

ICAC Technical Briefing on Mercury Control Technologies

For U.S. Environmental Protection Agency's Office of Water

The Institute of Clean Air Companies (ICAC) is the national trade association of companies that supplies air pollution control and monitoring systems, equipment, and services for stationary sources. For 60 years, ICAC member companies have helped to clean the air by developing and installing reliable, cost-effective control and monitoring systems. We believe that improved air quality and industrial growth best occur when achievable, cost-effective policies are paired with innovative technologies. We are providing this briefing to support the EPA Office of Water's understanding of mercury control technologies used at US coal-fired electric generating units (EGUs), with a specific focus on halogens.

In February 2012, EPA published the final Mercury and Air Toxics Standard (MATS). By April 2016, all coal-fired electric generating units (EGUs) greater than 25 MW were mandated to meet mercury emissions limits set by the MATS rule.

There are several mercury control strategies available to EGUs in the US. The relative effectiveness of these various strategies varies by plant and is influenced by parameters, including coal type, halogen and sulfur contents, boiler operating conditions, and air pollution control equipment type and operation. A review of air pollution control strategies reported to EPA in 2018, available through the Air Markets program, was conducted to determine the configurations currently in operation at EGUs that are required to comply with MATS. These data were supplemented with coal supply and use data reported to the Energy Information Agency (EIA) for the 12-month period December 2017-November 2018. Figure 1 provides an overview of the mercury control technologies in use at US EGUs. Additional descriptions of the technologies will be provided in the next section.



The data reported to EPA and EIA, summarized in Figure 1, suggest that approximately 58% of bituminous-fired EGUs, 92% of subbituminous-fired EGUs, and 99% of lignite-fired EGUs utilize supplemental halogens (on the coal, into the boiler or in the form of halogenated powdered activated carbon, or HPAC) as part of a mercury control strategy.

In addition to supplemental halogens, all coal contain some level of native halogen. A scatterplot of the chlorine (Cl) and bromine (Br) content in parts per million (ppm) for various ranks (grades) of coal produced in 110 counties in the US is presented in Figure 2. As shown, the contents of Br in coal are commonly about 2 percent of the Cl content (Br/Cl = 0.02), the ratio generally ranging from 1 to 4 percent (dashed lines indicate this range). The content of iodine in coal is not often measured. United States Geological Survey (USGS) data from several central and northern Appalachian coals indicate that the iodine concentration is typically between 1 and 10 ppm.

¹ Data compiled from https://ampd.epa.gov/ampd/ and https://www.eia.gov/electricity/data/eia923/. In Figure 1: RC = IRS Section 45 Refined Coal, CA = halogen-based coal additives, HPAC = halogen-treated powdered activated carbon, PAC = powdered activated carbon, including non-halogenated oxidizing PAC, WFGD = wet flue gas desulfurization. Note that "Dry" in Figure 1 includes dry flue gas desulfurization, dry sorbent injection and fluidized bed combustion. Oxidizing sorbents without the use of halogens and non-carbon-based sorbents are not independently represented in this figure.



*Figure 2. Scatterplot of chlorine and bromine content of coal produced in 110 counties*²

The number of EGUs employing wet flue gas desulfurization (WFGD) for SO₂ control has increased significantly since 2005 in response to increasingly stringent air pollution control regulations. The resulting decrease in SO₂ emissions is shown in Figure 3. By 2018, 60% of operating EGUs were configured with WFGDs. Although halogen emissions are not measured or reported continuously, reductions in SO₂ emissions are expected to trend with reductions in halogen emissions at the stack. Halogens removed by the scrubber are expected to be present in scrubber effluent.



Figure 3. Reduction in SO2 emissions since 1990³

² Kolker, Allan, Jeffrey C. Quick, Connie L. Senior, and Harvey E. Belkin. Mercury and Halogens in Coal—Their Role in Determining Mercury Emissions from Coal Combustion. USGS Fact Sheet 2012–3122. November 2012

³ (https://www3.epa.gov/airmarkets/progress/datatrends/index.html)

Although an exhaustive review of EGU National Pollutant Discharge Elimination System (NPDES) permits has not been conducted, a preliminary subset of EGUs has been compiled of units that utilize WFGD systems and add halogens (on the coal, into the boiler or in the form of HPAC) for mercury control. This subset fired 33% of all coal used at US EGUs for the previous 12 months. This percentage increases to 45% for the subset of EGUs with WFGDs that fire bituminous coal with higher halogen contents. All of these plants could be affected if a federal change to the Effluent Limitation Guidelines that limits halogen discharges was promulgated.

