Options for Compliance Mercury Monitoring at Coal-Fired Power and Cement Producing Plants

Mercury emissions from coal-fired power and cement producing plants have been recently regulated in the U.S. by the Mercury and Air Toxics Standards and National Emission Standards for Hazardous Air Pollutants from the Portland Cement Manufacturing Industry. These rules are anticipated to significantly reduce mercury emissions and consequently lower the concentration of mercury in the flue gas effluent from these facilities. This article overviews the respective regulations and discusses compliance options for mercury monitoring available to plant operators. One of these options is the installation and use of sorbent trap mercury monitoring systems (STMMS), which have the ability to accurately and reliably measure a wide range of mercury concentrations including the very low levels expected to result from these regulations.

> *"The cement and electric utility industries have come under increased pressure to control and reduce their mercury emissions."*

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Mercury emissions from industrial sources have received continuous attention from regulators in the U.S. over the past couple of years. As a result, on February 12, 2013, the U.S. Environmental Protection Agency (US EPA) promulgated the final amendments to the National Emissions Standard for Hazardous Air Pollutants from Portland Cement Manufacturing Industry, also known as the PC MACT [1]. In addition, on March 28, 2013, the US EPA submitted for publication, the final amendments of the Mercury and Air Toxics Standards (MATS), establishing national emissions limitations and work practice standards for mercury and certain other hazardous air pollutants (HAP) emitted from coal-fired and oil-fired electric utility generating units (EGU) [2]. Each rule requires significant reduction in mercury emission.

The mercury emission standards in the PC MACT apply to all new and existing cement kilns and are based on the production rates of clinker, the manufactured product from the kiln. They correspond to equivalent average flue gas concentrations of approximately 5 µg/m^3 for new kilns and 12 µg/m^3 for existing kilns. These limits apply to normal operation and are assessed on a 30-operating-day rolling average. Compliance with these standards will be determined through continuous monitoring. All kilns must install and operate a mercury monitoring system by September 9, 2015.

The EGU MATS affects over 1000 fossil-fired utility boilers in the U.S. with an anticipated compliance date for existing sources in spring of 2015. The mercury emission limits are based on the date on which a facility is constructed or substantially modified and the type of fuel burned to produce electricity. These limits are applicable based on four source categories: coal-fired units designed to burn coal with a gross calorific value (GCV) ≥ 8,300 Btu/lb, coal-fired units designed to burn low-rank virgin coal (GCV < 8,300 Btu/lb), Integrated Gasification Combined Cycle (IGCC) units and solid oil-derived fuel (i.e., petroleum coke)-fired units.

Certain units can comply with the rule by qualifying as "Low-Emitting EGUs" (LEEs). For mercury, a LEE is an existing unit that emits at less than 10% of the applicable emissions limit, or has the potential to emit no more than 29.0 lb of mercury per year. This option may not be used for new units or existing units with configurations that allow them to bypass their wet flue gas desulphurisation scrubbers. Similar to the requirements for the PC MACT, units that don't qualify as a LEE must continuously monitor mercury (excluding oil-fired units) and report their emissions on a 30-operating-day rolling average.

Figure 1 illustrates the MATS limits for three source categories. The limits are converted to the approximate equivalent unit of µg/m^3 for easier comparison to readings normally obtained from mercury monitoring systems. Comparison of the LEE limits with the existing non-LEE limits provides an operating envelope for monitoring systems at existing units. For example, existing units firing coal with a GCV ≥ 8,300 Btu are anticipated to generate emissions bounded on the low end by the LEE limit of 0.14 µg/m^3 and on the upper end by the existing non-LEE limit of 1.4 µg/m^3.

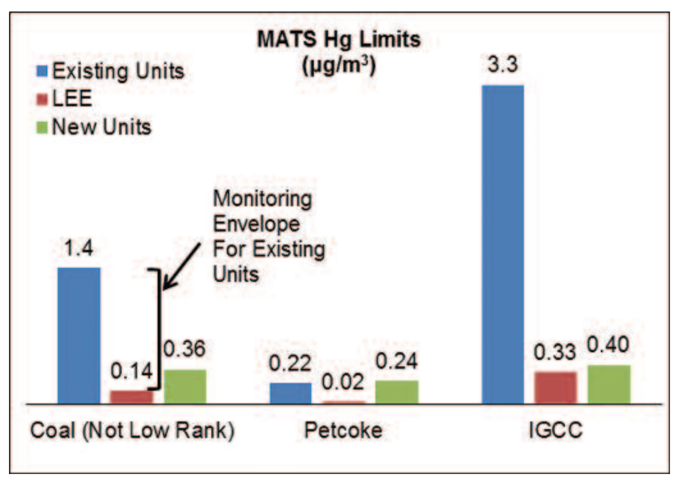

Figure 1: MATS mercury limits for various fuel types, illustrating monitoring envelope for existing coal-fired units.

