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Mercury Emissions Control Technology Selection – Let Installed Air Quality Control System (AQCS) Equipment Guide Technology Choice

Authors:

M. Gadgil

S. Feeney

*Babcock & Wilcox
Barberton, Ohio, U.S.A.*

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AUTHORS

Mandar Gadgil (The Babcock & Wilcox Company) – Lead
Steven Feeney (The Babcock & Wilcox Company)

ABSTRACT

A variety of technologies are available for mercury emissions reduction from coal-fired power plant stack gas. Some of the most common technologies are: 1) halogen addition to the coal for mercury oxidation, with subsequent capture; 2) various sorbent additions to the coal and/or injections into the flue gas; and 3) addition of chemicals and/or sorbents into the wet flue gas desulfurization (FGD) absorbers or dry FGD vessels. These technology choices are driven by the equipment in place. One approach would be favored for a plant having only a cold-side electrostatic precipitator (ESP) and no FGD, whereas another would be more effective for a dry FGD with a fabric filter baghouse. Data will be presented from a number of tests conducted during the past few years showing how the technology choice was driven by the site-specific conditions of each plant. Cost comparison analysis will be presented for different technologies for mercury emissions compliance. Finally, data will also be presented from recent testing using the electrochemical noise (ECN) probe technique to determine the rate of air heater corrosion when adding halogen to coal for mercury oxidation.

INTRODUCTION

There is a worldwide effort to control mercury emissions from coal and biomass fired power plants [1]. The United States Environmental Protection Agency (USEPA) requires electric generating power plants firing bituminous and subbituminous coals to limit the stack mercury emission at or below 1.2 lb/TBtu (approximately 1.3 ug/m³) as per the Mercury and Air Toxic Standards (MATS) rule. There are many proven technologies available for mercury emission control. The control technologies include use of mercury sorbents such as brominated or non-brominated activated carbon, or various forms of phyllo-silicates to capture mercury within the solid matrix of the injected particulate. Halogens such as bromine or iodine can be added to the coal to increase gas-phase mercury oxidation, with subsequent removal of the oxidized mercury in downstream emissions control equipment. With wet FGD systems, the readily dissolved oxidized forms of mercury in the gas-phase can be absorbed in the liquid phase and removed in combination with one or more suitable additives. Each control technology has its advantages and disadvantages. The objective of this paper is to perform an analysis of the different mercury capture technologies from the perspective of cost effectiveness, and potential balance of plant (BoP) impacts.

MERCURY CAPTURE TECHNOLOGIES

HALOGEN ADDITION FOR MERCURY OXIDATION

The simplicity of addition and ease of maintenance is a distinct advantage of adding halogen directly to the coal for mercury oxidation (or even the virtual equivalent of adding a halogen to the flue gas stream separate from the coal). Adding halogen to the coal has been used for different types of coal with different AQCS equipment downstream of the boiler. Chlorine, bromine, and to a lesser extent, iodine have been the halogens of choice for mercury oxidation. The addition of bromine to the coal as a solution of calcium bromide has been the most prevalent based on cost and effectiveness.

The application rate of bromine or any halogen to achieve a particular level of gas-phase mercury oxidation depends in large part upon the presence or absence of a selective catalytic reduction (SCR) system used for nitrogen oxides (NO_x) control. For example, when an SCR system is installed, the SCR catalyst can reduce the application rate of bromine by 50 to 80% compared to the application rate of bromine when there is no SCR.

INJECTION OF ACTIVATED CARBON FOR MERCURY CONTROL

Injection of powdered activated carbon (PAC) in the flue gas exiting the boiler is also an effective and common mercury emissions control technology. The carbon can either be non-brominated or brominated. The non-brominated PAC can only remove the oxidized mercury from flue gas, whereas the brominated PAC can remove both oxidized and elemental mercury, since the bromine in the PAC acts as a mercury oxidizer. The PAC is injected pneumatically using injection lances and is then removed from the gas by an ESP or fabric filter along with the mercury adsorbed on the surface of PAC.

EFFECTIVENESS OF BROMINE INJECTION FOR MERCURY EMISSIONS CONTROL

Testing was performed at a 220 MW electric generating unit in the midwestern United States. The plant burns subbituminous Powder River Basin (PRB) coal and is equipped with SCR, circulating dry scrubber (CDS) and fabric filter as AQCS equipment. The plant also uses brominated PAC injection on site for mercury emissions control. Testing was performed with brominated PAC injection into the flue gas after the air heater and with calcium chloride and calcium bromide injection to the coal to measure mercury emissions reductions. The data from the testing is shown in Table 1. The objective was to achieve stack mercury emissions below 1.2 lb/Tbtu (1.3 ug/m³) for an 8-hour period as a result of the additive injection.

