

Advances in Refined Coal Technology for Emissions Reduction

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ABSTRACT

Refined Coal technology is widely used in coal-fired power plants for emissions reduction. The technology is successfully implemented for different types of coals and combustion configurations resulting in reduction in both NO_x and mercury emissions. Refined coal additives are a cost-effective alternative to activated carbon injection (ACI) for mercury emission control. Recent developments have been made to optimize the refined coal process so as to enhance its benefits. One such improvement is reduction in the halogen addition to the coal for mercury control. Data will be presented demonstrating various balance-of-plant benefits of halogen reduction. For example, halogen reduction lowers bromine discharge for coal-fired units with wet flue gas desulfurization (WFGD) systems and can give a corresponding decrease in trihalomethane (THM) levels in downstream drinking water systems.

INTRODUCTION

Mercury can enter the environment from a number of natural and man-made sources, including coal combustion for power generation. Mercury poses an ecological threat when it enters water bodies, where aquatic organisms convert it to methyl mercury – a highly toxic form. This form of mercury can migrate up the food chain and pose a health threat to humans, particularly those who rely on fish as a key element in their diet. Consequently there is a need to control mercury from solid fossil-fuel-fired power generators.¹ One method for mercury control is refined coal technology using pretreatment with Chem-Mod chemicals.^{2,3} The Chem-Mod technology is a dual-reagent coal pretreatment method which uses a halogen for mercury oxidation and a dry-powder sorbent for capture of mercury and other oxidized metals. Refined coal plants using the Chem-Mod technology are installed at more than 40 power and industrial plants in the US with capacity to refine over 100,000,000 tons per year of steam coal.

In general, coal-fired steam generator balance-of-plant (BoP) impacts associated with Chem-Mod refined coal are due to the added bromine. These include increased fouling rates on reheat and low-temperature superheat tube banks and increased corrosion rates on cold-end air heater baskets when burning low-rank coals. In plants with WFGD systems, bromine concentration in effluent streams has in some cases resulted in increased THM levels in downstream drinking water plant distribution systems. Consequently, Chem-Mod is optimizing bromine addition rates with the goal of eliminating or minimizing these impacts. One alternative that Chem-Mod is pursuing with B&W is the use of a third chemical, Mitagent™, which promotes mercury and heavy metal oxidation, and consequently reduces halogen addition requirements. This paper presents the emissions results of development work at bench-, pilot- and full-scale, and the consequent BoP benefits.

PROJECT APPROACH

Mercury Emissions Testing

Pilot-scale Test Facilities and Procedures

Pilot-scale simulation emissions tests were carried out using the Combustion Test Facility (CTF) at the University of North Dakota's Energy and Environmental Research Center (EERC). The CTF is a small (30-inch ID), refractory-lined test furnace which utilizes firing rates between 550,000 and 750,000 Btu/hr to simulate combustion in full-scale boiler furnaces. It has an extensive history of use to investigate a number of emissions topics, including transformation of toxic trace metals (primarily Hg) during the combustion of coal. The test facility also is equipped with a number of post-furnace devices to simulate air quality control (AQC) equipment, including an electrostatic precipitator (ESP) or fabric filter (FF) baghouse for particulate control, a selective catalytic reduction (SCR) column for NO_x control, and a wet scrubber column for control of sulfur emissions. A schematic of the CTF is given in Figure 1.

The CTF produces gas and particulate samples which are representative of those produced in pulverized coal-fired industrial and power boilers. It fires pulverized coal (p.c.) at a rate sufficient to match the furnace exit gas temperature (FEGT) of the specified commercial boiler furnace. For subbituminous coals, a firing rate between 600,000 and 650,000 Btu/hr produces a FEGT between 2100° and 2250°F. For bituminous coals, a firing rate between 650,000 and 750,000 Btu/hr produces a FEGT between 2250° and 2400°F. Combustion air is provided by a forced-draft (FD) fan in this balanced-draft system. The induced-draft (ID) fan at the back of the system is used to maintain a slight vacuum in the combustion zone and to exhaust the combustion flue gases to a stack. Combustion air is preheated using an electric heater and is split between primary and secondary air. Over-fire air (OFA) is diverted from the secondary air flow and is introduced through a separate port near the furnace exit. An adjustable-swirl burner is used to maintain a stable flame.