Sorbent Trap Mercury Monitoring

Meeting the mercury monitoring requirements of these new rules will be a challenge. Continuous monitoring using on-line analyser-based technology to provide real-time mercury concentration data is available. However, recent U.S. utility experience indicates that this approach may be difficult and costly to implement as a continuous compliance reporting tool [3].

A sorbent trap mercury monitoring system (STMMS) following U.S. EPA Performance Specification 12B (PS12B) [4] is an alternative to the continuous analyser approach and is gaining wide-spread recognition as the preferred method for continuous compliance reporting. An STMMS provides an average mercury concentration that is integrated over a period of time that could be hours, days, or even weeks. Flue gas is sampled through a pair of traps filled with a sorbent that captures mercury. The rate at which the sample passes through the sorbent is varied in proportion to the flue gas flow rate in the stack to provide so-called proportional sampling. After a period of time (up to 14 days), the

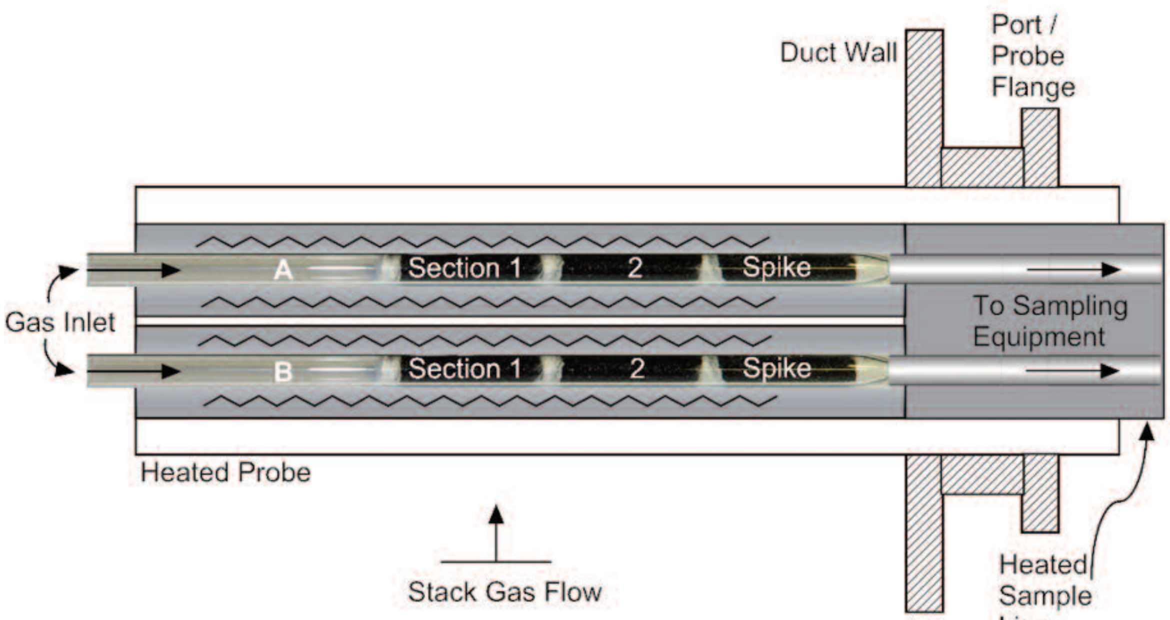

Figure 2: Principles of sorbent trap monitoring

sorbent traps are removed and replaced. The retrieved sorbent traps are analysed for total mercury using spectroscopic analytical techniques. The mass of mercury trapped divided by the volume of gas sampled is then used to determine the average mercury concentration over the sample period. Since the sorbent continuously captures mercury during a monitoring run and in turn pre-concentrates the analyte prior to analysis, this monitoring approach has an inherent ability to measure very low concentrations. The lowest level that can be measured is essentially limited only by the time available to collect the sample. Mercury concentrations as low as 0.001 µg/m³ are not uncommon for one week sampling runs.

Sorbent traps intended for continuous compliance reporting of mercury emissions are required to consist of three equal sections of a sorbent that is able to selectively capture total gaseous mercury. A schematic of a sorbent trap sampling probe is shown in Figure 2. The first two sections of sorbent are used to collect total gaseous mercury and ensure that there is no breakthrough. PS12B requires that no more than 5% of the total collected sample be present in the second section. In addition, PS12B calls for duplicate samples to be taken and the results for these traps need to agree within ± 10% relative deviation (RD). The third sorbent section is spiked and contains a known quantity of elemental mercury ranging from 50% to 150% of the anticipated mercury mass loading captured in the first section during a sampling run. Laboratory recoveries of the spike amount must range between 75 to 125%. Recoveries outside this range will lead to an invalidated trap pair.