This briefing provides an overview of the mercury control technologies in use at US plants and a discussion on optimization and developments that have or may reduce reliance on halogens for mercury control.

Review of Mercury Control Technologies in Use at US EGUs

The combustion of coal results in the release of mercury into the flue gas in the form of particulate, gaseous elemental and gaseous oxidized mercury. Particulate mercury is removed via existing particulate control devices. Oxidized mercury can be efficiently captured in the vapor phase by current technologies. Re-emission control may be required for WFGD-equipped units to preclude the reduction of oxidized mercury (Hg²⁺) and re-emission as gaseous elemental mercury (Hg⁰). Current re-emission control strategies have been shown to be effective.

Elemental mercury is more problematic and generally needs to be oxidized in order to be collected. The higher the elemental mercury level in comparison with the target emission rate, the more difficult it will be to meet the emission limit. Oxidizing agents, such as halogens, and non-halogenated oxidizing agents are effective at converting elemental mercury to the oxidized form, which is critical to removing mercury from flue gas or in WFGDs. A review of reported mercury control strategies, including Refined Coal treatment, suggests that 80% of EGUs rely on halogen coal additives and/or HPAC for mercury control, as measured by the cumulative amount of coal fired. Non-oxidizing complexing additives, such as transition metal derivatives, have also been employed but to a lesser degree of success.

Coal Additives

Coal additives are chemicals that are added to the fuel or to the boiler. These additives increase the oxidized fraction of mercury in the combustion gas with little to no impact on the total mercury concentration. The most widely used additives are halogen-containing salts, primarily bromine-based salts. Bromine-based additives are nominally 10x more effective in flue gas than chlorine-based additives on a mass basis, as illustrated in Figure 4. Iodine-based additives are also used. Iodine additives require nominally 1/10th the mass for a similar mercury oxidation effect when compared to bromine-based additives. Iodine-based additives are rarely used at a dosage above 10 ppm.⁴ Nominally, 80% of the coal treated with halogen-based additives in the US is treated with bromine salts, and the balance is treated with iodine salts.

⁴ Gadgil, M.; Davis, K. Corrosion Rate Measurements when Adding Iodine and Bromine for Hg Oxidation." Presented at Reinhold NOx-Combustion Roundtable, Richmond, VA, February 23-24, 2015.



Figure 4. Improved mercury oxidation with bromine salts compared to chlorine salts⁵

Over about a five-year period, the Electric Power Research Institute (EPRI) analyzed 72 coalfired units using halogen additives that responded to survey questions. Forty-eight units used boiler bromine additives as part of the Section 45 Refined Coal Initiative. Seventeen used boiler bromine addition to meet state or federal mercury emissions regulations. Seven used boiler bromine addition for both Section 45 and mercury emissions compliance. Bromine addition rates reported ranges from 10 to 440 parts per million of bromine on the coal on a dry basis. The reported distribution of bromine addition rates is shown in Table 1.

Bromine addition	PRB-fired	Bituminous-	All Units
rate, ppm (dry basis)	units	fired units	
<50	18	0	18
50 to 99	4	2	6
100 to 149	23	1	24
150 to 199	4	1	5
>200 ppm	4	14	18
Total	53	18	71

Table 1. Distribution of bromine addition rates for units in EPRI survey⁶

⁵ Richardson, C.; Dombrowski, K.; Chang, R. Mercury Control Evaluation of Halogen Injection into Coal-Fired Furnaces. Presented at EUEC, Tucson, AZ, January 22-25, 2006.

⁶ Murray, Abbot, et al. Advances in Refined Coal Technology for Emissions Reduction. Presented at the Power Plant Pollutant Control and Carbon Management "MEGA" Symposium, Baltimore, MD, August 19-22, 2014.

