

MERCURY CONTROL ALTERNATIVES FOR COAL-FIRED POWER PLANTS

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ABSTRACT

Coal-fired power plants in the United States may have to reduce their mercury emissions by up to 90% by 2007 - 2009 due to proposed regulations that could affect up to 1,100 utility boilers. Air pollution control system components such as electrostatic precipitators, baghouses, NOx reduction catalysts, SO₂ scrubbers, and their various configurations in utility applications significantly impact mercury emission rates. Furthermore, several additional techniques are available to augment the removal of mercury by particulate control systems and/or flue gas desulfurization systems found in coal-fired power plants.

Considerable experience controlling mercury emissions has been gained in more than 60 US and 120 international waste-to-energy plants. These commercial plants burn municipal or industrial waste or sewage sludge. In waste-to-energy plants, the ratio of Cl to Hg is relatively high, and therefore the ratio of ionic Hg to elemental Hg in the flue gas is also high. In coal-fired plants, the ratio of Cl to Hg is lower, resulting in a higher fraction of elemental Hg. Since the removal of elemental Hg is generally more difficult to accomplish than removal of ionic Hg, this presents a daunting challenge for meeting the high removal requirements in proposed legislation.

Sorbents and reagents have been commercially proven in waste-to-energy plants to augment the removal of mercury. These include activated carbon, lignite coke, sulfur containing chemicals, or combinations of these compounds. For example, injecting polysulfide compounds such as sodium tetrasulfide (Na₂S₄) into the flue gas promotes the formation of mercuric sulfide from elemental Hg. The overall effectiveness of these techniques is a strong function of introducing the compounds in the appropriate flue gas conditions to promote the removal of elemental Hg. Actual commercial experience using sorbents and reagents in combination with SO₂, NOx and particulate control to reduce Hg emissions is discussed in detail. Experience from sewage sludge incineration is especially relevant since the flue gas characteristics (e.g., high SO₂ and low HCl levels) are comparable to coal combustion flue gas characteristics.

INTRODUCTION

US coal-fired power plants may have to reduce their mercury emissions by up to 90% by 2007 - 2009. Proposed regulations may affect over 1,140 coal-fired utility boilers. In general, experience with coal-fired power plant emission control shows that mercury removal already occurs to some extent as part of other gas cleaning processes such as selective catalytic reduction (SCR) for NO_x control, flue gas desulfurization (FGD) for SO₂ control, and precipitators / baghouses for particulate control. The mercury removal efficiency of these gas cleaning steps is strongly influenced not only by their individual process details, but also by the mercury speciation in the flue gas. Elemental, ionic, and particulate bound Hg species have dramatically different behavior in the air pollution control (APC) system.

Published empirical data clearly shows that additional mercury-specific control technologies will be required to meet proposed regulations. Babcock Borsig Power (BBP) has considerable experience with mercury removal in more than 60 waste-to-energy plants burning municipal or industrial waste and sewage sludge. There can be important and significant differences between flue gas streams from coal-fired boilers and municipal waste combustors. Therefore, considerable care must be taken when applying commercially proven Hg removal processes to new applications on coal-fired utility boilers. Activated carbon, for example, is widely used at MWC facilities to meet regulatory mandates. However, preliminary tests indicated that extremely high carbon dose rates may be required for applications that have a high fraction of elemental mercury (e.g., PRB coals). These high carbon dose rates lead to other operational problems in downstream components, and also negatively impact fly ash disposal. Other mercury-specific control alternatives may be required for coal-fired utilities facing future stringent mercury reduction requirements.

MERCURY EMISSIONS COAL-FIRED POWER PLANTS

Estimates of mercury emissions from coal-fired utility boilers in the United States vary from 45 to 57 tons per year. Since there are approximately 1,140 utility coal-fired boilers operating, this means that the “average” plant emits about 80 pounds per year. While the individual plant emission rates are low, coal-fired boilers in the aggregate are the largest source of man-made mercury emissions in the US. For comparison, Municipal Waste Combustors (MWCs) were previously the second largest source emitting approximately 34 tons annually. However, the MWC emissions have been reduced more than ten fold to less than 3 tons per year.

EPA has formulated a goal to reduce mercury emissions from coal-fired power plants 50 to 70% by 2005 and 90% by 2010. Senator Jeffords has proposed a 90% reduction in Hg emissions by 2007. President Bush’s Clear Skies proposal has two steps in Hg reduction, 45% by 2008 and 67% by 2018. Regardless of the details of future legislation, a major challenge in controlling mercury emissions from coal-fired boilers is the high degree of Hg captures required in combination with the very low Hg concentration in typical boiler flue gas. Uncleaned coal contains between 3 and 4,000 µg/kg of mercury, resulting in flue gas concentrations between 1 and 130 µg/Nm³, as determined in the EPA measurement program. Over 80% of the boilers have mercury concentrations (at the exit of the boiler) that are below 10 µg/Nm³. Underlining the complexity of the issue surrounding Hg emissions, it must be noted that there is no uniform

control for all plant configurations, coal types, and existing flue gas controls used for other pollutant control.

