

The Balance-of-Plant Impacts of Calcium Bromide Injection as a Mercury Oxidation Technology in Power Plants

Paper # 27

A&WMA Mega Symposium, August 25 – 28, 2008, Baltimore MD (USA)

Katherine Dombrowski, Sara McDowell

URS Corporation, 9400 Amberglen Boulevard, Austin, TX 78729

Mark Berry, April Freeman Sibley

Southern Company Services, PO Box 2641 BIN 14N-8195 Birmingham, Alabama 35291

Ramsay Chang

EPRI, 3412 Hillview Avenue, Palo Alto, CA 94304

Bernhard Vosteen

Vosteen Consulting GmbH, Leopold-Gmelin-Strasse 80, Cologne, Germany

ABSTRACT

The use of calcium bromide as a mercury oxidizing agent may result in elevated concentrations of bromine (as HBr or Br₂) in the fly ash, FGD byproducts, and/or flue gas. EPRI has initiated a project to evaluate the fate of bromide/bromine in coal-fired power plants and its potential balance of plant impacts. Data for this project are being gathered from bromine injection tests completed recently and from on-going calcium bromide injection testing where samples are obtained from flue gas, fly ash, and wet scrubbers. Samples are analyzed for impacts of bromine on flue gas bromine emissions, ash use, bromine leaching, bromine related corrosion in the boiler and in the scrubber, and the partitioning of bromine and mercury between the FGD liquor and solids. This paper summarizes the results from Southern Company's Plant Miller, the first field site to be tested as part of this EPRI-funded balance of plant survey.

INTRODUCTION

The speciation of mercury in flue gas can affect the ability of various environmental control devices to remove it. Flue gas derived from Powder River Basin (PRB) coal typically contains a high fraction of elemental mercury. This form is insoluble in water and therefore not easily removed across wet scrubbers. Several methods are being investigated by EPRI and others to oxidize the elemental mercury in flue gas, thereby improving mercury removal across a wet scrubber. These methods include catalytic and chemical injection processes.

The results of previous studies have shown that the addition of bromide-containing salts to a full-scale coal combustion unit can result in increased levels of oxidized mercury in the flue gas. This technology is likely to be employed at units firing low-rank, low-chloride coals. Although long-

term balance-of-plant impacts at these facilities are unknown, some areas of concern can be investigated by short-term tests (approximately two weeks in duration) of calcium bromide addition, including:

- Effect of bromine on fly ash for concrete use
- Leachability of bromine from fly ash
- Effectiveness of bromine capture by wet FGD
- Bromine concentrations and partitioning in wet FGD systems (liquor vs. solids)
- Effect of bromine on mercury partitioning between wet FGD liquor and solids
- Effect of bromine on mercury re-emissions from wet FGD.

EPRI has funded a study to evaluate the fate of bromide/bromine in coal-fired power plant systems and its potential balance of plant impacts. Data for this project are being gathered from a survey of available literature, from calcium bromide injection field demonstrations planned for 2008, and from laboratory corrosion and bench-scale FGD testing. This paper reports on results obtained from Plant Miller, the first field site to be tested as part of this survey.

Full-scale furnace injection tests of calcium bromide injection^{1,2} was conducted under a license grant from Vosteen Consulting GmbH, Cologne, Germany, at Alabama Power Company's Plant Miller Unit 4, which fires PRB coal. This project is the continuation of a 2006 EPRI-funded program at Plant Miller Unit 4 which demonstrated that adding very small amounts of bromide to the furnace increased the oxidation of mercury in the Plant Miller flue gas to >90%³. In the 2006 program, the tests were short-term in nature and did not evaluate the removal of oxidized mercury across a wet scrubber. A pilot scale flue gas desulfurization (FGD) scrubber was installed for this most recent round of testing to determine the mercury removal that might be achieved. Continuous injection tests were conducted for several days so that flue gas, ash, and FGD samples could be obtained to evaluate the balance of plant impacts of the calcium bromide injection technology.

EXPERIMENTAL

This test program consisted of a series of parametric tests to determine the effectiveness of calcium bromide solution in oxidizing mercury at several different injection concentrations. Parametric testing was performed to determine the lowest bromine concentration required to achieve adequate oxidation of mercury. Then two longer-term injection tests were conducted to evaluate how mercury oxidation and removal were sustained over several days and to collect samples to evaluate balance of plant effects of bromide injection.

Description of Host Site

Calcium bromide injection testing was performed at Plant Miller on Unit 4. Unit 4 is a 700 MW pulverized coal unit that fires exclusively PRB coal in a wall-fired furnace. It is equipped with an SCR and cold-side electrostatic precipitator (ESP). Table 1 lists the average composition and heating value of the PRB coal that was fired during the test program in early 2008. PRB coal typically produces flue gas in which the oxidized mercury concentration ranges 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 selective catalytic reduction (SCR) catalyst chambers, each upstream of 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) with three catalyst layers and space available for an additional layer. The design gas velocity through the catalyst is 17.2 ft/sec. The SCR was designed for 90% NO_x removal with an ammonia slip of less than 2 ppm. At the time of this test program, the current catalyst had been in service for four ozone seasons.

