

MERCURY CONTROL EVALUATION OF CALCIUM BROMIDE INJECTION INTO A PRB-FIRED FURNACE WITH AN SCR

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ABSTRACT

One mercury control option for power plants burning low-chloride coal is to add halogens into the furnace to oxidize the flue gas mercury into a soluble species, thereby enhancing mercury removal in downstream wet control devices. This paper summarizes EPRI- and Southern Company-funded full-scale calcium bromide injection tests conducted at Southern Company's Alabama Power Plant Miller. Miller fires PRB coal and is equipped with an SCR and a cold-side ESP. Calcium bromide was injected into the furnace at injection rates ranging from 2 to 230 ppm Br in the coal. The resulting changes in mercury speciation were measured at the SCR inlet, SCR outlet, air heater outlet, and ESP outlet. The plant does not have a wet FGD scrubber, so mercury removal by the scrubber could not be measured.

During baseline operation, the flue gas mercury at the ESP outlet was approximately 60% oxidized. The mercury oxidation at the ESP outlet increased to 90% at an injection rate of 5 ppm Br in the coal. The SCR played a significant role in the oxidation of mercury in the system. An injection rate of 115 ppm Br in the coal was required to achieve similarly high levels of mercury oxidation at the SCR inlet. The results from this program show that calcium bromide injection is an effective technology for achieving high levels of mercury oxidation for PRB plants equipped with an SCR. The technology may also be effective for PRB plants without an SCR, although higher injection rates may be needed.

Plant Miller also sells 100% of the fly ash that is captured within the ESP. Ash samples were subjected to testing to determine if the addition of calcium bromide had any effects that would preclude the use of the fly ash in concrete ad mixtures.

INTRODUCTION

The speciation of mercury in flue gas can affect the ability of various control devices to remove mercury. Mercury in flue gas derived from low-chloride coals such as Texas Lignite, PRB, and North Dakota lignite can contain a high fraction of elemental mercury, ranging from 40 to 95% of the total vapor-phase mercury. Elemental mercury is insoluble and is not well removed across wet scrubbers. EPRI has investigated a number of potential ways to increase mercury removal across wet and dry scrubbers by increasing the fraction of flue gas mercury present as oxidized mercury (which can be soluble in wet scrubbers). Evaluated processes have ranged from the use of catalysts (high and low temperature) to the addition of chemical reagents at various locations along the flue gas path.

This paper reports on EPRI-funded, full-scale calcium bromide injection tests conducted at Southern Company's Plant Miller Unit 4, which fires PRB coal. Unit 4 is equipped with an SCR for NO_x control and an ESP for particulate control. Plant Miller will be installing a wet FGD scrubber for SO₂ control, and Southern Company is interested in capitalizing on the possibility of capturing mercury in the wet scrubber as a co-benefit.

As the first step in this evaluation, a parametric test program was carried out at Plant Miller to evaluate the effectiveness of calcium bromide injection into the furnace. A calcium bromide solution was injected at feed rates ranging from 3 to 328 ppm Br in the coal (dry basis). Flue gas mercury measurements were made with mercury SCEMs (semi-continuous emissions monitors) at the SCR inlet, SCR outlet, ESP inlet, and ESP outlet. Mercury measurements were made with alternate methods to verify the results.

Data from this program show how halogen injection technology affects mercury removal and oxidation across the SCR, air heater, and ESP in PRB flue gas. Because Plant Miller is not currently equipped with an FGD scrubber, it was not possible to measure the ability of the oxidized mercury to be scrubbed and retained by the FGD.

This test program was conducted under a license agreement between Vosteen Consulting GmbH and Southern Company Services, Inc., as signed in August 2006. These tests were also performed under an extension of Agreement 05-0292KC between Vosteen Consulting GmbH and EPRI. Fundamentals and corresponding experimental laboratory results comparing the differences between chlorine and bromine based mercury oxidation and sorption in units with SCR catalysts were previously presented^{1,2}.

EXPERIMENTAL

This test program consisted of a series of parametric tests to determine the effectiveness of the bromide solution in oxidizing mercury at several different injection concentrations. Parametric testing was performed to determine the lowest bromine concentration that still resulted in adequate oxidation of mercury. All parametric tests were conducted with the selective catalytic reduction (SCR) reactor in service. A calcium bromide solution was injected at feed rates ranging from 3 to 328 ppm Br in the coal (dry basis).