Mercury Speciation – Elemental vs. Ionic Forms

At higher temperatures, mercury compounds are not thermally stable; therefore, mercury is primarily in the elemental form in the gaseous state at the high temperature in the combustion chamber, largely independent of the coal composition. The minimal retention of mercury in the slag is due to its high vapor pressure, and is much less than 5% of the total mercury input as shown in various investigations. Other metals, on the other hand, such as copper, chromium, or nickel have a slag retention rate of more than 90%. Table 1 presents the physical properties of various Hg compounds found in flue gas.

Table 1
Physical Properties of Hg Compounds Found in Flue Gas

	Melting /Sublimation	In Furnace	Vapor pressure	Water solubility
	[°C] 1 atm	>850°C 1 atm	[µg/m ³] 20°C, 1 atm	[µg/l] 20°C, 1 atm
Hg ⁰ liquid	-39	Gaseous (boils @ 357°C)	14,000	≈20
Hg ₂ Cl ₂ solid	383	Conversion to gaseous Hg ⁰	-	2.1
HgCl ₂ solid	276	Conversion to gaseous Hg ⁰	800	69,000,000
HgS solid	584	Conversion to gaseous Hg ⁰	≈0.1	0.0013
CH ₃ HgCl solid	170	Not existing in flue gas	54,000	5,000,000

The elemental mercury vapor from the combustion process reacts and mixes with the flue gas and enters the convection section, which is an integral part of the boiler. Due to the decreasing gas temperature, the elemental mercury is able to react with other flue gas components. One of the first reactions of the mercury vapor is the formation of mercury (II) chloride (HgCl₂) out of the gaseous hydrochloric acid (HCl) and elemental mercury (Hg⁰) under the oxidizing conditions of the off-gases downstream of the boiler. There is sufficient HCl from most coal combustion for this reaction to take place. The exact mechanism of this reduction reaction has not yet been completely understood, but is usually described as follows:

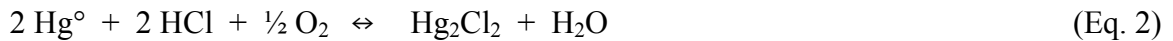


On decreasing temperature, the equilibrium of this reaction shifts more and more to the right side. However, the reaction is not only dependent on temperature. Other flue gas components, such as O₂, sulfur compounds, and HCl, as well as the residence time in a certain temperature range, influence the reaction equilibrium.

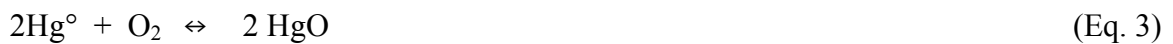
The thermodynamic balance of the above-mentioned reaction appears to be blocked kinetically. Therefore, a complete transformation of the Hg° into HgCl_2 cannot be expected. The mercury chloride thus formed has a high volatility and is found in the gas phase in the boiler (see Table I).

In addition to the formation of mercury (II) chloride, other reactions of mercury in the gaseous phase are possible:

- Elemental mercury can be oxidized to mercury (I) chloride (Hg_2Cl_2):



- Elemental mercury can be oxidized to mercury oxide (HgO):



However, at more elevated temperatures, the above described, simplified reaction possibilities (Eq. 2 and Eq. 3) are of less importance, since Hg_2Cl_2 , and HgO are not stable at temperatures above 400°C . Above this temperature, Hg_2Cl_2 decomposes into Hg° and HgCl_2 respectively and HgO into $\text{Hg}^\circ + \frac{1}{2} \text{O}_2$.

A higher amount of mercury (I) chloride could be formed out of HgCl_2 in the presence of reducing effects, for example by fly ash or SO_2 . At the boiler's outlet temperature, the Hg_2Cl_2 is solid, and will be removed with the fly ash (sublimation temperature 383°C , see Table I). Up to 10% of the total mercury amount can be removed in this way.

The influence of other flue gas constituents is not completely understood. NO_x seems to enhance the oxidation at low concentrations, but to inhibit it at high concentrations. SO_2 in more than minute concentrations and water vapor inhibit the oxidation. In the ductwork of a power plant the equilibrium conditions will rarely be reached. Therefore, the content of elemental mercury will typically be above equilibrium conditions.

The elemental mercury fraction can increase drastically in two ways:

1. if the amount of SO_2 exceeds the amount of HCl by an order of magnitude, or
2. if there is no residence time for the HgCl_2 formation due to simple quenching.

The portion of elemental mercury in the flue gas originating from a sewage sludge incinerator or a coal-fired power station is usually about 30 to 50%. A characteristic of both Hg° and HgCl_2 is their high vapor pressure, even at temperatures as low as 200°C (400°F). Accordingly, since a large portion of the mercury species is in the vapor phase, the particulate removal equipment, which is usually arranged downstream of the boiler, is unable to act as an effective mercury removal device.

