent is evenly distributed across the flue duct. The injection lance design therefore is very important and should be considered carefully. A fabric filter located downstream of the sorbent injection location can also improve sorbent utilization as well as further lower acid gas emissions. Figure 1 illustrates a typical flue gas path from a pulverized coal (PC) fired boiler with no wet FGD. Sorbents can be injected in the economizer region but more typically is injected either immediately just prior to the air preheater (APH) or immediately after.



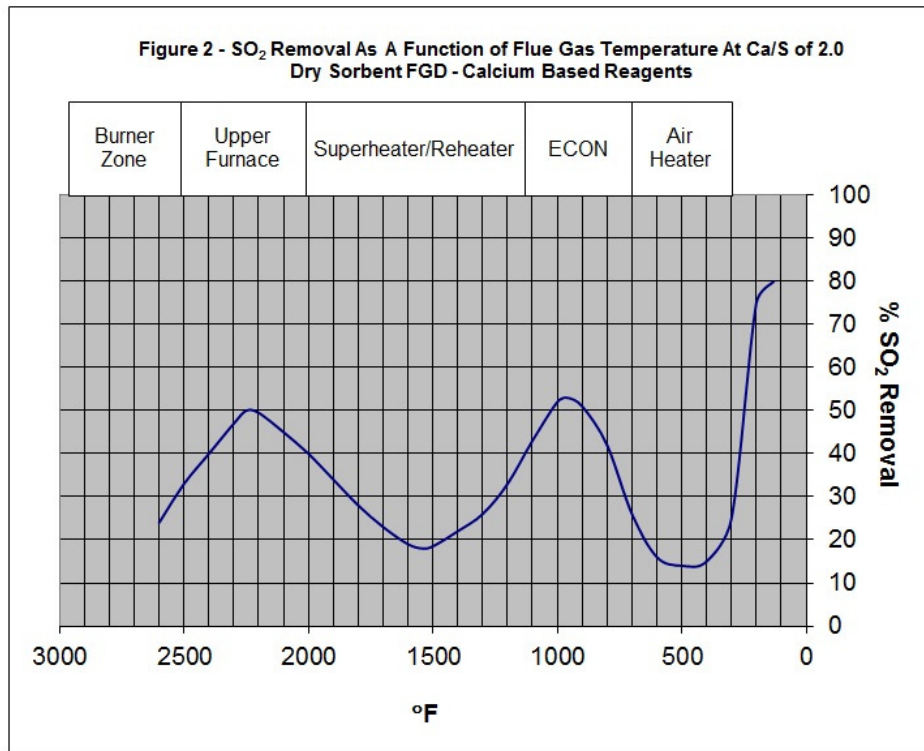
Generally, power plants employing DSI burn lower sulfur bituminous or Powder River Basin (PRB) coal or a blend of the two. Calcium and sodium-based sorbents are both leading choices for DSI flue gas treatment (FGT). The amount of PM contributed by reagents could increase significantly depending on the dose required to achieve MATS compliance. With final MATS rules only specifying a limit on filterable PM, it is likely that plants already having properly tuned and maintained ESP's should be able to achieve PM emission compliance without installing bag house filters. It is felt by many that calcium based reagents, not being conductive at typical cold ESP operating conditions, would cause operational problems that increase opacity. We will see later that in tests Carmeuse has participated in, no problems of this type were evident.

All reagents also indirectly influence mercury removal through reduction of HCl or SO<sub>3</sub>. Reduced SO<sub>3</sub> in flue gas helps powdered activated carbon (PAC) to absorb more mercury by preventing SO<sub>3</sub> deposition as sulfurous acid onto PAC and blocking its pores. While it is well known that HCl in flue gas can help oxidize mercury, it is not yet clear that once mercury is oxidized, whether a lower HCl level can make mercury more prone to be reduced back to an elemental state.

