

# FUNDAMENTAL SCIENCE AND ENGINEERING OF MERCURY CONTROL IN COAL-FIRED POWER PLANTS<sup>1</sup>

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## **ABSTRACT**

Electric utilities must deal with impending regulation of mercury from coal-fired power plants in the most cost-effective manner. Mercury (Hg) can be controlled by existing air pollution control devices or by retrofit technologies. Choosing the best approach for any given unit requires knowledge of the chemistry of mercury in flue gas, including its behavior in existing air pollution control devices abetted with retrofit technologies such as activated carbon injection. Furthermore, the impact of fuel switching and blending on the efficiency of mercury control must also be understood. In this paper, we discuss the existing knowledge base applicable to mercury control in coal-fired boilers and outline the gaps in knowledge that can be filled by experimentation and data gathering. While laboratory-scale experiments are important, pilot- and full-scale test data are needed to adequately understand the control of Hg in coal-fired units. We review current speciation and capture models and use them to interpret recent pilot- and full-scale test results. Finally, we discuss further research needed to understand the mechanisms that control the behavior of mercury in the many coal-combustion-control technology combinations that are used at coal-fired electric generating stations.

## **INTRODUCTION**

A study by the National Academy of Sciences (NAS) concluded that human exposure to methylmercury from eating contaminated fish and seafood is associated with adverse neurological and developmental health effects. The U.S. Environmental Protection Agency's (EPA's) report to Congress on the risks hazardous air pollutants (HAPs) from electric utility generating stations concluded that there is a plausible link between mercury (Hg) emissions and adverse health effects in humans. In December 2000, the EPA announced plans to develop HAP emission regulations that will limit Hg emissions from coal-fired electric utility stations.

The U.S. Department of Energy (DOE), the Electric Power Research Institute (EPRI), EPA and other organizations are developing Hg control technologies for coal-fired electrical

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<sup>1</sup> Paper presented at the Air Quality IV Conference, September 22-24, 2003, Arlington, VA.

generating units. The capture of mercury in air pollution control devices depends on its speciation, so a scientific understanding of mechanisms that govern its speciation and capture is crucial to the development of effective control technologies. Factors that determine the speciation and capture of Hg from coal combustion exhausts include the type of coal, combustion conditions, and flue gas cleaning equipment used at each power plant.

## **BACKGROUND**

Flue gas from coal combustion may contain elemental mercury ( $\text{Hg}^0$ ), mercury chloride ( $\text{HgCl}_2$ ), mercury oxide ( $\text{HgO}$ ), mercury sulfate ( $\text{HgSO}_4$ ), mercuric nitrate [ $\text{Hg}(\text{NO}_3)_2$ ], and a number of other compounds. Each of these species has different properties that determine its solubility in water and its potential for adsorption onto solid surfaces. Available measurement techniques only allow for the routine measurement of ionic mercury ( $\text{Hg}^{2+}$ ), particulate bound mercury ( $\text{Hg}_p$ ), and  $\text{Hg}^0$  in flue gas. The determination of these three forms of mercury in flue gas is called the speciation of mercury.

Insights on Hg speciation and capture can be obtained from laboratory and pilot-scale experiments, as well as from the study of mercury speciation measurements on full-scale units. Starting at the laboratory scale, a large body of work exists on the behavior of mercury in particle-free, synthetic combustion gas mixtures and on the interaction of mercury with fly ash and sorbents like activated carbon. Experimental correlations, chemical equilibrium calculations, homogeneous reaction models, heterogeneous reaction models, and other studies have all aided in the characterization of Hg speciation and capture.