Table 1: Estimated Mercury Emission Control Costs with Different Technologies

Day	Additive	Injection Rate	8 hours Average Stack Hg in lb/TBtu	Expected Operating Cost US\$/hr	Expected Capital Cost US\$Million
1	Baseline	0.0	4.8 (5.3 ug/m ³)	0.0	0.0
	Brominated PAC	52 lb/hr (24 kg/hr)	1.0 (1.1 ug/m ³)	58	0.8 to 1.0
3	Calcium Chloride Solution	300 ppm (29 kg/hr) to coal	1.8 (2.0 ug/m ³)	36.5	0.20
4	Calcium Bromide Solution	40 ppm (4 kg/hr) to coal	1.1 (1.2 ug/m ³)	50	0.20
5	Powdered Calcium Bromide	30 ppm (3 kg/hr) to coal	1.2(1.3 ug/m ³)	37.5	0.5 to 0.7

As seen from the data the baseline emission was 4.8 lb/TBtu. With the injection of brominated PAC at the air heater outlet, the plant stack mercury emission was 1.0 lb/TBtu. The injection rate was 24 kg/hr of brominated PAC which resulted into an expected operating cost of US\$58/hr to achieve MATS emissions limits. Two different types of halogens were tested at the plant to investigate their effectiveness for mercury oxidation. With an addition of 300 ppm of calcium chloride to the coal, in the form of a solution of calcium chloride, the mercury oxidation improved from 30% under the baseline conditions to 51% at the air heater outlet; the stack mercury was reduced to 1.8 lb/TBtu. This reduction was not sufficient to achieve MATS emissions limits.

Two different forms of bromine injection were also investigated. On the first day, bromine in the form of a solution of calcium bromide was added to the coal using simple pump injection skids. With an addition of 40 ppm of bromine to the coal on a dry basis, the mercury oxidation was 76% at the air heater outlet and the stack mercury was 1.1 lb/TBtu. The expected operating cost was US\$50 per hour. This was comparable to that of brominated PAC. On the second day of injection, calcium bromide was added to the coal in a powder form. The objective was to determine if the powdered calcium bromide can provide the same performance as that of liquid calcium bromide injected into the coal. As seen from the data the performance was essentially the same for both powder and liquid bromine injection. The powdered calcium bromide injection was more complicated and is resulting in certain operational difficulties. Therefore, powdered calcium bromide injection was not the injection method of choice for this application.

As seen from the Table 1, it would appear that calcium bromide injection in liquid form will offer small operating cost savings as compared to activated carbon injection. The main savings is in the capital cost as the calcium bromide injection requires a simple injection skid set-up that can cost approximately US\$200,000 compared to an almost US\$1.0 million investment required for the PAC addition equipment. In addition to the extra cost, PAC injection can also potentially affect flyash sales due to the presence of carbon in the ash. In applications with a CDS in which the ash is recirculated back from the fabric filter to the CDS via air slides, the presence of PAC presents fire safety design concerns that must be addressed. There is also a possibility of adsorbed mercury leaching from the PAC under landfill conditions.

As a result, for many subbituminous units with FGD, either with, or without SCR, the use of a calcium bromide addition to the coal is a common technology to achieve MATS emissions limits. Many units which have PAC systems installed, only use it as additional control if halogen injections are insufficient. For subbituminous units with only an ESP or a fabric filter, the technology of choice is typically brominated PAC.

INJECTION EFFECTS

BALANCE OF PLANT (BOP) EFFECTS OF HALOGEN INJECTION FOR MERCURY OXIDATION

As bromine addition to the coal has become more common for mercury oxidation and emissions control, in some cases there have been negative balance of plant impacts due to bromine application. These effects include an increased rate of corrosion, especially in the air heaters, an increased formation of tri-halo methanes (THM) in water, and also, at times, an increase in certain selenium compounds in water. Formation of THM is an undesired side effect of bromine injection for mercury oxidation. Many jurisdictions impose limits on THMs. This THM phenomenon can be observed with both bromine injection for mercury oxidation and also with use of brominated PAC. Bromine cannot be removed by more conventional wastewater treatment (WWT) methods (such as chemical precipitation) or even more advanced techniques such as bio-reactors. THM formation is dependent on bromine/chlorine in water and the most cost effective method of reducing the THM formation is reduction in the use of bromine application for mercury oxidation.

EFFECT OF HALOGEN INJECTION ON SELENIUM SPECIATION IN COMBUSTION SYSTEMS

Due to its affinity for halogens such as chloride, its several oxidation states in the aqueous phase, and the relatively low boiling point of certain selenium halogen compounds, selenium emissions control from power plant flue gas can be a very difficult and challenging task. A possible mitigation or control technology could involve improving the performance of plant particulate collection devices, since a portion of gas-phase selenium can be adsorbed onto ash particles. However, there are practical limitations to the ability of particulate collection devices for removing very fine aerosols. Based on the U.S. EPA database, power plants equipped with fabric filters can achieve higher removal (80 to 90%) for particulate selenium as compared to power plants equipped with ESPs, which can achieve around 60 to 70% of selenium removal in particulate phase. Calcium selenate is an order of magnitude more soluble than calcium sulfate, so on power plants equipped with wet limestone FGD units, selenium in the wastewater is a concern. Within the limestone forced oxidation (LSFO) wet FGD systems, the dominant forms of aqueous selenium are selenite (Se^{+4}) and selenate (Se^{+6}). Selenium removal from wet FGD wastewater becomes more challenging if it is in its selenate state. In its selenite (Se^{+4}) state, most selenium is in the solid form in the scrubber slurry and therefore can be removed comparatively easily by the physical and chemical process. If selenium is in its selenate (Se^{+6}) phase, a more substantial dissolved phase in the slurry can result, and hence it cannot be removed by the conventional chemical precipitation waste treatment technology. It therefore enters the wastewater and special and expensive treatment equipment, such as bio-reactors, may be required. Regulation of selenium from wastewater discharge has been proposed by the EPA in the draft Effluent Limitation Guidelines (ELG).

