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## **TECHNICAL PUBLICATION**

# ADVANCED TECHNOLOGY TO CONTROL MERCURY EMISSIONS

by

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### BABCOCK BORSIG POWER®

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#### INTRODUCTION

U.S. coal fired power plants may have to reduce their mercury emissions by up to 90% by 2007-2009. The pending regulations may affect over 1,100 utility boilers. This paper discusses the impact of mercury emissions from system configurations such as ESPs, baghouses, SCRs, and scrubbers. Babcock Borsig Power (BBP) has gained considerable experience with mercury removal in more than 60 waste-to-energy plants burning municipal or industrial waste and sewage sludge. A technology base exists for the removal of mercury (Hg) by particulate control systems such as ESP or fabric filters in combination with FGD systems found in coal fired plants.

In waste-to-energy plants, the ratio of Cl<sup>-</sup> to Hg is relatively high, and therefore the ratio of ionic Hg to elemental Hg is also high. The collection of ionic Hg is easier to accomplish than emissions of elemental Hg. In coal fired plants, these ratios are lower and the collection of elemental Hg is a challenge. Sewage sludge incineration has fluegas characteristics that are comparable with coal combustion, high levels of SO<sub>2</sub>, and low amounts of HCl. The sorbents used to remove mercury are activated carbon, lignite coke, and/or sulfur-containing chemicals such as sodium tetrasulfide (Na<sub>2</sub>S<sub>4</sub>). Injecting polysulfide compounds into the flue gas promotes the formation of mercury sulfide from elemental Hg (Hg<sup>0</sup>). Ionic mercury (Hg<sup>+</sup>) is thermally stable up to 480°C (900°F). Finding the appropriate flue gas conditions enhance the removal of elementary Hg. Contrary to Na<sub>2</sub>S, the use of Na<sub>2</sub>S<sub>4</sub> in particular permits the removal of elementary mercury. Thus, it will be of substantial importance because of the predominant concentration of elemental mercury in the flue gas of coal fired plants. This experience will be presented in detail, including examples using flue gas treatment by BBP to reduce mercury in combination with SO<sub>2</sub> control. The paper will discuss the transfer of these technologies to control mercury emissions to coal fired power plants.

#### **Mercury Emissions**

Emissions of Hg from coal fired utility boilers 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 emissions are low as an industry group, coal fired boilers are the largest source of man-made mercury emissions in the U.S. Municipal Waste Combustors (MWCs) were the second largest source at 34 tons. However, the MWC emissions have been reduced to less than 3 tons per year.

EPA has formulated a goal to reduce mercury emissions from 50-70% by 2005 and 90% by 2010. Nevertheless, over 80% of the total mercury values exiting the boilers are below 10µg/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 the existing flue gas controls used for other pollutant control.

The distribution of the Hg from the boiler to the stack is also well known; although the capture of mercury from different coals was reported to show a broad variation. Hg emissions from Powder River Basin (PRB) coals are associated with the fly ash up to 30%, but lignite to bituminous coal reaches only 10-20% of Hg in fly ash. Wet FGD systems can remove about 90% of ionic Hg (Hg<sup>2+</sup>) when firing bituminous coal, but only about 60% firing lignite coal. The ratio between elemental Hg<sup>0</sup> and ionic Hg<sup>2+</sup> in the flue gas varies from 90:10 and 10:90, with a nominal ratio  $70(\text{Hg}^0):30(\text{Hg}^{2+})$ , so that the removal rate with wet FGD depends strongly on the ratio Hg<sup>0</sup>/ Hg<sup>2+</sup>. Additionally, an apparent increase of non-ionic Hg from 7-40% at the outlet of wet FGDs was found in U.S. test data. Current FGD systems need to improve operating conditions to increase Hg removal rates.

#### 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  $Hg^0$  to  $Hg^+$  after the air heaters, and the downstream ESPs and FGD systems collected more of the total Hg emissions.

German investigations in three dry bottom furnaces and a slag tap boiler with highdust SCR systems all revealed that metallic mercury is also oxidized. 40 to 60% metallic mercury was found upstream of SCR systems and 1 to 12% downstream of SCR systems. The total concentration of mercury from combustion of pulverized coal was 17  $\mu g/m^3$ , Standard Temperature and Pressure (STP), of which 6 to 7  $\mu g/m^3$  (STP) of metallic mercury were found upstream of the SCR system, and less than 1  $\mu g/m^3$  (STP) downstream of the SCR system.

