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Reducing Operating Costs and Risks of Hg Control with Fuel Additives

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ABSTRACT
As compliance with the MATS and IB MACT rules approaches, coal-fired boilers have many options for mercury control. Once in compliance, plants will need to keep the operating costs of mercury control systems in check. Coal additives are used to increase the oxidation of mercury in the flue gas and improve the effectiveness of activated carbon. Bromine is currently the most commonly used coal additive. While effective, bromine addition has been associated with balance-of-plant problems, notably corrosion of components such as air preheaters, leaching into effluents that eventually discharge into waterways, and ancillary emissions. ADA’s patented M-Prove™ coal additive has been used successfully on PRB- and lignite-fired boilers to increase mercury oxidation and reduce PAC consumption for mercury control. After treating over 100 million tons of coal for several years, there has been no indication or evidence of corrosion in the flue gas path, or issues associated with water treatment, leaching, or ancillary emissions. In this paper, examples of the use of M-Prove, including opportunities to reduce carbon consumption and minimize balance-of-plant impacts, will be presented.

INTRODUCTION
For nearly two decades, ADA has conducted more than 100 mercury control demonstrations at coal-fired plants and sold activated carbon injection systems maintaining mercury control for more than 140 boilers. Our portfolio of products has grown to address limitations in coal composition, balance-of-plant impacts from alternate approaches, and operational challenges introduced by other technologies. We were the first to understand these environmental issues and provide a range of commercial solutions to the industry.

ADA delivers an important combination of hands-on experience, industry expertise, demonstrated commercial products, and commitment to collaborating with customers. Our track record includes securing more than 35 US patents, with additional US and international patents pending, and receiving numerous prestigious industry awards for emissions control technology and systems. No matter the challenges our customers face, ADA will continue to focus its significant expertise and resources to innovating for a cleaner energy future.
Legislation and Environmental Regulations
Air emissions from coal-fired boilers and industrial sources are regulated under the federal Clean Air Act as well as under state rules. These are multi-pollutant rules, which can increase the complexity of finding a compliance solution. The control of particulate matter (PM) must be accomplished while controlling both acid gases and mercury (Hg). As summarized below, specific federal rules apply to each source category.

Federal Mercury and Air Toxic Standards (MATS)
On December 16, 2011, the EPA issued the final MATS rule, which took effect on April 16, 2012. Affected units had to be in compliance on April 16, 2015, unless they received a one-year extension of the compliance date to April 16, 2016. The MATS rule is based on the maximum achievable control technology (MACT) framework for hazardous air pollutant (HAP) regulations. The rule is applicable to coal and oil-fired Electric Utility Steam Generating Units (EGUs) that generate electricity via steam turbines and provides for, among other provisions, control of mercury and particulate matter, and control of acid gases and other HAPs.

State Mercury and Air Toxics Regulations Affecting EGUs
In addition to federal MATS rules, certain states have their own mercury rules that are similar to, or more stringent than MATS. Power plants around the country are also subject to consent decrees that require the control of acid gases and particulate matter, in addition to mercury emissions. Seventeen states have mercury-specific rules that affect more than 260 generating units.

Industrial Boiler MACT
On December 20, 2012, the EPA finalized a specific set of adjustments to the MACT-based air toxics standards originally finalized in March 2011 for industrial boilers. Starting January 31, 2016, industrial boilers must begin compliance with the Industrial Boiler (IB) MACT which limits emissions of mercury, acid gases, particulate matter, and carbon monoxide. Some boiler owners may be granted a one year extension delaying the compliance date until January 31, 2017. Within 180 days of the compliance date, industrial boilers operators must demonstrate compliance. The EPA estimates that approximately 600 coal-fired boilers will be affected by the IB MACT in industries such as pulp and paper.

MERCURY CONTROL STRATEGIES FOR COAL-FIRED BOILERS
There are only two pathways by which mercury can be removed from coal-fired boilers: collection of mercury that has been adsorbed on surfaces (e.g., fly ash, sorbents) and absorption of oxidized gaseous mercury species (collectively, Hg^{2+}) in aqueous media. Any mercury control strategy must utilize one or both of these pathways, either by removing particulate-bound Hg using the particulate collection device or by removing gaseous Hg^{2+} in a flue gas desulfurization (FGD) scrubber.
Oxidation of Mercury in Flue Gas
Oxidation of the elemental mercury (Hg\(^0\)) that is present in the flame zone is the key step in the transformation of mercury into forms that can adsorb and/or absorb in downstream air pollution control equipment. Halogen compounds have long been identified as the most important species for oxidizing mercury in coal combustion systems. Chlorine is the most abundant halogen in coal. The chlorine contents of coals from the U.S. span two orders of magnitude,\(^1\) and this large variation resulted in the observation that coal chlorine content had a strong influence on the oxidation state of mercury in the flue gas, as well as the removal of mercury in certain air pollution control devices.