At the 2012 Power Plant Air Pollution Control Mega Symposium, it was reported by others that when calcium bromide was injected for mercury oxidation, a significant increase in selenium concentration in the wet FGD system was also observed [2]. No gas-phase selenium sampling or selenium speciation determinations were performed at the time when making these observations.

FIELD RESEARCH ON SELENIUM EMISSIONS

During two different field tests performed by Babcock & Wilcox (B&W) involving bromide injection, gas-phase selenium sampling was performed at an ESP inlet at one site (Site A). Site A burns Eastern bituminous coal. It has an SCR, ESP and wet FGD as air quality control system (AQCS) equipment. Calcium bromide injection was performed for mercury oxidation. The data for Site A is shown in Table 2.

Table 2: Site A — Effect of Halide Injection on Trace Elements Emission

	ESP Inlet A Side Duct (ug/dscf)	ESP Inlet B Side Duct (ug/dscf)
Baseline selenium	7.41×10^{-6}	3.24×10^{-6}
Selenium with bromide injection	3.94×10^{-5}	3.35×10^{-6}

The flue gas sampling was performed both on A side duct and B side duct. The results for gas-phase selenium emissions are reported in units of ug/dscf. For selenium it was observed that on the B side, the amount of gas-phase selenium remained relatively the same with and without injection of bromide for mercury oxidation. On the A side there was a considerable increase in gas-phase selenium with injection of bromide for mercury control. The wet FGD slurry samples collected during this test period also showed a significant increase in the selenium content. This observation was in line with observations reported at the Mega Symposium [2]. Based on this observation, it is possible that gas-phase bromide was reacting with selenium adsorbed on ash and releasing it back in the gas phase. This reaction is possibly taking place after the air heater in the cooler gas temperatures. Whatever the ultimate mechanism may be, there was an increase in gas-phase selenium with injection of bromide to the coal. This same phenomenon has been observed with injection of brominated PAC at the air heater outlet location, and therefore is not limited to use of calcium bromide injection to the coal.

CORROSION

AIR HEATER CORROSION

In the early days of calcium bromide injection on units burning lower rank fuels, a number of cases of air heater corrosion were observed. This is especially true in the last several inches of the cold-end basket where the coldest temperatures occur within the air heater [3]. In many cases, air heater corrosion occurred very quickly, sometimes within months of the start of the calcium bromide injection process. The rate of corrosion depends upon the operation of the unit (in particular with respect to load swings), whether a steam coil air heater is used to preheat the cold air, materials of construction, and the application rate of calcium bromide. The most likely mechanism for the air heater corrosion is direct condensation of hydrogen bromide (HBr) gas on the metal. Even though the dew point of HBr is lower than that of SO₃, on low halogen, low sulfur coals when adding a halogen for

mercury oxidation, the air heater corrosion is mainly from HBr and not from SO₃. This is because the concentration of SO₃ in the flue gas is much less than the concentration of HBr. Depending upon the moisture content of the flue gas and the HBr concentration in the gas phase, the dew point of HBr can be as low as 125F (51.7C). The metal temperature of the cold end of the air heater as it rotates back into the flue gas stream can be below the acid dew point temperature of HBr. This can therefore provide the sites for the HBr from the gas phase to condense on the metal. As a result, the possibility of cold-end corrosion for air heater baskets increases.

LOW-TEMPERATURE CORROSION

Air heater corrosion is a risk with use of bromine on low-rank (high-moisture) subbituminous or lignite coals. Like hydrochloric acid, hydrobromic acid is aggressive in the presence of moisture below its dew point temperature. The dew point temperature depends on the concentrations of both acid and moisture in the flue gas. An example of acid dew point temperature versus HBr concentration for a flue gas containing 12.5% moisture (typical of 8,900 Btu/lb PRB coal burned with 3% excess oxygen) is given in Figure 1. Acid dew point temperature is reduced by 10F (5.6C) by reducing the bromine addition rate from 200 ppm (0.02%) to 50 ppm (0.005%) [4]. The greatest risk for corrosion of this type is in the cold-end air heater baskets during rotation from the air duct into the flue gas duct. Experience has shown that the air heater cold-end basket corrosion risk is dramatically reduced at and below 50 ppm addition rates of bromine (dry coal basis) to PRB coals. The main preventive measure is to maintain metal temperatures above the acid dew point or saturation temperature of the flue gas by using air preheat steam coils for those units exceeding an approximate 50 ppm bromine addition rate. As an extra precaution, cold-end baskets may be coated with enamel to protect the metal against acid attack.