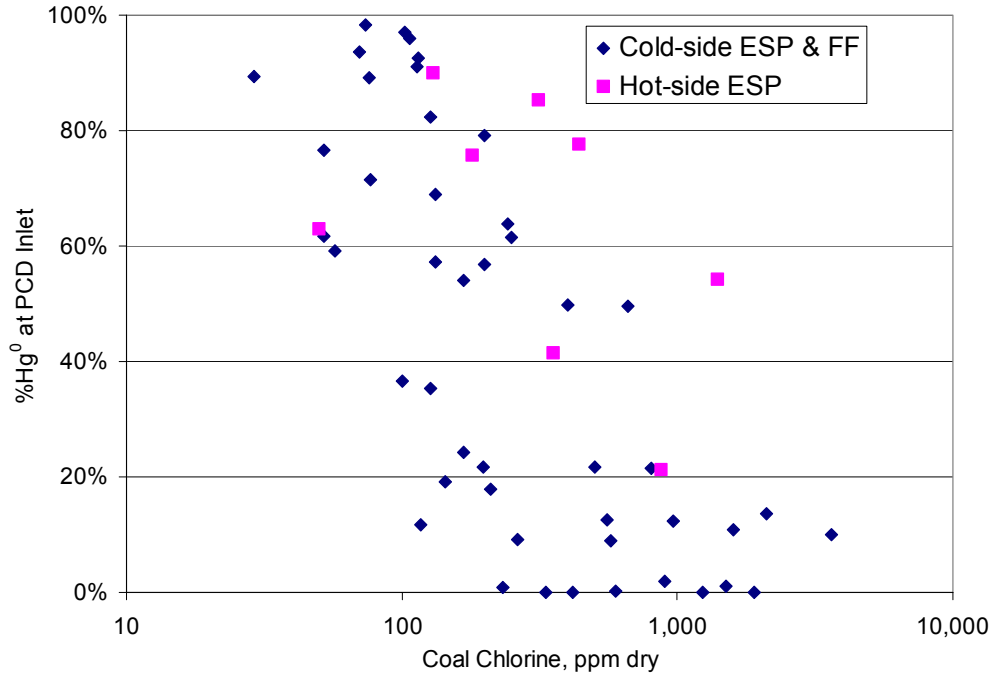
## **MERCURY BEHAVIOR IN FLUE GAS**

Mercury exists as  $\text{Hg}^0$  in the high temperature regions of coal-fired boilers. As the flue gas is cooled, a series of complex reactions begin to convert the  $\text{Hg}^0$  to  $\text{Hg}^{2+}$  and  $\text{Hg}_p$ . In the presence of chlorine, gas-phase equilibrium conditions favor the formation of  $\text{HgCl}_2$  at flue gas cleaning temperatures. However, the oxidation of  $\text{Hg}^0$  is kinetically limited by the gas-phase (homogeneous) and gas-solid (heterogeneous) reaction rates. As a result, mercury enters the flue gas cleaning device(s) as a mixture of  $\text{Hg}_p$ ,  $\text{Hg}^{2+}$ , and  $\text{Hg}^0$ .

The extent of conversion of  $\text{Hg}^0$  to  $\text{Hg}^{2+}$  and  $\text{Hg}_p$  depends on the flue gas composition, the amount and properties of fly ash, and the flue gas quench rate. These factors are, in turn, dependent on the type (and properties) of coal, the combustion conditions, and the design of boiler and downstream heat extraction equipment. Important coal properties include the coal sulfur, chlorine, nitrogen, and mineral content. Flue gas composition is important because some components enhance Hg capture while others diminish capture. The properties of fly ash are important because fly ash can both oxidize  $\text{Hg}^0$  and capture  $\text{Hg}^0$  and  $\text{Hg}^{2+}$ .

Data on mercury speciation from full-scale utility boilers provide insight into Hg chemistry in flue gas. Utility boiler field-test data show that the chlorine content of the coal has some impact on the speciation of mercury at the inlet to the air pollution control device(s). Figure 1 shows the fraction of  $\text{Hg}^0$  in flue gas at the inlet to the electrostatic precipitator (ESP) particulate control device for samples taken as part of EPA's Information Collection Request (ICR).<sup>1</sup> While there is considerable scatter in the data, it is clear that coals containing "low" chlorine (less than 100-300  $\mu\text{g/g}$  Cl) result in flue gas in which  $\text{Hg}^0$  predominates whereas

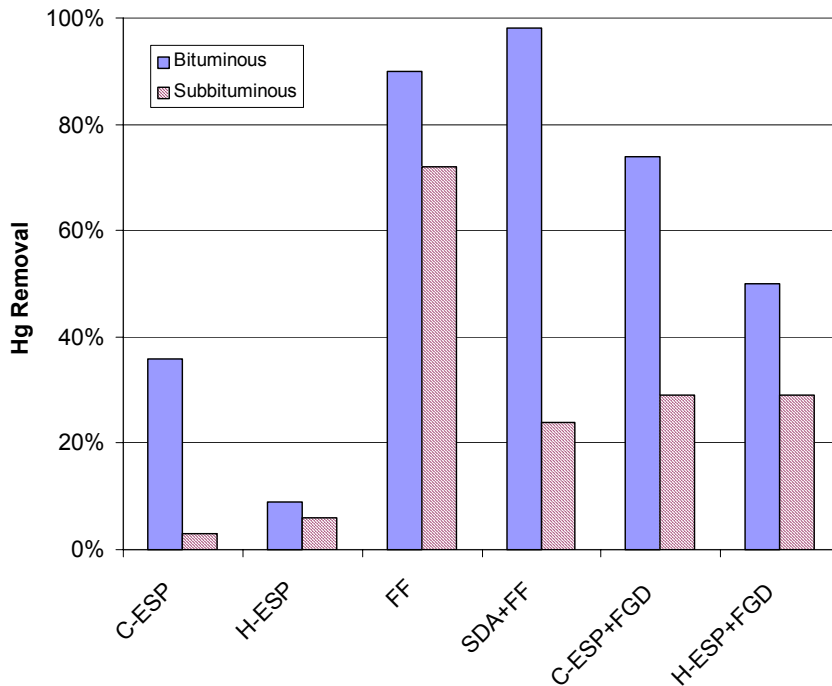
flue gas from coals containing “high” chlorine (more than about 500  $\mu\text{g/g}$  Cl) have relatively little  $\text{Hg}^0$ . The scatter in the data may be due to a number of factors not accounted for in the ICR data, particularly the amount of unburned carbon (UBC) in the fly ash.