Table 1. Average Composition of Plant Miller PRB Coal Samples from Spring 2008 Test.

Fuel Parameter	Value (dry basis, except where noted)
Heating Value	11958 Btu/lb
Carbon	68.6 wt. %
Hydrogen	4.6 wt. %
Nitrogen	1.0 wt. %
Oxygen	19.1 wt. %
Ash	6.3 wt. %
Sulfur	0.35 wt. %
Moisture (as received)	27.2 wt. %
Mercury	0.066 ppm
Chloride	26 ppm
Bromide	<1 ppm

For the program described in this paper, halogen injection tests were performed with the SCR both in and out of service. Due to a service outage for the ammonia (NH₃) feed system, the SCR was not operated with ammonia; thus, it was not reducing NO_x. With the SCR in this mode of operation, the NO in the flue gas would have been partially converted into water soluble NO₂, resulting in an increased nitrite input to the FGD absorber subsequently causing a higher concentration of sulfur-nitrogen species in the FGD liquor. The absence of ammonia in the SCR is advantageous for mercury oxidation across the SCR; therefore, the results obtained from this 2008 test program may be more optimistic than results obtained had the SCR been operating with ammonia. The design velocity of 17.2 ft/sec is low enough to allow for mercury oxidation with the SCR in service and operated with ammonia, as demonstrated in the 2006 test program.³ Additional halogen injection testing will be performed in Fall 2008 with the SCR in service and operated with ammonia.

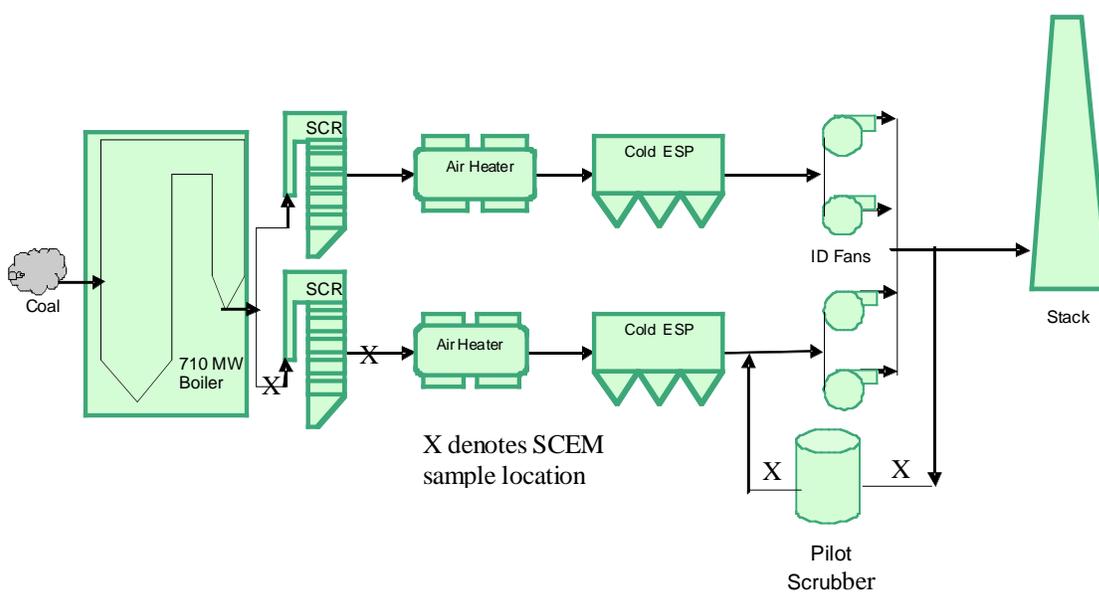
A 2 MWe pilot scrubber was installed at the ESP outlet (Figure 1) to evaluate the removal of oxidized mercury across an FGD unit. The pilot scrubber was a double contact flow scrubber designed by Advatech, similar in configuration to the full-scale scrubbers that are being installed at Plant Miller. The scrubber operated with a limestone reagent slurry to remove SO₂ at high efficiency. For this test program the scrubber operated at a pH of 5.5 – 5.6 with an SO₂ removal efficiency greater than 94%, which was sufficient for this test program. The scrubber could have been operated for higher SO₂ removal (up to 99%), but SO₂ removal was not the focus of this program.

During the initial startup of the FGD scrubber (and prior to the initiation of the baseline test period), the FGD slurry was spiked with calcium chloride to raise the soluble chloride content to approximately 3000 ppm, which is the anticipated steady-state chloride concentration of the full-scale scrubber liquor. Because of the low chloride content of the PRB coal fired at Miller, it would have taken over a month to have achieved this liquor chloride concentration naturally.