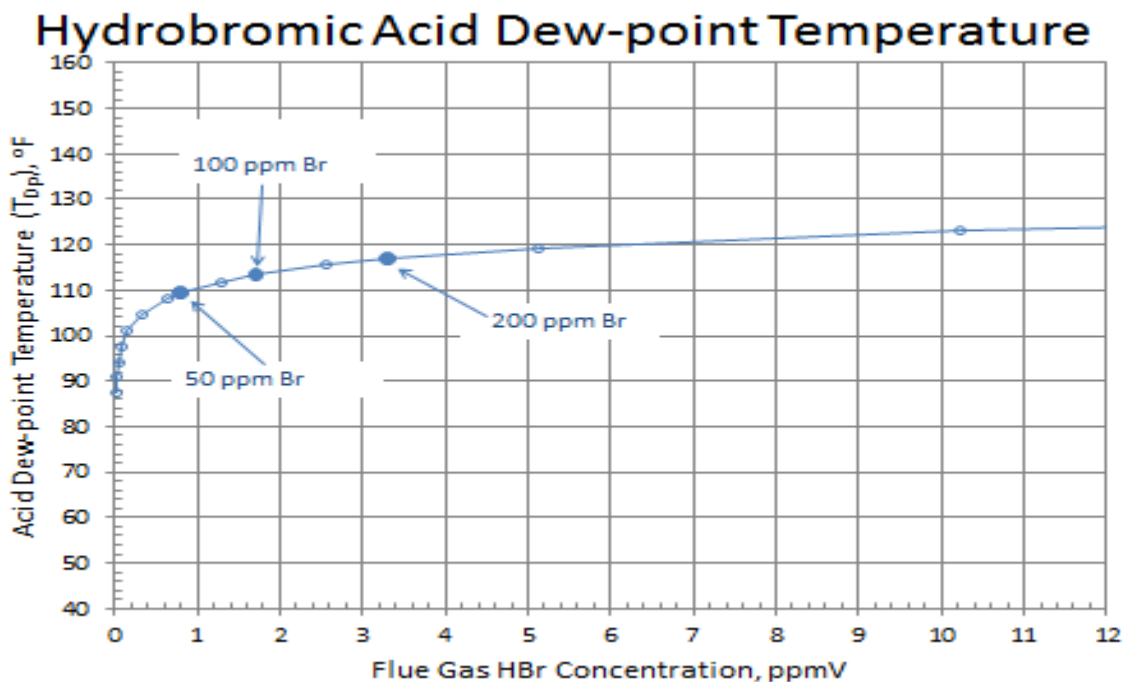


Figure 1: Acid Dew Point Temperature vs. Flue Gas HBr Concentration (12.5% Moisture).

ELECTROCHEMICAL NOISE MONITORING

To obtain a real-time indication of corrosion to air heater baskets during halogen addition, a measurement system based on electrochemical noise (EN) sensing was utilized. 'Traditional' corrosion monitoring instrumentation such as electrical resistance or linear polarization measurement equipment is unable to provide meaningful results in this service.

The principle of operation of EN corrosion sensing technique is that spontaneous fluctuations in the measured electrical potential and current signals are generated during electrochemical corrosion activity [5].

CORROSION RATE MEASUREMENT TESTING

There were two main objectives for the corrosion rate measurement testing using the ECN probe.

- 1) To investigate the halogen injection rate required to obtain high (90% plus) mercury oxidation
- 2) To measure the rate of corrosion associated with the rate of halogen injection needed to achieve this 90% gas-phase mercury oxidation.

To achieve these two objectives, testing was performed at an 80 MW power generating unit in the mid-western U.S. The unit is corner fired with an ESP as the only AQCS equipment. Bromine in the form of a calcium bromide solution and iodine in the form of a potassium iodine solution were used for the testing.

MONITORING EQUIPMENT

The corrosion monitoring system is shown in Figure 2 and consists of an air-cooled cross-flow probe with sensor elements machined from materials representative of those used in the location of interest, an instrument box, and a control computer. The sensor element alloy chosen for this campaign, A-192, is a plain carbon steel that is a common selection for air heater basket elements. Other common basket materials, such as low alloy Corten (weathering steel), or enamel-coated carbon steel, are more resistant to corrosion over long periods. It would not be meaningful to conduct short-term tests on either of these materials. Enamel coating prevents attack of the underlying air heater element metal as long as the integrity of the enamel coating is not compromised. The corrosion protection mechanism of Corten is different. It can be more resistant to corrosion longer-term but this is reliant upon the development of a finely divided and tightly adherent corrosion product. Consequently, Corten initially may exhibit similar, or possibly even higher, rates of corrosion than plain carbon steel. However, multiple wetting and drying cycles develop a patina over the course of weeks or months and then the subsequent corrosion rate is lower than that of carbon steel. Therefore, corrosion rates measured over a period of a few days will not be representative of long-term material loss.



Figure 2. Corrosion monitoring system (clockwise from upper left), a) instrument box, b) inserted probe, c) corrosion probe with sensor elements, d) control computer.

It should be noted that corrosion rates measured in this campaign are difficult to extrapolate to long-term rates expected on air heater elements. The sensor elements were held at a constant temperature, whereas air heater basket metal temperatures are cyclic in time, due to the air heater rotation into the cold incoming combustion air, which is often pulled from outside the boiler house, then cycling back into hot flue gas with higher acid concentrations, which immediately condenses on the cold metal and then re-evaporates, concentrating as it does so. Table 3 shows the results obtained from the corrosion testing. Both bromine and iodine additions to the coal were able to achieve the high mercury oxidation as required. The high oxidation was achieved at an injection rate of 150 ppm of bromine added to the coal whereas with iodine, the same high percentage of oxidation was obtained at 10 ppm addition rate to the coal.