Fate of Mercury Through Typical Power Plant Air Pollution Control Systems

The fate of mercury compounds as they travel through the boiler to the stack has been studied and reported in various publications. In general, the capture of mercury compounds varies

dramatically with power plant configuration. The data also shows a broad variation as a function of coal type, which is known to have a controlling influence on mercury speciation. The US EPA has reported the following Hg capture data for different control technologies and coals.

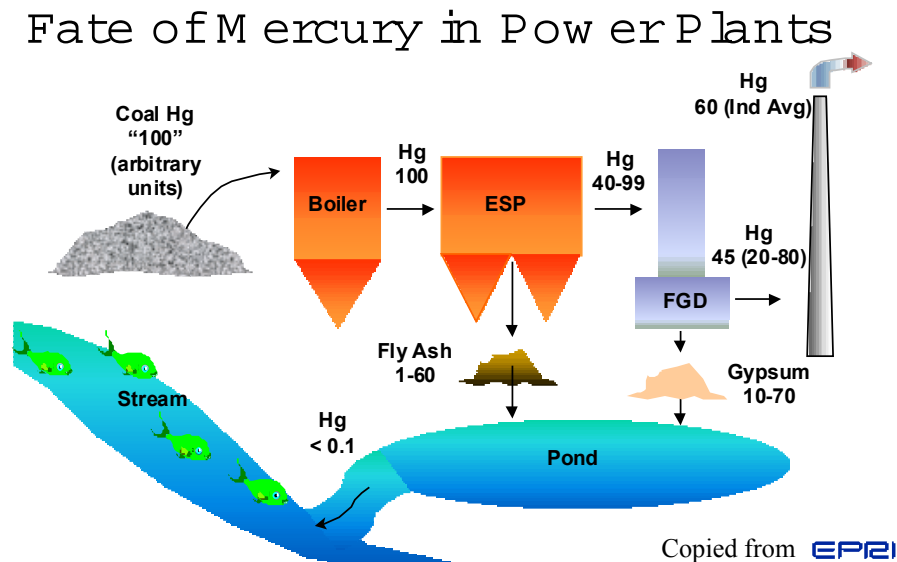
Table 2
Mercury Capture as a Function of Coal Type and APC Equipment

	% Mercury Capture		
	<u>Bituminous</u>	<u>Sub-bituminous</u>	<u>Lignite</u>
W/ PM Controls			
Cold ESP	46	16	0
Hot ESP	12	13	?
Fabric Filter (FF)	83	72	?
Wet Scrubber	14	0	33
W/ FGD Controls			
Spray Dryer/FF	98	3	17
Hot ESP & Wet FGD	55	33	?
Cold ESP & Wet FGD	81	35	44
FF & Wet FGD	96	?	?

Some general observations can be drawn from the EPA's ICR database and other reports. Mercury associated with the fly ash (which is capable of downstream removal by other devices) can be as high as 30% for Powder River Basin (PRB) coals, while typically only as high as 10 to 20% for lignite and bituminous coals. Wet FGD systems can remove as much as 90% of ionic Hg (Hg^{2+}) when firing bituminous coal, but typically only about 60% firing lignite coal. The overall Hg removal rate with wet FGD depends strongly on the ratio of Hg^0 to Hg^{2+} in the flue gas, which can vary from 90:10 to 10:90, with a nominal ratio of approximately 60(Hg^0):40(Hg^{2+}). Additionally, an apparent increase of non-ionic Hg from 7 to 40% at the outlet of wet FGD's was found in US test data. A wet FGD requires stable operating conditions for consistent Hg removal since FGD systems can "store" mercury that can be released back to the flue gas with changing operating conditions in the scrubber. In addition to such storage effects, absorption/desorption of mercury on the walls of an absorber vessel or downstream ductwork could occur and contribute to non-controlled mercury release ("memory-effects"). FGD systems in general are ineffective in trapping elemental mercury.

If an SCR is present, additional factors influence the fate of mercury through the APC system. In the SCR reactor, the catalyst will support gas phase oxidation of elemental mercury. Therefore, flue gas conditions favoring gas phase Hg oxidation will help in the SCR reactor as well. Effects of SCR on mercury speciation ranging from no influence to nearly quantitative oxidation of elemental mercury have been observed. For good oxidation of mercury in an SCR, a high redox potential and sufficient concentration of hydrogen chloride as a reaction partner at a temperature significantly below 400 °C (750 °F) is necessary.

Figure 1



Impact of SCRs on Hg Emissions

Experience gained in Germany has shown that, when burning bituminous coals in boilers after the plants were equipped with high dust SCRs to control NO_x, these plants substantially reduced their Hg emissions. The test data shows that there is a shift from Hg⁰ to Hg⁺ after the air heaters and the ESPs, and FGD systems collected more of the total Hg emissions. German investigations in three dry-bottom furnaces and a slag-tap boiler with high dust SCR systems revealed that elemental mercury is oxidized to some extent. Mercury upstream of SCR systems was approximately 40 to 60% in the elemental form, while only about 1 to 12% was in the elemental form downstream of the SCR systems. The total concentration of mercury from combustion of pulverized coal was 17 µg/Nm³, of which 6 to 7 µg/Nm³ of metallic mercury were found upstream of the SCR system, and less than 1 µg/Nm³ downstream.