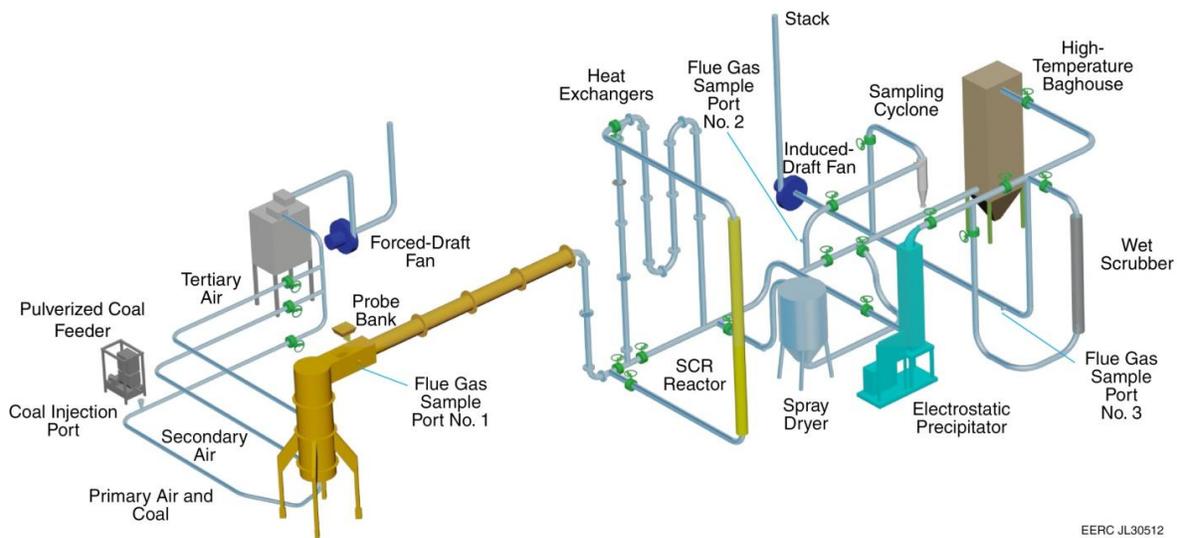


Figure 1. UND EERC Combustion Test Facility

Combustion gas is analyzed for O_2 , CO_2 , CO , SO_2 , and NO_x using continuous emission monitors (CEMs) at two locations: the furnace exit, which is used to monitor and maintain a specified excess air level for all test periods, and the outlet of the AQC device of interest. This is usually the particulate control device (ESP or FF), but also can be a WFGD unit where it is the last AQC equipment before the stack. Continuous mercury monitors (CMMs) manufactured by Tekran[®] Instruments Corporation are used to collect flue gas concentration data at the outlet of the control device of interest. The flue gas is conditioned to remove moisture, CO_2 and SO_2 to prevent interference with the ability of the CMM to accurately measure mercury concentration. Since all mercury analyzers can only measure elemental mercury (Hg^0), the total mercury ($Hg_{(T)}$) concentration is obtained by reducing the oxidized mercury portion (Hg^{2+}) with a 10% NaOH solution containing stannous chloride. The Tekran instrument traps Hg^0 from the conditioned sample onto a cartridge containing an ultrapure gold adsorbent. The amalgamated mercury is then thermally desorbed and detected using cold-vapor atomic fluorescence spectrometry. A dual-cartridge design enables alternate sampling and desorption, resulting in continuous measurement of the sample stream. All gas emissions data are reported on a dry-gas basis to provide consistency for sample comparison, eliminating effects of sample moisture variability. All gas analyses are continuously monitored and recorded by the CTF data acquisition system.