During baseline testing, the bromide concentration of the liquor was allowed to increase naturally from the bromide in the coal. The bromide concentration of the liquor was 40 –50 ppm during baseline. During parametric calcium bromide injection, the bromide concentration was also allowed to increase naturally, and ranged from 185 to 290 ppm. On the first day of the continuous injection test at 25 ppm Br in the coal, calcium bromide was artificially spiked into the scrubber to achieve a level of 1400 ppm Br in the liquor. The bromide concentration remained in the 1400 – 1500 ppm range for five days, until another spike was introduced to raise the liquor bromide level to 2600 ppm. The last three days of 25 ppm injection test and the entirety of the 50 ppm injection test were performed at liquor bromide concentrations ranging from 2500 – 2900 ppm. At the end of the test program, the chloride and bromide concentrations in the liquor were each approximately 2800 ppm.

Absorber slurry samples were collected and processed daily during this test period to monitor scrubber chemistry. Analysis of these samples showed that sulfite levels in the scrubber were elevated (115 to 170 ppm) throughout the test program. In a typical limestone forced oxidation scrubber, a sulfite concentration below 80 ppm is considered ideal; analysis of the gypsum product showed that the pilot FGD scrubber was otherwise operating well. The elevated sulfite levels could potentially have resulted from operating the SCR without ammonia, as discussed above. Sulfur-nitrogen species accounted for approximately half of the total hydrolysable sulfur content in the liquor.

Figure 1: Schematic of Plant Miller Unit 4 and Pilot FGD Scrubber



Measurement Methods

Various bromide and mercury measurements were made on the flue gas, coal, fly ash, and FGD samples. Flue gas mercury measurements were made with EPRI mercury semi-continuous emissions monitors (SCEMs) at the SCR inlet, SCR outlet, pilot FGD scrubber inlet, and pilot FGD scrubber outlet to characterize oxidation and removal of mercury across the SCR, ESP, and scrubber. Previous field and laboratory measurements have indicated a possibility for bromine to bias flue gas mercury measurements.⁴ Laboratory tests showed that reactive surfaces such as stainless steel and glass exacerbate this measurement bias; therefore, these surfaces were avoided where possible in the SCCEM systems used for this test program. Sorbent tube and Ontario Hydro measurements were collected throughout the test period to verify the mercury SCCEM measurements. Sorbent tubes were collected at both the FGD inlet and outlet, while Ontario Hydro measurements were collected at the FGD inlet only. Comparison of the SCCEM data to sorbent trap and Ontario Hydro data indicated good agreement and that measures taken to reduce the bromine-induced bias during this test program were effective at the FGD inlet and outlet. These measures included:

- *Use of Teflon impingers during the early part of the test program.* These impingers were used at all locations upstream of the FGD scrubber throughout most of the parametric testing. This measure was particularly important during testing at high injection rates. At the end of the parametric tests and during the long-term injection testing, the use of glass impingers was resumed at the FGD inlet location and no indication of a bias was observed. Injection rates were less than or equal to 50 ppm Br during these test periods.
- *Use of a Teflon probe at the FGD inlet location.* At the FGD inlet location, a probe made of Teflon tubing was used instead of the standard blower loop, which eliminated flue gas contact with stainless steel surfaces.

At the SCR inlet and outlet locations, high particulate concentrations and gas temperatures required the use of a stainless steel, filtered probe. Little to no bromine-induced mercury measurement bias was observed at the SCR inlet, while at the SCR outlet, a bromine-induced mercury measurement bias was observed, resulting in low total mercury concentrations and over-prediction of mercury oxidation.