**Figure 1. Fraction of elemental mercury in flue gas at inlet to particulate control device as a function of coal chlorine content (Source: ICR data).**

Research has shown that Hg is adsorbed onto the UBC in fly ash, forming  $\text{Hg}_p$ . The capture of  $\text{Hg}_p$  in an existing air pollution control device is sometimes called “natural” capture<sup>2</sup>. In general, increases in the UBC content of fly ash lead to increases in Hg capture in particulate matter (PM) control devices. Coal char from the combustion of low rank coals is very reactive, and the resulting fly ash typically has low concentrations of UBC. Furthermore, fixed-bed, bench-scale testing has shown that the presence of HCl in simulated flue gas promotes adsorption of  $\text{Hg}^0$  by carbon. Low rank fuels contain low amounts of chlorine, typically less than 100  $\mu\text{g/g}$ , resulting in flue gas with low HCl concentrations in which  $\text{Hg}^0$  is the predominant Hg specie. Thus, lower natural removal of Hg in PM control devices is expected in plants burning low rank fuels.

Accordingly, cold-side ESP’s (C-ESP’s) and fabric filter baghouses (FF’s) exhibit levels of natural Hg capture that are dependent on the type of coal burned. The ICR data in Figure 2 shows the average Hg removal for different coal and control technology combinations.<sup>2</sup> While units that burned bituminous coal and were equipped with a C-ESP had an average Hg removal of 36%, removals as high as 90% were measured. Many units that burn subbituminous coal exhibit little, if any, capture of Hg in C-ESPs. In general, FF’s show higher Hg removals than C-ESP’s because of the additional Hg capture that occurs as flue gas passes through the FF filter cake. For units equipped with a FF, the average Hg removal was better for bituminous coals (90%) than for subbituminous coals (72%).



**Figure 2. Average removal across air pollution control devices as a function of coal rank (Source: ICR data).**

Dry flue gas desulfurization (FGD) scrubbers capture Hg by adsorption onto both the alkaline sorbent particles used for SO<sub>2</sub> control and the UBC in fly ash. The most common dry scrubber system used by the electric utility industry is a spray dryer adsorber (SDA) followed by either an ESP or a FF. Bench-scale experiments have shown that HgCl<sub>2</sub> is easily adsorbed onto hydrated lime, the most common

sorbent used in SDA's. For the same type of coal, SDA-FF systems are more effective in capturing Hg than SDA-ESP systems because of Hg capture in the filter cake. The capture of Hg from bituminous coal flue gas is typically much higher than the capture of Hg from low rank coal flue gas because of the higher proportion of Hg<sub>p</sub> and Hg<sup>2+</sup> in bituminous coal exhausts.

The ICR data indicate that the capture of Hg from bituminous coal flue gas is better in units equipped with a SDA/FF system than those equipped with a FF alone. This is because of the effective capture of Hg<sup>2+</sup> by alkaline sorbents. Conversely, the capture of Hg from units burning subbituminous coal was better for units equipped with a FF than those equipped with a SDA-FF system. Alkaline sorbents do not capture Hg<sup>0</sup>, and they adsorb HCl, reducing the availability of chlorine for Hg<sup>0</sup> oxidation and capture.

Wet FGD systems consist of a PM control device (ESP or FF) followed by an alkaline scrubber, the most common being a limestone scrubber. The PM control device can capture Hg<sub>p</sub>, and the wet FGD scrubber can capture soluble compounds of Hg<sup>2+</sup>. The ICR data show that the average Hg removal across wet FGD scrubbers is well over 50% for bituminous coals but only about 30% for subbituminous coals (see Figure 2). Owing to the differences in speciation of mercury entering the air pollution control devices, the removal of Hg across scrubbers depends on the rank of coal being burned. Scrubbers on units equipped with a FF tend to exhibit higher Hg capture than units equipped with an ESP because of increased Hg<sup>0</sup> oxidation across the filter cake.

The capture of Hg in wet scrubbers is also affected by scrubber design and operating conditions. For example, low liquid-to-gas ratios may limit the mass transfer of pollutants, and the scrubber chemistry may result in the reduction of dissolved  $\text{Hg}^{2+}$  and the subsequent re-emission of  $\text{Hg}^0$ . Some units are equipped with combined PM and FGD scrubbers. These scrubbers will probably exhibit lower Hg capture efficiencies than FGD systems equipped with an ESP or FF. Wet PM scrubbers are not efficient collectors of fine particulate ( $\text{Hg}_p$ ), and they do not enhance oxidation of  $\text{Hg}^0$ , as does an ESP or FF.

Based on ICR data, about 90% of the incoming oxidized mercury was removed across wet FGD's. Virtually no elemental mercury was removed. The chemistry of Hg in scrubbers is important, and several problems associated with the capture of Hg in wet scrubbers must be resolved by further research. Potential problems include the need to oxidize additional  $\text{Hg}^0$  to  $\text{Hg}^{2+}$ , effective dissolution of  $\text{Hg}^{2+}$  in the scrubbing liquor, prevention of  $\text{Hg}^{2+}$  reduction reactions, absorption of  $\text{Hg}^{2+}$  onto solids in the scrubbing liquor, and separation of solids from the scrubber liquor.