Work carried out in Europe on the effect of bromine on mercury emissions in incinerators\(^2\) spurred numerous investigations on the impact of bromine addition to coal combustion systems. On an equivalent molar basis, bromine is more effective than chlorine for the homogeneous oxidation of mercury in combustion flue gas. There is not enough native bromine in most US coals to affect mercury oxidation in coal-fired boilers: the bromine content of US coals is 1% to 4% of the chlorine content.\(^3\) Therefore, bromine has been added to the coal before combustion or to the flue gas, if additional mercury oxidation is desired.

Addition of halogens to the fuel or flue gas finds the best application on boilers burning low-chlorine coals (subbituminous or lignite coals). A sampling of data from full-scale studies\(^4,5,6,7\) shows that, in most cases, the amount of oxidized mercury at the ESP outlet levels off at about 80-90% with the addition of 100 µg Br/g coal, which might indicate kinetic limitations on the process. ADA discovered that adding low-levels of iodine can also be very effective at oxidizing mercury, and that the addition of iron or other metals can act as a catalyst to improve the effectiveness of halogens for mercury oxidation. Leveraging years of research and technical expertise, ADA has secured 13 patents incorporating M-Prove technology, with more pending in the US and foreign patent offices.

Adsorption of Mercury in Flue Gas
Mercury adsorption on carbon surfaces is used in many applications to capture mercury both from gas and liquid media. The presence of both oxidized and elemental mercury in coal combustion flue gas originally posed challenges for design of effective sorbents. In other applications, municipal solid waste combustors, for example, mercury is almost entirely in an oxidized form, which has proven easier to adsorb on activated carbon than the elemental form.

In a coal-fired power plant, the fly ash often contains unburned carbon from less-than-complete combustion of the coal. This unburned carbon can adsorb mercury. Activated carbon sorbents are more effective than unburned carbon in fly ash because of higher specific surface area and, in some cases, an optimized pore structure or surface treatments specific to mercury capture.
The presence of halogen compounds in the flue gas promotes mercury adsorption by activated carbon, which has been attributed to its activation of the catalytic sites on the carbon, at which mercury is oxidized. Pre-treating the carbon with aqueous chloride, aqueous bromide or gas-phase halogen has a similar promotional effect on the adsorption of elemental mercury. ADA’s portfolio includes patents that cover the combined use of halogen-based coal additives and mercury sorbents, including activated carbon.

With low concentrations of halogens in the flue gas, activated carbon is not very effective at adsorbing mercury in coal-fired boilers. Low concentrations of halogens mean that most of the gaseous mercury will be in the elemental form and elemental mercury requires halogens to activate binding sites. The effectiveness of activated carbon is increased by either adding halogen to the flue gas (e.g., bromine or other halogen addition to the coal) or by pretreating the activated carbon with a halogen. The use of brominated activated carbon or a halogen additive in conjunction with non-brominated carbon is typically necessary when the flue gas contains low concentrations of halogens, for example, when subbituminous or lignite coals are burned in a boiler.

**Absorption of Mercury in Scrubbers**

Absorption of mercury in flue gas desulfurization (FGD) scrubbers is one of the ways to remove mercury from the flue gas in coal-fired boilers. As with gas-phase mercury chemistry, what seems simple at first turns out to be quite complex. The solubility of HgCl$_2$ in water is relatively high and close to the solubility of HCl in water. The solubility of elemental mercury is 10$^6$ times lower.$^8$ The removal of oxidized mercury by wet FGD scrubbers typically exceeds 90%.$^9$ In some scrubbers, however, some of the absorbed Hg$^{2+}$ in the liquid is reduced back to elemental mercury. Because of the very limited solubility of elemental mercury, the result of this reduction reaction is increased elemental mercury in the gas phase.

