CALCIUM BROMIDE TECHNOLOGY FOR MERCURY EMISSIONS REDUCTIONS

Great Lakes SOLUTIONS

a Chemtura business

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by William R. Fielding
Great Lakes Solutions, a Chemtura business

Bromine and bromine-based products have been shown to be effective in oxidizing elemental mercury which enhances its removal from the flue gas of coal-fired power plants by conventional APC devices. Calcium bromide has been found to be especially effective either alone or in conjunction with sorbents such as activated carbon. Data supporting calcium bromide's use for mercury reduction follows.

On December 16, 2011, the United States Environmental Protection Agency (EPA) signed a rule to reduce emissions of toxic air pollutants from power plants. The Mercury and Air Toxic Standards (MATS) are designed to reduce emissions from oil and coal-fired electric utility generating units (EGU). The rule provides up to three years for compliance by all sources and the potential for a one year extension under certain circumstances.*

A number of technologies have been investigated over the past ten years to remove mercury from EGU's emission streams. The use of calcium bromide is one of the technologies which has been shown to enhance the reduction of mercury emissions by traditional Air Pollution Control (APC) technologies in a cost-effective manner. Great Lakes Solutions, a Chemtura business, has developed this White Paper to demonstrate the enhanced mercury reduction achieved from the use of calcium bromide and to provide data from sources that have implemented the calcium bromide mercury reduction technology.

GeoBrom®

GeoBrom® products have been designed for incorporation into new technologies that use bromine or brominated derivatives products for the efficient reduction of toxic mercury emission from coal-fired boilers and power plant installations.

The GeoBrom® product line provides sustainable, secure, U.S. manufactured brominated products for mercury control by a company with proven ability to solve complex customer logistical challenges and requirements.

*http://www.epa.gov/airquality/powerplanttoxics/pdfs/20111221MATSsummaryfs.pdf)

COAL-FIRED POWER PLANTS AS A SOURCE OF MERCURY EMISSIONS TO THE ENVIRONMENT

Mercury is a natural part of the earth's crust with an estimated average concentration of 50 parts per billion. Like all minerals, concentrated deposits are found in specific areas such as coal or limestone. Because it is a natural element it cannot be destroyed, only changed in form. Mercury is generally found in an oxidized form as a salt. Mercury is released to the biosphere through natural processes such as volcanic eruptions or weathering of the earth's crust when it is changed from a bound, non-transportable form to the elemental form that can be transported by air or water. It can also be released by anthropogenic processes, such as fossil fuel combustion or industrial processes like gold mining, in which it is converted to the elemental form and released as a vapor.

Mercury deposited in aqueous ecosystems such as ponds, lakes, or wetlands can be transformed into methylmercury by sulfate-processing bacteria. Methylmercury can be adsorbed onto plankton which, when consumed, become the primary entry point into the food chain. Methylmercury is absorbed rapidly and excreted slowly allowing bioaccumulation at each level of the food chain.

Methyl mercury is a toxic form of mercury affecting the nervous, immune, and enzyme systems. A developing fetus is five to ten times more sensitive to methylmercury than an adult. Therefore, children born to women who consume large quantities of contaminated fish are at risk for neurological damage.[1,2] The neurological damage suffered by the fetus can result in children being born with learning disabilities.[3,4]

CONTROL OF MERCURY EMISSIONS WITH APC DEVICES

Coal-fired power plants account for about 50% of the anthropogenic mercury in the United States.[4] Mercury concentrations in coal range from 0.04 to 0.19 ppm depending on the type of coal and where it is mined. Coal contains a number of other impurities which influence how it burns, the type and amount of pollutants released, and the type of abatement equipment required to control its emissions. Among the pollutants found in the flue gas are unburned carbon, fly ash, sulfur oxides (SOx), nitrogen oxides (NOx) and particulate matter.

The coal-fired power industry is composed of over 1300 boiler operations. To reduce the emission of pollutants from these boilers, air pollution control (APC) devices, such as electrostatic precipitators (ESP), flue gas desulfurization units (FGD), and selective catalytic reduction (SCR) units have been added to power plants to control SOx, NOx and particulate matter over the past 30 years. These APC devices can also help to remove mercury from the flue gas stream. Of the 1300 plus boilers in the United States, 37% use an ESP as their primary APC device. The remaining 63% of the boilers use one of ten different types of APC configurations[5]. The coal type and source, the boiler configuration and operation, and the APC configurations all contribute to the complexity of choosing a mercury-specific control technology.