The accuracy of sorbent trap data hinge on accurate measurement of two key quantities – the mass of mercury captured on the sorbent, and the volume of gas sampled through the traps. Traceability to NIST standards is incorporated into each of these measurements. The elemental mercury solutions used for trap spiking and the oxidised mercury solutions used for instrument calibration in the laboratory analyses are traceable to NIST references. Flow sensors used in the gas sample volumetric measurements are all compared against NIST-traceable references on a quarterly basis. This approach ensures that the accuracy of each sorbent trap measurement can be traced back to verifiable NIST standards.

Typical Sorbent Trap Monitoring Results

The following figures illustrate the actual implementation of some of the quality assurance and control (QA/QC) criteria for day-to-day sorbent trap monitoring described earlier at low mercury concentrations. The data displayed are from actual installations of sorbent trap monitoring systems used for compliance monitoring. Figure 3 shows spike recoveries from more than 500 sorbent traps collected over a three-year period at Dominion Energy's Salem Harbor Power Station in Salem, Massachusetts. From 2008 through 2010, Dominion used three CleanAir MET-80 STMMS to comply with the Massachusetts Mercury Rule [5]. More than 97% of all the traps sampled during this period met the applicable spike recovery criteria, which are also indicated in Figure 3. The average concentration of mercury emissions from the three units during this time was less than 1 µg/m³, which is similar to concentrations expected under MATS for existing units.

A good indicator of precision of each STMMS measurement is the agreement between the paired trap results, often expressed as relative deviation (RD). Figure 4 shows the precision of sorbent trap monitoring data over a period of over five months. Individual results of each of the two traps (A and B) of a STMMS used for weekly measurements at a utility firing Powder River Basin coal are displayed. During this period, the mercury concentrations measured ranged from 0.10 to 0.35 µg/m³, which are mercury levels similar to those under MATS. The chart shows excellent precision of the measurements, with the RD between the traps averaging 2.4%.

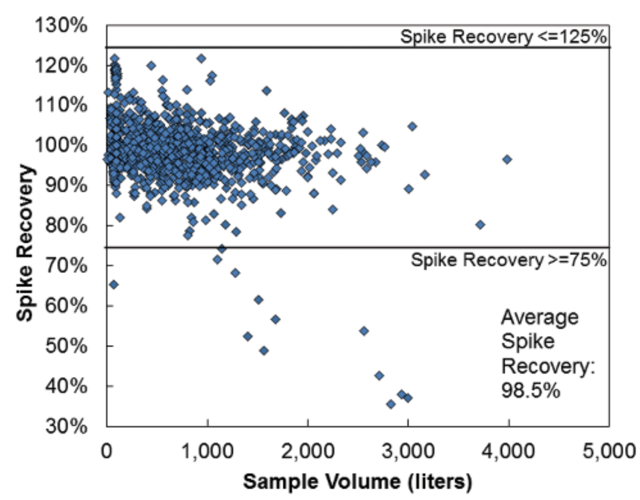

Figure 3: Spike recovery results for Salem Harbor Power Station, Salem, Massachusetts, from 2008 to 2010

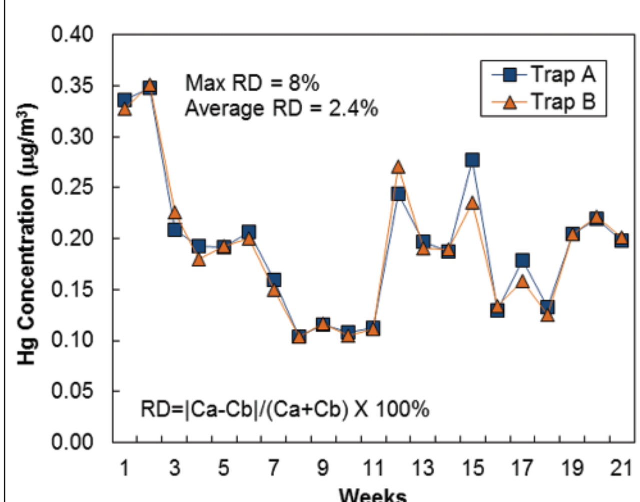

Figure 4: STMMS paired trap agreement expressed as Percent Relative Deviation (RD) for 21 trap pairs sampled at a Powder River Basin coal-fired facility. Ca and Cb refer to the mercury concentrations measured by trap A and B, respectively.