In wet FGD scrubbers, mercury can be found either in the aqueous phase or in the solid phase. Once in the solid phase, mercury is not observed to be reduced back to elemental form. In the solid gypsum product from forced-oxidation scrubbers, mercury appears to be in a phase containing Al, Fe or both.$^{10}$ Mercury is associated with the finest solids, which are sometimes included in the gypsum product in a forced-oxidation scrubber and sometimes separated.$^{11}$

Further complicating the picture, scrubbers do not always operate at steady-state conditions. Process changes can cause changes in the composition of the scrubber solution and can result in transient emissions of elemental mercury from the scrubber. Such transient events can result in significant emissions of mercury because of the large reservoir of liquid in a typical scrubber.

In summary, there are two primary mercury control strategies used today in coal-fired power plants. First, the existing air pollution control devices may be able to remove sufficient mercury without the addition of new equipment dedicated to mercury control, sometimes
called a “co-benefits” strategy. Certain measures can be taken to increase the capture of mercury, including: burning coal blends to increase the halogen in the coal; using oxidizing agents or catalysts to increase oxidized Hg; addition of a scrubber to removed oxidized Hg. Second, sorbents can be used to adsorb Hg from the flue gas, which involves adding additional equipment to inject sorbents into the flue gas, typically upstream of a particulate control device. The most commonly used sorbents are powdered activated carbons (PACs). These might be doped with halogens (typically bromine) or halogens might be added to the coal in conjunction with non-halogenated PAC. Halogen addition is often an important component of a plant’s mercury control strategy.

HALOGEN ADDITION TO COAL-FIRED BOILERS
Addition of halogen compounds, either to the fuel or to the flue gas, has been demonstrated as an effective way to increase the amount of oxidized mercury in the flue gas, which can improve mercury emissions control. Configurations in which adding halogens to the fuel or flue gas is advantageous for mercury emissions control include the following:

- A low-halogen fuel and the use of a non-brominated PAC (in the hope that this combination would be cheaper than brominated PAC by itself);
- A low-halogen fuel on a unit with a wet or dry FGD with the intent of using the scrubber as the primary mercury removal device;
- Refined Fuel use in an EGU boiler, which is a modification of the fuel to result in in sufficient demonstrated emission reductions, typically of NOx and mercury to qualify for tax credits under a US tax regulation (IRS Section 45). This tax credit only applies to the qualified fuel purchase and does not affect compliance with the MATS rule. Most refined coal systems achieve mercury control by adding halogens to the coal.
When additional Hg oxidation is needed in the flue gas, bromine has typically been the halogen used. However, there are balance-of-plant effects of bromine addition that have been noted after several years of bromine usage at coal-fired utility boilers, including: corrosion in the flue gas path, selenium partitioning in the flue gas, and potential discharges of bromide in scrubber wastewater.

An ongoing study by EPRI\textsuperscript{12,13} on the balance of plant effects of bromine addition (including direct bromine addition and injection of brominated PAC) has, to date, identified corrosion as the major observed impact. The most commonly reported corrosion locations in the EPRI study associated with bromine addition were the cold-end baskets of air pre-heaters (APHs). This corrosion was only observed on boilers firing subbituminous coals or subbituminous-bituminous blends. Furthermore, most of the corrosion identified in boilers in which bromine was added to the fuel took place in boilers with bromine addition rates greater than 100 $\mu$g Br/g coal.

The addition of bromine compounds to the flue gas has been observed to increase the concentration of selenium in the flue gas downstream of the air heater\textsuperscript{14} and in a wet scrubber slurry.\textsuperscript{11} It appears that the presence of bromine compounds in the flue gas can result in a shift of selenium from the fly ash to the flue gas leaving the particulate control device. Increasing the concentration of selenium in the scrubber slurry might result in an increase in selenium in the FGD discharge stream. Selenium, particularly the most oxidized form (Se[VI]) cannot be removed efficiently by conventional wastewater treatment units. This may be of concern to utility boilers because of the limits on discharge of Se in power plant wastewater promulgated in the federal Effluent Limitation Guidelines.