Full-scale Testing Configurations and Procedures

Full-scale emissions tests have been carried out at several units with variable AQC equipment, including ESP only, ESP+WFGD, SCR+ESP+WFGD, and SCR+Circulating Dry Scrubber (CDS)+FF. Chem-Mod and B&W chemicals were added to the coal at the discharge end of each of the coal feeders. The Calcium Bromide is added through a nozzle onto the end of the coal belt, and the blended S-Sorb III and Mitagent powders are pneumatically transported and applied at the end of the belt. The treated coal falls through the vertical coal line to the pulverizer where the chemicals are further mixed with the coal in the grinding process. Stack emissions measurements are made using a variety of equipment and gas sampling methods, including CEMs, CMMs, and

EPA Methods 29 and 30B. Tests are typically conducted on a daily basis for a period of one week or more.

Water Testing

Studies have shown that increasing bromide levels in the raw water intake of a drinking water treatment plant can potentially cause an increase in THM and haloacetic acid (HAA) formation in the finished water distribution system.⁴ To assess the impact of reducing bromine in the power plant effluent on downstream drinking water distribution system THM and HAA levels, Chem-Mod and Santee Cooper contracted with Meridian Energy & Environment, LLC (Meridian) to conduct a bench-scale study of THM and HAA formation at five simulated bromide ion levels (including blank baseline) in a conventional drinking water treatment scheme using chloramine disinfectant.

Test samples were prepared to represent potential raw water intake composition at various bromide levels entering the drinking water treatment plant. Raw water at the intake to the drinking water treatment facility was simulated by blending lake water with representative plant wastewater discharges. The wastewater discharges were comprised of mixtures of ash pond water and hydroclone overflow. Hydroclone overflow is produced by the facility's SO₂ scrubber system and is the primary source of bromide in the facility's wastewater. Various bromide levels in the simulated raw water intake were produced using different amounts of the hydroclone overflow. Scenarios were developed to evaluate two levels (low and high) of bromide use (0.015% and 0.025% application rate) at one or more power plants. Five scenarios were tested: 1. One plant, low-Bromide loading, 2. Two plants, low-Bromide loading, 3. One plant, high-Bromide loading, 4. Two plants, high-Bromide loading, and 5. No Bromide use (Blank).

The bench-scale study was designed to simulate the drinking water plant process by subjecting the raw water sample to coagulants (aluminum sulfate and polymer) at doses practiced at the facility and removing the resulting solids by vacuum filtration through Whatman No. 2 filter paper. The filtered sample was then dosed with chlorine (sodium hypochlorite) and nitrogen (ammonium sulfate) to generate a chloramine disinfectant with a representative concentration of 3.8 mg/L as total chlorine. The dosed samples were analyzed for THMs and HAAs after 24, 48, 72 and 96 hours following the dosing. Samples were screened at Meridian using a Hach DR 2800 Spectrophotometer and duplicate samples were sent to a contract laboratory for comparison. Trihalomethanes were analyzed by Method SW846 8260B⁵ and haloacetic acids by EPA Method 552.3.⁶

RESULTS AND DISCUSSION

Mercury Emission Test Results

Pilot-scale Test Results

The objective of the pilot testing was to demonstrate the reduction in the bromine application rate as a result of applying the Mitagent additive. Both bituminous and sub-bituminous coals were tested. Table 1 gives results for a sub-bituminous Powder River Basin (PRB) coal for an ESP Only AQC configuration. It is seen that the mercury emission is reduced from 2.73 lb/TBtu to 1.08 lb/TBtu with typical addition rates of 0.02% MerSorb and 0.3% S-Sorb III to make refined PRB coal. By substituting Mitagent for S-Sorb III at a level of 25% of the total dry powder rate, the rate of bromine was reduced by 50% while still achieving similar mercury reduction for the refined coal.

Table 1: EERC CTF Results for PRB Coal with ESP Only AQC Configuration.

MerSorb Rate (%, coal basis)	S SORB III Rate (%, coal basis)	Mitagent Rate (%, coal basis)	Bromine Reduction (%)	Hg (lb/TBtu)
0.00	0.000	0.000	0.0	2.73
0.02	0.300	0.000	0.0	1.08
0.01	0.175	0.075	50.0	1.15

Full-scale Test Results

Based on these pilot-scale test results, a full-scale test was performed at a nominal 80 MW electric generating unit with similar AQC configuration. The objectives for this test were twofold:

1. To prove a similar reduction in bromine level with the use of Mitagent as demonstrated at pilot-scale, and
2. To demonstrate stack mercury emission level below the 1.2 lb/TBtu MATS standard with a mixture of MerSorb (CaBr₂ solution)+S-Sorb III+ Mitagent.