Description of Plant Miller Unit 4

Calcium bromide injection testing was performed at Plant Miller on Unit 4. The unit is equipped with an SCR and a cold-side electrostatic precipitator (ESP). Table 1 lists key operating parameters for the unit. Unit 4 is a 700 MW pulverized coal unit that fires exclusively PRB coal in a wall-fired furnace. PRB coal produces flue gas in which the oxidized mercury concentration can range from 5 to 60% of the total mercury concentration. The oxidation of mercury in the baseline flue gas at Plant Miller was at the upper end of this range.

Unit 4 has two SCR catalyst chambers. Each chamber precedes a Lungstrom air preheater with a design operating temperature of 720°F. Each of the two catalyst chambers contains high activity Cormetech Honeycomb catalyst (9.2 mm pitch). Each reactor currently contains three catalyst layers and there is space available for an additional layer at some point in the future. The design gas velocity through the catalyst is 17.2 ft/sec. The SCR is designed for 90% NO_x removal with ammonia slip less than 2 ppm. The catalyst had been in service for four ozone seasons when the test program was executed.

A schematic of Plant Miller, along with the locations for vapor phase mercury measurements, is shown in Figure 1. Flue gas mercury measurements were made with mercury SCEMs (semi-continuous emissions monitors) at the SCR inlet, SCR outlet, ESP inlet, and ESP outlet. Mercury measurements were made with alternate methods (sorberent traps and Ontario Hydro) to verify the results.

Table 1. Key Design and Operational Parameters of Plant Miller Unit 4.

Unit	Capacity (MW)	Fuel	Furnace Type	Existing Controls	Air Heater Outlet Temperature (°F)	Stack Flow at Full Load (kscfm, wet)
Miller 4	700	PRB coal	Wall fired	SCR, ESP	310-330	1750

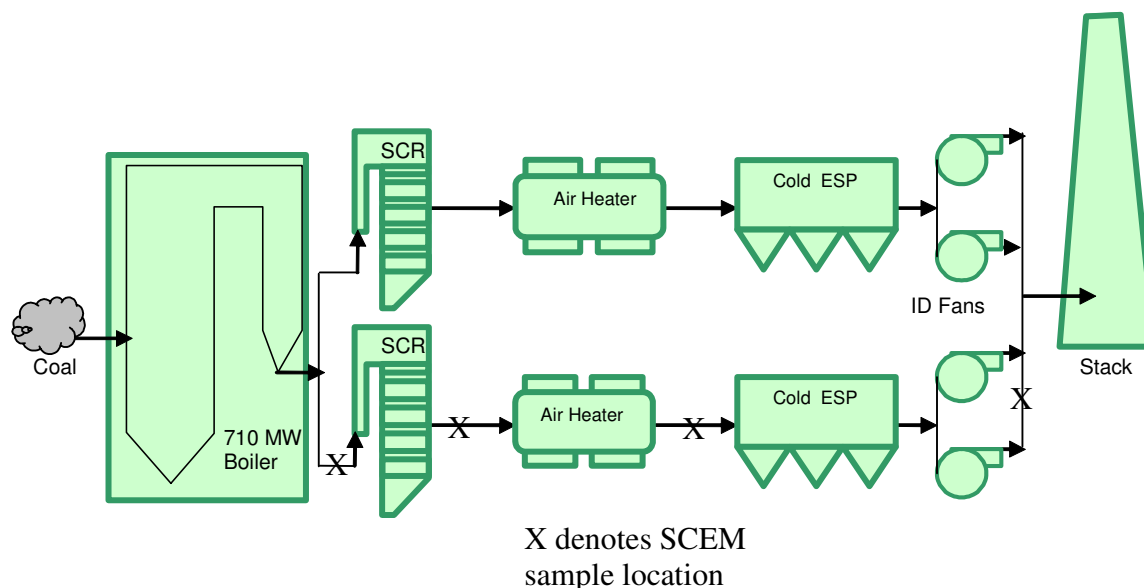


Figure 1. Schematic of Plant Miller Unit 4.

