WHITE PAPER: CONDUCTING A SUCCESSFUL MERCURY CONTROL DEMONSTRATION TEST AT A COAL-FIRED POWER BOILER

INSTITUTE OF CLEAN AIR COMPANIES 2013

The Institute's mission is to assure a strong and workable air quality policy that promotes public health, environmental quality and industrial progress. As the primary representative of the air pollution control industry, the Institute seeks to evaluate and respond to regulatory initiatives and establish technical standards to the benefit of all citizens.

Conducting a Successful Mercury Control Demonstration Test at a Coal-Fired Power Boiler

This publication provides guidance on how to conduct a successful demonstration of mercury control technology at a coal-fired boiler. Planning is a critical part of conducting any test; identifying clear objectives is critical to beginning the process. Options for measurements and for mercury control technologies are discussed. The uses of demonstration data for compliance planning and equipment procurement are discussed.

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1. HISTORY

This document is the first version of ICAC's "Conducting a Successful Mercury Control Demonstration Test at a Coal-Fired Power Boiler." It was adopted in 2013, due to the need for testing mercury control technologies for coal-fired power plants as part of preparation for compliance with regulations, such as the U.S. Environmental Protection Agency (EPA), Mercury and Air Toxics Standards (MATS), and the Industrial Boiler Maximum Achievable Control Technology (MACT) rule. The Mercury Control Technology Division of the Institute of Clean Air Companies prepared this new document in order to assure that appropriate and consistent information for the testing of mercury control technologies is provided to both boiler operators and testing groups.

2. OBJECTIVE

The objective of this publication is to help owners and operators of coal-fired boilers carry out demonstrations of mercury control technology that will yield meaningful data, which can be used to evaluate the technical and economic feasibility of mercury control technology. This white paper covers the planning and execution of programs to test mercury control technologies, and it considers how the results of test programs are used in making decisions on commercial equipment for mercury control. This document does not recommend specific mercury control technologies or vendors.

3. PROBLEM DEFINITION

Test programs at coal-fired power plants can be expensive, complex, and challenging to manage. It is critical to define objectives, and carefully examine, and clearly communicate the goals of the program in advance. Starting with the external or internal drivers for the assessment; derive specific goals, timing, scope, and budget. Clearly define the program to meet each of the goals. However, actual demonstrations rarely go exactly as planned. Therefore having the contingency plan in place allows changes to be made as circumstances change which maximizes the overall chance of success.

3.1 Identify Objectives of the Test Program

Possible objectives include the following.

- Evaluating or troubleshooting the reliability of a known and established configuration for continuous operation.
- Extrapolating results from short-term tests to performance of permanently installed systems.
- Evaluation of coal switching options.
- Evaluation of a retrofit control technology that is not yet in place;
  - Timing for demonstration, design and procurement;
  - Balance of plant impacts;
  - Comparison among alternatives, including reliability and costs;
  - Integration and sequencing of multiple technology demonstrations;
  - Multi-pollutant control impacts.
- Comparing or selecting competing suppliers of a given technology.
- Determining the effectiveness of possible future retrofits without all equipment installed (pilot or surrogate testing).
- Making decisions in a pre-defined time frame, such as within six months or by the end of 2013. If MATS compliance evaluation is the goal, timing is paramount.
- Deciding on compliance measurement methodology.

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3.2 Outline Detailed Demonstration Program – The Test Plan

Based on the objectives defined in the initial effort, a scope of effort can be defined. Items to identify and decide on to develop a clear plan include the following.