## **Hydrated Lime Effect on SO<sub>2</sub>, SO<sub>3</sub> and HCl**

Hydrated lime's reactivity with any particular acid gas is influenced by several things. Mainly there is competition in flue gas for hydrated lime between CO<sub>2</sub>, SO<sub>2</sub>, SO<sub>3</sub>, HCl and HF; but the degree that hydrated lime is reactive to any of these flue gases depends on the temperature at which hydrated lime and the particular gas first come into contact.

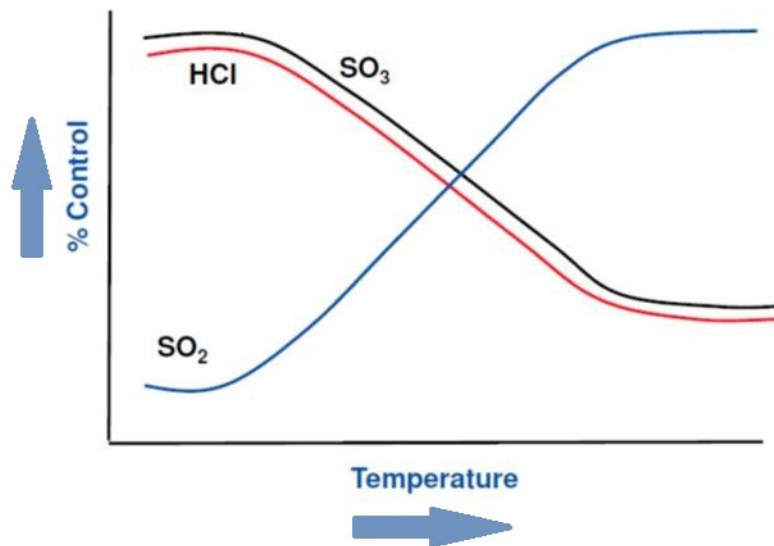
Figure 2<sup>2</sup> is the result of work conducted by Hamon-Research-Cottrell in their pilot combustor facility that trends injected hydrated lime reactivity with SO<sub>2</sub> over a temperature range along the flue gas path from the boiler through to near saturation at a constant Ca/S stoichiometric ratio of 2.0. Three distinct temperature regimes exist where calcium reactivity with SO<sub>2</sub> peaks, along with temperature regimes where calcium reactivity with SO<sub>2</sub> is minimal.



These peaks and troughs are explained by the fact that  $\text{CaSO}_4$  is the only stable species at temperatures greater than 2000°F while  $\text{CaCO}_3$  is more stable at lower temperatures. Hydrate reactivity with  $\text{SO}_2$  gains the upper hand again at around 1000°F but is heavily influenced by physical attributes of hydrated lime like surface area and pore volume. The final peak illustrates increased reactivity between calcium and  $\text{SO}_2$  as flue gas cools and approaches saturation for water vapor.

Other acid gases compete for hydrated lime but also are affected by the temperature at which hydrated lime is injected. Figure 3<sup>3</sup> illustrates in general reactivity of hydrated lime with other prominent acid gases over a temperature range beginning around 250°F to around 850°F. Clearly if both  $\text{SO}_2$  and  $\text{HCl}$  are required to be treated through DSI, hydrated lime would need to be injected at different flue gas temperatures depending on the degree of acid gas removal desired.

Figure 3 - Impact of competing acid gases for hydrated lime as a function of temperature.



## Hydrated Lime Effect on Mercury

Acid gas removal with DSI has both positive and negative effects to removal of mercury (Hg) from flue gas. Mercury is not removed by hydrated lime but is affected negatively by HCl removal with alkaline sorbents and positively from SO<sub>3</sub> reduction. While it is well known that HCl in flue gas can help oxidize mercury, which in turn makes it easier to be absorbed by powdered activated carbon (PAC), it is not yet clear that once oxidized, the presence of chlorine (HCl) is necessary to prevent reduction of Hg. On the other hand, SO<sub>3</sub> has a tendency to precipitate onto the pores of PAC as flue gas is cooled. Its removal from flue gas keeps the pores of PAC open to absorb Hg more effectively.