SCEM Data Verification

Previous field and laboratory measurements have indicated a possibility for bromine to bias flue gas mercury measurements; therefore, sorbent tube and Ontario Hydro measurements were collected throughout the test period to verify the mercury SCEM (semi-continuous emissions monitor) measurements. When measuring the baseline flue gas (no bromine present), no bias was observed in the total and elemental mercury concentration measurements by the SCEM. When bromine was present in the flue gas (i.e., during furnace injection of calcium bromide), the comparison of the SCEM data to the sorbent trap and Ontario Hydro methods indicated a negative bias of 15 to 40% in the measurement of total mercury concentration by the SCEM. However, there appeared to be little to no bias in the measurement of elemental mercury concentrations by the SCEM when compared to the Ontario Hydro Method. Both the SCEM and the Ontario Hydro methods measured very low concentrations of elemental mercury during the bromine injection tests, and were within acceptable agreement for measurements made below $1\mu\text{g}/\text{Nm}^3$. For this report, to quantify mercury oxidation and removal during bromine injection tests, the total mercury concentrations measured by the sorbent tube method were coupled with the elemental mercury concentrations measured by the SCEM.

Bromide Salt Injection System Design

Bromide was added to the Plant Miller Unit 4 boiler as a salt solution of calcium bromide. The premise of this method was that the bromide from the salt solution would be vaporized in the boiler and subsequently increase the Br_2/HBr concentration in the downstream flue gas.

The bromide salt chosen for these tests was calcium bromide (CaBr_2). It was purchased as a 52 wt% solution at a delivered cost of \$0.90/lb. The salt solution was obtained in its most concentrated form to minimize the volume of solution being shipped. It was diluted with plant water into 2500-gal plastic holding tanks. The diluted solution was pumped up 60 feet to the coal feeder deck level and then sprayed onto the coal as it fell off the weigh belt into the pulverizer.

A schematic of the coal feeding system is given in Figure 2. The furnace has three burner elevations on the front-side, labeled A, G, and B, and four burner elevations on the back side, labeled C, E, D, and F. Each burner elevation on each side is served by its own coal bunker, stock feeder, and pulverizer. Each pulverizer feeds eight fuel pipes that span the width of the furnace.

The project team chose to inject into the stock feeders for pulverizers F and G because each pulverizer feeds the mid to lower levels of different sides of the furnace and because these two feeders were closest to the pump skid. The

bromide solution was pumped through hose to the stock feeder for each pulverizer, where it was sprayed onto the coal as it fell off the weigh belt. The coal and bromide solution mixed in the pulverizer before traveling through the fuel pipes to the furnace.

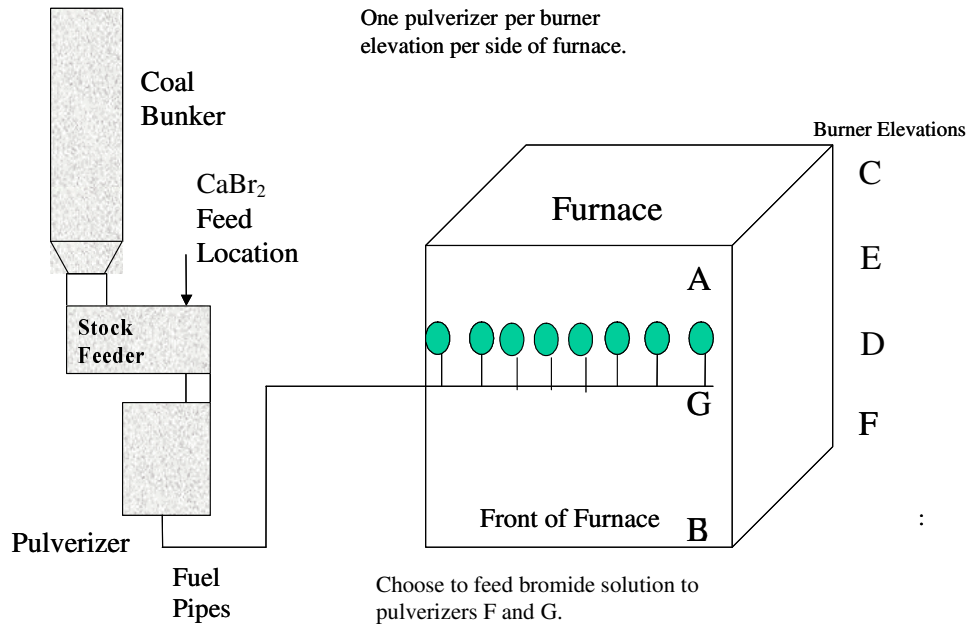


Figure 2. Coal handling system layout.

