Calcium Bromide technology for mercury emissions reduction

Kasturirangan Kannah
Chemtura, Manchester, UK
k.kannah@chemtura.com

Jon Lehmkuhler
Chemtura, Philadelphia, USA
jon.lehmkuhler@chemtura.com

Abstract : The UN Minamata Convention on mercury has captured the attention of regulatory authorities around the world. Every signatory country is obliged to produce national plans on how to manage their mercury emissions . Coal combustion is a dominant source of mercury emissions in India, accounting for an estimated 85% of total mercury emitted from man-made sources. As India moves ahead with its plans for expanding available, reliable and sustainable electric power to its citizens, the need for more effective control of emissions to the atmosphere become paramount.

In December 2015, MoEF mandated regulations on SOx, NOx, particulates and mercury from coal fired thermal power plants. The new limits are seen as challenging by the industry and will necessitate substantial capital expenditure in the next few years. This paper compares various options to minimize emissions, highlighting some techniques which have found widespread application in the United States.

The effectiveness of bromide compounds to enhance the reduction of mercury emissions from coal-fired power plants has been well documented. In addition to mercury, SOx and NOx levels can also be reduced through chemical additive techniques. Bromide based technologies can be an effective part of a comprehensive co-benefit strategy to reduce mercury emissions in conjunction with other pollutant control strategies. Limited available data indicates that the use of bromide can be a viable option for achieving mercury emission reductions that would significantly contribute to India's compliance with the MoEF regulations. We provide this paper to demonstrate the enhanced mercury reduction achieved from the use of calcium bromide in coal fired plants in the USA and to provide data from sources that have implemented the calcium bromide mercury reduction technology. We discuss the relevance of this technology for Indian thermal power plants.

Mercury in the environment – the issue

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 can not 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 methyl mercury by sulfate-processing bacteria. Methyl mercury can be adsorbed onto plankton which, when consumed, become the primary entry point into the food chain. Methyl mercury 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 methyl mercury 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 Air Pollution Control Devices

Coal- fired power plants account for a significant proportion of the anthropogenic mercury globally. 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.

To reduce the emission of pollutants from coal fired boilers, air pollution control (APC) devices , such as electrostatic precipitators (ESP), flue gas desulfurization units (FGD), and selective catalytic reduction (SCR) units are installed in power plants to control SOx, NOx and particulate matter.. These APC devices can also help to remove some 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/	HS-ESP/	SCR	SCR/
			FGD	FGD	CS-ESP	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 Activated Carbon & Calcium Bromide

	% Mercury Removed					
	FF	CS-ESP	SDA/CS-ESP	SDA / FF	SCR / FGD	SCR/
Equipment*					CS-ESP	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]

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

A UN Regulation called the Minamata Convention governing the releases of mercury to the environment is expected to be ratified in 2017. Once ratified, this Regulation will become legally binding on the Parties which are a signatory to the Convention. India became a signatory to the Minamata Convention on 30th September 2014.

The regulatory framework in India for air pollution from coal fired power plants

The Ministry of Environment and Forests (MoEF) issued norms in December 2015 for coal fired thermal power plants, targeted at the following pollutants – particulate matter, SOx, NOx and mercury (Table 3). The deadline for compliance is December 2017.

Table 3: Notified Air Pollution Control Norms for TPPs – India (Ministry of Environment & Forests, 8th December 2015)

Age of unit	**Parameter**	**Proposed limits**
TPPs installed before Dec 31st 2003	Particulate matter	100 mg/Nm3
	Sulphur dioxide	600 mg/NM3 (<500MW) 200 mg/NM3 (>500 MW)
	Oxides of nitrogen	600 mg/NM3
	Mercury	0.03 mg/NM3 (500 MW and above)
TPPs installed between 1/1/2004 and 31/12/2006	Particulate matter	50 mg/NM3
	Sulphur dioxide	200 mg/NM3
	Oxides of nitrogen	300 mg/NM3
	Mercury	0.03 mg/NM3

TPPs installed from 1/1/2017	Particulate matter	30 mg / NM3
	Sulphur dioxide	100 mg/NM3
	Oxides of nitrogen	100 mg/NM3
	Mercury	0.03 mg/NM3

TPPs (units) shall meet the limits within two years from the date of publication of this notification.

Discussion

Due to the impending deadline, it is reported that power sector operators are urgently assessing their options. It has also been estimated that the overall cost of compliance will be in the region of Rs 2 lakh crores and increase the national power tariff by up to 23%. This is due to the large capital expenditures necessitated by systems such as Flue Gas Desulphurisation (FGD) for SOx and and Selective Catalytic Reduction (SCR) for NOx and upgrading of Electrostatic Precipitators (ESPs). It is outside the scope of this paper to discuss these systems in detail, however there are other technology options such as furnace sorbent technologies that are far more cost effective and it is probable that such systems will enter the Indian market in the years to come. These systems can be well integrated with the mercury control techniques described in this paper.

In terms of mercury content in Indian coals, CIMFR compiled a comprehensive report published in February 2014 on behalf of the UN Chemicals Division and funded by the European Union. The mean value of mercury from an assay of 66 samples was found to be 0.14 g/tonne, which is fairly representative of the global mean. Within these samples, the variation was 0.003 to 0.34 g/tonne. The mercury concentration in the flue gases was measured at three units at 14.84, 11.5 and 4.24 µg/Nm3 ; this is within the emission limit specified for mercury in the MoEF Notification at 30 µg/Nm3, although the sample size is comparatively small. The initial conclusion that can be drawn from this report is that it is possible to meet the current emission limit for mercury without any additional abatement. However, it must be borne in mind that the emission limit is not representative of modern regulatory regimes such as in the USA and the European Union, where limits are typically below 10 µg/Nm3. Further, with the coming into force of the Minamata Convention and the public recognition of the toxic effects of mercury on human health and the environment, it would be prudent to anticipate that emission limits will become more stringent, in keeping with the other air pollutants such as particulates, SOx and NOx and plan accordingly.