Table 3: Effects of Halogen Injection on Mercury Oxidation and Air Heater Corrosion

Test ID	Hg Oxidation @ AHO %	Rate of Corrosion Mil/year	Expected Injection Cost \$/hr
Baseline	50.0	0.16	0.0
25 ppm Br	78.0	0.26	8.0
75 ppb Br	83.0	0.39	25.0
150 ppm Br	94.5	1.2	50.0
10 ppm Iodine	93.0	0.16	28.0
25 ppm Iodine	99.0	0.31	76.0

The results from Table 3 suggest iodine may be a better mercury oxidation additive when all impacts are considered: expected injection cost, ability to exceed 90% mercury oxidation, and rate of corrosion. While only 10 ppm of iodine achieves 93% mercury oxidation, a rate of 150 ppm bromine is needed for similar oxidation. Further, the rate of corrosion is an order of magnitude greater for the required bromine addition rate. More data will be necessary to confirm the observation from this particular test.

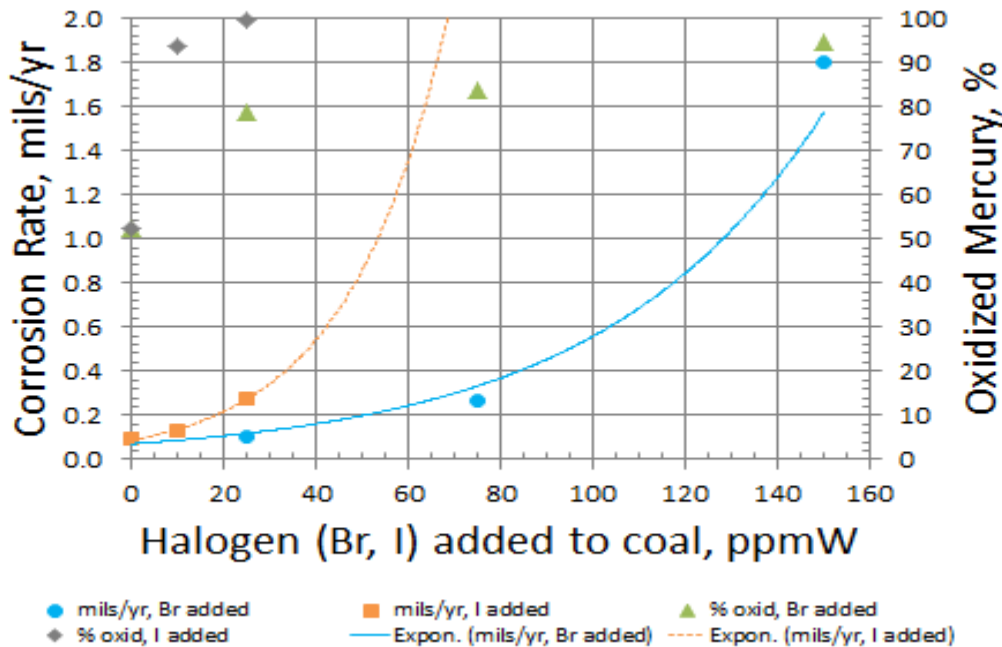


Figure 3: The rate of corrosion as a function of injection concentration of bromine and iodine [6].

As seen from Figure 3, the corrosion rate is a function of the application rate of bromine to the coal. As the application concentration of bromine increases, the rate of corrosion also increases. This is where the presence of an SCR catalyst that can efficiently convert the added bromine from HBr to the diatomic bromine (Br_2) is of great importance. As a result of the presence of an SCR, high mercury oxidation can be obtained at low injection rates of bromine. Many units do not have SCRs installed and as such, they require higher injection rates of bromine as the conversion of HBr to Br_2 is low in absence of a catalyst. A lack of an SCR results in a higher required injection rate of bromine to the coal creating a potential additional concern.

MITAGENT ADDITIVE

BENEFITS FROM MITAGENT ADDITIVE FOR REDUCTION OF HALOGEN INJECTION RATE FOR MERCURY CONTROL

As discussed above, the rate of corrosion depends on the addition rate of bromine to coal. In the combustion process the added bromine forms HBr gas in the furnace. A portion of the HBr gas converts into Br_2 that can then react with elemental mercury to form $HgBr_2$ or the oxidized mercury.

These reactions are as shown in Equations 1 and 2.



The unconverted HBr gas is the main cause of air heater corrosion as the dew point of HBr is around 125F (51.7C). Reduction of the HBr concentration in the flue gas should result in a reduction in the corrosion rate as well as seen from Figure 3. B&W's Mitagent additive, which provides among other things a method by which to tie up gas-phase phosphorus, also has been shown to achieve a reduction in the application rate of bromine or a bromine-containing compound regardless of whether or not an SCR is installed. While not wishing to be bound to any one theory, it is believed that B&W's Mitagent additive accomplishes this via catalyzation of the bromine Deacon Reaction, reducing the needed application rate of bromine for equivalent levels of gas-phase mercury oxidation. The data presented below from full-scale unit testing demonstrates the reduction in bromine usage for units without an SCR [4]. The full-scale test was performed at a midwestern U.S. power plant with an 82 MW gross electric generating unit burning subbituminous PRB coal. This unit only has an ESP as the AQCS equipment. The objective of the field testing was to demonstrate similar or better mercury oxidation using B&W's Mitagent combustion additive with lower bromine application rate than the oxidation obtained with higher bromine application rates. For the testing, the oxidized mercury at the stack was measured by the U.S. EPA method 30B (modified for speciation) also known as the modified sorbent trap method. Table 4 shows the mercury oxidation measured at the stack as a result of the Mitagent additive to the coal.