RESULTS

Baseline Mercury Measurement at Miller Unit 4

Flue gas mercury concentrations at the SCR inlet ranged from 7 to 13 $\mu\text{g}/\text{dNm}^3$ (normalized to 3% O₂) with between 18% and 42% of the flue gas mercury present in the oxidized form. The total vapor-phase mercury concentration measured at the SCR inlet correlated reasonably well with coal mercury data. Flue gas mercury concentrations at the SCR outlet ranged from 7 – 13 $\mu\text{g}/\text{Nm}^3$ (normalized to 3% O₂) with up to 56% present in the oxidized form, indicating oxidation of mercury across the SCR.

Flue gas mercury concentrations at the ESP inlet were 6 – 10 $\mu\text{g}/\text{Nm}^3$, with 34 – 41% oxidation. At the ESP outlet, mercury concentrations ranged from 5 – 10 $\mu\text{g}/\text{Nm}^3$, with about 60% of the mercury present as oxidized mercury.

The baseline mercury removal across the system (SCR inlet to ESP outlet) was approximately 20%, with most of the removal occurring across the air heater. Little to no mercury removal was measured across the SCR and ESP.

The baseline coal chlorine content ranged from <5 to 45 ppm Cl in the coal (dry basis). The baseline flue gas HCl concentration was 1.5 ppm (dry, 3% O₂) at both the ESP inlet and outlet. The measured chloride content of the flue gas agreed reasonably well with the variable coal chloride concentration.

The baseline flue gas HBr concentration was less than the Method 26 detection limit of 0.08 ppm (dry, 3% O₂). The baseline coal bromine content averaged 5.8 ppm (dry basis). Bromine was not detected in the baseline ash (detection limit of 1 ppm).

Calcium Bromide Injection Results at Miller Unit 4

Flue Gas HBr Enhancement

Calcium bromide was added to the furnace at rates ranging between 3 and 328 ppm Br in the coal (dry basis). The resulting flue gas bromide levels were measured at the ESP inlet and the ESP outlet (Figure 3). The flue gas bromide content increased with increasing calcium bromide injection, up to an injection rate of 165 ppm Br in the coal (dry basis). At this point, the flue gas bromide concentration plateaued at 3.6 ppm HBr in the gas (dry basis, 3% O₂). It is unclear why the flue gas bromide concentration did not increase further when the injection rate was increased to 328 ppm Br in the coal (dry basis), so it may be the result of an anomalous measurement.

The measured flue gas bromide concentrations were less than the theoretically predicted bromide concentrations, as calculated from native coal Br content and calcium bromide addition rate. The discrepancy between the theoretical and measured concentrations increased with increasing injection rate.

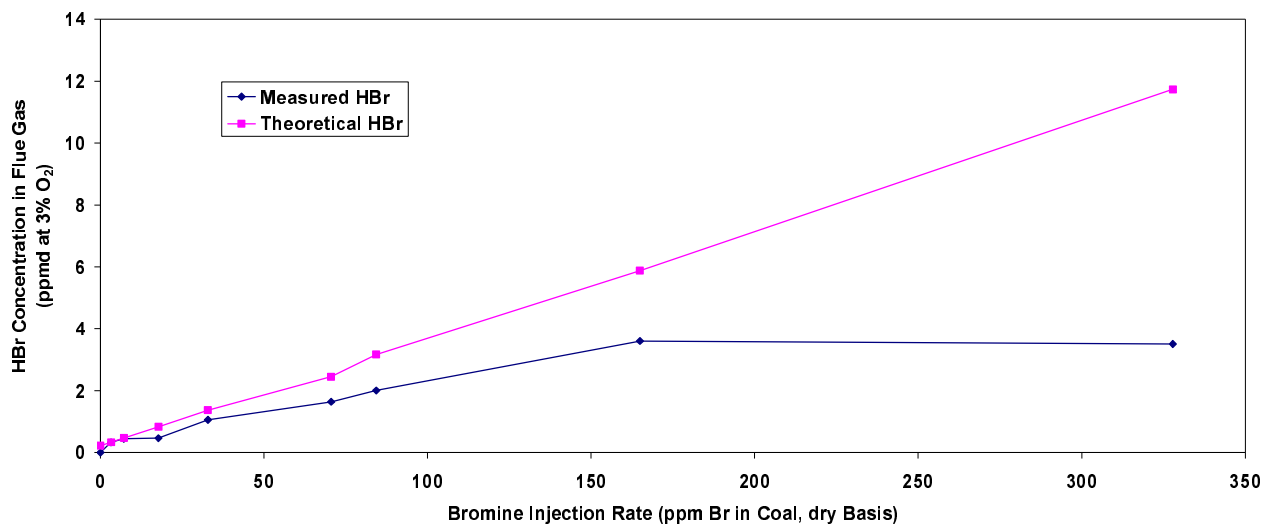


Figure 3. Flue gas HBr enhancement due to boiler injection of calcium bromide.