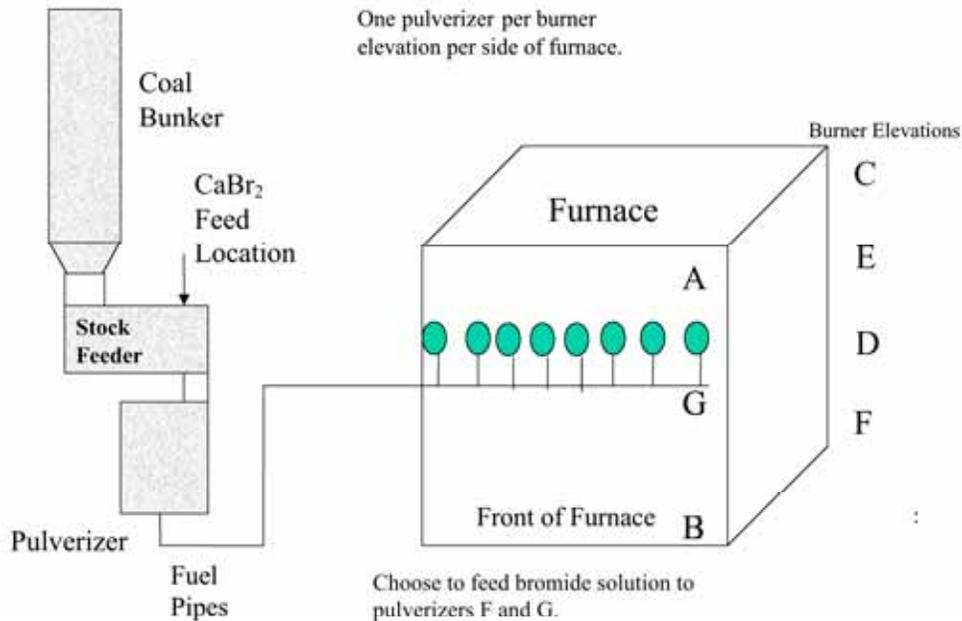
Bromide Salt Injection System Design

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 Br₂/HBr concentration in the downstream flue gas. The bromide salt chosen for these tests was calcium bromide (CaBr₂). 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.

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 tubing 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 Measurements at Miller Unit 4

Baseline data were collected on days specifically set aside as baseline days and in the mornings on parametric test days before injection began. Flue gas mercury concentrations at the SCR inlet ranged from 10 to 17 $\mu\text{g}/\text{dNm}^3$ (normalized to 3% O₂) with less than 5% of the flue gas mercury present in the oxidized form. During the 2006 test program, the mercury at the SCR inlet was more oxidized (18-28%). As compared to the coal fired in the 2006 test program, the coal fired during this 2008 test program (Table 1) had a significantly lower native bromide content (<1 ppm vs. 5.8 ppm) and a slightly higher chloride content (26 ppm vs. 13 ppm). The higher bromide content in 2006 may have resulted in higher mercury oxidation at the SCR inlet during baseline testing.

Baseline data at the SCR outlet were collected soon after the SCR was placed in service. During this measurement period the SCR adsorbed mercury, resulting in lower outlet mercury

concentrations. Over the course of six days, the SCR progressed toward adsorption equilibrium. On the fifth day with the SCR in service, at which point the SCR appeared to be closest to steady state, flue gas mercury concentrations measured at the SCR inlet ranged from 15 – 18 $\mu\text{g}/\text{dNm}^3$ (normalized to 3% O_2) and the flue gas concentrations measured at the SCR outlet ranged between 10 and 15 $\mu\text{g}/\text{dNm}^3$ (normalized to 3% O_2).

Baseline flue gas mercury concentrations at the FGD inlet typically ranged from 4 to 10 $\mu\text{g}/\text{dNm}^3$, indicating some adsorption of mercury by the fly ash. Flue gas mercury at the FGD inlet was appreciably more oxidized than at the SCR outlet, indicating significant oxidation of mercury across the air heater and ESP. During baseline testing with the SCR out of service, the FGD inlet mercury oxidation ranged from 35 - 57%, and total mercury removal across the FGD ranged from 23 - 55%. FGD outlet total mercury concentrations ranged from 2 to 6 $\mu\text{g}/\text{dNm}^3$. With the SCR in service (no NH_3), the FGD inlet mercury oxidation increased to 65 - 85%; likewise, total mercury removal across the FGD increased to 72 - 85%. With the SCR in service, FGD outlet total mercury concentrations ranged from 2 to 4 $\mu\text{g}/\text{dNm}^3$.

Calcium Bromide Injection Results

The calcium bromide test program for Spring 2008 was divided into the following phases:

- Parametric injection testing (30 – 234 ppm Br to the coal) with the SCR off ;
- Parametric injection testing (2 – 54 ppm Br to the coal) with the SCR on (no NH_3);
- Six days of continuous injection at 25 ppm Br to the coal (SCR on, no NH_3); and
- Three days of continuous injection at 50 ppm Br to the coal (SCR on, no NH_3).

During the injection test program, the following parameters were monitored: flue gas mercury oxidation resulting from calcium bromide injection, mercury removal across the pilot FGD scrubber, and the balance of plant effects of calcium bromide injection.

Mercury Oxidation Resulting from Bromide Injection

The furnace injection of calcium bromide resulted in increased mercury oxidation of the flue gas. Three injection rates were evaluated during parametric testing with the SCR off: 234 ppm, 90 ppm, and 30 ppm Br in the coal. At an injection rate of 234 ppm, the mercury oxidation at the FGD inlet was 97%. This oxidation percentage decreased with decreasing injection rate to approximately 69% at the lowest tested rate of 30 ppm.