Adding a halogen, such as bromine, to the flue gas has been demonstrated to increase the concentration of bromide ions in the liquid phase of a wet FGD scrubber.\textsuperscript{5} If halogens in the scrubber liquor are increased and the materials of construction were not designed for those increased halogen levels, corrosion could result.\textsuperscript{12} In particular, scrubbers designed to operate on boilers firing Powder River Basin subbituminous coals, which typically have 25 $\mu$g/g chlorine or less, might not be constructed of the right materials for long-term operation with addition of greater than 100 $\mu$g/g bromine.

In at least one case, an increase in brominated organic compounds in the wet FGD scrubber discharge has been observed with bromine addition to the fuel, although not at high enough concentrations to be of concern.\textsuperscript{12} Increase of halogens (chloride, bromide, etc.) in wet scrubber liquid discharge could potentially be a problem if the waters are discharged to a body of water with a drinking water treatment plant downstream. In public drinking water systems, the US EPA sets a limit of 80 parts per billion ($\mu$g/L) on the total concentration of four trihalomethanes (THMs): chloroform, bromoform, bromochloromethane, and dibromochloromethane.\textsuperscript{15} In the chlorine disinfection process in the treatment plant, THMs containing bromine can be formed and there is a concern about the toxicity of brominated
THMs. For this reason, concern has also been raised about bromide in rivers and lakes that supply municipal water treatment plants.\textsuperscript{16,17}

Addition of halogens for increasing mercury oxidation in coal combustion flue gas can be a part of a plant’s mercury control strategy. However, the balance-of-plant effects of halogens must be considered in order to make an informed compliance decision. ADA’s M-Prove can be paired with an ADA-patented approach to remove the halogen from scrubber water to limit build-up in the scrubber as well as mitigate discharge concerns.

**M-PROVE TECHNOLOGY FOR MERCURY OXIDATION**

ADA’s patented M-Prove Technology was developed to provide the benefits of halogen addition for mercury control, without the negative impacts that have been observed with bromine. We use a form of halogen that can be applied at very low levels. This essentially eliminates the risk associated with bromine injection at higher levels while achieving similar mercury control benefits.

The proprietary liquid coal additive product for enhanced mercury oxidation and removal in coal-fired boilers can be applied at various stages of the coal feed process. Typically, eight to ten times less M-Prove additive is required to achieve similar oxidation and Hg removal results as with bromine. This mitigates balance-of-plant impacts.

To date, over 57 full-scale tests of M-Prove technology have been conducted on plants with various air pollution control devices (APCDs) as shown in Table 1. Since 2009, over 100 million tons of coal have been treated with M-Prove additive, primarily PRB subbituminous coal, with no reported balance-of-plant impacts.

**Table 1. Feedstock and APCD configurations from M-Prove demonstrations at full-scale coal-fired power plants.**

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>APCD Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>PRB / PRB Blend (&gt;85%)</td>
<td>SCR/C-ESP</td>
</tr>
<tr>
<td>PRB / PRB Blend (&gt;85%)</td>
<td>C-ESP, FF</td>
</tr>
<tr>
<td>PRB / PRB Blend (&gt;85%)</td>
<td>SCR or SNCR/C-ESP/WFGD</td>
</tr>
<tr>
<td>100% PRB</td>
<td>H-ESP</td>
</tr>
<tr>
<td>100% Lignite</td>
<td>SNCR/C-ESP/WFGD</td>
</tr>
<tr>
<td>Lignite Blend (&gt; 90%)</td>
<td>C-ESP/WFGD</td>
</tr>
<tr>
<td>100% Lignite</td>
<td>FF, C-ESP/WFGD</td>
</tr>
<tr>
<td>Bituminous</td>
<td>SCR/DSI/C-ESP/WFGD</td>
</tr>
</tbody>
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Hg Removal Case Studies

*M-Prove Technology* has been used successfully with PAC injection to control mercury to the levels required by the MATS or IB MACT rules. Data from seven boilers firing low rank (subbituminous or lignite coal) are summarized in the following two graphs for units with ESPs and fabric filters (Figure 1 and Figure 2, respectively). Injection temperatures ranged from 222-365°F across all tested units, with a mean injection temperature of 324°F. Non-brominated PAC was used alone or in conjunction with typical *M-Prove* addition rates. The greatest benefit of *M-Prove* was observed at lower PAC injection concentrations. Being able to reduce the PAC injection rate can save on the cost of PAC. A further economic benefit can be realized for plants that sell their fly ash for concrete manufacture, because lowering the PAC addition rate can allow the fly ash to be sold instead of landfilled.