Elemental Mercury Results

Table 2 shows the average elemental mercury concentrations measured by the SCEMs for all four analyzer locations during baseline and injection testing. These data show that once the Hg was oxidized in the SCR, it remained oxidized through the rest of the emission control systems. This result is important because the FGD system that will be installed at Plant Miller will be located after the ESP. At an injection rate of 3 ppm Br in the coal, the ESP outlet elemental mercury concentration had decreased to 1.0 $\mu\text{g}/\text{dNm}^3$, compared to a baseline value of 3.1 $\mu\text{g}/\text{dNm}^3$. The elemental mercury concentration decreased to 0.7 $\mu\text{g}/\text{dNm}^3$ at injection rates of 7 and 18 ppm Br in the coal. At injection rates of 23 ppm and higher, the outlet mercury concentration was consistently between 0.4 and 0.6 $\mu\text{g}/\text{dNm}^3$.

Table 2. Average Elemental Hg Concentrations Measured Across Unit 4.

Date & Time	Avg. Bromine Injection Rate (ppm in coal)	SCR Inlet Avg. Hg ⁰ (µg/dNm ³)	SCR Outlet Avg. Hg ⁰ (µg/dNm ³)	ESP Inlet Avg. Hg ⁰ (µg/dNm ³)	ESP Outlet Avg. Hg ⁰ (µg/dNm ³)	% of Hg ⁰ Oxidized Across SCR [#]
Baseline	0	8.2	6.7	4.7	3.1	18%
10/17/06 9:00 - 15:00	3	7.6	1.7	2.1	1.0	78%
10/16/06 9:00 - 12:10	7	11.4	0.4	1.1	0.7	96%
10/15/06 10:00 - 17:56	18	6.3	0.4	1.7	0.7	94%
10/13/06 15:15 - 17:00	23	3.7	0.3	0.4	0.4	92%
10/13/06 11:58 - 14:15	33	3.0	0.3	0.4	0.4	90%
10/12/06 12:15 - 17:00	71	4.3	0.3	0.4	0.5	93%
10/18/06 8:00 - 12:20	84	5.2	1.1	0.4	0.4	79%
10/17/06 16:00 - 19:00	86	3.0	0.4	0.6	0.6	87%
10/11/06 11:12 - 16:22	165	0.2	0.8	0.4	0.5	-300%
10/10/06 11:52 - 17:52	328	0.4	1.2	0.3	0.4	-200%

$$\# \% \text{ Hg}^0 \text{ Oxidized Across SCR} = [1 - (\text{Hg}^0_{\text{SCR,outlet}})/(\text{Hg}^0_{\text{SCR,inlet}})] * 100$$

Mercury Oxidation Results Across the SCR

The oxidation of elemental mercury across the SCR was calculated as

$$\% \text{ Hg}^0 \text{ Oxidized Across SCR} = [1 - (\text{Hg}^0_{\text{SCR,outlet}})/(\text{Hg}^0_{\text{SCR,inlet}})] * 100$$

This calculation is independent of the SCEM total mercury concentrations, which were shown to have a possible bias associated with them.

The data in Table 2 indicate that only a small amount of bromine addition is required to affect the oxidation of mercury across the SCR. At an injection rate of 3 ppm Br in the coal, approximately 78% of the elemental mercury was oxidized across the SCR. Higher bromide injection rates were tested (up 328 ppm Br in the coal), but the measured Hg oxidation across the SCR for these higher injection rates ranged anywhere from 79% to 96%. These data indicate the oxidation of mercury can be quite high; the variability may be due to process conditions or measurement uncertainty.

A brief comment should be made about the last two rows of data in Table 2, which represent mercury measurements at the highest tested injection rates of 165 and 328 ppm Br in the coal. In both of these tests, a very high level of oxidation was measured at the SCR inlet and the elemental mercury concentration was very low (0.3 µg/dNm³). At these high injection rates, there was sufficient bromide to effectively oxidize all of the mercury upstream of the SCR. The SCR outlet elemental mercury concentrations were low (~1.0 µg/dNm³), but higher than the inlet mercury concentrations, thus resulting in a negative value of percent of elemental mercury oxidized across the SCR.