Table 2 shows mercury oxidation as measured at the stack as a result of Mitagent addition to the coal. Baseline mercury oxidation is 38%, which is common for low-halogen coals. Mercury oxidation for two levels of bromine addition is 46.5% and 62.5%, respectively for 70 ppm and 100 ppm bromine addition on a dry coal basis. As in the pilot-scale testing, substitution of Mitagent for 25% of the S-Sorb III gave 56% mercury oxidation at only 40 ppm bromine addition, or roughly one-half the rate (70-100 ppm) without Mitagent.

Table 2: Full-scale Unit Results for PRB Coal with ESP Only AQC Configuration.

Test Date	Bromine Rate (ppm, dry coal)	Coal Mercury (lb/TBtu)	Mitagent Rate (lb/hr)	Oxidized Mercury (%)
12/9/2013	0	8.52	0	38.0
12/10/2013	70	5.65	0	46.5
	100	7.20	0	62.5
12/11/2013	40	4.95	25	56.0

Figure 2 shows the results of a test demonstrating the second objective conducted on 12/12/2013. Stack mercury emissions are reduced from a baseline level of roughly 1.8 lb/TBtu to 0.6 lb/TBtu on average over a period of approximately eight hours. The stack mercury emissions returned to baseline levels once the coal treatment was stopped. One key advantage of this Chem-Mod/B&W coal pretreatment method is that the mercury is chemically bound in the S-Sorb III particulate phase. It is demonstrated that the bound mercury and other heavy metals are not leachable by the TCLP test.² It also is beneficial that mercury captured in this manner prior to a WFGD unit is not then removed in the scrubber effluent.