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 HgCl<sub>2</sub>) can be observed after the second and third layers. Presumably the first layer has less oxidizing effect owing to greater loading with ammonia.

Investigations in a tailend SCR system (after the FGD system) revealed a distinct but insignificant tendency to oxidation, albeit not to the extent seen in high-dust SCR systems. This insignificant effect could be attributed to the absence of hydrogen chloride in the treated gas downstream of the FGD system.

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, after which mercury oxide reacts with hydrogen chloride to form mercury chloride. The equilibrium of this reaction depends upon the equilibrium between metallic mercury and mercury chloride described above.
- 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 U.S. on plants firing PRB coal indicate that there was no change in ratio of  $Hg^0$  /  $Hg^+$  before and after the SCR. Some have theorized that the PRB has lower  $Cl^-$  content or that 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 on these test programs.

#### **MWC Data Base**

A significant database of mercury emissions and control technologies has been developed from the MWC (Municipal Waste Combustor) 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 there exists a base of knowledge gained from the MWCs, there are several significant differences as shown below. Note that this data is "general" and varies significantly by boiler type and type of coal.

#### Emission Forms of Hg (Uncontrolled)

	% Composition	
	<u>Coal</u>	MWC
Hg <sup>o</sup> (vapor)	50	15
$Hg^{2+}$ (Cl or $SO_4^{2-}$ )	30	80
Hg, (particulate)	20	5

#### Flue Gas Characteristics

	<u>Coal</u>	MWC
Uncontrolled Hg emissions	5 to 20 μg/dscm	200 to 600 µg/dscm
HCI concentration	10 to 20 ppm	400 to 900 ppm
Boiler exit temperature	700 °F	450 °F
SO <sub>2</sub> concentration	≈1500 to 8000 ppm	≈200 to 800 ppm

From this summary, it is easy to see that controlling Hg emissions from coal fired plants is different than MWCs.

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Carbon adsorption is one of the key technologies used to control Hg emissions. Most activated carbons have an excellent capacity to capture ionic Hg, but do a poor job in the capture of Hg<sup>0</sup>. Due to the high percentage of Hg<sup>0</sup> in the flue gas, it is expected that high dose rates of carbon will be required.

When choosing among the various technologies for mercury control for flue gases of coal fired boilers, ecological and economical criteria are decisive in restricting power production costs to a justifiable rate. The use of additives provides a significant potential, especially for plants already equipped with a spray dryer/bag house system for achieving compliance at relatively low cost.

The use of sodium tetrasulfide  $(Na_2S_4)$  as an additive for the control of mercury emissions is presented as a possibility to combine both ecology and economy. Particularly with the pending requirements in the U.S., this technology offers the opportunity for most plants to significantly reduce their Hg emissions.

The new proposed regulations have raised concerns with the owners and operators of coal-fired power plants for the following reasons:

- There is very little longterm 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 different air pollution control technologies in multiple stages and having different economic impacts.
- It will require using significantly more activated carbon in order to operate at the lower Hg levels. This raises additional questions. What impact will this additional activated carbon 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?

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

The major advantage of the Na<sub>2</sub>S<sub>4</sub> technology is that it controls elemental, as well as ionic forms of Hg, and due to dissociation in the flue gas, H<sub>2</sub>S under normal operating conditions is not a problem.

Other advantages of the Na<sub>2</sub>S<sub>4</sub> technology are:

- The reaction yields stable inert reaction products.
- Na<sub>2</sub>S<sub>4</sub> is a liquid and is easier and safer to handle than powered activated carbon. Being a liquid, Na<sub>2</sub>S<sub>4</sub> feeding and control is simpler and more positive than powdered activated carbon.
- The higher ratio of elemental Hg fraction produced,in industrial/hazardous waste incinerators, sewage sludge incinerators, and coal fired power plants is easier to control with Na<sub>2</sub>S<sub>4</sub> than with powdered activated carbon.
- Activated carbon is abrasive and results in higher maintenance cost due to replacement of conveying pipes and rotary equipment.