Figure 4 plots the elemental mercury concentrations measured at each location for the various tested injection rates. The plot shows that at an injection rate of 7 ppm Br in the coal, the elemental mercury concentrations at the SCR outlet and ESP outlet have reached the lowest achievable value for the injection configuration. At the SCR inlet,

however, the elemental mercury concentration is considerably higher. The low elemental mercury concentrations achieved at the SCR inlet at higher injection rates (≥ 165 ppm Br in coal) indicate that units that do not have an SCR may still be able to achieve high levels of mercury oxidation. Plants without an SCR may require an order of magnitude more bromide than plants with an SCR.

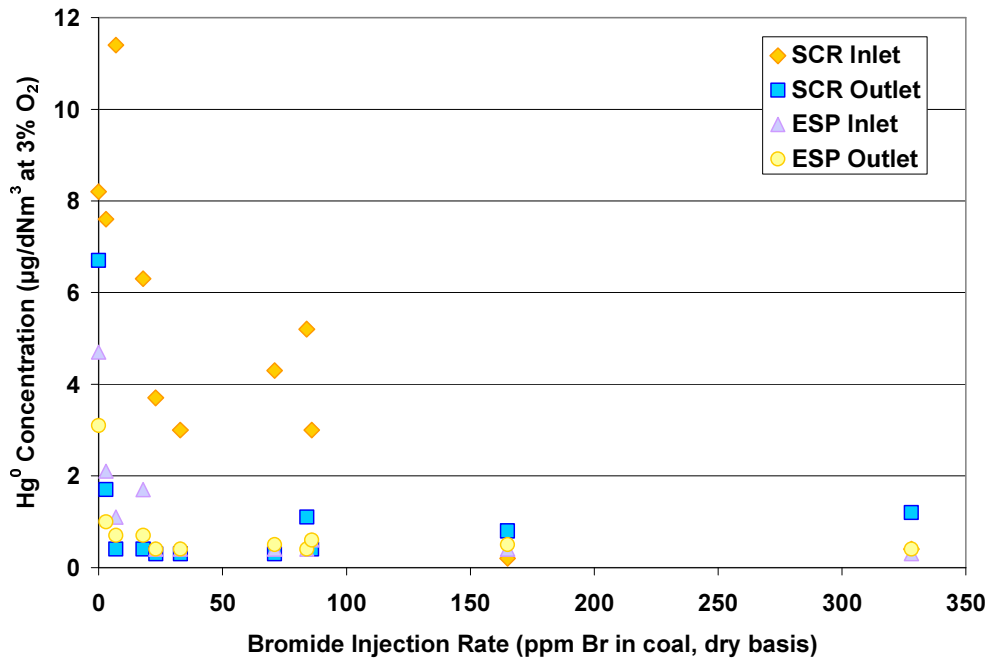


Figure 4. Average elemental mercury concentrations measured during each bromide injection test.

This observation is affirmed by results obtained from a DOE-NETL funded calcium bromide injection test program at TXU’s Monticello Steam Electric Station (MoSES).³ MoSES is not equipped with an SCR. As part the DOE-NETL program, mercury oxidation was measured at the ESP outlet at various calcium bromide injection rates. Table 3 compares results from the ESP outlet at MoSES to the SCR inlet at Plant Miller. When comparing results from the two programs, it should be recognized that there is a difference in coal type (MoSES fires a Texas Lignite/PRB blend) and sampling location (MoSES measurements were made downstream of the air heater, where further mercury oxidation can occur). For both plants, injection concentrations between 55 and 86 ppm Br in the coal (dry basis), the oxidation of mercury ranged from 55% - 67%. To achieve greater than 90% oxidation, injection rates greater than 150 ppm Br in the coal (dry basis) were required.

Table 3. Comparison of Plant Miller Results to TXU Monticello Results.

Results from Plant Miller		Results from TXU’s Monticello	
Injection Rate (ppm Br in the coal, dry basis)	% Hg Oxidation* Measured at SCR inlet	Injection Rate (ppm Br in the coal, dry basis)	% Hg Oxidation# Measured at ESP outlet
71	55%	55	67%
86	63%	113	85%
165	98%	193	91%
328	96%	330	83%

* Percent Oxidation calculate from SCEM elemental mercury concentration and SCEM total mercury concentration (no bias suspected at SCR inlet).