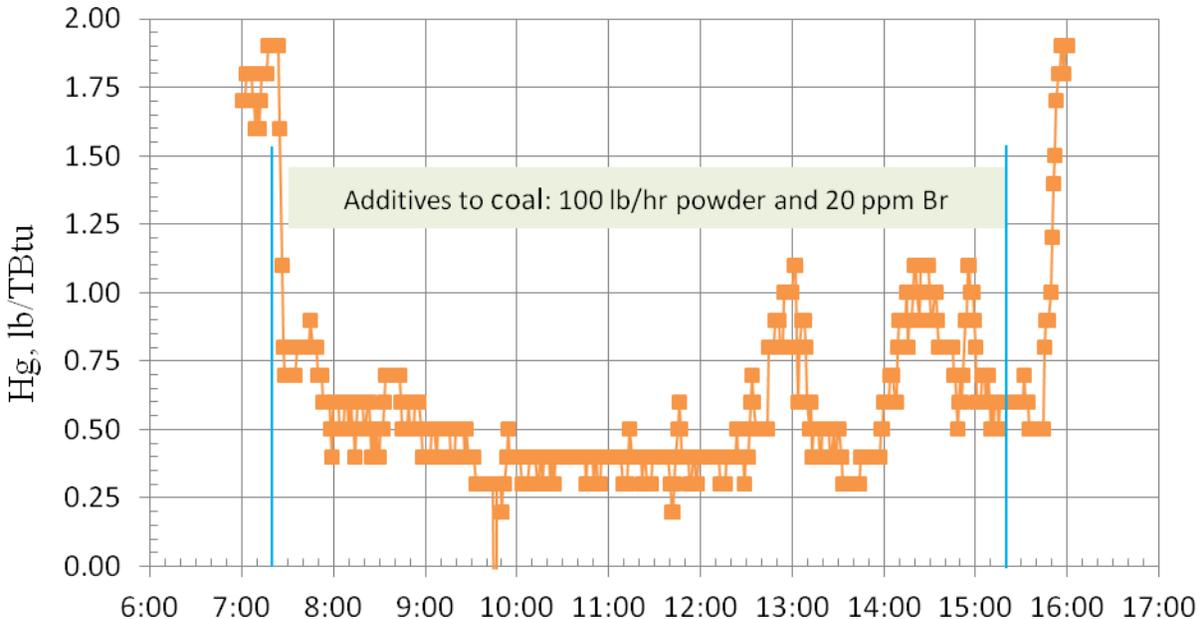


Figure 2: Full-scale Unit (ESP Only) Data for 12/12 Test with 20 ppm Bromine and 100 lb/hr Powder (75 lb/hr S-Sorb III and 25 lb/hr Mitagent) on As-Fired PRB Coal Basis.

Figure 3 shows the results of a week-long test in a nominal 250MW unit equipped with SCR, CDS and FF. Each day constituted a change in coal pretreatment. The first day is a baseline test with no pretreatment of the PRB coal. The second day included treatment of the coal with 100 ppm of MerSorb (Calcium Bromide solution), which corresponds to 41.6 ppm bromine on an as-fired coal basis. On the third day Mitagent was added to the coal at a rate of 30 lb/hr. Finally, on day four the coal was treated with 100 ppm of MerSorb and 100 lb/hr (435 ppm) of dry powder additive, 70% (305 ppm) S-Sorb III and 30% (130 ppm) Mitagent. Coal treated with Chem-Mod chemicals plus Mitagent was burned from 8:00 AM to 5:30 PM (17:30). Mercury reduction with

Chem-Mod technology coal treatment and Mitagent is 73% compared to baseline. MATS compliance mercury emission levels ($0.77 \mu\text{g}/\text{m}^3$ or $0.7 \text{ lb}/\text{Tbtu}$) are achieved with this level of treatment for the specific PRB coal source and unit AQC configuration.

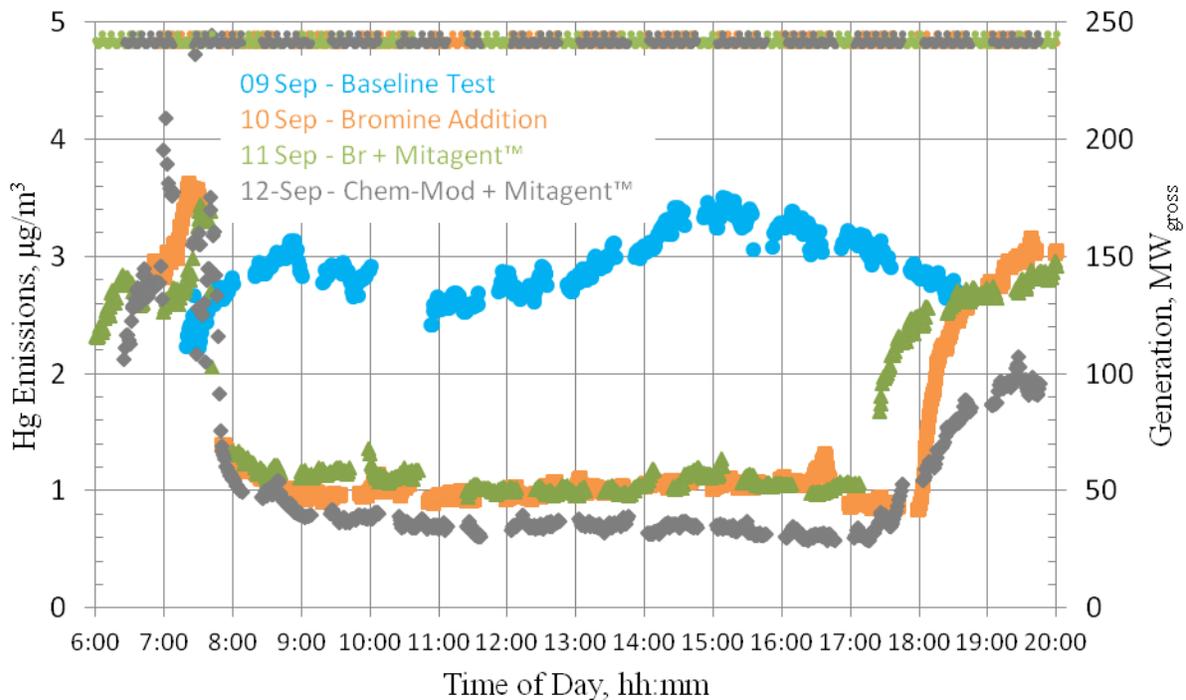


Figure 3: Full-scale (SCR+CDS+FF) Data for Three Single-day Tests Burning PRB Coal, including Baseline, Bromine Only Addition, Bromine plus Mitagent and Chem-Mod Chemicals plus Mitagent.