- Identify the Testing Project Manager, who will define the test program, obtain bids, and interface with the plant (this may be an A&E firm, an internal engineer or project manager, or a consultant).
- Identify a single point of contact at the plant. This is a person who can write work orders and purchase orders to get contractors lined up and who can get plant support for testing needs such as: compressed air, cleaning out test ports, scaffolding, electrical supply, shipping and receiving, etc. This is not the Testing Project Manager necessarily.
- Establish key parameters for testing and develop a test matrix, including "replicate", "baseline", "high", "low," and "center" point test conditions.
  - Give consideration to how long to test at each condition, including consideration of the time to reach steady state and/or the time needed to observe balance-of-plant effects of the technology.
  - Establish the priority of the test parameters. Depending on the time allotted for the test, some test conditions may have to be eliminated. Testing at too many conditions, particularly if the testing schedule is compressed, can give results at non-steady-state conditions, which are difficult to interpret.
- Check with the appropriate regulatory agency as to whether permission is required to conduct your program, and allow time for submittal of test plans, etc. Obtaining a testing permit can require as much as much as *four to six months*, depending on the agency.
- How will each component of the program be supplied and supported (equipment, sorbents, measurements, etc.)? Make sure the logistics are covered at the site during testing. Give the plant contact the punch list of items needed to support the test well in advance so the plant can plan the work and labor accordingly. Check the status of preparations with the plant a week before the test start date.
- Work out procurement activities with adequate notice prior to the need to be onsite. Ensure all necessary agreements are in place.
- Make sure the right people are available at the site and/or available for decision-making.
- Based on all needs, develop and track a detailed schedule.
- It is very important to enlist plant Operations support to define operating conditions as well as to schedule loads and other conditions at the right time. Considerations include where injection and measurements need to be made, and whether ports are in place.
- Assure that the fuel fired during the testing program is controlled during testing. Firing coal from a storage pile can add significant variability to a test program depending on the fuel supply.
- Determine if the tests will result in requirements to manage combustion byproducts differently. For example, if fly ash is currently sold and a test of activated carbon injection is being planned, disposal of the ash during the test period will need to be arranged. Depending on the test, ash salability may be compromised for a period of time after completion of testing. Discuss this with your ash broker and test contractor.
- Plan for appropriate safety training at the site. Determine if a Process Safety Management review is required. Conduct discussions between the Plant's Safety department and representatives of every organization that will be present during the testing to address personal protection equipment (PPE) requirements. The discussions should also cover Safety Department approval to deliver any chemicals needed for the testing.
- When examining and selecting control technologies to test, make sure the appropriate expertise is enlisted to determine the impact of flue gas chemistry, coal type, temperatures, and existing as well as future emissions equipment. These all play into the specific tests that need to be run and the technology solutions available.

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3.3 Examples of Typical Test Durations

For a mercury oxidation improvement test using a product containing bromide fuel or boiler additive, the increase in mercury oxidation occurs quickly after the chemical is introduced to the furnace. Due to the relatively quick reaction time, a minimum test period would be one week (Monday to Friday) with Monday as a baseline day. This will allow time for baseline measurements and parametric testing with different additive injection rates and, possibly, different load conditions. An improvement on this test plan would be to turn off the feed rate over the weekend and repeat the test for a second week.

When activated carbon is injected upstream of an ESP, the carbon reacts quickly with mercury and it is possible to conduct at least two parametric tests in a ten-hour day. To obtain meaningful data, a minimum activated carbon injection test period can be a one-week duration (Monday to Friday) with Monday as a baseline day.

When activated carbon is injected upstream of a baghouse, the baghouse solids residence time typically range from 20 minutes to many hours, depending on the cleaning cycle. The test schedule must allow sufficient time for the baghouse to reach steady-state operation and typically would include more than one cleaning cycle. One week would be a minimum test period, if several carbon feed rates are desired or if different carbons are going to be tested.

For a test of mercury re-emission from a wet scrubber, a minimum of two weeks is recommended to obtain meaningful test results, due to the liquid residence time in the absorber.

3.4 Measurement Methods

In any technology demonstration, measurement methodology must be carefully selected to support the project objectives. Answer the following questions:

- Which data from existing instrumentation should be logged for evaluation of the results?
- What measurements will require an outside test company to be on site?
- What is(are) the best method(s) for flue gas mercury measurement based on my needs – consider speciation, location along the flue gas path, grab samples (sorbent traps or manual wet chemistry methods) versus CEMS?
- What solid samples (e.g., coal, ash, scrubber solids) are needed in order to be able to answer questions on balance of plant impacts?
- Is it a priority to demonstrate the ultimate compliance method during the test program?
- What other streams and components need to be monitored to establish balance-of-plant (BOP) impacts?
- What other measurements can be taken to support compliance with regulations for other hazardous air pollutants (HAPs), for example, stack particulate measurements during activated carbon injection (ACI) testing.

These answers lead to an outline of measurement needs that can then be put into a test plan for field program definition, scoping, pricing and scheduling.

3.5 Review Available Data in Hand

There have been many public and private technology demonstrations for mercury control. Draw on any past work on the specific unit, including measurements made and operating data for that unit. Keep in mind the changes that have occurred since earlier tests such as coal, temperatures, and air pollution control (APC)

configuration including the age of the catalyst in the SCR.