IMPROVEMENT OF ABATEMENT OF MERCURY EMISSIONS VIA OXIDATION WITH BROMINE COMPOUNDS

Mercury is released when coal is burned and takes three forms in the flue gas: elemental, oxidized, and particulate. Oxidized and particulate mercury can be controlled by abatement equipment designed for other pollutants such as ESP or FGD units. However, elemental mercury is gaseous at combustion temperatures and is difficult to capture. Therefore, chemical additives have been developed to oxidize the elemental mercury in the flue gas, converting it to a form which can be captured by current abatement equipment.

Calcium bromide ($CaBr_2$) is one of the chemical additives that has been developed as a mercury-specific control technology. When used in combination with a number of APC configurations, $CaBr_2$ is effective in reducing total mercury emissions by oxidizing elemental mercury that is then captured by the abatement equipment. The percent reduction of mercury emissions from several APC configurations are shown in Table 1.

The baseline data indicates the percentage of mercury removed by the APC configuration without any mercury specific control technology. The mercury removed by these APC configurations is oxidized or particulate mercury. With the addition of calcium bromide the percentage of mercury removed increases with each abatement configuration. The increased removal of mercury indicates that calcium bromide effectively oxidizes previously uncaptured elemental mercury, which is then collected by the APC devices. In addition, these results highlight the ability of calcium bromide to improve mercury removal from the flue gas across a variety of abatement configurations.

Table 1: Mercury Removal with the Addition of Calcium Bromide

% Mercury Removed						
Equipment*	**FF**	**CS-ESP**	**CS-ESP/ FGD**	**HS-ESP/ FGD**	**SCR CS-ESP**	**SCR SDA / FF**
Baseline	**19**	**28**	**28**	**44**	**60**	**20**
$CaBr_2$	**>55**	**60**	**86**	**>80**	**90***	**85**
References	***6***	***7***	***8***	***9***	***10,11,12,13***	***14***

*Fly ash passed concrete use test

FF (fabric filter bag house)
CS-ESP (cold-side electrostatic precipitator)
CS-ESP / FGD (cold-side electrostatic precipitator / flue gas desulfurization unit)
HS-ESP / FGD (hot-side electrostatic precipitator / flue gas desulfurization unit)
SCR / CS-ESP (selective catalytic reduction / cold-side electrostatic precipitator)
SCR / SDA / FF (selective catalytic reduction / spray dryer absorber / fabric filter)

Sorbents, such as activated carbon (AC), are another mercury-specific control technology which has been successful in reducing mercury in flue gas streams. Table 2 shows a number of abatement configurations where calcium bromide has been used in combination with activated carbon. The data indicate that the addition of calcium bromide improves the effectiveness of activated carbon in removing mercury.

Table 2: Mercury Removal with Activate Carbon & Calcium Bromide

% Mercury Removed						
Equipment*	**FF**	**CS-ESP**	**CS-ESP/ FGD**	**HS-ESP/ FGD**	**SCR CS-ESP**	**SCR SDA / FF**
Baseline	**19**	**28**	**18**	**20**	**15**	**20**
AC only	**58**	**73**				**48**
$CaBr_2$ / AC	**>90**	**88**	**>80**	**86**	**90**	**>90**
References	***6***	***7***	***15***	***15***	***15***	***14***

FF (fabric filter bag house)
CS-ESP (cold-side electrostatic precipitator)
SDA / CS-ESP (spray dryer absorber / cold-side electrostatic precipitator)
SDA / FF (spray dryer absorber / fabric filter bag house)
SCR / FGD (selective catalytic reduction / flue gas desulfurization unit)
SCR / SDA / FF (selective catalytic reduction / spray dryer absorber / fabric filter bag house)

In some APC configurations, such as electrostatic precipitators or fabric filters, the combination of calcium bromide and activated carbon to enhance mercury removal may allow plants to achieve the necessary reductions without the need for changes to existing control devices. For example, in older or smaller plants the APC units may be undersized to handle the increased particulate loading of activated carbon injection that would be needed to achieve a high level of mercury removal. In these plants, the addition of calcium bromide to promote the oxidation of elemental mercury can reduce the level of activated carbon needed. In many cases this would allow the plant to use existing equipment minimizing the cost to achieve reduced mercury emissions.