## DRY SORBENT INJECTION TESTING USING HYDRATED LIME

Carmeuse has been fortunate to participate in full scale DSI tests for HCl mitigation at several different power plants that have burned a variety of low sulfur fuels; employing either ESP's or bag houses for particulate control. Three of the several plants where DSI tests were conducted had unique characteristics that are identified in Table 1.

**Table 1.** DSI Test Plant Characteristics

<b>Plant</b>	<b>One</b>	<b>Two</b>	<b>Three</b>
Fuel	Low Sulfur, High Chlorine, CAPP	PRB Blend	Columbian Coal
Particulate Removal	ESP	Baghouse	ESP

Two of the three test sites offered the opportunity to inject hydrated lime immediately upstream and downstream of the unit's air preheater (APH) at temperatures of 600 to 650°F and 300 to 350°F, respectively. EPA Method 26A was used to measure baseline and reduced concentrations of HCl downstream of particulate removal. As a back-up, Fourier Transform Infrared (FTIR) instrumentation was also used to measure several flue gas components including SO<sub>2</sub> and HCl. The third test site injected hydrated lime immediately downstream of the APH at a temperature of 300°F and monitored SO<sub>2</sub>, HCl, and HF by a combination of Continuous Emission Monitoring Systems (CEMS) and FTIR.

## Test Site One

Plant One is a B&W single-wall-fired, pulverized-coal boiler with a capacity of less than 150 MWe. The unit combusts CAPP coal that has 1.2 lbs/MMBtu sulfur content and is equipped with low NO<sub>x</sub> burners. Particulate control is accomplished with mechanical separators followed by a cold-side electrostatic precipitator (ESP) that has an SCA of nearly 600 ft<sup>2</sup>/1,000 acfm. The unit also has a Ljungstrom air pre-heater, selective non-catalytic reduction (SNCR) system and PAC injection. At the time of the trial, the SNCR and PAC injection were not in service. CEMS installed on this unit monitors opacity, NO<sub>x</sub>, SO<sub>2</sub>, Hg, and CO<sub>2</sub>.

The HCl baseline data at the stack as recorded by FTIR during the trial was an emission rate of 0.111 lb/MMBtu. The HCl baseline data recorded using the EPA Method 26A procedure was 0.076 lb/MMBtu.

Approximately 11 tons of hydrated lime was injected at the air pre-heater outlet with a feed rate of 8400 lbs/hr. This resulted in an approximate removal rate of 99.96 percent and emission rate of 0.00003 lb/MMBtu, measured by EPA Method 26A.

Approximately 12 tons of hydrated lime was injected at the entrance to the air pre-heater at varying feed rates of 3800 lbs/hr and 7800 lbs/hr. The 3800 lbs/hr test resulted in an emission of 0.006 lb/MMBtu and removal rate of 91.7 percent. The 7800 lbs/hr test resulted in an emission of 0.001 lb/MMBtu, a removal rate of 98.9 percent, which was within the 2015 MATS emission compliance limit for this site. Table 2 summarizes these results.

**Table 2.** Plant One HCl Results

<b>HCl Results ( EPA Method 26A )</b>				<b>APH Inlet</b>	<b>APH Inlet</b>	<b>APH Outlet</b>
	<b>Units</b>	<b>Baseline</b>	<b>Objective</b>			
Feed Rate	# / Hr	-	-	3800	7800	8400
Sorbent / Acid Gas	# / #	-	-	2.3	4.7	5.1
HCl Results	# / MMBtu	0.076	0.002	0.0063	0.0008	0.00003
Removal	%	-	97.4%	91.7%	98.9%	99.96%

<b>HCl Results ( FTIR )</b>				<b>APH Inlet</b>	<b>APH Inlet</b>	<b>APH Outlet</b>
	<b>Units</b>	<b>Baseline</b>	<b>Objective</b>			
Feed Rate	# / Hr	-	-	3800	7800	8400
Sorbent / Acid Gas	# / #	-	-	2.3	4.7	5.1
HCl Results	# / MMBtu	0.111	0.002	0.0176	0.0017	0.001
Removal	%	-	98.2%	84.1%	98.5%	99.1%

Data recorded using permanent CEMS equipment during the trial is shown in Table 3. The baseline data for SO<sub>2</sub> emissions was 1.11 lb/MMBtu.