In some instances,  $\text{Hg}^0$  is oxidized by the vanadium-based catalysts used in selective catalytic reduction (SCR) units. Pilot- and full-scale tests have shown that oxidation of  $\text{Hg}^0$  in SCR catalyst systems is limited to units burning bituminous coal. The presence of ammonia (the reducing agent) often reduces the amount of  $\text{Hg}^0$  oxidation as does aging of the catalyst. Measurements along a length of catalyst indicate competition between ammonia and  $\text{Hg}^0$  for active surface sites. While a certain amount of HCl in the flue gas appears to be necessary for  $\text{Hg}^0$  oxidation<sup>3,4</sup>, the exact mechanisms for  $\text{Hg}^0$  oxidation by vanadium catalysts and its dependence on flue gas properties are currently unknown.

## MODELING MERCURY CHEMISTRY

Bench-, pilot-, and full-scale research has led to the development of theoretical models that attempt to explain the speciation and capture of Hg in coal-combustion flue gases. The transformation of  $\text{Hg}^0$  to  $\text{Hg}^{2+}$  involves both homogeneous and heterogeneous reactions. Key elements of these models as formulated by Sliger, Fujiwara, Niksa, Senior, Olsen, and others<sup>5-10</sup>.

The primary gas-phase  $\text{Hg}^0$  oxidation product is believed to be  $\text{HgCl}_2$ , the specie favored by equilibrium conditions. The gas-phase transformation pathway involves the oxidation of  $\text{Hg}^0$  by atomic Cl. The concentration of Cl, in turn, depends on a complex series of gas-phase reactions involving oxygen, water vapor, hydrocarbons, chlorine compounds, and sulfur compounds. A number of critical reactions limit the concentration of Cl and the subsequent conversion of  $\text{Hg}^0$  to  $\text{HgCl}$  and then to  $\text{HgCl}_2$ . Although  $\text{NO}_2$  has been shown to oxidize  $\text{Hg}^0$  in laboratory experiments, it is not believed to play a major role in homogeneous  $\text{Hg}^0$  oxidation reactions.

The cooling rate in the flue gas has also been shown to strongly influence homogeneous oxidation of  $\text{Hg}^0$ . High flue gas cooling rates between the air heater inlet and air pollution control device inlet limit reaction rates associated with homogeneous oxidation reactions. The effects of cooling rates on heterogeneous reactions are unknown.

Heterogeneous reactions involve absorption and desorption reactions that lead to the adsorption of gas-phase Hg onto solid particles ( $Hg_p$ ) and the formation of  $Hg^{2+}$ .<sup>10</sup> In a “first-generation” heterogeneous speciation mechanism proposed by Niksa, HCl is adsorbed onto the UBC in fly ash, forming chlorinated surface active sites for the chemisorptions of  $Hg^0$ . Niksa’s mechanism currently uses experimental data from the combustion of specific coals to characterize the concentration and properties of the reactive UBC sites on coal fly ash.<sup>9</sup>

A multi-step heterogeneous model has been proposed by researchers at the University of North Dakota – Energy and Environmental Research Center (UND–EERC) to characterize the adsorption and oxidation of Hg by activated carbons.<sup>10</sup> Two mechanisms are postulated: a binding site mechanism and an oxidation mechanism. Both are based on the concept of zig-zag carbene structures, the spaces between aromatic rings. These structures are postulated to be the location of Lewis sites for binding and oxidization of Hg. Lewis acid sites are created at these locations by reactions involving HCl,  $SO_2$ ,  $H_2SO_4$ ,  $NO_2$ , and other flue gas constituents.

In an alternate heterogeneous oxidation mechanism, the metals in fly ash can produce Cl atoms via the Deacon process reaction to oxidize  $Hg^0$  to  $HgCl$ , followed by reactions that form  $HgCl_2$ .<sup>11</sup> It has been recognized for many years that certain metals in fly ash can produce Cl atoms from HCl; copper was identified as a metal that catalyzed this decomposition in order to form dioxins in municipal solid waste combustors. More recently, both copper oxide and iron oxide have been shown to promote oxidation of  $Hg^0$  in the presence of HCl in simulated flue gas.<sup>11</sup>

The presence of chlorine is necessary for all three of these proposed heterogeneous reaction mechanisms. Carbon surfaces are essential for two of the mechanisms, and one or more metals, such as Fe, are required for the third mechanism. The mechanism involving carbon structures and Lewis acid reactions require HCl and a number of other flue gas constituents ( $H_2SO_4$  and  $NO_2$ ).<sup>10</sup> The validity and relative importance of each of these mechanisms is currently unknown.

Models for the homogeneous oxidation of mercury in flue gas have been developed and seem to predict laboratory data fairly well.<sup>8</sup> Both homogeneous and heterogeneous oxidation pathways may be important in coal combustion flue gas. Models for heterogeneous oxidation of mercury in flue gas have been proposed, but are not as mature as gas-phase models. Work has begun on the modeling of  $Hg^0$  oxidation in SCR catalysts, but a heterogeneous oxidation mechanism has not been formally proposed. More work, both experimental and theoretical, is needed to bring mercury models to a state that will allow them to accurately predict the effects of process and fuel changes on mercury oxidation and capture in coal combustion flue gases.