Test data from the US indicates that the oxidation shift only takes place in boilers that are burning "high" chlorine coals, and does not occur when burning coals low chlorine coals such as PRB coal.

Measurements between individual catalyst layers revealed that the first layer caused no significant change in metallic mercury concentration, whereas a distinct reduction in metallic mercury concentration (or an increase in HgCl₂) can be observed after the second and third layers. Presumably, the first layer has less oxidizing effect owing to greater loading with ammonia, or a higher dust loading on the catalyst surface.

Investigations in a tail end SCR (after the FGD system) system revealed a measurable but small tendency to oxidation, albeit not to the extent seen in high dust SCR systems. This minor effect could be attributed to the absence of hydrogen chloride in the treated gas downstream of the FGD system. New Hg emission information has been released from tests conducted at German waste-to-energy plants with tail-end systems. The test data has shown that when the plants experience higher than normal HCl emissions, Hg^0 that was absorbed in the catalyst is released, causing spikes that could put these plants in violation of their Hg emission limits. It is believed that the HCl reacts with Hg^0 that had been captured in the catalyst and is released as HgCl .

There are two conceivable mechanisms for the formation of mercury chloride on the SCR catalyst:

1. Mercury is oxidized (by flue gas oxygen) to mercury oxide, which then reacts with hydrogen chloride to form mercury chloride. The equilibrium of this reaction depends upon the equilibrium between metallic mercury and mercury chloride described at the beginning of the paper.
2. Formation of free chlorine from hydrogen chloride according to the Deacon equilibrium, and subsequent reaction with metallic mercury to form mercury chloride.

However, tests conducted in the US on plants firing PRB coal indicate that there was no change in the ratio of Hg^0 to Hg^+ before and after the SCR. Some have theorized that the lower Cl content of PRB coal, or the higher calcium content in the fly ash, does not permit the conversion to HgCl_2 . At this time we are awaiting further details and information from these test programs.

Impact of Wet FGD's on Hg Emissions

Every coal-fired power plant in Germany has an FGD system. Bituminous-fired plants in Germany have SCRs while lignite units generally do not have SCRs. At the present time there are no specific emission regulations for mercury from coal-fired power plants. However, the existing air pollution controls on these plants result in a significant reduction in mercury emission rates. BBP, the major provider of FGD systems in Europe, has conducted a number of test programs on its air pollution control systems. These tests have shown that 90% of the ionic Hg can be controlled with a system firing bituminous coals. One of the primary reasons that high overall reduction is achieved is that most units have high efficiency ESPs prior to the FGD systems.

To achieve a reduction of ionic mercury of 90 % in a wet FGD system, the following points need to be met:

- Particles with reducing properties have to be removed in an upstream particle removal system.
- The scrubbing solution has to be kept under oxidizing conditions in all situations to prevent the reduction of mercury. Reduced mercury cannot be present in the absorber.
- The pH of the scrubbing solution has to be kept constant. To prevent the release of mercury on pH fluctuations, a chemical additive can be used. One advantage of our dual loop FGD design is that a constant pH is easier to maintain under all operating conditions.

- The liquid to gas ratio has to be sufficiently high (16-20 L/m³).

Empirical data shows that at times the outlet Hg emissions from an FGD system can be greater than the Hg measured at the inlet. While the exact cause of this condition has not been determined, it is believed that changes in the pH of the absorber slurry can cause a release of captured Hg. Precipitating chemicals can be added into the scrubber to prevent this. BBP has experience using chemical additives in FGD system to ensure that captured ionic mercury is retained in the absorber slurry. Depending on the circumstances, BBP has used TMT 15 or Nalco 71281/Nalmet. Both chemicals can be dosed directly into the scrubbing circuit. The chemicals are delivered as solutions in suitable containers, and only a dosing device is required. The concentrations needed depend on the heavy metal concentrations in the flue gas. Neither of these two compounds impacts the ability to remove SO₂ in the system, or the ability to make high quality gypsum.

Additional options exist to prevent the mercury in the absorber slurry from being released under changing chemical conditions:

- Mercury can be bound in the buffer tank of the scrubber solution with NaS. However, if NaS is overdosed, the oxidation in the scrubber can be inhibited due to the formation of Na₂S₂O₃.
- Mercury can be removed with an ion exchanger from the scrubber solution circulation. This measure requires filtered liquid and upstream precipitation processes.
- Mercury can be removed from the scrubbing solution by reducing it in an electrical cell and extracting the liquid metal. Due to the high particle content in the scrubber solution, a clogging of the cell would be probable and additional measures have to be taken.

The latter two processes are only useful if mercury content restrictions in the gypsum do not allow precipitated mercury complexes or mercury compounds formed by reactions with precipitating agents.

Impact of Wet ESPs on Hg Emissions

With pending regulations concerning SO₃, PM_{2.5}, and Regional Haze being evaluated, there is growing interest in the application of wet ESPs integrated into FGD systems. One of the additional benefits of integrating wet ESPs into new or retrofitted FGD systems is that they can control Hg⁺ emissions.