**Table 3.** Plant One SO<sub>2</sub> Results

<b>SO<sub>2</sub> Results (CEMS)</b>			<b>APH Inlet</b>	<b>APH Inlet</b>	<b>APH Outlet</b>
	<b>Units</b>	<b>Baseline</b>			
Feed Rate	# / Hr	-	3800	7800	8400
Sorbent / Acid Gas	# / #	-	2.3	4.7	5.1
SO <sub>2</sub> Results	# / MMBtu	1.11	1.02	0.9	0.86
Removal	%	-	8.1%	18.9%	22.5%

Injection of hydrated lime reduced SO<sub>2</sub> emissions by 22.5 percent or 0.86 lb/MMBtu emission rate at the air pre-heater outlet and up to 18.9 percent or 0.90 lb/MMBtu emission rate at the air pre-heater inlet. These results were expected at the injection temperatures tested, approximately 300 and 600°F, and are in-line with work conducted by Hamon-Research-Cottrell.

## Test Site Two

Plant Two is a B&W opposed-wall fired, wet-bottom, cyclone-burner boiler with a capacity of less than 200 MWe. There are four cyclones on the unit. The unit combusts PRB coal with 0.4 percent sulfur content. This unit uses the overfire air (OFA) portion of a retrofitted gas reburn system for NO<sub>x</sub> control and is equipped with a reverse-gas style baghouse with a design air-to-cloth ratio of 1.96 ft<sup>2</sup>/1000 acfm. CEMS monitors at this site include NO<sub>x</sub>, CO<sub>2</sub>, SO<sub>2</sub>, and opacity. The APH inlet and APH outlet injection locations were tested.

Baseline data from EPA Method 26A measurements indicated that this test site was already near compliance at 0.0035 lb/MMBtu for HCl. Approximately 10 tons of hydrated lime was injected at the APH outlet with a feed rate varying from 920 to 3380 lbs/hr. This resulted in

92.3 to 93.7 percent removal by FTIR measurement and a 96.9 percent removal at 3380 lbs/hr using the EPA Method 26A measurement.

Approximately 12 tons of hydrated lime was injected at the entrance to the APH over a two day period at a rate 1440 to 3540 lbs/hr. This resulted in 94 percent removal by FTIR at injection rates of 1440 to 3540 lbs/hr and 96.8 percent removal at an injection rate of 3380 lbs/hr using the EPA Method 26A measurement. These results are shown in Table 4.

**Table 4.** Plant Two HCl Mitigation Results

HCl Results ( EPA Method 26a )				APH Outlet	APH Outlet	APH Outlet	APH Inlet	APH Inlet
	Units	Baseline	Objective					
Feed Rate	# / Hr	-	-	920	2500	3380	1440	3540
Sorbent / Acid Gas	# / #	-	-	0.71	1.95	2.60	1.12	2.77
HCl Results	# / MMBtu	0.00350	0.002	-	-	0.00011	-	0.00011
Removal	%	-	42.9%	-	-	96.9%	-	96.9%

HCl Results ( FTIR )				APH Outlet	APH Outlet	APH Outlet	APH Inlet	APH Inlet
	Units	Baseline	Objective					
Feed Rate	# / Hr	-	-	920	2500	3380	1440	3540
Sorbent / Acid Gas	# / #	-	-	0.71	1.95	2.60	1.12	2.77
HCl Results	# / MMBtu	0.00619	0.002	0.00039	0.00048	0.00048	0.00034	0.00034
Removal	%	-	67.7%	93.7%	92.3%	92.3%	94.5%	94.4%

SO<sub>2</sub> data recorded using permanent CEMS equipment during the trial is shown in Table 5.