Table 4: Effect of Mitagent Additive on Halogen Addition and Mercury Oxidation

Bromine addition rate to coal In mg/kg	Mitagent addition rate to coal In kg/hr	% oxidized Hg at Stack
0	0	38
60	0	47
100	0	62.5
40	15	56

The data in Table 4 shows that the average mercury oxidation was 38% without addition of halogen and Mitagent additive to the coal. With the addition of 60 mg/kg of bromine to the coal, the average mercury oxidation without the Mitagent additive was 47%. With the addition of 100 mg/kg of bromine to the coal, the mercury oxidation without the Mitagent additive was 62.5%. With the Mitagent additive to the coal at 15 kg/hr and bromine at 40 mg/kg, the average mercury oxidation at the stack was 56%. This testing demonstrated that with the addition of B&W's Mitagent additive to the coal, the bromine addition rate can be reduced significantly (potentially even by half in some instances tested) while achieving the same gas-phase mercury oxidation. The benefits of reducing the bromine addition rate to the coal include reduction in cost, a reduction in the rate of corrosion, and depending on AQCS equipment configuration, less bromine discharged from the plant.

FIELD TESTING

FIELD TEST FOR MERCURY EMISSIONS COMPLIANCE

The second objective of the field testing described above was to achieve stack mercury emission below 1.2 lb/TBtu as a result of the addition of various sorbent additives. These chemicals were tested because some hold the possibility of removing gas-phase oxidized mercury similar to non-brominated PAC but at a lower price. The performance demonstration testing took place from December 10, 2013, through December 12, 2013. Proprietary Sorbent A was added to the coal along with halogen and the Mitagent additive on December 12. With the addition of only 20 ppm of bromine to the coal and a mixture of solid sorbents added to the coal at a rate of 100 lb/hr (45.4 kg/hr), the average total mercury in the stack was 0.6 lb/TBtu as shown in Figure 4. The spike on the graph was the result of sorbent injection issues near the end of the test.

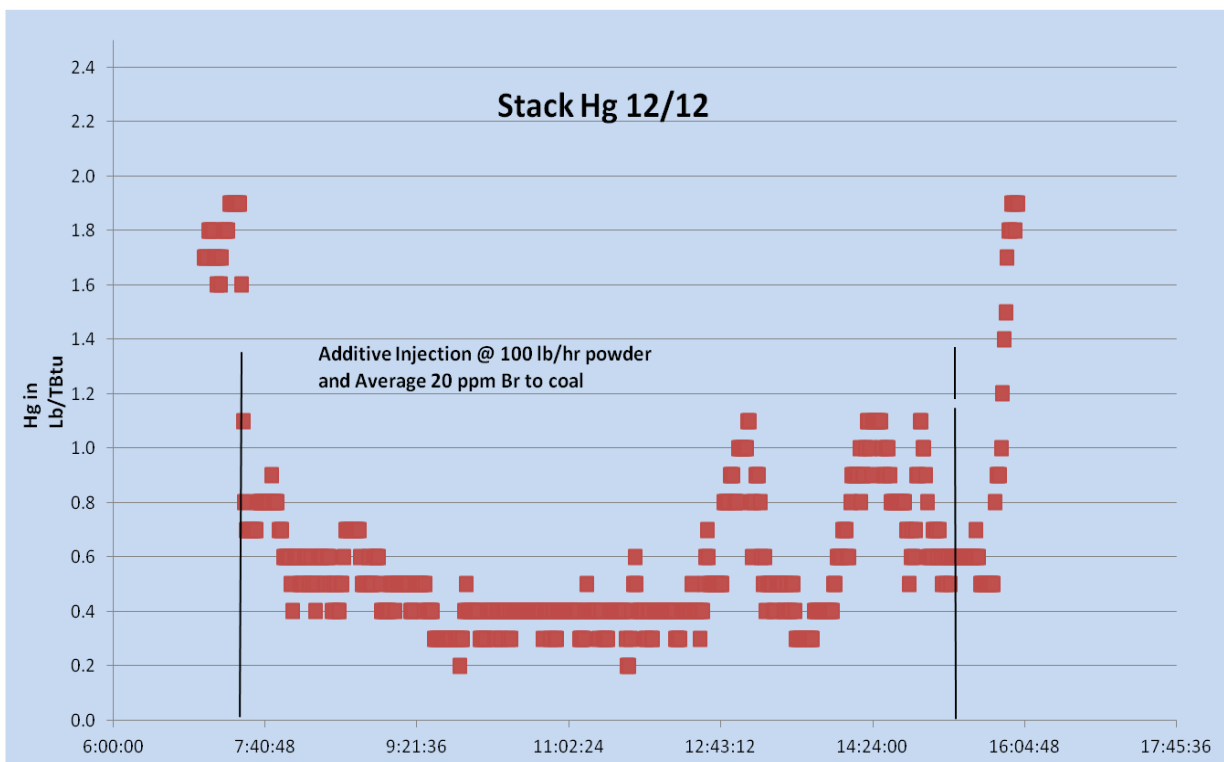


Figure 4: Stack mercury emissions with additive injection.