The three-reagent coal pretreatment also is being tested at a nominal 600 MW unit equipped with SCR, ESP and WFGD. The unit burns bituminous coal from multiple mine sources. The as-fired coal treatment rates for the three chemicals are 100 ppm MerSorb, 3375 ppm S-Sorb III and 1125 ppm Mitagent. In mid-May Method 30b sampling was conducted both prior to the scrubber and at the stack. Four individual tests were conducted on each day. Average results for each test day are shown in Table 3. On average, between 75% and 80% of the mercury is captured by the fly ash and S-Sorb III in the particulate phase prior to the scrubber, and another 10% is captured in the scrubber. Mercury speciation measurements at the scrubber inlet show that over 96% of the mercury is in the oxidized state. It is readily captured by both the Chem-Mod S-Sorb III and the scrubber liquor. These results also demonstrate compliance with MATS regulations.

Table 3: Mercury in Coal and Flue Gas.

Test Day	Coal Hg, lb/TBtu	Flue Gas Hg, lb/TBtu (% Reduction)		
		Scrubber Inlet M30b		Stack M30b
		Oxidized	Total	Total
1	9.38	2.20	2.27 (76)	1.04 (88)
2	7.30	1.41	1.46 (80)	1.02 (86)

Water Study Test Results

Full-scale Test Results

A study also is ongoing to measure bromides in the scrubber and wastewater treatment ponds at the same 600 MW unit. Refining the coal with MerSorb (250 ppm) and S-Sorb III (4500 ppm) began in August 2013, which led to a corresponding increase in bromides in the scrubber basin to measured levels between 800-1000 ppm and 90-110 ppm in the final wastewater treatment pond. Beginning in February 2014, a triple-reagent treatment process was initiated using one-half the MerSorb treatment rate (100 ppm) in combination with the S-Sorb III (3375 ppm) and Mitagent (1125 ppm) powders. Although equilibrium behavior in the ponds is not entirely established at this point, a proportional decrease is observed between coal pretreatment bromine levels (250 ppm vs. 100 ppm) and bromides in each of the ponds, i.e., levels of roughly one-half those ranges noted above.

Meridian Bench-scale Test Results

The two-fold objective of the contracted Meridian bench-scale simulation is:

1. To determine the impact of bromine level in the water treatment plant raw water intake on the potential to produce THMs in the drinking water system, and
2. To determine whether the reduced bromine levels can give THM levels that both meet the regulatory standard and are consistent with THM levels prior to refining the coal.

A general trend of increasing total THM (TTHM) levels with increased bromide loading is observed in the bench-scale Water Study test results. There is a strong positive correlation between bromide levels and TTHM formation across the range of bromide levels and at all sampling intervals. The sole exception is the blank sample (Run 5) with no bromide loading where the predominant THMs are primarily chlorinated species. It is noteworthy that none of the results exceed the regulatory standard of 80 µg/L for TTHMs. Furthermore, the THM results for low-bromide application rates (Run 2 is shown in Figure 5) are in the same range as the 2008-2009 water treatment system monitoring results before Chem-Mod was used, and significantly less than the monitoring results for 2010 to 2012 after Chem-Mod was first applied (Figure 6).

Analytical data for THM speciation at different bromide levels further support this trend. The more-brominated species predominate at higher bromide levels, i.e., dibromochloromethane is in higher concentrations compared to dichlorobromomethane at higher bromide levels. Chloroform levels also decrease at higher bromide levels. Chloroform is the predominant disinfection byproduct (DBP) following chlorination when no bromide is present.