Five injection rates were evaluated during parametric testing with the SCR on (no NH_3), ranging from 2 to 54 ppm Br in the coal. When compared with the parametric data collected with the SCR off, these data show the important role the SCR plays in oxidizing mercury. At an injection rate of 28 ppm Br in the coal with the SCR on (no NH_3), the percent of mercury oxidized at the FGD inlet was 99%. With the SCR off, an injection rate of 234 ppm Br in the coal was required to achieve >95% mercury oxidation.

During a six-day continuous injection test at 25 ppm Br in the coal, mercury oxidation at the FGD inlet increased over the first three days of the test period from 83% to 97%; mercury oxidation was sustained at 97% for the last three days of the 25 ppm Br test period. Increasing

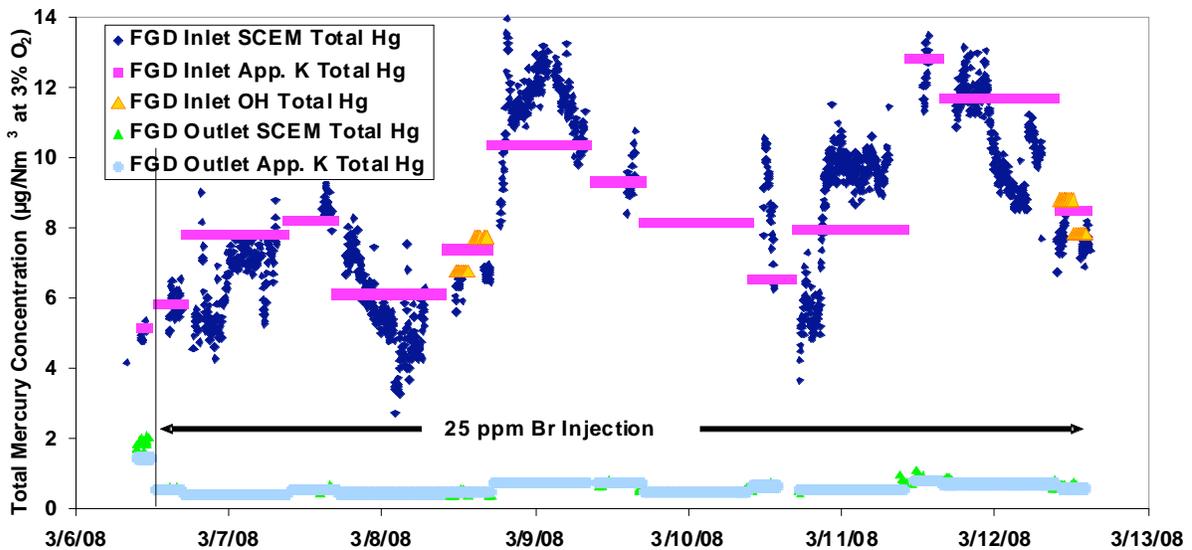
the injection rate to 50 ppm Br in the coal resulted in a very slight increase of mercury oxidation at the FGD inlet to 98%, which was sustained over the three-day test period.

Mercury Removal across the FGD Scrubber

In this test program, a pilot wet FGD scrubber was operated using a slipstream of flue gas from the ESP outlet. Flue gas mercury measurements confirmed that mercury oxidized by the calcium bromide injection process was scrubbed with >95% removal efficiency. Net removal of mercury was limited by re-emissions when the SCR was not in operation, both during baseline (0 to 33% oxidized Hg re-emitted) and bromide injection testing (0 to 21% oxidized Hg re-emitted). Mercury re-emissions were not observed when the SCR was in operation (no NH₃) during either baseline or bromide injection testing.

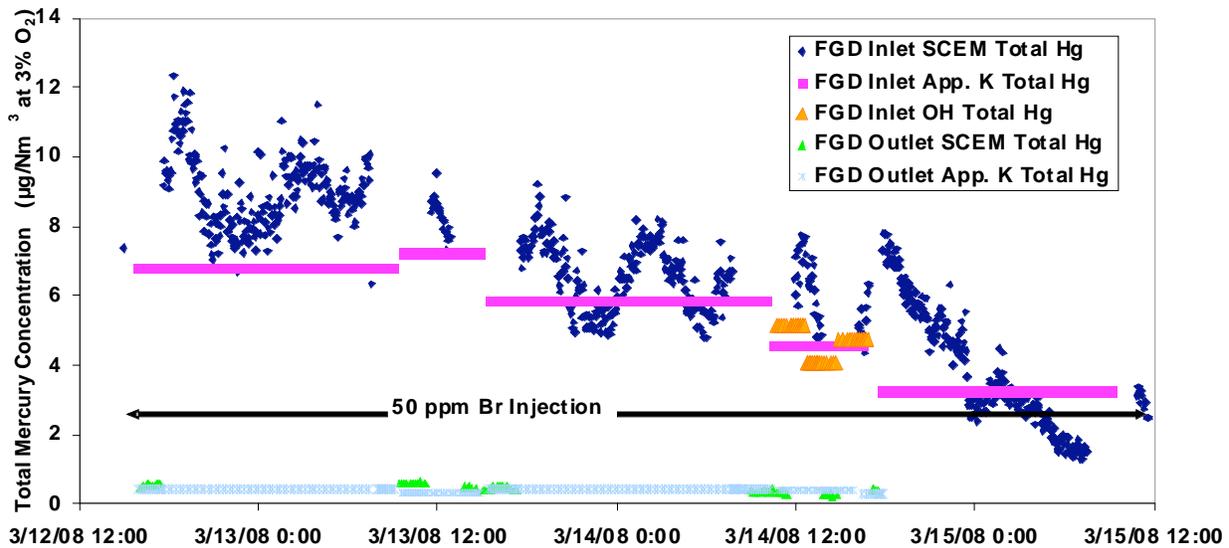
Based on the parametric injection tests, injection rates of 25 ppm and 50 ppm Br to the coal were selected for longer-term continuous injection tests. During a six-day continuous test of 25 ppm Br injection, FGD outlet mercury concentrations ranged from 0.4 to 0.9 µg/dNm³, as compared to coal inlet mercury concentrations of 6 to 9 µg/dNm³ (Figure 3). An overall system mercury removal of >90% was sustained for the six-day test. Oxidized mercury removal across the FGD averaged 95%, and total mercury removal across the scrubber averaged 93%. No re-emissions of absorbed oxidized mercury were observed.