#### **Mercury From Coal Fired Power Plants**

At higher temperatures, mercury compounds are not very thermally stable; therefore, the mercury is gaseous at a temperature of 850°C in the combustion chamber, independent of the kind of compound that is taken into the refuse combustion plant. The minimal retention of mercury in the slag is due to its highvapor pressure and is less than 5% of the total mercury input as shown in various investigations. Other metals such as copper, chromium, or nickel have a slag retention rate of more than 90%. Table 1 presents the physical properties of Hg compounds.

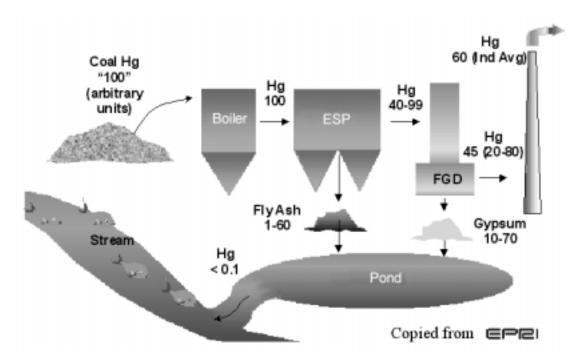


Figure 1 Fate of Mercury in Power Plants

Table 1 Physical Properties of Hg Compounds

	Melting /Sublimation	In furnace	Vapor pressure	Water solubility
	[°C]	>850°C	[µg/m³]	[μg/l]
	1 atm	1 atm	20°C, 1 atm	20°C, 1 atm
Hg⁰ liguid	-39	Gaseous (boils @ 357°C)	14,000	≈20
Hg <sub>2</sub> Cl <sub>2</sub> solid	383	Conversion to gaseous Hg <sup>o</sup>	-	2.1
HgCl <sub>2</sub> solid	276	Conversion to gaseous Hg <sup>o</sup>	800	69,000,000
HgS solid	584	Conversion to gaseous Hg <sup>o</sup>	≈0.1	0.0013
Ch3HgCl solid	170	Not existing in flue gas	54,000	5,000,000

The mercury vapor from the combustion process reacts and mixes with the flue gas and enters the convective section, which is an integral part of the boiler. Due to the decreasing gas temperature, the elemental mercury is able to react with other fluegas components.

One of the first reactions of the mercury vapor in MWC is the formation of mercury (II) chloride (HgCl<sub>2</sub>) out of the gaseous hydrochloric acid (HCl) and elemental mercury (Hg<sup>0</sup>) under oxidizing conditions of the offgases downstream of the boiler. There is sufficient HCl

from most coal combustion for this reaction to take place. Although the exact mechanism of this reduction reaction is not completely understood, it is usually described as follows:

$$Hg^0 + 2 HCl \Leftrightarrow HgCl_2 + H_2O$$
 (Eq. 1)

In case of 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 O<sub>2</sub>, sulfur compounds, and HCl, as well as, the residence time in a certain temperature range influence the reaction equilibrium.

The thermodynamic balance of the abovementioned reaction appears to be blocked kinetically. Therefore, a complete transformation of the  $Hg^0$  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 1).

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<sub>2</sub>Cl<sub>2</sub>):

$$2 \text{ Hg}^0 + 2 \text{ HCl} + \frac{1}{2} \text{ O}_2 \Leftrightarrow \text{Hg}_2\text{Cl}_2 + \text{H}_2\text{O}$$
 (Eq. 2)

• Elemental mercury can be oxidized to mercury oxide (Hg0):

$$2Hg^0 + O_2 \Leftrightarrow 2Hg^0$$
 (Eq. 3)

However, at more elevated temperatures, the above described, simplified reaction possibilities (Eq. 2 and Eq. 3) are of less importance as  $Hg_2Cl_2$ , and  $Hg^0$  are not stable at temperatures above 400°C. Above this temperature,  $Hg_2Cl_2$  decomposes into  $Hg^0$  and  $HgCl_2$  respectively and  $Hg^0$  into  $Hg^0 + \frac{1}{2}O_2$ .