Wet ESPs are characterized by their ability to separate microscopic particles, fumes, and fine aerosols from flue gases saturated with water vapor. Many years of industrial applications have demonstrated that wet ESPs have the following characteristics;

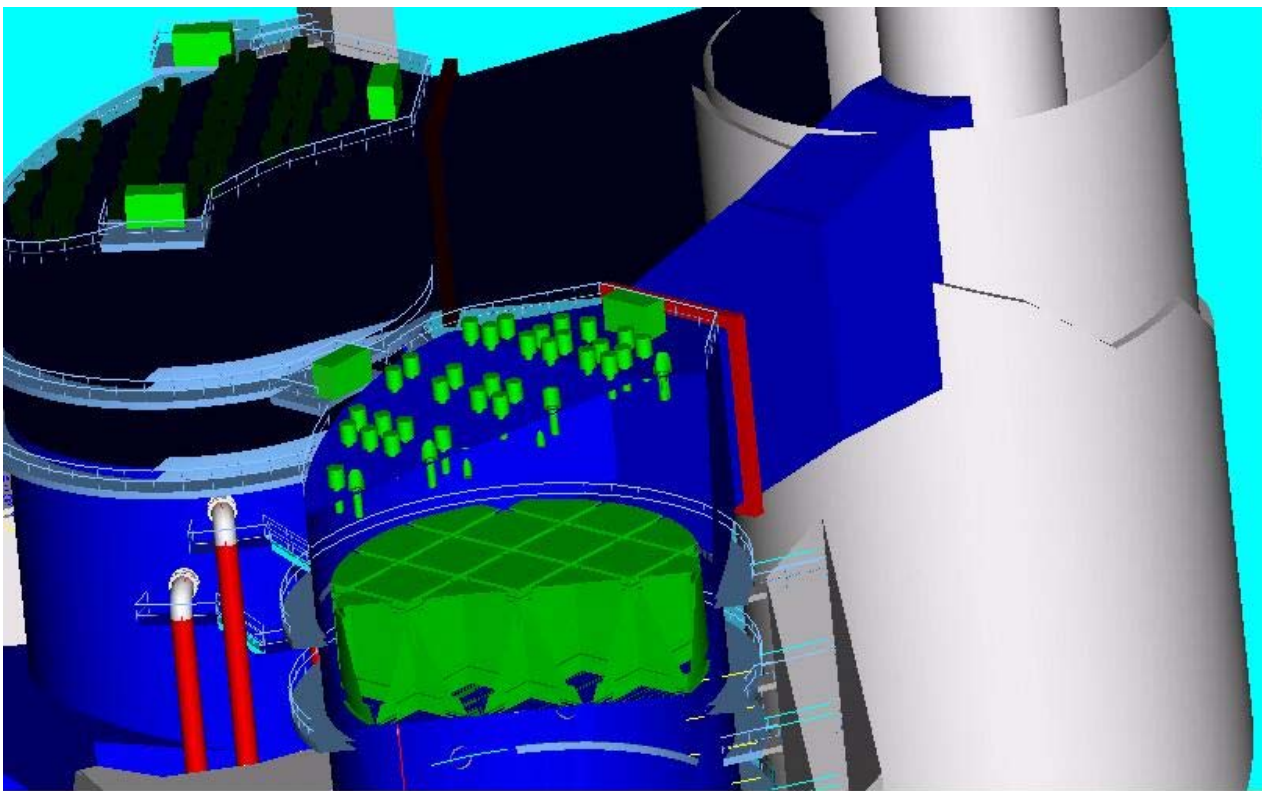
- Very high removal rate of microscopic particles
- Low pressure drop losses
- Low energy consumption
- High availability and low maintenance requirements

In the wet ESP, particles of water/aerosols that have been separated from the flue gas exiting the FGD absorber form a layer of humidity on the precipitation electrodes. Particulate matter and

mercury particles mix with this layer of humidity. To keep the collection surfaces clean, they are washed with clean water on regular intervals, and the water is retained in the absorber vessel as make-up water for the FGD system. Pilot plant test data have shown that 80 to 90% of ionic Hg can be removed in wet ESPs.

Wet ESPs can be integrated into the FGD vessel or can be added as a separate system after the vessel. The prime advantages of the integrated vessel design are that no additional space is required, and that highly acidic liquids do not need be handled since the liquids drain internally to the scrubber vessel. Figure 2 shows an integrated wet ESP and FGD vessel.

Figure 2



MERCURY-SPECIFIC CONTROL TECHNIQUES

Municipal Waste Combustor (MWC) Experience Base

A significant experience base of mercury emissions and control technologies has been developed from the MWC industry. Today all large MWCs in the US and in central Europe have mercury controls. Many of the MWCs in Asia either have controls or are installing them. While this base of knowledge gained from the MWCs exists, there are several significant differences in mercury speciation and flue gas composition between MWCs and coal-fired power plants, as shown below. Note that this data is general and varies significantly by boiler type and type of coal.