As shown in Figure 4, the stack mercury emissions before the start of the injection was approximately 1.8 lb/TBtu. With the injection of the additive to the coal, the stack mercury emission was reduced to an average value of 0.6 lb/TBtu during the injection period from 8 AM to 3:30 PM. The stack mercury increased back to the baseline mercury values once the injection was stopped. One of the most important advantages of the blended additive used for mercury control is that it can remove the mercury in a particulate bound form [4]. This advantage could be very beneficial for units with wet FGD systems, as the removal of the majority of the mercury before the wet

FGD will reduce the concerns associated with mercury in the gypsum or the wet FGD wastewater. Table 5 compares the expected cost of achieving the mercury emissions compliance target with use of brominated PAC, non-brominated PAC and a proprietary additive mixture. This comparison is based on the expected injection rates necessary to keep stack mercury emissions below 1.0 lb/TBtu (approximately 1.1 ug/m³).

Table 5: Mercury Emission Control Costs with Different Technologies

Sorbent	Injection Rate Kg/hr	Bromine injection rate ppm	Stack Hg emission	Expected Operating Cost \$/hr	Expected Capital Cost \$Million
Brominated PAC	25	NA	1.0	60.5	0.7-1.0
Non Brominated PAC	25	100	1.0	65	0.8-1.0
Proprietary Sorbent B	25	NA	1.0	70	0.7-1.0
Proprietary Sorbent A	45	40	1.0	40	1.0-1.2

It can be seen from the data in Table 5 that the injection rates of the different sorbents are almost the same for both types of PACs and Proprietary Sorbent B, whereas the rates of the blend of the Mitagent additive and the proprietary additives (as used in the testing shown in Figure 4) is higher. With respect to the operating cost, the blended sorbent with Mitagent additive has the lowest cost. This is mainly because the materials used in the Mitagent additive blend are inexpensive, naturally occurring, and widely available in the U.S. as compared to the other sorbents that must be manufactured. The capital cost is expected to be somewhat higher for the proprietary blended sorbent due to the higher injection rates.

Overall for power plants firing subbituminous coals, the bromine addition to the boiler and use of suitable mercury sorbents can be a lower-cost option for mercury emissions control as compared to injection of brominated PAC, as long as the bromine addition rate is low enough so that the effects on the balance of plant can be minimized.

BITUMINOUS COAL MERCURY EMISSIONS CONTROL

For units operating with bituminous coals, the mercury emissions control strategy can be achieved by using multiples technologies such as PAC injection or by using the oxidation of mercury and capture with FGD. Many of the bituminous coals have wet FGD for SO₂ emissions control. Due to the higher sulfur contents in the coal, the SO₃ concentration in the flue gas is higher than lower rank fuels. This higher SO₃ concentration makes it difficult to use PAC injection by itself as SO₃ preferentially occupies valuable sites on the PAC surfaces and therefore, crowds out sites for the capture of mercury. If SO₃ is adsorbed on the carbon instead of mercury, even more PAC must be added. One frequent method to overcome this limitation is installing a dry sorbent injection (DSI) system upstream of the PAC injection system. This can significantly increase the cost of mercury emissions control. Additionally, wet FGD systems can pose additional challenges. Once the wet FGD system becomes saturated with elemental mercury (Hg⁰), stripping occurs. However, if the oxidized mercury level in the wet FGD liquor can be held below saturation, this allows enough room for the elemental mercury to remain sub-saturated. Commonly referred to as mercury *re-emission*, this is a saturation issue resulting from not satisfying the mercury mass

balance across the wet FGD system. Chemical additives, generally various forms of sulfides, can be added to the wet FGD system to precipitate mercury from the aqueous phase of the slurry liquor to maintain sub-saturation. B&W's patented Absorption Plus (Hg)[®] process uses an inexpensive sulfide to eliminate what is commonly referred to as mercury re-emission. B&W's Absorption Plus (Hg) additive was developed for the same purpose and the following field testing data demonstrates the capability of mercury emissions control on a bituminous coal-fired unit with SCR and FGD by only adding bromine to the coal and Absorption Plus (Hg) to the wet FGD.

In the first quarter of 2014, testing was performed at a 930 MW unit in the mid-western U.S. The objective was to determine the effectiveness of certain additives and their impact on mercury emissions. The testing was carried out on unit #2, a 930 MW unit burning eastern high sulfur coal. Both units 1 and 2 at the plant are equipped with a plumb-bob scrubber designed to remove both particulate and SO₂. The wet scrubber uses magnesium lime-based scrubbing with sodium thiosulfate to inhibit oxidation. The purpose of the bromine addition was to achieve high mercury oxidation because at the time of the testing, the SCR catalyst was experiencing high ammonia slip. As discussed earlier, the mercury re-emission effect is caused by mercury saturation of the scrubber slurry aqueous phase, and can be eliminated once the system is sub-saturated with respect to elemental mercury. This mercury sub-saturation can be achieved either via the use of activated carbon injection into the scrubber, or the use of sulfide-based precipitating agents. Figure 5 shows the mercury concentrations data for Absorption Plus (Hg) injection testing as identified by MRE2 on the graph. The graph not only includes the mercury concentrations, but the boiler load, bromine addition rate onto the coal, and sulfide addition rate.