If there is not information from previous testing on the specific unit, you can review test programs from similar units, Information Collection Request (ICR) data, published papers, discussions with colleagues, suppliers and experts, etc. Good sources of information on previous work include documentation of test programs sponsored by the Department of Energy, National Energy Technology Laboratory (available at www.netl.doe.gov) and proceedings of conferences such as the DOE-EPA-EPRI-AWMA Power Plant Air Pollution "Mega" Symposium, the Electric Utilities Environmental Conference or the Air Quality Conference.

3.6 Communication and Decision Process Defined

Test programs rarely go exactly as conceived. The more challenging the objectives you have defined, the more likely it is that decisions will need to be made based on actual results during the test. It is more important to stick to the overall test objectives than to continue running a predefined parametric matrix that is not working.

The objectives should be clearly laid out to ensure that each team member on site knows to whom to go to with any concerns or changes. Establish a clear go-to leader for the project, who fully understands the big picture objectives and has the ability and authority to make changes and decisions on the fly. Make sure that all test program participants understand what decisions are within their authority and when they need to go to the leader.

The testing team must know they should proactively interface with the plant operators, and this communication goes in two directions. When significant changes are being made (e.g., turning sorbent feed on or off) or when test personnel are working in certain areas of the plant, the Control Room should always be notified. During the testing, if team members notice anomalous results, they should communicate with the Control Room to determine if there have been any changes in plant operation (load changes, equipment malfunctions, etc.). Instruct testing personnel to touch base with the plant operators during the day to discuss how the plant is operating, e.g., have they noted any changes in their operation today? These practices will increase the likelihood that testing personnel remain abreast of changes in operation that are affecting performance.

Before the test begins, make certain there are no other operational tests also taking place, such as a turbine output test, a stack CEMs periodic calibration in which the CEMs would be out of service, or a coal blending test. Have the plant point of contact speak with the Operations superintendent or the with the Control Room operator to determine if there are any other tests taking place.

Allow time well in advance to "Schedule" unit load, especially if full load is required during the test period or if sufficient coal must be set aside for the testing period. Then one week before the test starts, follow-up with the Operations personnel to verify that preparations are in place.

4. MEASUREMENTS

4.1 Mercury Measurement Methods

4.1.1 Hg CEMS

Mercury continuous emissions monitoring systems (Hg CEMS) are used to monitor flue gas for concentration of different species of mercury that exist in the flue gas at a given location. Hg CEMS are currently used as a means to comply with air emission standards such as the U.S. EPA's MATS rule, the Portland Cement MACT, federal emission programs, state permitted emission standards or to study Hg levels within an industrial plant process. Facilities employ Hg CEMS to continuously collect, record, and report the required emissions data.

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A typical compliance-type Hg CEMS consists of a sample probe, filter, sample line (umbilical), gas conditioning system, calibration gas system, and an analyzer which reports the concentrations being monitored. These Hg CEMS are not entirely unlike CEM systems used for NO_x/SO_2, but contain some special components for sample handling.

A small sample of flue gas is extracted, by means of a pump, into the CEM system via a sample probe. Dilution with clean, dry air or nitrogen is often used because the effluent gas can be hot, wet and, with some pollutants, sticky. Once diluted to the appropriate ratio, the sample is transported through a sample line (typically referred to as an umbilical) to a manifold from which the analyzer may extract a sample.

In many cases, full extractive 'hot-wet' systems are also used to make the measurements. These extractive systems require high-temperature sample lines and heated measurement modules. They isokinetically extract a representative sample of flue gas at high flow rate and transport it to the Hg CEMS. At the Hg CEMS, an isokinetic subsample from that high flow rate stream is then collected by way of a small pump, which the Hg CEMS will then analyze. The remaining volume of flue gas is then returned to the stack. These systems often utilize an eductor as the motive force which pulls the high flow by using compressed air or a blower.

During demonstration programs, non-compliance Hg CEMS are often used. Although these may contain commercial components, they are often research-grade systems suited for short-term demonstrations. These systems typically include a sampling filter, either impinger-based or catalyst-based conditioning modules, a hot-line, and an analyzer. The calibration system may be calibration gas or wet-chemistry based. The accuracy and reliability of these systems is often lower than the compliance systems and additional time may be required during the testing programs for calibrations and system maintenance. Additional quality assurance oversight is recommended if these research-grade systems are incorporated into a testing program.