**Table 5.** Plant Two SO<sub>2</sub> Mitigation Results

SO <sub>2</sub> Results ( CEMS )			APH Outlet	APH Outlet	APH Outlet	APH Inlet	APH Inlet
	Units	Baseline					
Feed Rate	# / Hr	-	920	2500	3380	1440	3540
Sorbent / Acid Gas	# / #	-	0.71	1.95	2.60	1.12	2.77
SO <sub>2</sub> Results	# / MMBtu	0.58	0.32	0.29	0.33	0.24	0.27
Removal	%	-	44.3%	49.6%	42.4%	59.4%	52.9%

Hydrated lime injection at the APH outlet resulted in a SO<sub>2</sub> removal rate of up to 49.6 percent or 0.29 lb/MMBtu. The air pre-heater inlet test resulted in a SO<sub>2</sub> mitigation rate peak of 59.4 percent or 0.24 lb/MMBtu. This result was at the lowest hydrated lime injection rate at the APH inlet and can be discounted as a fluctuation in coal sulfur.



## Test Site Three

Test three was conducted at Alabama Power Company Plant Barry Unit 4. Unit 4 is a tangential-fired, pulverized-coal boiler with a capacity of less than 370 MWe. The unit combusts a Columbian coal that has 1.0 lb/MMBtu sulfur content and is equipped with low NO<sub>x</sub> burners. Particulate control is accomplished by a series of cold-side electrostatic precipitators with a SCA ranging from 250 to 370 ft<sup>2</sup> per 1,000 acfm. The unit also has a Ljungstrom air pre-heater, SNCR, and a temporary PAC injection system. CEMS equipment installed on this unit monitors opacity, NO<sub>x</sub>, SO<sub>2</sub>, Hg, and CO<sub>2</sub>.

The dry sorbent injection test was conducted at the APH outlet and occurred over a five day period at varying loads and feed rates. The load ranged from 250 to 350 MWe while varying the hydrated lime and activated carbon feed rates. HCl and HF emissions were measured by a continuous MKS FTIR located at the stack. Baseline data from FTIR indicated that this test site was already in MATS compliance at 0.0007-0.001 lb/MMBtu for HCl while using a Colombian coal, shown by day in Table 6.

**Table 6.** Test Site Three HCl Reduction by FTIR

Load	MW	250	300	350	350	350
Sorbent Feed Rate	# / Hr	3000	3600	4000	Varied	4000
Sorbent / Acid Gas	# / #	0.9	0.94	1.12	-	1.18
ACI Feed Rate	# / Hr	200	250	350	350	350
Avg. Baseline HCl	# / MMBtu	0.0009	0.0008	0.0007	0.0010	0.0010
Avg. Controlled HCl	# / MMBtu	0.00027	0.00018	0.00026	0.00015	0.00024
Avg. HCl Removal		71%	78%	64%	84%	77%

At a load of 250 MWe, the feed rate of hydrated lime was 3000 lbs/hr while activated carbon was 200 lbs/hr. Taking the mass of SO<sub>2</sub> as reported with a continuous emission monitor and adding it to HCl and HF emissions recorded by the FTIR gave an average sorbent to acid gas ratio of 0.90. At these conditions, the average HCl removal of 71 percent resulted in a 0.00027 lb/MMBtu emission rate. At a load of 300 MWe, the feed rate of hydrated lime was 3600 lbs/hr while activated carbon was 250 lbs/hr. This set of conditions resulted in an average HCl removal rate of 78 percent and a 0.00018 lb/MMBtu emission rate with an average sorbent to acid gas ratio of 0.94. Three days of testing were conducted at a load of 350 MWe. Hydrated lime was injected 4000 lbs/hr while activated carbon was 350 lbs/hr. This set of conditions resulted in an HCl removal rate between 64 and 77 percent resulting in a 0.00026 to 0.00024 lb/MMBtu emission rate, respectively. The sorbent to acid gas ratio was 1.12 to 1.18 at these conditions.