Figure 3: Total Vapor Phase Mercury Measurements Made Around the FGD Scrubber During Long-Term Injection at 25 ppm Br (SCR in service, no NH₃)



Increasing the injection rate to 50 ppm Br to the coal resulted in only a slight increase in mercury removal across the FGD. During the three-day test at 50 ppm Br, the FGD outlet mercury concentrations ranged from 0.3 to 0.6 µg/dNm³ (Figure 4); mercury removal across the scrubber averaged 94%. Once again, no re-emissions of absorbed oxidized mercury were observed. FGD inlet vapor-phase mercury concentrations decreased over the three-day test at 50 ppm Br; however, a similar decrease was also observed on Unit 3, which was not being treated with calcium bromide.

Figure 4: Total Vapor Phase Mercury Measurements Made Around the FGD Scrubber During Long-Term Injection at 50 ppm (SCR in service, no NH₃)



Balance of Plant Effects

While furnace injection of calcium bromide has been demonstrated at Plant Miller and several other PRB test sites as an effective mercury oxidizing agent, these tests have been very short in duration. Few data are available regarding the possible balance of plant effects when this technology is employed over a long-term basis. During this test program at Plant Miller, gas, solid, and liquid samples were analyzed to gather data on the following balance of plant effects:

- Effectiveness of bromine capture by the wet FGD absorber;
- Bromide uptake by fly ash, its effect on fly ash use in concrete, and bromide leaching from fly ash;
- Effect of bromide injection on mercury adsorption by fly ash; and
- Effect of bromide injection on mercury partitioning between wet FGD liquor and solids.

Capture of Flue Gas HBr/Br₂ by FGD

During parametric testing, calcium bromide was added to the furnace at rates ranging between 2 and 234 ppm Br in the coal (dry basis). The resulting flue gas bromide levels were measured at the FGD inlet and outlet. The flue gas bromide concentration increased with increasing calcium bromide injection rate, up to the maximum injection rate of 234 ppm Br in the coal (dry basis), at which point the measured flue gas bromine concentration reached 4.2 ppm in the gas (dry basis, 3% O₂), calculated as HBr. The speciation of HBr and Br₂ in SO₂-rich boiler flue gas by wet impinger techniques is not possible, due to the immediate reduction of water-soluble Br₂ back to HBr by absorbed SO₂.⁴ For injection rates of 25 to 234 ppm Br to the coal, the measured flue gas bromide concentrations were 50–60 % of theoretical predictions, assuming that all injected calcium bromide converted to flue gas HBr or Br₂. The “missing” bromine was not found in the fly ash and may be a result of measurement biases associated with Method 26.

Both HBr and Br₂ are highly soluble in water and should be readily scrubbed by the FGD scrubber. Flue gas total bromine concentrations (expressed as ppm HBr) were measured at the FGD inlet and outlet on several days during the continuous injection tests. At the long-term injection rate of 25 ppm Br, the flue gas total bromine concentration averaged 0.51 ppm as HBr (dry, 3% O₂) at the FGD inlet and 0.02 ppm as HBr at the FGD outlet. At the long-term injection rate of 50 ppm Br, the flue gas total bromine concentration averaged 0.90 ppm as HBr at the FGD inlet and 0.05 ppm as HBr at the FGD outlet. The removal of total bromine across the FGD scrubber ranged from 94 – 96%, which was similar to the SO₂ scrubbing efficiency of the FGD system. The FGD scrubber efficiently removed bromine from the flue gas.