Typical Emission Forms of Hg (Uncontrolled)

	% Composition	
	<u>Coal</u>	<u>MWC</u>
Hg ⁰ (vapor)	50	15
Hg ²⁺ (Cl ⁻ or SO ₄ ²⁻)	30	80
Hg _p (particulate)	20	5

Typical Flue Gas Characteristics

	<u>Coal</u>	<u>MWC</u>
Uncontrolled Hg emissions	5 to 20 µg/dscm	200 to 600 µg/dscm
HCl concentration	10 to 20 ppm	400 to 900 ppm
Boiler exit temperature	370 °C (700 °F)	230 °C (450 °F)
SO ₂ concentration	1500 to 8000 ppm	200 to 800 ppm

Carbon adsorption is one of the primary technologies used to control Hg emissions. In these so-called entrained-flow processes, activated carbon is typically injected into the flue gas duct and spent carbon is removed by means of a downstream fabric filter. Most activated carbons have an excellent capacity to capture ionic Hg, but do a poor job in the capture of Hg⁰. It is expected that high carbon dose rates will be required for coal-fired applications due to the high percentage of elemental Hg in the flue gas.

Elemental and ionic mercury can be captured in special filters. Activated carbon fixed-bed filters (ACRs) are the proven and reliable method to separate both forms of mercury in MWCs down to the detection limit. Removal rates for total Hg greater than 98% are common at MWCs by forming HgSO₄ at the surface of the carbon (lignite coke). Recently, alternative processes specifically for the separation of elemental mercury have been proposed. These include the application of zeolite in the so-called medisorbon process, and amalgamation on precious metals. However, all such filtration processes share the fundamental disadvantage of involving a separate apparatus in the flue gas path. In addition, the disposal of the spent, heavily contaminated sorbent frequently presents severe problems. The high investment and operating costs for the filters adversely affect the economics of such systems.

Alternatively, the use of sodium tetrasulfide (Na₂S₄) as a reagent for the control of mercury emissions has been commercially applied successfully on MWCs, and has proven to be effective on both ionic and elemental forms of mercury. Sodium tetrasulfide's high capture rate of elemental mercury is a significant advantage over carbon adsorption, and the process does not suffer from the disadvantages of the filtration processes described above.

The applicability of MWC experience to meet proposed regulations in the United States has raised general concerns with the owners and operators of coal-fired power plants for the following reasons:

- There is very little long-term operating data on Hg emissions control using activated carbon adsorption to maintain continuous compliance at 5 to 20 µg/dscm.

- Most MWCs have operating experience at this emission level using several air pollution control technologies in multiple stages with different economic impacts.
- Significantly higher dose rates of activated carbon may be required in order to achieve the required reductions at the lower Hg concentrations and correspondingly higher elemental fraction. This raises the following additional questions:
 - What impact will this high activated carbon dose rate have on plant operations?
 - What will the cost of activated carbon be in the future as demand increases?
 - Will sufficient amounts of activated carbon be available?

Sodium Tetrasulfide for Mercury Control

L. & C. Steinmüller GmbH, now part of BBP Environment GmbH, developed a new technology - sodium tetrasulfide (Na_2S_4) - that addresses the problematic issues associated with other Hg separation processes. This technology should not be confused with sodium sulfide Na_2S that was tried in both Europe and the U.S. without success. The shortcomings of Na_2S are that it can leave a strong odor of hydrogen sulfide (H_2S) in the ash, and it does not control all species of Hg.

The major advantages of the Na_2S_4 technology are that it controls elemental, as well as ionic forms of Hg, and, due to dissociation in the flue gas, H_2S under normal operating conditions is not a problem.

Other advantages of the Na_2S_4 technology are:

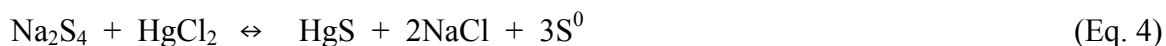
- The reaction yields stable inert reaction products.
- Na_2S_4 is a liquid and is easier and safer to handle than powdered activated carbon. Also, being a liquid, the feeding and control of Na_2S_4 is simpler and more positive than powdered activated carbon.
- The higher fraction of elemental Hg produced in sewage sludge incinerators and coal-fired power plants are easier to control with Na_2S_4 than with powdered activated carbon.
- Activated carbon is abrasive and results in higher maintenance cost due to replacement of conveying pipes and rotary equipment.

The Na_2S_4 Process for Mercury Separation

The principles of Hg removal with Na_2S_4 are as follows:

- Sodium tetrasulfide (Na_2S_4) decomposes in flue gas into elemental sulfur (S°) and ionic sulfide (S^{-2})
- Elemental sulfur reacts with Hg° to form mercury sulfide (HgS)
- Ionic sulfide reacts with ionic mercury to form mercury sulfide
- Mercury sulfide is a non-toxic solid that transforms to cinnabar, which is thermally stable up to 480°C (900°F).