This trial also monitored hydrofluoric (HF) acid by FTIR although mitigation is not currently required in MATS. Reviewing the baseline data for HF in Table 7, it shows that the emission of HF was actually higher than HCl.

**Table 7.** Test Site Three HF Reduction by FTIR

Load	MW	250	300	350	350	350
Sorbent Feed Rate	# / Hr	3000	3600	4000	Varied	4000
Sorbent / Acid Gas	# / #	0.9	0.94	1.12	-	1.18
ACI Feed Rate	# / Hr	200	250	350	350	350
Avg. Baseline HF	# / MMBtu	0.0021	0.0015	0.0009	0.0017	0.0010
Avg. Controlled HF	# / MMBtu	0.00042	0.00042	0.0002	0.0002	0.0002
Avg. HF Removal		80%	72%	79%	89%	82%

At the previously stated conditions, the 250 MWe test resulted in an average HF removal of 80 percent with a 0.00042 lb/MMBtu emission rate. The 300 MWe test resulted in an average HF removal rate of 72 percent with a 0.00042 lb/MMBtu emission rate. Over three days of testing conducted at a load of 350 MWe, hydrated lime removed between 79 and 82 percent of the HF resulting in a 0.0002 emission rate.

SO<sub>2</sub> emissions were tracked using CEM equipment during the trial and are shown in Table 8.

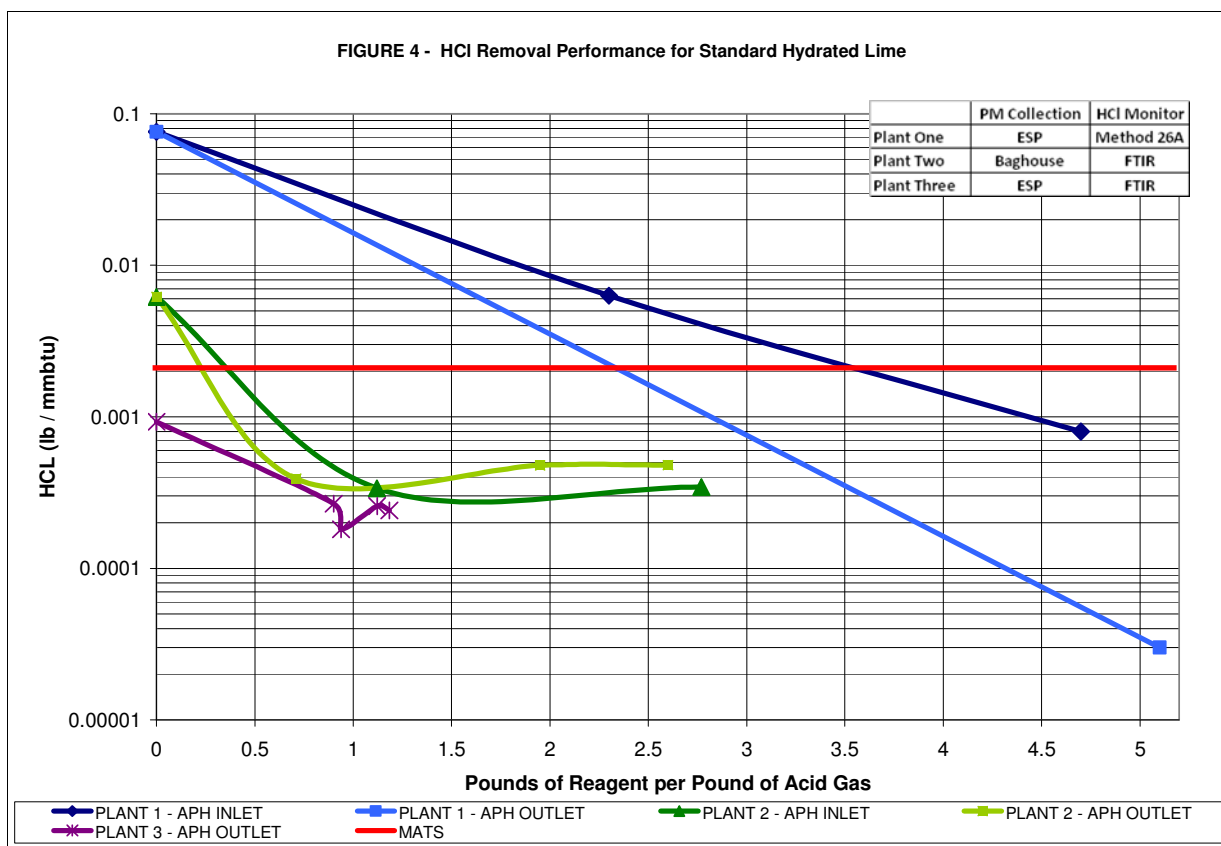
**Table 8.** Test Site Three SO<sub>2</sub> Reduction by CEM