Fly Ash Results

Fly ash samples collected during both baseline and continuous testing were analyzed for total bromide content (Table 2). Only 1% of the bromide injected into the furnace was adsorbed by the fly ash. Leaching tests were performed on the ash samples to determine the amount of bromide that might be released from the ash in a landfill situation. The bromide concentration in the leachate was small, ranging from 0.18 – 0.36 mg Br/L, and represented 50% of the total ash bromide concentration. Fly ash samples from this test program were tested to determine whether the increased bromide content affects the ash’s suitability as a cement replacement for making concrete. There was no adverse effect on quality of concrete made with ash collected during tests with injection rates of 25 ppm Br and 50 ppm Br in the coal.⁵

Table 2. Total Bromide Content and Bromide Leaching Results of First Field Fly Ash Samples.

Date of Sample	Injection Condition	Ash Br Content by Neutron Activation (µg Br/g ash)	Br Content of SPLP leachate (mg Br/L leachate)
2/22/08	Baseline	1.2	0.03
2/23/08	Baseline	<0.5	0.03
3/8/08	25 ppm Br	10.6	0.36
3/9/08	25 ppm Br	9.3	0.18
3/12/08	25 ppm Br	12.2	0.34
3/15/08	50 ppm Br	8.3	0.16

Fly ash samples collected from Miller Unit 4, which was treated with calcium bromide, were compared with fly ash samples from Miller Units 1-3, which were not treated with bromide. The fly ash mercury concentrations of both sets of samples were similar throughout the test program (Table 3), indicating that bromide injection did not result in increased mercury adsorption by the fly ash. These results were affirmed by flue gas mercury measurements made by the plant’s uncertified stack mercury monitors, which showed similar trends in mercury concentrations for Unit 3 (untreated) and Unit 4 (treated). The unburned carbon (UBC) content of the fly ash was low, ranging from 0.25% to 0.45% for all samples.

Table 3. Mercury Concentrations of Composite Fly Ash Samples.

Date of Sample	Injection Condition	Unit 4 (Treated) Ash Hg (ppm)	Units 1-3 (Untreated) Ash Hg (ppm)
3/9/08, 3/7/08*	25 ppm	0.382	0.169
3/12/08	25 ppm	0.154	0.300
3/15/08	50 ppm	0.580	0.570

*Unit 4 (treated) sample gathered on 3/9/08; Unit 1-3 (untreated) sample gathered on 3/7/08.

FGD Slurry Results

FGD slurry samples were collected each day and were filtered on-site to separate the liquor from the solids. Analysis of these samples (Table 4) showed that the scrubber liquor contained approximately 0.1% of the mercury in the slurry, with the remaining mercury present in the solids. The mercury content of the liquor did not appreciably increase during calcium bromide injection, while the mercury concentration in the solids increased by approximately 50%. The bulk of the mercury present in the liquor (>75%) was either dissolved or present as particulate mercury less than 0.02 μm in diameter, making it difficult to remove by filtration. The remaining mercury in the liquor (<25%) was present as particulate mercury ranging in size from 0.02 to 0.45 μm .

Table 4. Mercury Concentrations in Absorber Solids and Liquor.

Date	Injection Condition	SCR Operation	Hg in Liquor ($\mu\text{g/L}$)	Hg in Solids ($\mu\text{g/g}$)	Wt % Solids	% Absorber Hg in Liquor	% Absorber Hg in Solids
2/22/2008	0 ppm Br	off	1.52	2.17	34.1	0.1%	99.9%
2/23/2008	0 ppm Br	off	1.14	2.35	27.5	0.1%	99.9%
3/8/2008	25 ppm Br	on / no NH_3	1.76	3.49	28.9	0.1%	99.9%
3/9/2008	25 ppm Br	on / no NH_3	1.63	3.47	32.1	0.1%	99.9%
3/12/2008	25 ppm Br	on / no NH_3	1.98	3.36	30.4	0.1%	99.9%
3/15/2008	50 ppm Br	on / no NH_3	1.62	3.00	29.0	0.1%	99.9%

For the pilot scrubber at Plant Miller, a primary hydroclone was operated and samples of the overflow and underflow were analyzed to determine how mercury partitioned between the two streams. The results are summarized in Table 5. During the 25 ppm Br injection test, the solids entering the hydroclone had a higher mercury concentration of 3.47 ppm as compared to baseline concentration of 2.35 ppm. The hydroclone overflow solids were slightly enriched in mercury (3.60 ppm) and the hydroclone underflow solids had a slightly lower mercury concentration (3.15 ppm). The increase in mercury concentration in the overflow was expected as mercury

concentration is typically higher in the smaller gypsum particles. The mercury partitioning across the hydroclone was very similar to baseline, indicating that the presence of bromide in the scrubber did not fundamentally affect how mercury partitioned to the various gypsum particle sizes. The bromide concentration of the FGD solids was below the detection limit of 0.02 ppm.