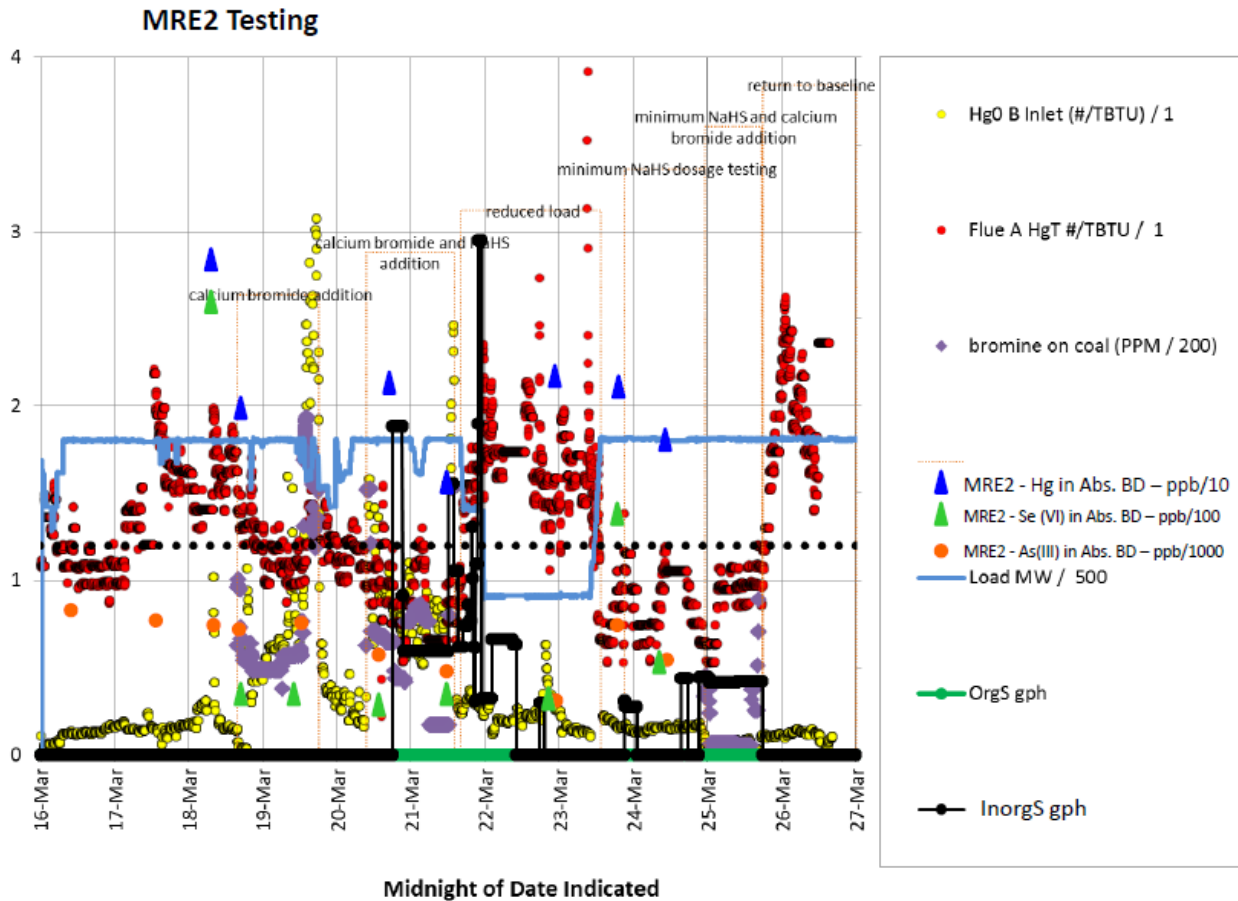


Fig. 5 – MRE2 testing Results from Unit #2 [7].

Plant load is shown in the blue line. The plant was operating under full load conditions for most of the test period with some operation at reduced load. The total mercury at the wet FGD inlet is shown in red and it was generally around 1.5 lb/Tbtu with some higher values at around 3 lb/Tbtu. The stack mercury is shown in yellow and it can be seen that it was often higher than 1.2 lb/Tbtu. The bromine addition rates were around 150 to 200 ppm of bromine added to the coal. The injection of Absorption Plus (Hg) additive is shown by the solid black lines. It can be seen that with the injection of the Absorption Plus (Hg) additive, the stack mercury emissions were always significantly lower than 1.2 lb/Tbtu indicating the injection of Absorption Plus (Hg) additive was able to achieve mercury emissions rate below the MATS limit with use of bromine for mercury oxidation.

CONCLUSION

Out of the technologies available for mercury emissions compliance, use of halogens such as bromine or iodine for mercury oxidation and subsequent removal of the oxidized mercury, either by FGD or by sorbents, can be a reliable yet cost effective option as compared to injection of brominated PAC for low sulfur subbituminous coals. For high sulfur coals with wet FGD, use of bromine or iodine for mercury oxidation (for units without SCR) and Absorption Plus (Hg) additive can be a reliable yet cost effective option as compared to injection of brominated

PAC and DSI injection. In both the cases the addition rates of bromine or iodine can be reduced by roughly 50% by using Mitagent additive to minimize the balance of plant issues that can arise from use of halogens for mercury oxidation.

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