Optimization efforts to reduce bromine addition rates have been ongoing. In 2014, results demonstrated that equivalent mercury removal could be achieved with lower bromine treatment rates. In the full-scale test results cited, the initial Refined Coal bromine treatment dose was 70 to 100 ppm. By co-injection with a proprietary chemical, the bromine treatment rate was reduced to 40 ppm.⁷ Prior to starting the trial to reduce bromine use, the holding pond used for FGD wastewater and the wastewater treatment pond were sampled for bromides. When Refined Coal treatment of the coal began, there was an increase in bromides in both the FGD holding pond and the wastewater treatment pond. When bromine addition to the coal was cut in half, there was a proportional decrease in bromides in the ponds.

A current Refined Coal user reported that they have reduced their treatment dose of bromine from 200 ppm prior to 2015, to 20 ppm since 2015. Bromine providers concur that the amount of bromine delivered for Refined Coal is consistent with this magnitude of optimization.

While it may not be reasonable to completely remove bromide from WFGD discharge water because coal contains bromide, ICAC members are actively developing and implementing technologies that are less reliant on added bromine. As recently as 2017, a major utility group chose not to pursue the application of bromide salt as mercury emissions trim control on a small subset of their plants; however, this does not constitute a universal compliance strategy away from halogens across their entire fleet.⁸

Mercury Oxidation Across SCRs

Selective catalytic reduction (SCR) systems are primarily installed for controlling NOx emissions. SCRs also promote the reaction between halogen and mercury to form Hg²⁺. This is beneficial to mercury capture when the SCR is paired with a WFGD because Hg²⁺ is highly aqueous soluble and in turn is thus easily captured in the WFGD, whereas Hg⁰ is not. Thus, for EGUs with SCRs and WFGDs, oxidization additives, such as halogens, can often be reduced or eliminated.

Current catalyst technology was developed for NO_x reduction while maintaining low SO_2 oxidation rates. These catalysts are active for mercury oxidation, but they were not designed to do so. However, new SCR catalysts that explore the design space to optimize NO_x reduction, SO_2 oxidation, and Hg oxidation are in development.

Regardless of the catalyst type, careful management of catalyst operating conditions is paramount to achieving high mercury oxidation rates and capture. Because mercury oxidation is a reaction in equilibrium, the theoretical maximum oxidation is highly dependent on operating temperature. Increasing temperatures lead to lower mercury oxidation rates. The extent of mercury oxidation is also heavily impacted by both the type of halogen (i.e. Cl vs Br vs I) and the concentration, particularly at low halogen concentrations. Other contributing factors

 ⁷ Murray, Abbot, et al. Advances in Refined Coal Technology for Emissions Reduction. Presented at the Power Plant Pollutant Control and Carbon Management "MEGA" Symposium, Baltimore, MD, August 19-22, 2014.
⁸ Hatcher, Larry E. (June 12, 2017), Ltr to Willets, Wm NCDEQ, Mercury and Air Toxics Standards (MATS); 40 CFR 63, Subpart UUUUU Rescission Request to Use Halide Salts as a Mercury Control Strategy.

https://www.southernenvironment.org/uploads/words_docs/withdrew_re_SIGNED_Submittal_(3).pdf

include, but are not limited to, the concentration of ammonia and the space velocity. Because SCRs are typically installed for NOx reduction and mercury oxidation is considered a "cobenefit", it is often not possible to maximize mercury oxidation because it may negatively impact NOx reduction effectiveness.

Injection of Powdered Activated Carbon

Prior to the development and implementation of halogen addition to PAC, EGUs tested nonoxidizing carbons to capture mercury. The US Department of Energy (DOE) sponsored several full-scale demonstrations of activated carbon injection for evaluating mercury control technologies, including those included in Figure 5 below. ⁹ While the DOE study did not cover all possible EGU configurations, a reasonable breadth of information for activated carbon technology at the time was provided.¹⁰ Prior to initiating a broad study, DOE concluded from their testing that it would cost \$50,000 to \$70,000 per lb. of mercury removed to capture 50%-70% of the mercury.¹¹ Because this cost was deemed prohibitively high, DOE funded mercury control technology development projects that resulted in the development of halogenated technologies, increased the achievable mercury reduction level to at least 90%, and reduced the cost of control to approximately 10% of the 2002 level.¹²

EGUs with fabric filters (FFs) and/or electrostatic precipitators (ESPs) provide an opportunity to employ sorbents for mercury removal. The most prevalent is powdered activated carbon (PAC) that is introduced into the flue gas or combustion gas to transfer mercury from the gas phase to the solid phase where it is captured on the sorbent and/or is associated with the fly ash in a particulate control device.