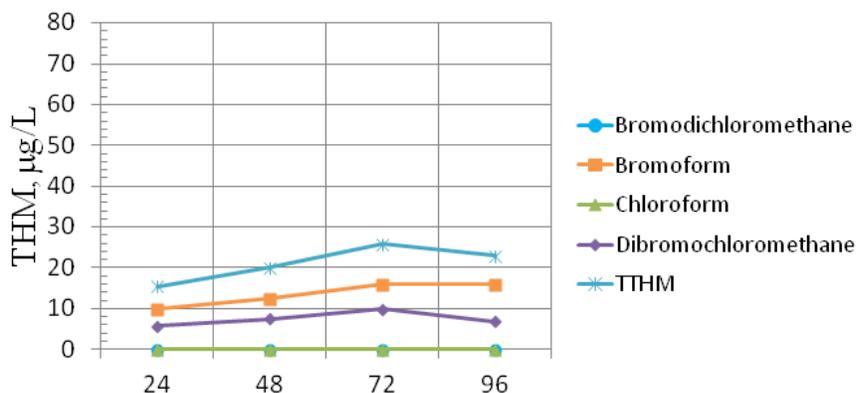


Figure 5: TTHM and Speciated THM Results for Run 2, Two Plants, Low-Bromide Loading.

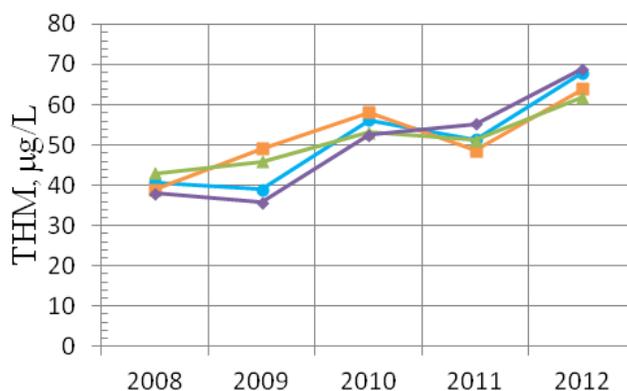


Figure 6: Average Historical TTHM Results for Four Individual Sites in the Water Treatment System.

The total HAA data does not correlate as strongly as total THM data with bromide levels, however the HAA speciation results show that chlorinated species are replaced by brominated species with increasing bromide levels. This shift toward brominated species is observed in the absence of monochloroacetic acid, the reduction in dichloroacetic acid, and the increased concentration of dibromochloroacetic acid. These HAA results agree with those of other studies.² Also, the speciation results for the blank show a predominance of chlorinated species over brominated species.

Refined Coal Balance-of-Plant Benefits

Bromine discharge

The full-scale Water Study results show that both Scrubber and Low-Volume Waste effluent are reduced at lower bromine addition rates to the coal. The bench-scale results show a strong positive correlation between raw water bromide levels and THM/HAA formation and support the DBP mitigation effort of limiting the bromide dosage to the coal feedstock at the coal plant to reduce the downstream formation rate of DBPs in the finished water distribution system.

Fouling

When burning low-rank subbituminous (e.g., PRB) or lignite coals, two problematic deposit types can form on reheat and primary superheat tube banks in the boiler back-pass. These are referred to as silicate- or sulfate-based deposits. Silicate-based deposits are sintered ash deposits that form between 1900°F and 2100°F (high-temperature), or below typical ash fusion temperatures. Sulfate-based deposits form due to sulfation of alkaline earth (Ca) or alkali (Na and K) elements in deposits between 1200°F and 1800°F (low temperature), the maximum rate occurring between 1500°F and 1600°F. Both the sintering and sulfation processes require time to form high-strength deposits which may not be readily removed by normal soot-blowing operations. Bromine can accelerate the development of low-temperature fouling deposit strength by forming an intermediate phase in the alkaline earth element sulfation process. This reduces the time required to develop strength in these deposits. Since it is a concentration-dependent process, lower bromine addition rates reduce both gas-phase concentration and rate of reaction. Tube spacing and bundle depth in these horizontal banks, and sootblower coverage and sequencing are critical factors for controlling these deposits. If uncontrolled, these deposits bridge and plug flue gas lanes in these tube bundles, causing unit shutdown because ID fan power limits or duct pressure limits are exceeded.