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 countries like India, China and South Africa as they implement mercury reduction strategies.

References

[1]*Human Health Criteria, Methylmercury Fish Tissue Criterion*, Fact Sheet: January 2001.

http://www.epa.gov/waterscience/criteria/methymercury/factsheet.html

[2]USGS *Mercury in the Environment,* Fact Sheet 146-00, October 2000. http://www.usgs.gov/themes/factsheet/146-00/

[3]Praveen, A., Mercury Emissions from Coal-Fired Power Plants, NESCAUM, 2003.

www.nescaum.org/documents/rpt031104mercury.pdf/

[4]Johnson, K., B. Wemhoff, *Mercury Emissions Frequently Asked Questions*, National Rural Electric Cooperative Association Environmental Affairs Unit, July 2004.

http://www.nreca.org/Documents/PublicPolicy/MercuryEmmisionsFAQ.pdf

[5] Mercury Control Technology Selection Guide, EPRI, Palo Alto, CA, September 2006

[6]Dutton, R., et al. *Options for High Mercury Removal at PRB-fired Units Equipped with Fabric Filters with Emphasis on Preserving Fly Ash Sales*. Proceedings of the Power Plant Air Pollutant Control “Mega” Symposium, Baltimore, MD, August 25-28, 2008.

[7]Durham, M.D., et al. *Mercury Control for PRB and PRB/Bituminous Blends*. Proceedings of the Power-Gen Renewable Energy Conference, Las Vegas, NV, March 1-3, 2005.

[8]*Large-Scale Mercury Control Technology Testing for Lignite-Fired Utilities – Oxidation Systems for Wet FGD,* Final Report to U.S. Department of Energy under Cooperative Agreement No. DE-FC26-03NT41991, URS Corporation, March 2007, http://www.netl.doe.gov/technoligies/coalpower/ewr/mercury/control-tech/pubs/41991/41991%20Final%20Report.pdf

[9]Renninger, S., et al. *Testing of Nalco's Mercontrol 7895 for Mercury Removal at Arizona Electric Power's Apache Station*, Proceedings of the Air Quality VII Conference, Arlington, VA, October 26-29, 2009.

[10]Berry, M., *Mercury Control Evaluation of Calcium Bromide Injection into a PRB-Fired Furnace with an SCR*, Proceedings of the Air Quality VI Conference, Arlington, VA, September 24-27, 2007.

[11]*Southern Company Evaluates Novel, Cost-Effective Mercury Control Technologies,* EPRI Newsletter, Palo Alto, CA, September 2009, http://mydocs.epri.com/docs/public/000000000001020183.pdf

[12]Dombrowski, K, et al. *The Balance-of Plant Impacts of Calcium Bromide Injection as a Mercury Oxidation Technology in Power Plants*, Proceedings of the Power Plant Air Pollutant Control "Mega" Symposium, Baltimore, MD, August 25-28, 2008.

[13]Larrimore, L., et al. *Effect of Bromine Addition on Fly Ash Use in Concrete,* Proceedings of the Power Plant Air Pollutant Control "Mega" Symposium, Baltimore, MD, August 25-28, 2008.

[14]Amrhein, J., et al. *Mercury Control at New Generation Western PC Plants,* Proceedings of the Power Plant Air Pollutant Control "Mega" Symposium, Baltimore, MD, August 25-28, 2008.

[15]Rini, M., et al. *Full-scale Test Results From a 600 MW PRB-fired Unit Using Alstom's KNX™ Technology for Mercury Emissions Control,* Proceedings of the Power Plant Air Pollutant Control "Mega" Symposium, Baltimore, MD, August 25-28, 2008.

[16]Chang, R. et al. *Near and Long Term Options for Controlling Mercury Emissions from Power Plants.* Proceedings of the Power Plant Air Pollutant Control "Mega" Symposium, Baltimore, MD, August 25-28, 2008.

[17]GAO, Report to the Chairman, Subcommittee on the Clean Air and Nuclear Safety,

Senate Committee on Environment and Public Works, *Mercury Control Technologies at Coal-Fired Power Plants Have Achieved Substantial Emissions Reductions*, GAO-10-47 (Oct. 2009), *available at* http://www.gao.gov/products/GAO-10-47

[18] *Energy Information Administration / Annual Energy Review 2008, Table 7.3 Coal Consumption by Sector, Selected Years, 1949-2008,* available at

http://www.eia.doe.gov/aer/pdf/pages/sec7_9.pdf

[19] *Technologies for Control and Measurement of Mercury Emissions from Coal-Fired Power Plants in the United States: A 2010 Status Report*, NESCAUM, July 2010, pgs. 1-2 & 3.

[20]USGS Mineral Commodity Summaries 2010, January 2010. http://minerals.usgs.gov/minerals/pubs/mcs/2010/mcs2010.pdf

[21]Jones, A.P., T.J. Feeley, III, *DOE/NETL's Mercury Control Technology Field Testing Program, Preliminary Economic Analysis of Wet FGD Co-Benefit Enhancement Technologies,* May 2008., p. 16.

[22] *Technologies for Control and Measurement of Mercury Emissions from Coal-Fired Power Plants in the United States: A 2010 Status Report*, NESCAUM, July 2010, pgs. 1-47 & 48.

Energy World, 22nd February 2016

Assessment of the mercury content of the coals fed to power plants and the study of mercury emissions from the sector in India, report prepared by CIMR, Dhanbad, February 2014 for UNEP Chemicals Branch, Geneva