Percent Oxidation calculated from SCEM elemental mercury concentration and coal mercury concentration.

Mercury Oxidation Results at the ESP Outlet

As a result of the bias in SCEM total Hg measurements observed during this program, the sorbent tube total Hg results were used for the total vapor-phase Hg concentrations in the flue gas at the ESP outlet. Table 4 gives the sorbent tube results and the SCEM elemental Hg measurements collected at the ESP outlet, along with the percent oxidation at the outlet calculated using these data. Based on the data in the table, it appears that the percent mercury oxidation at the ESP outlet begins to plateau at an injection rate of 7 ppm bromine in the coal; this rate results in approximately 92% oxidation of the Hg in the flue gas. Increasing the bromine injection rate past this point does not appear to produce a comparable increase in oxidation.

Table 4. Mercury Oxidation at the ESP Outlet.

Date & Time	Avg. Bromine Injection Rate (ppm in coal)	Sorbent Tube Total Hg ($\mu\text{g}/\text{Nm}^3$)	ESP Outlet Avg. Hg⁰ ($\mu\text{g}/\text{Nm}^3$)	% Hg Oxidation
Baseline 10/17/06	0	7.2	3.1	58%
9:00 - 15:00 10/16/06	3	7.2	1.0	86%
9:00 - 12:10 10/15/06	7	8.5	0.7	92%
10:00 - 17:56 10/13/06	18	6.5	0.7	90%
15:15 - 17:00 10/13/06	23	6.6	0.4	94%
11:58 - 14:15 10/12/06	33	6.6	0.4	94%
12:15 - 17:00 10/18/06	71	5.7	0.5	91%
8:00 - 12:20 10/17/06	84	9.1	0.4	95%
16:00 - 19:00 10/11/06	86	7.2	0.6	92%
11:12 - 16:22 10/10/06	165	6.8	0.5	92%
11:52 - 17:52	328	7.9	0.4	94%

Effects on Unit Operation

Long-term impacts of chemical addition are uncertain. During this short test program, no adverse effects of calcium bromide injection were noted on the coal feeder or boiler operation. Ash samples collected during bromide injection did show an appreciable increase in bromide concentration. The effects of bromide on concrete ash admixtures were evaluated. The set time, air content, and slump were not affected for concrete made from bromide-containing ashes. There was a 15% decrease in compressive strength for the concrete specimens produced with ash from the calcium bromide addition. This screening is not conclusive because of the limited number of samples and the broad range of bromide addition rates; however, the results do warrant further investigation. The properties of the concrete ash admixtures will be further investigated in the Plant Miller calcium bromide injection test program scheduled for Winter 2008.

CONCLUSIONS

The results showed that the injection of calcium bromide into the furnace holds promise for converting elemental mercury to oxidized mercury and improving mercury removal for PRB fired units. During baseline operation, the flue gas mercury at the ESP outlet was approximately 60% oxidized. The mercury oxidation at the ESP outlet

increased to 90% at an injection rate of 5 ppm Br in the coal. The SCR played a significant role in the oxidation of mercury in the system. An injection rate of 115 ppm Br in the coal was required to achieve similarly high levels of mercury oxidation at the SCR inlet. The results from this program show that calcium bromide injection is an effective technology for achieving high levels of mercury oxidation for PRB plants equipped with an SCR. The technology may also be effective for PRB plants without an SCR, although higher injection rates may be needed.

Further work will be needed to address key issues with this technology:

- This test program should be repeated on a unit equipped with either a pilot- or full-scale wet scrubber to demonstrate the solubility of the oxidized mercury in the scrubber liquor and to demonstrate that mercury re-emissions are minimal.
- The stack emission of bromine/bromide needs to be determined downstream of the wet scrubber and evaluated with respect to permitted limits.
- The increased levels of bromide in the scrubber liquor should be evaluated for effects on selection of scrubber materials of construction and blowdown rate.
- This test program should be carried out when the SCR is not in service to determine the calcium bromide's effectiveness for units not equipped with an SCR.
- Long-term furnace impacts should be evaluated via corrosion coupons or periodic boiler tube corrosion inspections.
- The increased concentration of bromide in the fly ash should be evaluated for impact on ESP ash disposal or re-use.

REFERENCES

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