Mercury separation using Na₂S₄ captures both ionic HgCl₂ and Hg⁰ in accordance with the following simplified reactions:



It is sufficient to inject an aqueous Na₂S₄ solution into the flue gas duct, and such a system can be easily retrofitted to an existing flue gas cleaning plant. The Na₂S₄ reacts with the mercury to form mercury sulfide (HgS) whose red allotrope is known as cinnabar. This is a non-poisonous insoluble salt that is thermally stable up to 480°C, and thus effectively immobilizes the mercury by chemical binding. The black allotrope, known as meta-cinnabarite, is found in waste combustion facilities. In the course of several years, it changes into the stable red allotrope.

Apart from the heat exchange with the flue gas, there is also a mass transfer between the droplets of the additive and the flue gas. The most likely mass transfer process between the liquid and the gaseous phase is the dissolving of strong acids like HCl in the droplets of the Na₂S₄, since aqueous alkaline liquids show a strong affinity towards the gaseous HCl, or possibly to SO₃.

Pilot Plant Test Program With ESPs for Particulate Control

There was considerable concern regarding the economics and viability of activated carbon injection technologies to meet the proposed Massachusetts mercury standard of 28 µg/dscm for MWCs, with no reduction exclusion on a long-term basis, especially on MWCs equipped with a spray dryer and ESP. Since the principal advantage of the Na₂S₄ technology is that it is more effective in controlling both elemental mercury (Hg⁰) and ionic mercury (Hg²⁺) than activated carbon, BBP Environment wanted to determine if the Na₂S₄ technology would be applicable. Na₂S₄ has been demonstrated to reduce Hg emissions in several European plants to the new proposed standard; however, there was no experience with the application of this technology to U.S. facilities.

In 1998 BBP Environment undertook a test program on a pilot plant MWC equipped with a spray dryer and ESP to determine the following:

- Could Na₂S₄ meet the new proposed emission standard during a short-term operating period?
- Would there be an advantage to using activated carbon injection and Na₂S₄ in combination to meet the proposed Hg emission standard on a short-term operating period?

Short term or typical stack tests were conducted during the activated carbon injection phase. Two different activated carbon injection rates (120 and 300 mg/dscm) were evaluated during the test program. Several dose rates of Na₂S₄ were evaluated and two dose rates were selected (80 and 120 mg/Nm³) for detailed test evaluations. In addition, several test runs and a 36-hour continuous test were made while injecting 90 mg/Nm³ of Na₂S₄ and 60 mg/dscm of activated carbon simultaneously.

Stack tests for Hg emissions were conducted using U.S. EPA Method 29. During parts of the testing program, a semi-continuous Hg analyzer, which required daily reagent replacement and maintenance, was used to assist in the evaluation program. BBP Environment developed the semi-continuous monitoring system to measure total Hg within the expected range of MWC operation. This system was used to measure the outlet Hg emissions during the Na₂S₄ only injection tests, and during the tests performed while simultaneously injecting both Na₂S₄ and activated carbon.

Activated Carbon Only Injection

Activated carbon injection tests were conducted at feed rates of 120 and 300 mg/dscm. However, the combined tests with Na₂S₄ and activated carbon were run at 57.5-mg/dscm of activated carbon. We did not measure any emission data at the 57.5-mg/dscm activated carbon feed rate due to time limitations. The following is a summary of the activated carbon test:

Dose Rate of Activated Carbon, mg/dscm (No Na₂S₄)	Average Hg Inlet $\mu\text{g/dscm @ 7\% O}_2$	Average Hg Outlet $\mu\text{g/dscm @ 7\% O}_2$	Hg Removal
120	250	20	92.0%
300	210	5	97.6%

The activated carbon injection test results were compared with the activated carbon injection model, with the test results comparing favorably with the model's projection. However, the actual test results showed slightly higher Hg removal than the model. Based on the test data and the use of our activated carbon modeling analysis, it was concluded that to meet a Hg emission limit of 28 $\mu\text{g/dscm}$ without a percent reduction with 95% confidence, approximately 230 mg/dscm of activated carbon would be required.

Na₂S₄ Only Injection

We conducted two test series at 80 mg/Nm³ and three test series at 120 mg/Nm³. Each of the test series was conducted over several days using both the continuous monitor (outlet only) and manual stack test (inlet and outlet). The following is a summary of the Na₂S₄ only injection test.

Dose Rate of Na₂S₄ mg/Nm³ (No activated carbon)	Average Hg Inlet $\mu\text{g/dscm @ 7\% O}_2$	Average Hg Outlet $\mu\text{g/dscm @ 7\% O}_2$	Hg Removal
80	148	26	82.4%
120	360	24	93.3%

Combined Test (Activated Carbon and Na₂S₄)

For the combined test, BBP Environment calculated that the optimum injection rate of 90 mg/Nm³ would achieve the required Hg reduction. Accordingly, a series of tests were conducted while simultaneously injecting Na₂S₄ at a dose rate of 90 mg/Nm³ with activated carbon at a dose rate of 57.5 mg/dscm. During these tests, the inlet concentration of Hg ranged from 170 - 250

µg/dscm at 7% O₂. All measured values at the outlet were below 20 µg/dscm at 7% O₂. As part of this evaluation, the continuous Hg analyzer was used, and the system was run for 36 hours.