4.1.1.1 Operating Principles and Sensitivity

Most Hg CEMS employ an analytical method called Cold Vapor Atomic Fluorescence (CVAF). In this technique, Hg atoms absorb ultraviolet (UV) light at ~253.5 nm, become excited, then decay back to the ground energy state, emitting (fluorescing) UV light at the same wavelength. Specifically,

Hg +hν (254nm)→Hg *→Hg +hν (~253.5 nm)
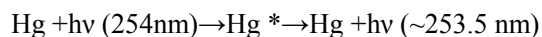
The sample is drawn into the fluorescence chamber, where UV light from a high energy Hg line source lamp excites the Hg atoms. The UV light is directed to the fluorescence chamber by a rejection mirror/beam splitter combination. A reference detector monitors the lamp intensity by viewing the transmitted light from the beam splitter. As the excited Hg atoms decay back to the ground energy state, they emit UV light that is proportional to the Hg concentration. Typical lower detectable limits are approximately 1 ng/m^3 at the analyzer. Hence, with a dilution system using 50:1 ratio, the system lower detectable limit is approximately 50 ng/m^3. Typical Hg concentrations in uncontrolled flue gas from coal-fired power plants range from 2-20 μg/m^3. The CVAF technique is similar to UV fluorescence used in SO_2 analyzers for the Acid Rain program and EPA reference method 6C.

An alternate method for Hg analysis uses Cold Vapor Atomic Absorption Spectroscopy (CVAAS), which measures the absorption of radiated light by free Hg atoms. This method is not as widely used in North America as CVAF due to interferences with SO_2 (which absorbs light at the same wavelength as Hg) and lower sensitivity. CVAF and CVAAS CEMS measure gaseous mercury only.

Another type of CEMS uses a patented reactive filter technology and nondestructive X-ray fluorescence (XRF)

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to measure both vapor-phase and particulate-bound mercury (as well as other metals). A sample of gas is extracted from a source, diluted, and drawn through a small spot on a chemically reactive filter tape. Vapor-phase Hg along with the particulate matter (if requested) are concentrated on that spot with a sample inlet designed to provide uniform sample deposition. The tape then advances, placing the collected sample spot in the analysis section of the instrument, while initiating collection of the next sample onto a previously unexposed spot on the tape. The sequence of sampling and analysis can continue automatically, limited only by the supply of filter tape. The duration of sample collection at each spot can be set at a constant interval, or varied to maintain detection performance in the face of varying concentration levels. The XRF Hg CEMS technique is similar to EPA Compendium Method IO-3.3: Determination of Metals in Ambient Particulate Matter Using X-Ray Fluorescence Spectroscopy.

Mercury and other metals determination in the XRF-based CEMS is based on the principle of energy-dispersive XRF (EDXRF), in which X-rays from a source cause the removal of an electron from an inner electronic shell of a metal atom in a sample. The vacancy in the inner shell is then filled by an electron from an outer shell, with resulting emission of an X-ray with a longer wavelength than that of the original excitation energy and characteristic of the metal under examination. EDXRF detector and electronics resolve the emitted X-rays based on their energy in kilo electron volts (KeV). The analyte line intensity (or peak intensity) is correlated to the amount of metal in the sample by comparison with NIST-traceable standards. The EDXRF technique allows use of a relatively simple optical path and a low power X-ray source, which lowers the instrument cost. EDXRF can very rapidly acquire a wide portion of the X-ray spectrum, and therefore detect multiple metals from the periodic table.

4.1.1.2 Calibration and QA/QC

In the U.S., periodic evaluations of the equipment must be reported and recorded for permanently installed CEMS, as described in Appendix A to Subpart UUUUU of 40 CFR Part 63 as published in the Federal Register on February 16, 2012. This includes initial certification and ongoing quality assurance/quality control (QA/QC) such as daily calibration error tests, weekly System Integrity Check, semi-annual (or annual) Relative Accuracy Audit Test (RATA), and bias tests. In power stations affected by the MATS Program, annual (or bi-annual) certification of the Hg CEMS must be performed by an independent firm. The firm will have an independent mercury measurement method temporarily in place to collect emissions data in parallel with the plant CEMS. This testing is referred to as a RATA. There are two methods of certifying an Hg CEMS: EPA Method 30A, which uses an optical instrumental reference, or EPA Method 30B, which uses sorbent traps. These are described in 40 CFR Part 60, Appendix A.

For a short-term demonstration, a QA/QC program should be followed that is similar in rigor as for a permanently-installed CEMS. Specifically, daily calibrations should be conducted with pass criteria that are at least as strict as prescribed in the EPA protocol. Although a full RATA test is typically impractical for a short-term demonstration, an initial relative accuracy test should be conducted where the Hg-CEMS measurement is compared to a reference method such as an EPA Method 30B.