## **CONTROL STRATEGIES**

Strategies for reducing Hg emissions include coal cleaning, the implementation of combustion and process change to enhance the natural capture of Hg by fly ash, the retrofit of existing flue gas cleaning equipment to improve Hg capture, and the use of additional flue gas cleaning devices (multipollutant controls) to limit emission of Hg and other pollutants.

## Pre-combustion Controls

Physical coal cleaning is widely used on bituminous coals to remove mining residues and to reduce ash and sulfur for the production of “SO<sub>2</sub>” compliance coals<sup>12</sup>. It has been estimated that current coal cleaning practices, used primarily for bituminous coals, reduce the potential emission of Hg by approximately 37%<sup>12</sup>. The use of advanced coal-cleaning processes to remove additional Hg is not believed to be competitive with other potential Hg control technologies. Further reductions in Hg emissions by coal beneficiation will depend on the ability of coal cleaning to provide other cost benefits, such as reduced transportation costs and boiler operating and maintenance costs.<sup>2</sup>

Subbituminous coals and lignites are not generally cleaned. Although DOE and EPRI no longer support coal-cleaning research, the private sector is promoting the development of a number of processes. An example is the K-fuel technology, which uses heat and pressure to physically and chemically transform low rank fuels into low-moisture, high-BTU solid fuels.<sup>13</sup> The K-fuel process removes ash and Hg from the coal and thus has the potential to produce fuels with a low mercury content and high heating value.

## Process Modifications

A number of techniques can be used to optimize the natural capture of mercury with existing combustion and flue gas cleaning equipment:

- The addition of reagents to coal or the high temperature combustion gases to promote oxidation of elemental mercury,<sup>14</sup>
- Combustion modifications that increase the amount or reactivity of UBC in fly ash to increase its adsorption of mercury and/or promote oxidation of elemental mercury,<sup>15</sup>
- The blending of coal to change the composition of flue gas and the properties of fly ash to increase formation of oxidized and/or particulate-bound mercury, and<sup>15,16</sup>
- Combinations of the above.

Recent research has shown that the addition of chemical reagents to the coal, coal burners, or furnace can promote oxidation of Hg<sup>0</sup>. This technique is intended for fuels with low chlorine content, primarily subbituminous coals and lignite.<sup>14</sup> EPRI-sponsored tests indicate that reagents containing chlorine can increase Hg<sup>0</sup> oxidation in the flue gas from these fuels. However, the increased oxidation did not always lead to increases in Hg capture. In addition, the different reagents tested exhibited varying degrees of detrimental balance-of-plant operating effects that must be resolved before utilities are willing to use reagents to enhance Hg oxidation and capture.<sup>14</sup>

Single burner pilot-scale tests have shown that combustion modifications and coal blending can be used to obtain high levels of Hg capture by the UBC in fly ash.<sup>15,16</sup> Combustion modification tests with bituminous coal indicated that gas-phase Hg reductions across a FF of greater than 90% were possible.<sup>15</sup> The use of subbituminous and bituminous coal blends in conjunction with combustion modification and combustion optimization techniques resulted in gas-phase Hg reductions across an ESP as high as 90%.<sup>15</sup> Although this research shows great promise, obtaining high levels of Hg capture in large coal-fired utility boilers with

multi-burner arrays will be difficult. In general, high levels of Hg control will require advanced combustion monitoring and control techniques and an appropriate bituminous coal. It will also require precise control of the coal blending methods, coal grind size, and the amount and distribution of coal and combustion air.

Combustion modification or other processes to enhance mercury oxidation may give high levels of oxidation in pilot-scale demonstrations, but such techniques may not give consistent results for a wide range of coals and operating conditions. However, these methods can be used to increase the natural capture of Hg in ESP's and FF's, reducing the amounts of sorbent needed to meet regulatory requirements. They can also be used to enhance Hg capture in wet scrubbers.

### Mercury Capture with Sorbents

Activated carbon injection (ACI) is the most mature technology for control of Hg emissions from coal-fired power plants. Figure 3 summarizes pilot- and full-scale Hg capture data for units that burn bituminous or Powder River Basin (PRB) coals and that are equipped with an ESP or FF. The symbols are for data from three full-scale tests conducted by ADA-ES under a cooperative agreement with DOE/NETL. While the coals and control technologies varied from site to site, the same group of commercial activated carbons were evaluated during parametric tests at each site. These full-scale data are discussed in more detail below. The region within the dashed lines depicts EPRI pilot-scale data from the three full-scale test sites and a variety of other sites.<sup>17</sup> The region with the dashed curves illustrate the effects of different flue gas properties on Hg capture efficiencies.