Measurement reliability is another area in which sorbent trap systems typically excel. Reliability can be assessed with "data availability", which is a measure of the number of hours in an operating period that the monitoring system provided reliable, quality-assured data. Data availability is generally expressed as a percentage of the operating hours. From 2008 through 2010, Salem Harbor Power Station reported data availability of their three CleanAir MET-80 STMMS of greater than 90%. Figure 5 shows data from the STMMS of Salem Harbor's Unit 3 boiler. From July, 2008, through December, 2010, the plant conducted 189 trap exchanges for this unit. Only one pair of traps failed the criteria for valid data set in PS12B and resulted in missing data. Four trap runs resulted in only one of the two traps meeting the validation criteria. In those cases, the data is reported using a single trap adjustment factor, or STAF. Overall, the data availability for this unit was 96% over the 2½-year time period.

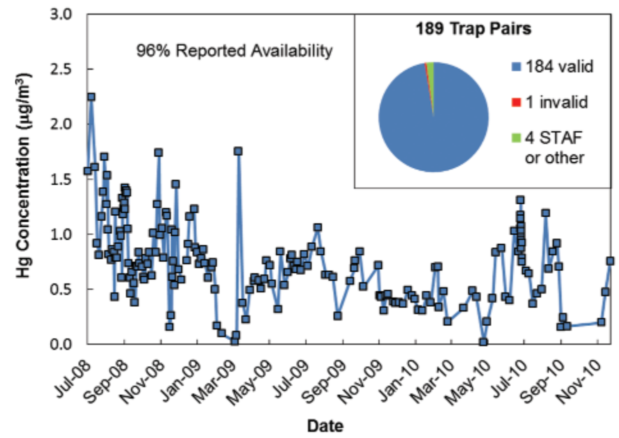

Figure 5: Reliability data for CleanAir's MET-80 at Unit 3 of Salem Harbor Power Station, Salem, Massachusetts, showing data availability and mercury concentration for 189 trap exchanges between July, 2008 and December, 2010. Each data point represents results for a sample period of 30 minutes up to several days.

Conclusions

The cement and electric utility industries have come under increased pressure to control and reduce their mercury emissions. As a result, recent regulations in the U.S. have been proposed that would significantly limit the amount of mercury that is emitted into the atmosphere by both industries. An integral part of these regulations is the ability to accurately and precisely measure mercury emissions. This is complicated by the low mercury levels that new emission controls will yield at electric utilities and perhaps some cement kilns. Although well within the analytical range of continuous mercury analysers, this technology falls short when including the measurement uncertainties introduced by the sample extraction, conditioning, and transport system. The resulting sensitivities are not sufficient to accurately quantify mercury at the low levels expected by the new regulations. In addition, there are concerns about the ability to quality-assure the resulting real-time data in a NIST traceable manner at these low levels.

Sorbent trap-based mercury monitoring systems, on the other hand, have proven their ruggedness and reliability at numerous installations at coal-fired power plants and cement kilns. Their inherent ability to accurately measure very low levels of mercury, combined with the fact that the generated results are NIST traceable, have made the sorbent trap-based monitoring approach the preferred approach for compliance monitoring.

References

[1] National Emission Standards for Hazardous Air Pollutants for the Portland Cement Manufacturing Industry and Standards of Performance for Portland Cement Plants; Final Rule, 2013. U.S. Environmental Protection Agency, Federal Register 78FR10005 (https://federalregister.gov/a/2012-31633).

[2] Reconsideration of Certain New Source Issues: National Emission Standards for Hazardous Air Pollutants from Coal- and Oil-fired Electric Utility Steam Generating Units and Standards of Performance for Fossil-Fuel-Fired Electric Utility, Industrial-Commercial-Institutional, and Small Industrial-Commercial-Institutional Steam Generating Units; Final Rule – Notice of final action on reconsideration, 2013. (http://epa.gov/airquality/powerplanttoxics/pdfs/20130328notice.pdf)

[3] Technologies for Control and Measurement of Mercury from Coal-Fired Power Plants in the United States: A 2010 Status Report, 2010. Northeast States for Coordinated Air Use Management (NESCAUM) (http://www.nescaum.org/documents/hg-control-and-measurement-techs-at-us-pps_201007.pdf).

[4] Performance Specification 12B – Specifications and Test Procedures for Monitoring Total Vapor Phase Mercury Emissions From Stationary Sources Using a Sorbent Trap Monitoring System, 2010. U.S. Environmental Protection Agency, Federal Register 75FR55042 (https://federalregister.gov/a/2010-21102).

[5] Massachusetts Emissions Standards for Power Plants, 2004, Massachusetts Department of Environmental Protection, Code of Massachusetts Regulations 310 CMR 7.29 (http://www.mass.gov/dep/air/laws/regulati.htm).

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