In 14 full-scale coal-fired power plant tests using calcium bromide to oxidize elemental mercury, greater than 90% of the mercury was oxidized with the addition of 25 to 300 ppm bromide by weight of coal. In a plant trial with an SCR in the abatement configuration, 90% mercury oxidation was achieved with <20 ppm bromide.[16]

In October 2009, the Government Accounting Office (GAO) published a report evaluating the effectiveness of sorbent injection systems for reducing mercury emissions from 25 fossil fuel-fired electric utility steam generating units (EGUs) from 14 coal-fired power plants.[17] The GAO Report reviewed data from these plants as well as data from the Department of Energy's comprehensive mercury control technology test program. The GAO Report concluded that these plants achieved mercury emissions reductions of about 90 percent. Sorbents that were chemically enhanced with halogens such as chlorine or bromine, which helped to convert mercury from an elemental form into an oxidized form, allowed the EGUs to achieve higher levels of mercury reduction across all coal types.

BROMINE & CALCIUM BROMIDE

The Energy Information Administration reported that in 2008, 1019 million short tons of coal were consumed in the United States by EGUs.[18] Of the coal used by EGUs about 45% was low rank coal and would require a mercury-specific control technology to achieve the proposed reductions in mercury emissions.[19] Using the 25 to 300 ppm range of bromide by weight of coal[15], the bromine demand would be from 5,700 short tons on the low end to 69,000 short tons on the high end per year to treat this amount of coal per year.

Elemental bromine and calcium bromide are readily available via a well developed commercial supply chain in the United States. In addition to mercury emissions abatement, bromine and calcium bromide are currently used as water treatment chemicals, oil drilling chemicals, flame retardant chemicals, and fine chemical production. The primary supply source within the United States is the Smackover formation in South Arkansas. With estimated reserves of eleven million tons of bromine, and an annual production capacity estimated at 226,000 tons, the U.S. supply is both stable and economical.[20]

ECONOMIC CONSIDERATIONS

The Department of Energy's National Energy Technology Laboratory (NETL) estimated the capital cost for $CaBr_2$ operation at a 500 megawatt plant to be $780,000. NETL estimated the cost per pound of mercury removed to be from $2800 (SCR) to $7000 (CS-ESP / wet FGD) for low rank coal on a 20-year level cost basis. The cost did not include any by-product impact because the use of calcium bromide does not affect the sale of fly ash.[21]

The data presented above demonstrates that calcium bromide can be used to enhance the reduction of mercury emissions with most existing APC systems. Calcium bromide is versatile enough that it can be added to the pulverized coal, injected into the boiler, or into the flue gas stream. The equipment to introduce calcium bromide requires moderate capital investment and has low impact on overall operating costs. Because the addition of calcium bromide is not harmful to boilers, adds minimal variable cost, and does not negatively affect the use of fly ash for sale to the concrete industry as a cement replacement, it has minimal impact on operating costs.[22]

MERCURY EMISSIONS CONTROL REGULATIONS

Regulations governing the abatement of mercury emissions are under development in several jurisdictions. These include state-level regulations in the United States, proposed new rules by the EPA, and preparation of a legally binding agreement on mercury by the United Nations Environment Programme (UNEP). Actions by EPA include proposed new rules to establish emission standards for specific categories of sources. The EPA is in the process of promulgating NESHAPs for ICI boilers, EGUs and Portland cement plants, all of which are anticipated to include emissions limits on mercury. As part of these rulemaking efforts, the EPA will be considering emissions data from control technologies for the specific types of emission sources. To the extent appropriate, we suggest that the EPA consider calcium bromide technology in establishing theses NESHAPs.

CONCLUSION

The effectiveness of bromine and bromide compounds to enhance the removal of mercury emissions from coal-fired power plants has been well-documented. As regulatory agencies evaluate the effectiveness of emissions abatement systems, the current or potential future use of calcium bromide and other bromine-based additive technologies should be considered in setting emissions limits and providing guidance on effective control technologies. We believe that the use of calcium bromide and other bromine-based additive technologies provide highly cost-effective controls for mercury emissions such that this technology should prove to be useful for regulated entities as they implement mercury reduction strategies at individual emissions units.

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