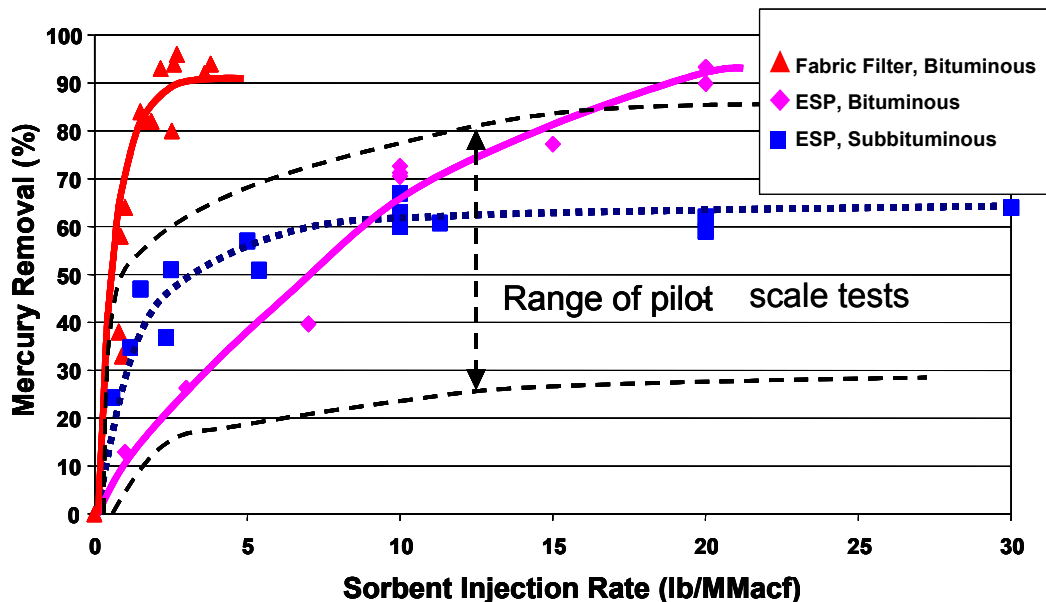


Figure 3. Removal of Hg across the particulate control device as a function of injection rate of activated carbon. (See text for references.)

### ***Cold-side ESP Retrofits for Bituminous Coals***

The combustion of low-sulfur bituminous coal often produces enough UBC and chlorine to oxidize and capture a significant fraction of the  $\text{Hg}^0$  that leaves the high-temperature regions of the boiler.<sup>18,19</sup> The use of low- $\text{NO}_x$  burners often results in fly ash UBC contents that range from several percent to more than ten percent. The minerals in bituminous coals can contain enough Fe and other reactive metals to permit  $\text{Hg}^0$  oxidation reaction via the Deacon process reaction.

Similar oxidation and capture mechanisms are believed to apply to both high- and low-sulfur bituminous coals when ACI is used to control Hg emissions. However, the higher  $\text{SO}_2$  concentrations from high-sulfur coals occupy a larger fraction of the surface active sites, decreasing the carbon adsorption capacity for  $\text{Hg}^0$ . With extended exposure to  $\text{SO}_2$  or  $\text{NO}_2$ , the  $\text{Hg}^0$  adsorbed by fly ash and activated carbon can be desorbed as  $\text{Hg}^{2+}$ . Therefore, to obtain the same Hg capture efficiency, higher carbon injection concentrations will generally be required for high-sulfur coals than for low-sulfur bituminous coals.

Activated carbon injection tests at Brayton Point illustrate site-specific factors that effect Hg capture in low-sulfur bituminous coals equipped with cold-side ESP's.<sup>19</sup> Brayton Point is equipped with low- $\text{NO}_x$  burners and typically has high levels of UBC in the fly ash as indicated by loss on ignition (LOI) measurements. The PM control system at Brayton Point is unusual in that it consists of two cold-ESP's in series. The long duct runs between the ESPs result in high levels of in-flight capture by UBC and ACI.

Previous measurements conducted at Brayton Point have shown natural Hg removal efficiencies ranging from 29% to 75%. During the ESP retrofit project conducted by ADA-ES, the average baseline removal efficiency across both ESPs averaged 90.8%, as measured during three tests with the OH method. During parametric tests a variety of activated carbons, including Darco-FGD, were injected just downstream of the first ESP. Incremental Hg removal efficiencies across the second ESP ranged from 3% to 93% depending on the carbon injection concentration (see ESP Bituminous data in Figure 3).<sup>19</sup> Total average Hg removal efficiencies across both ESPs averaged 94.5% during injection of Darco-FGD at 10 lb/MMacf. These high Hg capture efficiencies are considered to be atypical of other C-ESP units because of the high UBC concentrations, the two ESPs, and the long duct runs.

### ***Hot-Side ESP Retrofits for Bituminous Coals***

Hot-side ESPs (HS-ESPs) operate at temperatures where conventional sorbents do not effectively capture Hg. The only HS-ESP retrofit technology to be tested at full-scale is ACI injected upstream of a compact hybrid particulate collector (COHPAC™) system. COHPACs are normally used to improve the control of PM downstream of a hot-side ESP. The COHPAC tests were conducted by ADA-ES on Alabama Power's Gaston Plant, Unit 3.<sup>20</sup> The test unit has low- $\text{NO}_x$  burners and burns low-sulfur bituminous coal with chlorine content of approximately 0.03 %.