It is important to realize that the sorbents will add to the particulate loading on the FF and ESP. A few plants add activated carbon into the combustion gas prior to a WFGD system. In such a case, the WFGD serves both as a particle and sulfur capture device. In this configuration, the sorbent becomes part of the gypsum or scrubber by-product entering the wastewater treatment system where it may be separated with process equipment. In addition to injection of activated carbon upstream of the WFGD, some utilities add activated carbon directly within the WFGD recirculation water.^{13,14}

There are many grades and types of PAC products currently available. Since elemental mercury does not readily adsorb to activated carbon, only EGUs with sufficient oxidized mercury can rely on PAC without an added oxidizer, which is typically halogen-based. A review of data reported

⁹ Durham, M. et al, Full-Scale Evaluation of Sorbent Injection for Mercury Control on Power Plants Burning Bituminous and Subbituminous Coals, Powergen International 2002, Orlando, FL

¹⁰ "Mercury Emissions from Coal-Fired Power Plants: A Case for Regulatory Action," Northeast States for Coordinated Air Use Management, 2003.

¹¹ Mercury Control Technologies, Department of Energy

¹² Nelson, S, Advanced Utility Mercury-Sorbent Field-Testing Program, Final Report, December 31, 2007

¹³ Marsan, R. Mercury and Selenium. Presented at the APC Roundtable, St. Louis, MO, July 8-9, 2013.

¹⁴ Elliott, P. Mercury Control Strategy of a Wet Sodium Scrubber. Presented at the Power Plant Pollutant Control "MEGA" Symposium, Baltimore, MD, August 20-23, 2012.

to the EPA Air Markets Program suggests that only 8% of EGUs (on a coal-fired basis of tons burned) report relying on non-halogenated PAC in the absence of supplemental halogens.

Most commercially-available enhanced PACs treat the activated carbon with halogens to achieve sufficient mercury oxidation and capture. Additionally, oxidizing carbons without the use of halogens are currently available. Figure 5 provides an example of the improved removal achievable with PAC treated with bromine compared to non-brominated PAC. The use of a HPAC, or the combination of activated carbon with the use of a halogen-based coal additive, can often greatly increase the mercury capture performance versus non-halogenated activated carbon.

Several grades of HPACs are available, which contain a range of halogen content levels. The type of halogen, mass of halogen added, and halogen application method differ significantly between the different HPAC types. These differences will likely affect whether the added halogen remains in the carbon's porosity or volatizes to the gas phase. A low added mass of thermally stable halogen retained in the carbon porosity is unlikely to impact the WFGD effluent concentration of halogen.



Figure 5. Improved performance with bromine-treated PAC¹⁵

Advanced sorbents containing non-halogen oxidizing agents or mercury complexing agents have been available for over a decade. These sorbents have been tested in several configurations. Many EGUs are trialing next-generation "low" halogen chemistries or nonhalogenated sorbents currently being developed by various activated carbon manufacturers. For plants that depend on activated carbon for mercury emission, comparable performance has

¹⁵ Senior, et al. Multimedia Impacts of Halogen Injection for Mercury Control in Coal-Fired Boilers. Presented at EUEC, January 30, 2012

been demonstrated in some cases between standard halogenated PAC and these advanced non-halogen PACs^{16}

One type of PAC is being developed to incorporate a non-halogen oxidizing carbon that is chemically and physically enhanced to target gas and liquid phase removal of mercury in WFGD scrubbers. Recently, some promising trials have been completed where this PAC was directly injected within the WFGD recirculation slurry. Although only one utility uses this approach to mitigate Hg spikes when their coal mercury content is higher than normal, several trials suggest in due course that some EGUs may entertain this strategy in their efforts to meet compliance. Advanced non-halogen sorbents and additives may eventually contribute to a broad solution. However, there exist many challenged sites with complex flue gas chemistries or suboptimal air quality control systems (AQCS) where advanced non-halogen mercury compliance strategies have not been trialed. Many EGUs currently rely on some form of native mercury capture and/or co-benefit mercury removal (i.e., refined fuel, SCR, WFGD, etc.), in conjunction with PAC injection. Site considerations and EGU AQCS variability across the industry have not, to date, supported a singular solution. Technology development, product testing, commercial demonstration and phase-in over time have been a supported industry approach. It has been proposed that several years may be required fully commercialize advanced nonhalogen sorbents and additives.¹⁷