![Estimated Removal with M-Prove™ (ESP Applications)](image)

Figure 1. Reduced PAC usage for mercury control when using non-brominated PAC combined with *M-Prove* at typical addition rates on boilers with ESPs.
Figure 2. Reduced PAC usage for mercury control when using non-brominated PAC combined with M-Prove at typical addition rates on boilers with fabric filters.

M-Prove Technology has also been used on boilers with wet or dry flue gas desulfurization (FGD) scrubbers. Full-scale plant data for a lignite-fired unit with cold-side ESP and wet FGD are shown in Figure 3. In this case, non-brominated PAC was injected before the ESP, and M-Prove was added to the coal. The figure shows the total Hg concentration measured at the wet FGD inlet and in the stack with two levels of M-Prove addition, the typical baseline level (BL) and a lower addition rate.
Figure 3. Mercury concentrations at the wet FGD inlet and stack for plant firing a lignite coal.

In some cases, PAC is not required when M-Prove Technology is used with a scrubber. Figure 4 shows Hg stack emission data for a subbituminous-fired boiler in which M-Prove was added to the coal at a typical treatment level. The boiler had a spray dryer adsorber (SDA) followed by a fabric filter. In this case, no PAC was needed to achieve Hg stack emissions at or below the MATS limit.

M-Prove addition rates that are typically eight to ten times less than bromine addition rates have been shown to produce the high levels of mercury reduction needed for compliance with the MATS rule in conjunction with PAC or when used with wet or dry scrubbers.
Figure 4. Mercury concentrations at the stack for plant firing subbituminous coal with spray dryer adsorber and fabric filter; M-Prove added to coal at “BL-1” level, without the use of PAC.

Low Risk of Corrosion with M-Prove Technology

Recent results at both pilot and full-scale testing of corrosion rates using a real-time corrosion probe suggest that a hydrohalide condensation (i.e., dew point corrosion) mechanism is responsible for corrosion in flue gas at temperatures representative of air preheaters. Calculations for typical concentrations of bromine addition indicate dew points are in the 110-115°F range for high moisture PRB coal (Figure 5). The dew point of HBr was taken from Ganapathy. The dew point for M-Prove species was estimated from thermodynamic properties and is also shown in the figure. Since typical M-Prove addition rates are about ten times less than corresponding bromine addition rates, the dew point temperatures associated with M-Prove addition are expected to be 10 to 20°F less than those expected with HBr in the flue gas. This difference is significant because the dew point associated with M-Prove species is projected to be below cold-end metal temperatures in air preheaters. The cold end of air preheater baskets is the location where corrosion has been observed most often in PRB-fired plants that add bromine to the fuel.
**SUMMARY**

ADA’s M-Prove Technology provides a cost-effective alternative to other halogen-based coal additives used for enhanced mercury removal. Our product minimizes corrosion risks to cut maintenance and repair costs and enhances system reliability. M-Prove Technology also reduces additional halogen that could leach from fly ash or be present in the wastewater treatment system.

Key benefits of M-Prove are as follows:

- Effective at extremely low chemical treatment rates, typically eight to ten times lower than those used with bromine;
- Significantly reduces the balance-of-plant risks, including corrosion, attributed to other halogen-based coal treatments;
- Minimizes ancillary halogen emissions in the stack, fly ash, and wastewater;
- Reduces sorbent consumption for ACI systems;
- Facilitates enhanced mercury removal by other downstream pollution control devices (ESP, FF, FGD);
- Minimal capital investment.

ADA provides solutions for challenging industry problems. In the late 90s, we discovered that halogen was required to achieve high levels of mercury removal in plants firing sub-bituminous coals. We also know that adding too much halogen to a plant designed to burn
low-halogen coals can cause costly, unintended impacts to metal that comes in contact with flue gas. ADA has conducted extensive R&D and has been granted several patents associated with using halogen-based coal additives including:

- Iodine-based coal additives for mercury oxidation
- Iron plus halogen coal additive for enhanced mercury oxidation
- Halogen plus activated carbon for improved mercury control
- Iodine removal from wet scrubber water

M-Prove Technology is a liquid coal additive that can be applied at various stages of the coal feed process. We understand that adding a chemical to your process requires thoughtful consideration to minimize risks to the plant, and have developed a suite of solutions to assist in improving performance and mitigating risks.

REFERENCES