Table 5. Mercury Partitioning in Hydroclone.

Date in 2008	Injection Condition	SCR Operation	Absorber			Hydrocyclone Overflow			Hydrocyclone Underflow		
			Hg in Liquor (µg/L)	Hg in Solids (µg/g)	Wt % Solids	Hg in Liquor (µg/L)	Hg in Solids (µg/g)	Wt % Solids	Hg in Liquor (µg/L)	Hg in Solids (µg/g)	Wt % Solids
2/23	Baseline	off	1.14	2.35	27.5	0.37	2.64	16.9	0.45	2.06	53.3
3/9	25 ppm Br	on / no NH3	1.63	3.47	32.1	1.15	3.60	17.9	0.84	3.15	52.2

CONCLUSIONS

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. With the SCR in operation (no NH₃), mercury oxidation of the FGD inlet gas increased from 65 – 85% at baseline to 97% at an injection rate of 25 ppm Br to the coal. No increase in mercury adsorption by fly ash (with low UBC content) was observed. Over 98% of the oxidized mercury was removed in a pilot FGD scrubber, and no mercury re-emissions were observed. During a six-day continuous test of 25 ppm Br injection, FGD outlet mercury concentrations ranged from 0.4 to 0.9 µg/dNm³, as compared to coal inlet mercury concentrations of 6 to 9 µg/dNm³. An overall system mercury removal of >90% was sustained for the six-day test. This test will be repeated in Fall 2008 with the SCR operating with ammonia, as this is the planned year-round mode of operation for the host site.

Less than 1% of the injected bromide was detected in the fly ash. Approximately 50% of the fly ash bromide content was detected in leachate from a simulated landfill condition, and the leachate bromide concentration was small, ranging from 0.2 to 0.4 mg/L. There was no adverse effect on quality of concrete made with ash collected during tests with injection rates of 25 ppm Br and 50 ppm Br in the coal. During the six-day injection test at 25 ppm Br to the coal, the FGD inlet flue gas bromine concentration averaged 0.51 ppm as HBr. The flue gas bromide was scrubbed with 94 – 96% efficiency. For most of the 25 ppm Br injection test, the FGD liquor bromide concentration was controlled to 1500 ppm; none of the bromide was detected in the FGD solids. The increased bromide concentration of the FGD scrubber did not affect how mercury partitioned in the absorber or across the hydroclone filtration system.

The results from this program 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 equipped with an FGD unit. Further work is needed to address the following key issues:

- Longer-term tests are needed to demonstrate that mercury oxidation and removal can be sustained for units without an SCR. This test program demonstrated that >95% mercury oxidation could be achieved at an injection rate of 234 ppm Br, but this test was only five hours in duration. Similar short-term results were obtained at a TxL/PRB plant that did not have an SCR, with 91% oxidation at the FGD inlet at an injection rate of 193 ppm Br.⁶
- The effectiveness of this technology for bituminous coals needs to be investigated.
- Long-term furnace impacts should be evaluated via corrosion coupons or periodic boiler tube corrosion inspections.
- The increased levels of bromide in the scrubber liquor should be evaluated for effects on selection of scrubber materials of construction and blowdown rate.
- The increased concentration of bromide in the FGD liquor should be evaluated for impact on limits of wastewater discharges.

REFERENCES

1. Vosteen, B. et al., "Process for Removing Mercury from Flue Gases," United States Patent # 6,878,358 B2 (filed on May 6, 2003; issued on April 12, 2004) or German Patent # 102 33 173 B4 (filed on July 22, 2002; issued on March 23, 2006).
2. Vosteen, B. et al., "Bromine-enhanced Mercury Abatement from Combustion Flue Gases – Recent Industrial Applications and Laboratory Research", VGB PowerTech, Volume 86, Issue 3/2006, 70–75.
3. Berry, M. et al., "Mercury Control Evaluation of Calcium Bromide Injection into a PRB-Fired Furnace with an SCR," Air Quality VI, Arlington, VA, September 2007.
4. Kanefke, R., "Durch Quecksilberbromierung verbesserte Quecksilberabscheidung aus den Abgasen von Kohlekraftwerken und Abfallverbrennungsanlagen", Doctoral Thesis, Martin Luther University Halle-Wittenberg, April 15, 2008, Shaker Verlag, Aachen (ISBN 978-3-8322-7241-8, ISSN 1611-8057).
5. Larrimore, L. et al., "Effects of Bromine Addition on Flyash Use in Concrete," MEGA Symposium, Arlington, VA, August 2008.
6. Dombrowski, K. et al., "Mercury Control Field Testing at Monticello Steam Electric Station." Site Report for U.S. DOE-NETL Cooperative Agreement DE-FC26-03NT41991. November 2006.