Inorganic Sorbents

Inorganic (non-carbon) mercury sorbents are also applied as dry powders in manners and locations similar to activated carbon. These materials are effective on limited configurations and used for compliance at less than 1% of US EGUs.

Inorganic alkaline sorbents are also used for control of acid gases. The measured introduction of dry alkaline sorbents in the flue gas or exhaust gas is known is dry sorbent injection (DSI). DSI systems are employed to remove hydrogen chloride (HCl) and other acid gases.¹⁸ DSI is used for HCl control at coal-fired power plants and for hydrogen fluoride (HF) control at glass manufacturing facilities.^{19,20} While we have no published data to support such and properties of individual hydrogen halides differ, HCl and HF may be surrogates for other halogens when evaluating potential for control.

As stated above, elemental mercury generally needs to be oxidized in order to be collected in air pollution control devices. Oxidizing agents, such as halogens, are very effective at converting elemental mercury to the oxidized form. Alkaline sorbents, such as hydrated lime and trona,

¹⁶ Rodriguez, et al, How the Right Optimization Team Can Improve Your MATS Compliance Strategy. Presented at EUEC, March 5, 2018

¹⁷ Rodriguez, et al. Mercury Capture in the Wet FGD with WetJect[™]. Presented at Power Plant Pollutant and Effluent Control MEGA Symposium: Best Practices and Future Trends, August 23, 2018

¹⁸ <u>https://www.eia.gov/todayinenergy/detail.php?id=5430</u>

¹⁹ <u>https://www.epa.gov/airmarkets/national-electric-energy-data-system-needs-v6</u>

²⁰ Dickerman, J., Schantz, M., IMPROVED DSI PERFORMANCE WITH OPTIMIZED HYDRATED LIME, Air Quality IX, October 2013

show effectiveness for HCl capture and may effectively remove other halogens. However, this may also reduce the effectiveness of the halogens for mercury oxidation and, in some cases, reduce the effectiveness of certain mercury control strategies.

WFGD Additives

WFGDs operating at high sulfur capture rates theoretically should be able to remove nearly 100% of the oxidized mercury from combustion gas. However, in many cases oxidized mercury capture efficiencies are significantly less than theoretical. One demonstrated cause of the limited performance is mercury re-emission. Simply put, mercury re-emission is when elemental mercury concentration in the combustion gas entering the WFGD is lower than that of the stack gas or scrubbed gas. This occurs when oxidized mercury is absorbed into the scrubber liquor, and subsequently reduced (that is, the oxidation state of the mercury compound is lowered) in the aqueous phase to elemental mercury, which is then released back into the gas phase. Figure 6, below, depicts flue gas mercury absorption/desorption across WFGD. Higher bromine levels in the scrubber liquor have been associated with lower mercury re-emissions. WFGD additives or scrubber additives have been developed and demonstrated to reduce or eliminate the occurrence of mercury re-emission.



Figure 6. Illustration is provided of flue gas mercury absorption/desorption across WFGD²¹

²¹ Institute of Clean Air Companies, Improving Capture of Mercury Efficiency of WFDGs by Reducing Mercury Reemissions, June 2014, pp. 6.