Low-temperature Corrosion

Air heater corrosion is a risk with refined low-rank (high-moisture) subbituminous (PRB) 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.^{7,8} 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 7. Acid dew-point temperature is reduced by 10°F by reducing the bromine addition rate from 200 ppm (0.02%) to 50 ppm (0.005%). The greatest risk for corrosion of this type is in the cold-end AH 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.⁹ 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. As an extra precaution, cold-end baskets may be enamel-coated to protect the metal against acid attack.

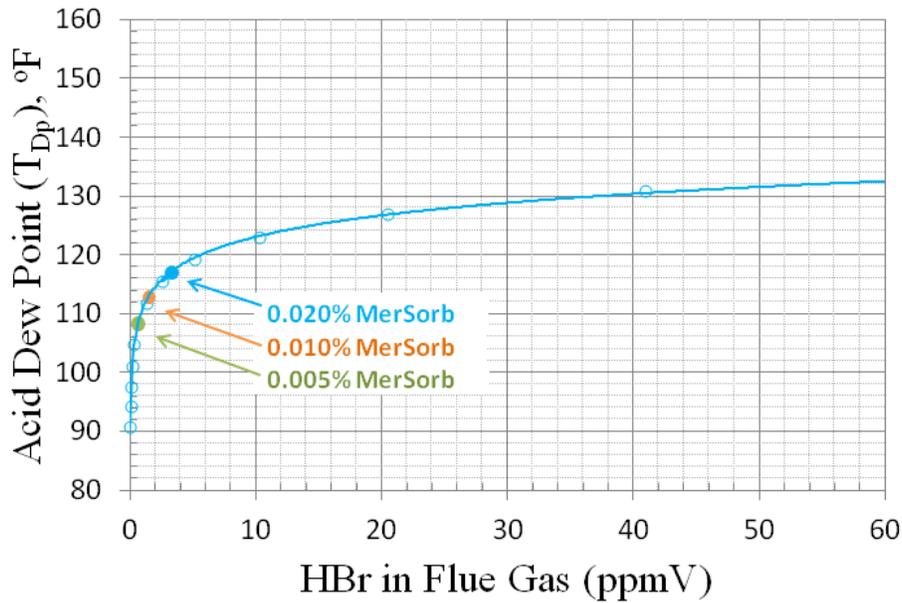


Figure 7: Acid Dew-Point Temperature vs. Flue Gas HBr Concentration (12.5% Moisture).

SCR Catalyst Lifetime

Improved SCR catalyst life has been reported for refined eastern bituminous coals. Calcium in the S-Sorb III reacts with and removes arsenic and other heavy metals from the flue gas stream, thus preventing their reaction with and “poisoning” the SCR catalyst surface. S-Sorb III potassium and phosphorus contents are more than an order-of-magnitude lower compared to the coal-ash levels and pose little or no risk for catalyst poisoning. Mitagent is shown to prevent phosphorus poisoning by reacting with gas-phase phosphorus.¹⁰ Therefore the triple-reagent refined coal reduces SCR catalyst poisoning when applied to high-phosphorus PRB coals.

SUMMARY

The Chem-Mod refined coal technology is now operating at a number of power plant sites. In the work described here Mitagent is demonstrated to give the added benefits of mitigating some observed BoP impacts linked to bromine, as well as preventing SCR catalyst poisoning for high-phosphorus PRB coals. Pilot- and full-scale furnace results are presented to demonstrate that bromine requirements for mercury oxidation can be reduced by 50% to 75%. Bench- and full-scale results are given to show that reducing bromine levels added to the coal results in lower levels of bromides in the scrubber effluent stream, and consequently lower THM levels in the water distribution system. In all cases shown THM levels did not exceed regulated limits.

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KEYWORDS

Coal, Emissions Control, Mercury, Refined Coal, Section 45 of IRS Tax Code, MATS, Halogens, Bromine, Sorbents,