A higher amount of mercury (I) chloride could be formed out of HgCl<sub>2</sub> in the presence of reducing effects, for example, by fly ash or SO<sub>2</sub>. At the boiler's outlet temperature, the Hg<sub>2</sub>Cl<sub>2</sub> is solid and will be separated together with the fly ash (sublimation temperature 383°C, see Table 1). Consequently, up to 10% of the total mercury amount can be removed.

The elemental mercury portion can increase drastically in two ways:

- 1. as the amount of SO<sub>2</sub> exceeds the amount of HCl by an order of magnitude, or
- 2. if there is no residence time for the HgCl<sub>2</sub> 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 - 50% as  $\mathrm{Hg^0}$ . A characteristic of both  $\mathrm{Hg^0}$  and  $\mathrm{HgCl_2}$  is their high vapor pressure, even at temperatures as low as  $200^{\circ}\mathrm{C}$  (395°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 sink.

#### **Measures for Mercury Control**

Besides the Hg separation via Na<sub>2</sub>S<sub>4</sub> as presented in this paper, there are other processes for Hg minimization in flue gas. Of course, ionic mercury as HgCl<sub>2</sub> can be successfully separated in wet scrubbers and in spray absorbers of a fluegas cleaning system as well. The disadvantage is that this equipment is ineffective in trapping metallic mercury. U.S. EPA has reported the following Hg capture data for different control technologies and coals.

#### % Mercury Capture

1 101 001111015			
	<b>Bituminous</b>	<u>Subbituminous</u>	<u>Lignite</u>
Cold ESP	46	16	0
Hot ESP	12	13	?
Fabric Filter (FF)	83	72	?
Wet Scrubber	14	0	33
FGD Controls			
Spray Dryer/FF	98	3	17
Hot ESP and Wet FGD	55	33	?
Cold ESP and Wet FGD	81	35	44
FF and Wet FGD	96	?	?

Metallic and ionic mercury can both be captured in special filters. Activated carbon fixedbed filters (ACR) are the tried and safest means to separate both forms of mercury down to the detection limit in MWCs. Removal rates for total Hg greater than 98% are common at MWCs by forming HgSO<sub>4</sub> on the surface of the lignite coke.

Furthermore, activated carbon can also be injected into the flue gas duct. Usually, in these entrained flow processes, spent activated carbon is again removed by means of a downstream fabric filter.

Alternative processes, especially for the separation of elemental mercury, have recently been proposed, e.g., the application of zeolite in the medisorbon process or the amalgamation of precious metals. However, all such filtration processes share the fundamental disadvantage of involving a separate apparatus in the fluegas path. In addition, the disposal of the spent, heavily contaminated sorbent frequently presents severe problems. The high investment and operating costs for the filters must call the economy of such a system into question.

#### The Na<sub>2</sub>S<sub>4</sub> Process for Mercury Separation

PM Controls

The principles of Hg removal with Na<sub>2</sub>S<sub>4</sub> are as follows:

- Sodium tetrasulfide ( $Na_2S_4$ ) decomposes in flue gas into elemental sulfur ( $S^0$ ) and ionic sulfide ( $S^{-2}$ )
- Elemental sulfur reacts with Hg<sup>0</sup> 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)

The disadvantages of the various conventional processes as described above forced Steinmüller/BBP Environment to develop its own principle of mercury separation using Na2S4 which can capture both ionic HgCl<sub>2</sub> and Hg<sup>0</sup> in accordance with the following simplified reactions:

$$Na_2S_4 + HgCl_2 \Leftrightarrow HgS + 2NaCl + 3S^0$$
 (Eq. 4)

$$S^0 + Hg^0 \Leftrightarrow HgS$$
 (Eq. 5)

It is sufficient to inject an aqueous  $Na_2S_4$  solution into the flue gas duct, and such a system can be easily retrofitted to an existing flue gas cleaning plant. The  $Na_2S_4$  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  $480^{\circ}C$  and thus effectively immobilizes the mercury by chemical binding. The black allotrope known as metacinnabarite found in waste combustion facilities changes into the stable red allotrope in the course of several years.

Apart from the heat exchange with the flue gas, there is also a mass transfer between the droplet 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  $Na_2S_4$  as aqueous alkaline liquids show a strong affinity towards the gaseous HCl or possibly to  $SO_3$ .