Several activated carbon suppliers provide carbon optimized for injection directly into a WFGD. These materials can decrease the fraction of dissolved mercury and the associated risk of reemissions by sequestering the liquor-solubilized mercury in the carbon solid-phase. The pore structure of PAC permits the adsorption and removal of mercury and allows for enhanced contact time through the recirculation of WFGD systems. Full-scale testing confirms that the PAC is effective at capturing dissolved mercury and lowering stack mercury emissions by controlling re-emissions.²²

Discussion of Halogen Treatment, Fate of Halogens in EGUs (Ash or WFGD)

For plants that discharge effluent into waterways, some of the halogen added to the system may report to the particulate and some may be incorporated into the effluent. However, insufficient data are currently available to determine the fate of all added halogens. Uses of HPACs incorporating a low mass of thermally stable halogen are likely to have limited impact on halogen content of the WFGD effluent. Use of these thermally stable halogen HPAC types, which have a proven record of mercury control success on a range of EGU sites, may be a way to address WFGD effluent concerns for at risk EGU sites. Alkaline sorbents, such as hydrated lime and trona, show effectiveness for HCl capture and may effectively remove other hydrogen halides with the particulate matter. However, as noted previously, this may also reduce the effectiveness of the halogens for mercury oxidation.

Data available from EPA's 2010 Information Collection Request that included HCl indicated that some HCl, and presumably other hydrogen halides, can be collected with the solids. Referring to Figure 7, for bituminous plants with cold-side ESPs (CESP), most HCl passes through. If the CESP is followed by a WFGD, the data suggests that most HCl is retained in the WFGD. For bituminous-fired units with a fabric filter (FF), nominally 50% of the HCl was captured in the FF. For subbituminous units, nominally 50% of the HCl was captured in a CESP and nominally 80% in a FF. Thus, the loading into a WFGD on a subbituminous-fired unit with either a CESP or FF would be lower. The data further indicates that the HCl capture on subbituminous units is lower at nominally 80%. If this data is representative of all halogens, one could extrapolate that on subbituminous units with WFGDs, nominally 40% of the halogen would be captured in the WFGD for a unit configured with a CESP, and 16% of the halogen would be captured in the WFGD for a unit configured with a FF.

²² Marsan, R. Mercury and Mercury Oxidation. Steag Energy Services LLC, Presented at Worldwide Pollution Control Association Southern Company Wastewater Treatment Seminar, April 2013.



Figure 7. Percent fuel chloride emitted at the stack²³

Discussion on Potential Impact of Effluent Halogen Restrictions on Power Plant Mercury Control Effectiveness and Reliability

Based on data reported to the EPA Air Markets Program and the EIA, 80% of US EGUs reported reliance on added halogens (either added to the fuel or boiler or in the form of halogenated PAC) for mercury control in 2018. Through optimization efforts, suppliers and users report that halogen use at individual plants is, on average, declining.

Restrictions on halogen in effluent from WFGDs could impact 45% of EGUs in the US. This population includes all units with WFGDs that discharge water and are either using halogen for mercury control, or fire higher halogen coal.

Closing Statement

ICAC remains committed to regulatory actions that support of environmental protection and protect human health. Through the work of many ICAC members and through extensive testing of many innovative ideas, halogen-based technologies were developed which now effectively control mercury emissions at the majority of coal-fired power plants, for a cost that can be borne by the EGUs. As a continuation of our commitment to good environmental practices, we believe that an assessment of the upstream sources of the halogen discharges, the relative contribution from those sources, and finally the fate of halogens from those sources is critical to understanding how to promulgate ELG rules that will improve public health in both water and air.

Figure 8 below shows various sources of potential bromide contribution to source water concentrations. The data represented in Figure 8 are several years old, and possibly outdated for contributions from coal-fired power plants due to the significant reductions in bromide

²³ Senior, et al. Multimedia Impacts of Halogen Injection for Mercury Control in Coal-Fired Boilers. Presented at EUEC, January 30, 2012.

additions since 2015. However, Figure 8 is valuable in pointing out the necessity of assessing all potential sources of halogen release upstream of drinking water treatment plants.



Figure 8. Bromide concentrations (mg/L on log scale) in natural waters, oil and gas produced waters, and coal-related wastewaters²⁴

In conclusion, the goals of protecting drinking water sources and preserving air quality need not be mutually exclusive, and for our part, ICAC members continue to develop innovative, advanced reduced-halogen and non-halogen technologies for mercury oxidation at EGUs. We believe that a better understanding of the potential contributors to halogen levels in surface waters will increase decision making capability, build awareness about this potential water pollution problem, and will lead to sound regulatory actions.

²⁴ VanBriesen, J.M., Potential Drinking Water Effects of Bromide Discharges from Coal-Fired Electric Power Plants, 2014.