Load	MW	250	300	350	350	350
Sorbent Feed Rate	# / Hr	3000	3600	4000	Varied	4000
Sorbent / Acid Gas	# / #	0.9	0.94	1.12	-	1.18
ACI Feed Rate	# / Hr	200	250	350	350	350
Avg. Baseline SO <sub>2</sub>	# / MMBtu	1.09	1.10	1.04	1.12	1.10
Avg. Controlled SO <sub>2</sub>	# / MMBtu	1.04	1.00	1.02	1.08	1.01
Avg. SO <sub>2</sub> Removal		4.5%	9.0%	2.4%	4.3%	8.2%

Injection of hydrated lime at 250 MWe reduced SO<sub>2</sub> emissions by 4.5 percent at the air pre-heater outlet. The 300 MWe test resulted in an average SO<sub>2</sub> reduction of 9.0 percent while the 350 MWe condition resulted in a reduction between 2.4 and 8.2 percent.

## SUMMARY

Figure 4 shows HCl reduction trends for the three tests as a function of reagent feed rate. Reagent feed rate is expressed as the mass ratio of reagent to the mass of total acid gases to be treated. Total acids gases are expressed as the sum of the masses of untreated SO<sub>2</sub>, HCl, and HF where applicable.



A significant finding at both plants was that MATS compliance for HCl (indicated by the red line in Figure 4) was achieved when hydrated lime was injected both upstream and downstream of the APH. Also while Plant Two with a bag house required significantly less hydrate to achieve MATS compliance for HCl than Plant One with the ESP, it should be noted that the mass of untreated HCl for Plant Two was an order of magnitude less than at Plant One.

## CONCLUSION

From full scale DSI testing and other subsequent testing at other plants since, hydrated lime is found to be a very effective reagent for removal of acid gases ( $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{HCl}$  and  $\text{HF}$ ) that are produced from power plants that burn coal.

Three distinct temperature regimes exist where calcium reactivity with  $\text{SO}_2$  peaks, along with temperature regimes where calcium reactivity with  $\text{SO}_2$  is minimal. Dry sorbent injection of hydrated lime immediately before or after an air heater constitutes a lower  $\text{SO}_2$  removal rate while utilizing a cold-side ESP and selectively reacts with other acid gases. The use of a cold-side ESP or baghouse would be ideal for potential users looking for surrogate  $\text{HCl}$  mitigation. These results reaffirm that a DSI trial is needed at each facility considering this technology for flue gas treatment.

It was seen that injection of hydrated lime did not adversely affect ESP operation by keeping opacity in-compliance, albeit toward the higher injection rates, hydrated lime became a significant portion of the total particulates entering the ESP.

At a minimum, BET specific surface area greater than  $20 \text{ m}^2/\text{g}$  and pore volumes greater than  $0.08 \text{ cm}^3/\text{g}$  are required to be reasonably reactive (and competitive); higher values are better but may be achieved only through use of expensive additives or drying of excess moisture. In the end, a cost effective reagent may be the best choice for meeting MATS compliance for a fossil fuel fired boiler of any size. Coupled with that is the fact that byproduct fly ash sales will probably not be affected and expensive hazardous ash disposal will not be required when hydrated lime is used as a DSI reagent.

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