Baseline test results showed that neither the HS-ESP nor COHPAC captured a significant amount of Hg. During ACI parametric tests, Hg capture efficiencies ranged from 25% to more than 90%, depending on the carbon injection rate. ACI concentrations of 3 lb/MMacf

resulted in gas-phase Hg reductions greater than 90% across the COHPAC (see FF Bituminous data in Figure 3).<sup>20</sup> The different activated carbons used in the parametric tests produced Hg capture efficiencies similar to Darco-FGD, the benchmark sorbent. Differences in sorbent particle size or base material (bituminous coal or lignite) did not result in appreciable performance differences.

Bag cleaning frequencies, which are controlled by baghouse pressure-drop, increased with increasing carbon injection rates. Because bag life decreases with increasing cleaning frequency, ACI concentrations were limited to 1.5 lb/MMacf during the long-term performance tests. During these tests Darco-FGD was injected 24 hr/day at 1.5 lb/MMacf. Mercury removal efficiencies averaged 78% and ranged from 36% to 90%, as measured by S-CEMs.<sup>20</sup>

While fabric filter bag strength and pH were unaffected by the ACI test project, it was concluded that longer tests (up to a year) would be needed to determine the impacts of ACI concentrations on bag life and outlet particulate emissions.

### ***ESP retrofits for Low Rank Coals***

The comprehensive C-ESP test program at Pleasant Prairie provided significant insights into the use of ACI to capture Hg from a subbituminous PRB coal flue gas.<sup>21</sup> The test unit does not use low-NO<sub>x</sub> burners and has fly ash with low UBC content. The chlorine content of the PRB coal was approximately 0.001%. Baseline tests using the OH method exhibited Hg capture in the ESP of about 5%. More than 70% of the Hg at the ESP inlet was Hg<sup>0</sup>.

Major parametric test variables included sorbent properties, sorbent injection concentration, and ESP inlet temperature. At low ACI concentrations, Hg reductions across the ESP were higher than expected, reaching 60% to 65% at injection concentrations near 10 lb/MMacf.<sup>21</sup> Increasing sorbent injection concentrations to 20 to 30 lb/MMacf increased Hg reduction efficiencies to only 70% (see ESP PRB test results in Figure 3).

Spray cooling to temperatures as low as 250 °F failed to improve the capture efficiency of Hg.<sup>21</sup> All sorbents evaluated during the parametric tests gave similar capture efficiencies of Hg regardless of mean particle size or other differences. Fly ash samples failed the foam index tests if they contained any activated carbon, and Pleasant Prairie fly ash could not be sold for use in cement manufacturing if it contained any activated carbon.

Subbituminous coals and lignites typically contain much lower concentrations of chlorine than bituminous coal.<sup>2</sup> Fly ash from these lower rank coals also contains relatively high concentrations of Ca and other alkaline elements. These coals are also more reactive than bituminous coals, and their fly ashes typically have a much lower percentage of UBC. The low concentrations of HCl in the flue gas from these coals can be partially absorbed by the alkaline components of fly ash, and little chlorine is available for Hg<sup>0</sup> oxidation reactions.<sup>2</sup> The natural capture of Hg by fly ash from low rank coals is typically very low.

The injection of activated carbon provides additional sites for Hg capture. However, if Hg<sup>0</sup> capture depends on adsorption-desorption reactions involving HCl, alkaline fly ash

associated with low rank coals may deplete the available HCl, and higher ACI concentrations may not significantly increase the oxidation and capture of Hg<sup>0</sup>. In the Pleasant Prairie tests, Hg removal efficiencies reached a plateau near 70%. Increasing activated carbon injection concentrations resulted in marginal increases in Hg capture efficiencies.

### **Spray Dryer Retrofits**

All of the ICR test units that fired bituminous coal and were equipped with SDA/FF systems exhibited average Hg captures greater than 90%.<sup>2</sup> This average may be somewhat high since two of the four tests units were also equipped with an SCR system. Mercury reductions for units burning subbituminous coal averaged 24% for three units with SDA/FF systems and 35% for three units with SDA/ESP systems. Two SDA/FF equipped units burning North Dakota lignite did not exhibit any significant Hg capture.<sup>2</sup>

Natural Hg capture appears to require a significant amount of coal chlorine and UBC. Units burning subbituminous coal and lignite typically fail to meet one or both of the requirements. Potential SDA retrofits include producing a higher carbon content fly ash by combustion modifications, use of ACI to provide absorption surface area, use of an Hg<sup>0</sup> oxidant in conjunction with ACI, or use of a special sorbent that can effectively capture Hg<sup>0</sup>.

The use of ACI on bituminous coal fired units is expected to provide removal efficiencies in excess of 90%. EPRI-sponsored ACI tests on a SDA/FF equipped unit burning North Dakota lignite resulted in maximum Hg removal efficiencies of 69% when untreated sorbents were used. Tests with iodated carbon resulted in removal efficiencies greater than 95% for injection concentrations greater than 1.0 µg/Nm<sup>3</sup>.<sup>22</sup> During one short test, EPRI injected a chloride salt solution (less than 0.1% of the coal feed rate) into the boiler at the same time that Darco FGD was being injected upstream of the SDA/FF system. This increased Hg capture across the SDA/FF to more than 90%, as compared with 69% to 77% capture in the absence of chloride.<sup>22</sup>

Dry scrubbing units that burn bituminous coal can easily use ACI to achieve high Hg emission reductions. Additional research on combustion modifications, additives, and special sorbents is needed to overcome problems associated with the control of Hg emissions from low rank coals.