Using our computer model, which predicts Hg removal efficiency by activated carbon, we determined that at a dose rate of 57.5 mg/dscm an 80.0% removal of Hg would be expected. Also, the estimated Hg removal efficiency at a Na₂S₄ only dose rate of 90 mg/Nm³ was calculated to be 83.4% over the expected range of uncontrolled Hg emissions. The testing with simultaneous injection of activated carbon and Na₂S₄ showed Hg removal rates that ranged between 89.6% and 92.6%. Therefore, we conclude that the combination of activated carbon injection and Na₂S₄ was more efficient than either technology applied separately.

Pilot Plant Test Program With Baghouse for Particulate Control

A pilot plant testing program was conducted at the MWC located in Kassel, Germany. The units in Kassel burn typical municipal solid waste. The Kassel plant has two units built in 1968, each capable of combusting 265 tons per day of waste. In 1996, the plant air pollution control system was upgraded to comply with the German requirements. The upgrade included installation of a spray dryer and baghouse (after the existing ESP) followed by an activated carbon reactor and an SCR. The activated carbon reactor is used to “protect” the SCR by removing SO₂ to trace levels. It was determined that additional reductions in mercury emissions were required so that the spent carbon from the activated carbon reactor could be returned to the boilers for disposal without creating a mercury cycle. The test program was undertaken to evaluate mercury reduction technologies. Na₂S₄ was tested under several operating conditions to determine the optimum dose rate and the effectiveness in removing Hg⁰, since the activated carbon filter may not reduce Hg⁰. The following is a summary of the pilot plant test results using Na₂S₄ as a sorbent.

Na ₂ S ₄ mg/m ³ dose rate	Dirty Gas µg/m ³		Cleaned Gas µg/m ³		% Removal	
	Hg ⁰	Hg ²⁺	Hg ⁰	Hg ²⁺	Hg ⁰	Hg ²⁺
31	19	153	1	101	96	29
42	17	203	1	15	94	93
48	17	185	2	9	91	95

The Kassel test program demonstrated that Na₂S₄ was an effective sorbent for reducing both total Hg and Hg⁰. Based on the pilot plant results, a full scale Na₂S₄ system was installed on both units.

SUMMARY AND CONCLUSION

BBP’s experience has demonstrated that several technologies can be employed to control mercury emissions from coal-fired power plants. Much of this experience has been gained with FGD systems on coal-fired power plants, and installations of various FGD and air pollution control systems on more than 60 waste treatment facilities.

Full scale and pilot plant tests have demonstrated that the Na₂S₄ process is both a technologically and an economically effective approach to controlling Hg emissions. Pilot plant and short-term tests have verified that the Na₂S₄ technology alone, or in combination with activated carbon

technologies, can achieve a controlled Hg emission rate approaching the expected regulatory requirements for coal-fired boilers. Longer test programs are planned to optimize the flue gas temperature regime and Na₂S₄ dose rate to reduce Hg emissions to extremely low levels. Since the efficiency of the Na₂S₄ process is influenced by mass transfer rates, the technology may be most effective on facilities equipped with fabric filters and wet FGD systems due to the additional retention and contact time.

Perhaps most importantly, the Na₂S₄ process is a commercially viable technique for capturing elemental mercury from coal-fired boilers. This has major significance for utilities with a high fraction of elemental mercury in the flue gas, and which potentially will be required to have high percentage mercury reduction.

REFERENCES

1. Schuettenhelm, W., Hartenstein, H.-U., and Licata, A., "An Optimization Concept for Flue Gas Cleaning Downstream of MWCs Using Sodium Tetrasulfide for Mercury Control" 6th Annual NAWTEC Conference, Miami Beach, FL., May 12, 1998.
2. Chandler, J., Gallant, J., and Hartenstein, H.-U., "A Retrofit of a WTE Facility with SCR for NO_x and PCDD/F Control and Na₂S₄ Injection for Mercury Control" 7th Annual NAWTEC Conference, Tampa, FL, May 17-19, 1999.
3. Clean Coal Today, Spring 2001, U.S.DOE(FE-24), Washington
4. Hester, G, Mercury: Knowns, Uncertainties & Future Directions, Presentation at CIBO NO_x Conference, 2000
5. Brown, T, Smith, D, et al., J. Air & Waste Management, Assoc. 49 (1999) 628-640
6. Gutberlet, H., Schlüter, A. and Licata, A., SCR Impacts on Mercury Emissions from Coal-Fired Boilers, EPRI SCR Workshop, April 18 – 21, 2000, Memphis, TN
7. König, Th, Dynamic Behavior of Hg on SCR DeNO_x Catalysts, DOE SCR Conference, May 2002, Pittsburgh, PA
8. US EPA Report, Control of Mercury Emissions from Coal-Fired Electric Utility Boilers: Interim Report Including Errata dated 3-21-02, EPA-600/R-01-109, April 2002

Key Words

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