Strong acids will decompose the existing Na2S4 in the droplets as follows:

$$Na_2S_4 + 2 HCl \Leftrightarrow H_2S + 3 S + 2 NaCl$$
 (Eq. 6)

After evaporation of the droplet, the  $H_2S$  injected into the flue gas is gaseous at a temperature of approximately 220°C. Elemental sulfur is then formed (melting point of sulfur = 119°C, boiling point = 445°C) and exists in liquid form as an aerosol with a diameter of <1 $\mu$ m. However, it is unlikely that the HCl will decompose all  $Na_2S_4$  molecules. Because  $Na_2S_4$  (melting point = 275°C) is stable at the existing temperatures, it is probable that  $Na_2S_4$  particles or coated fly ash particles can still be found in the flue gas after evaporation of the droplet.

In the entrained flow phase, the mercury reacts with  $H_2S$  (g),  $S^0$  (l), and  $Na_2S_4$ . According to the predominant opinion in literature and the steam pressure curve for pure components,  $Hg^0$  and  $HgCl_2$  can be found in the gaseous phase, including aerosols due to their high volatility.

Competitive reactions such as the oxidization of  $Na_2S_4$ ,  $H_2S$  or S into  $Na_2S_0$ 3,  $Na_2S_2O_3$ ,  $SO_2$ , and others cannot be excluded. Such competitive reactions would prevent the sulfur from further reactions with mercury. Moreover, sulfide formation of other heavy metals can cause competitive reactions as well. However, in the case of injection after upstream particulate control system, such reactions are of no consequence regarding the sulfur balance. Even if all heavy metals in the flue gas flow react to sulfides, only 4-10 % of the fed sulfur could be used up via the  $Na_2S_4$  injection. Simultaneously, an inerting of these heavy metals could be realized. Running a stoichiometric  $Na_2S_4$ : Hg more than 700:1, decomposition problems, as well as the reaction with other metal compounds in the flue gas, are compensated for without reaching an ultimately required  $Na_2S_4$  solution.

#### **Pilot Plant Test Program**

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 longterm basis. MWCs equipped with spray dryers and ESPs were of special concern. Since the principal advantage of the Na<sub>2</sub>S<sub>4</sub> technology is that it is more effective than activated carbon in controlling both elemental mercury (Hg<sup>0</sup>) and ionic mercury (Hg<sup>2+</sup>), BBP Environment wanted to determine if the Na<sub>2</sub>S<sub>4</sub> technology would be applicable. Na<sub>2</sub>S<sub>4</sub> 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 in U.S. facilities.

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

- Could Na<sub>2</sub>S<sub>4</sub> meet the new proposed emission standard on a short term operating period?
- Would there be an advantage to using activated carbon injection and Na<sub>2</sub>S<sub>4</sub> 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  $Na_2S_4$  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  $Na_2S_4$  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 Na<sub>2</sub>S<sub>4</sub> injection tests and during the tests performed while simultaneously injecting both Na<sub>2</sub>S<sub>4</sub> and activated carbon.

#### **Injection of Activated Carbon Only**

Activated carbon injection tests were conducted at feed rates of 120 and 300 mg/dscm. However, the combined tests with  $Na_2S_4$  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 Activated Carbon mg/dscm	Average Hg Inlet µg/dscm @ 7%O₂	Average Hg Outlet µg/dscm @ 7%O <sub>2</sub>	Hg Removal
<b>(No Na₂S₄)</b> 120	250	20	92.0%
300	210	5	97.6%

The activated carbon injection test results were compared with activated carbon injection model and the pilot plant test results compared favorably with the model projection. However, the actual test results showed slightly higher Hg removal than the model projects. Based on the test data and the use of our activated carbon modeling analysis, it was concluded that in order to meet a Hg emission limit of 28 µg/dscm without a percent reduction and a 95% confidence level, approximately 230 mg/dscm of activated carbon would be required.

#### Injection of Na<sub>2</sub>S<sub>4</sub> Only

We had two test series at  $80~\text{mg/Nm}^3$  and three test series at  $120~\text{mg/Nm}^3$ . 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  $Na_2S_4$  only injection test.