### **Wet Scrubber Retrofits**

In 1999, approximately 16% of coal-fired utility boilers used wet FGD scrubbers for SO<sub>2</sub> control. Conventional SO<sub>2</sub> scrubbers can capture Hg<sup>2+</sup> but do not capture Hg<sup>0</sup>, and the potential for Hg capture in scrubbers is limited by the amount of Hg<sup>0</sup> that is oxidized.

Research has shown that low-temperature catalysts can be used to oxidize Hg<sup>0</sup>, and long-term slip-stream performance tests are being conducted on pilot-scale units at two sites.<sup>23</sup> Bench-, pilot-, and full-scale test projects are also being conducted to evaluate and optimize Hg<sup>0</sup> oxidation in SCR reactors.<sup>3,4</sup> Several other techniques that employ gas-phase oxidation reactions are also being investigated. These techniques include addition of oxidation reagents to the coal, burners, or combustion gases<sup>16,22</sup>, the injection of ozone to provide free radicals for Hg oxidation, and the use a barrier discharge to produce oxidizing radicals.<sup>24,25</sup>

The reduction of dissolved  $\text{Hg}^{2+}$  to  $\text{Hg}^0$  in the scrubbing solution can be a problem in some scrubbers. McDermott Technologies (Babcock & Wilcox) recently completed a test project to evaluate a proprietary reagent to prevent reduction of  $\text{Hg}^{2+}$  in wet FGD scrubber liquors.<sup>26</sup> The McDermott reagent met performance goals in a wet limestone scrubber at Michigan South Central Power Authority's Endicott Station but failed to prevent  $\text{Hg}^{2+}$  reduction reaction in a thiosorbic lime scrubber at Cinergy's Zimmer Station.<sup>26</sup> Recent bench scale research has show that S(IV) compounds, which are normal products of FGD scrubbers, are unstable and lead to  $\text{Hg}^{2+}$  reduction reactions.<sup>27</sup> The recent progress made in understanding the chemistry of mercury in scrubbers is encouraging. Further work is needed to understand the chemistry of mercury in the scrubber solution and in the sludge.

## CONCLUSIONS

Insights into Hg chemistry have been obtained from laboratory and pilot-scale experiments as well as from studies of Hg speciation measurement in full-scale units. Although Hg leaves the combustion zone as gaseous  $\text{Hg}^0$ , varying amounts can be transformed to  $\text{Hg}^{2+}$  and  $\text{Hg}_p$  as the flue gas passes through the economizer and air heater. The efficiency of Hg capture by air pollution control devices depends on the gas-phase speciation as well as on the partitioning between gaseous and particulate forms. In turn, the coal composition (Cl and S content, ash composition) and boiler operation (LOI, gas cooling rate and residence time) affect the Hg speciation and partitioning in the flue gas. Existing air pollution control devices provide a range of "natural" Hg removals; fabric filters and scrubbers have the highest Hg removals, as much as 90%, for units burning bituminous coal. Moderate to low levels of natural capture are typically found in units that burn either subbituminous coals or lignites.

Models have been developed to predict the homogeneous and heterogeneous oxidation of Hg. Heterogeneous oxidation is not as well understood, and more work is needed to bring the level of understanding to a point where models can be considered truly predictive. Models for adsorption (on both fly ash and activated carbon) also require further development. Research has just begun on Hg oxidation across SCR catalysts, and further work is needed to adequately model this process.

The capture of Hg is dependent on the mechanisms that govern the behavior of mercury in coal-fired flue gases. The design and operation of mercury control technologies must take into consideration these fundamental principles. Coal composition, particularly coal chlorine and sulfur contents, have a large impact on the potential for Hg capture. Scrubbers are very effective when applied to bituminous coal-fired exhausts that primarily contain  $\text{Hg}_p$  and  $\text{Hg}^{2+}$ . PM control devices are also very effective when applied to bituminous coal-fired units with high amounts of  $\text{Hg}^{2+}$  and/or  $\text{Hg}_p$ . Processes that oxidize  $\text{Hg}^0$  (SCR's, dedicated Hg catalysts, ozone, or irradiation) can improve the effectiveness of scrubbers and, in some cases, PM control devices.

Activated carbon injection has been shown to be effective for removal of Hg in boilers that fire both bituminous and low rank coals. The effectiveness of ACI in capturing Hg from the combustion of subbituminous coals and lignite may be limited by the available HCl in the flue gas. Promising methods for increasing Hg capture from these flue gases include the use of chlorine-based additives or the use of impregnated carbons. In all cases, a sound

understanding of the chemistry of Hg in flue gas will be needed to implement Hg control technologies across a broad range of fuel types, boilers, and control technologies.

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