Dose Rate Na <sub>2</sub> S <sub>4</sub> - mg/Nm <sup>3</sup> (No activated carbon)	Average Hg Inlet µg/dscm @ 7%O <sub>3</sub>	Average Hg Outlet µg/dscm @ 7%O₂	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  $90 \text{ mg/Nm}^3$  would achieve the required Hg reduction. Accordingly, a series of tests were conducted while simultaneously injecting Na<sub>2</sub>S<sub>4</sub> at a dose rate of  $90 \text{-mg/Nm}^3$  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  $7\% \text{ O}_2$ . All measured values at the outlet were below 20 µg/dscm at  $7\% \text{ O}_2$ . As part of this evaluation, the continuous Hg analyzer was used and the system was run for 36 hours in this condition.

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 Na<sub>2</sub>S<sub>4</sub>-only dose rate of 90 mg/Nm<sup>3</sup> was calculated to be 83.4% over the expected range of uncontrolled Hg emissions. The testing with simultaneous injection of activated carbon and Na<sub>2</sub>S<sub>4</sub> showed Hg removal rates that ranged between 89.6% and 92.6%. Therefore, we conclude that the combination of activated carbon injection and Na<sub>2</sub>S<sub>4</sub> was more efficient than either technology applied separately.

#### Sewage Sludge and Industrial Waste Combustors

Sewage sludge and some industrial waste combustors have a flue gas composition closer to coal fired boilers than to MWCs. Sludge combustors typically have a higher sulfur to chloride ratio and a high Hg<sup>0</sup> to Hg<sup>+</sup> ratio. The following shows an example using Na<sub>2</sub>S<sub>4</sub> combined with activated carbon in air pollution control system for sludge combustors:

EVA Lünen: This sewage sludge plant is equipped with a spray dryer and fabric filter to capture Hg. The flue gas contained 700 ppm SO<sub>2</sub>, 120 ppm HCl, and 70 to 140 μg/dscm of Hg. Tests were initially conducted by injecting activated carbon prior to the spray dryer. With this arrangement the best Hg reduction that could be achieved was 61%. A Na<sub>2</sub>S<sub>4</sub> system was installed and the total Hg removed increased to 86%. Na<sub>2</sub>S<sub>4</sub> is currently being injected simultaneously with the activated carbon.

*SAVA Ebenhausen:* This industrial waste combustor is equipped with an ESP, scrubber, gas cooler and finally a wet ESP. The scrubber removes almost all of the HCl from the flue gas. Prior to the installation of the Na<sub>2</sub>S<sub>4</sub> system the maximum Hg removal in the system was 56%. When Na<sub>2</sub>S<sub>4</sub> was injected prior to the gas cooler the total system Hg removal rate was increased to 97%.

The test data from these combustors demonstrates that the Na<sub>2</sub>S<sub>4</sub> process can work in applications where there are low levels of HCl or and high ratios of Hg<sup>0</sup> to Hg<sup>+</sup>.

#### SUMMARY AND CONCLUSION

Both full scale and pilot plant tests have demonstrated that the Na<sub>2</sub>S<sub>4</sub> system is both a technologically and an economically effective approach to controlling Hg emissions. Pilot plant and shortterm tests have verified that the Na<sub>2</sub>S<sub>4</sub> technology alone or in combination

with activated carbon technologies can achieve a controlled emission rate on MWCs equipped with a spray dryer and ESP to levels approaching expected emissions from coal fired boilers. It would be beneficial to have a longer test program to optimize the dose rate of  $Na_2S_4$  to control Hg emissions at these low levels. Since the efficiency of the  $Na_2S_4$  is based on mass transfer, the technology would be even more effective on facilities equipped with fabric filters and wet FGD systems due to the additional retention and contact time.

Additionally, for each fuel and configuration of flue gas cleaning systems there must be proper positioning and boundary limits according to temperature and operating conditions for the successful dosing of Na<sub>2</sub>S<sub>4</sub> to remove mercury. Additional trials for the use of Na<sub>2</sub>S<sub>4</sub> technology for a variety of plant configurations will be required.

#### 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 NOx and PCDD/F Control and Na<sub>2</sub>S<sub>4</sub> 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, Licata, A, SCR Impacts on Mercury Emissions from Coal-Fired Boilers, EPRI SCR Workshop, April 18-21, 2000, Memphis, TN