Calibration and QA/QC for permanently installed Hg CEMS follow similar requirements as NO_x and SO_2 analyzers, with a few extra criteria. Systems typically employ gas vapor generators that use a Peltier cooler vapor and mass flow controllers to generate precise amounts of elemental mercury. This device generates calibration standards for use in establishing the initial calibration of the analyzer and subsequent adjustment of the background and coefficients for the analyzer calibration and system calibration of both the total and elemental channels.

During a calibration cycle, the calibration gas floods the probe and is drawn through the system back into the analyzer for measurement. This probe check is done in the absence of flue gas. If flue gas is causing any bias in the measurement, this check will not catch it. Research-grade systems may employ a different technique, which should be reviewed with the test team prior to testing.

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Permanent Hg CEMS that perform daily calibration error tests using elemental Hg are required to perform periodic checks using an oxidized Hg standard. This is referred to as a System Integrity Check. This QA requirement is intended to ensure that the Hg CEM does not have a low bias when measuring the oxidized fraction of the Hg in the sample. This test is often not included for temporarily-installed CEMS due to difficulties often encountered with transportation and site safety requirements associated with small cylinders of pressurized chlorine gas, which is required for this technique.

For the XRF-based CEMS, there are three steps to the calibration of the XRF analyzer: energy alignment, reference spectra library setup and quantitative calibration. In addition, daily and weekly calibration and system integrity checks are performed, as prescribed by the EPA for Hg CEMS in the Code of Federal Regulations.

The energy alignment must be performed before the acquisition of any reference spectra and assures that the spectral peaks for each element are at the correct energy (KeV). During the energy alignment, a source of copper is excited and the instrument automatically adjusts the system so that the peak centroid correlates with the channel at 8.041KeV.

The spectral deconvolution program (XRS-FP) employed by the XRF instrument requires the acquisition of reference spectra for every element of interest as well as interfering elements that could contribute to an unknown analysis spectrum. Thin film standards are used for building the spectral library because they most closely resemble the layer of a sample. XRS-FP uses a library of these characteristic elemental peak shapes to identify the sum of the intensity that each element is contributing to an unknown spectrum. It is these elemental shapes spectra that are fitted to the peaks in an unknown sample during spectral processing.

In the quantitative calibration of the XRF instrument, the relationship between spectral peak intensity and elemental concentration is established. Because most of the standards used for the reference spectra acquisition are quantitative, the same spectra used for the reference library may also be used for the quantitative calibration.

4.1.1.3 Operating Considerations of Hg CEMS

The objectives of the test, in terms of the desired level of mercury reduction, will suggest the limits of detection required from the Hg CEMS. The recently confirmed capability of NIST to certify Hg calibration gas generators down to 0.2 μg/m^3 will allow CVAF Hg CEMS to be calibrated for low-level measurements. The XRF CEMS has a detection limit for Hg of 0.01 μg/m^3 for a 30-minute sampling time (detection limits are determined using EPA I.O 3.3 standards of 95% confidence and interference-free data). Research-grade systems will need to be evaluated independently.

At sampling locations between the air preheater and the particulate control device, there can be a significant component of particulate-bound mercury present in the flue gas. Upstream of the air preheater or downstream of the particulate control device, the fraction of particulate-bound mercury is usually negligible. The CVAF Hg CEMS measure gaseous Hg only, while the XRF CEMS can measure gaseous and particulate mercury. For the latter method, the user may choose to quantify vapor-phase Hg only or to quantify both vapor-phase and particulate-phase Hg. When planning the test program and choosing sampling locations, the limitations of the measurement devices should be considered.

4.1.2 Wet Chemistry Methods

EPA developed several wet chemistry methods for measuring mercury in industrial stack gases in order to quantify emissions. Detailed descriptions of these methods can be found at the EPA website.[1] EPA Method 101A was developed for determination of gaseous and particulate mercury emissions from sewage sludge

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[1] US EPA, Technology Transfer Network, Emission Measurement Center, http://www.epa.gov/ttn/emc/. Accessed 16-December-2012.

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incinerators, but is often applied to coal-fired boilers to measure total mercury emissions. EPA Method 29 was developed to measure mercury and other metals in stack emissions. These two methods are appropriate if total mercury measurements are needed. Method 29 sampling train was not originally designed for mercury speciation analysis. The Ontario Hydro Method (ASTM Method D6784-02) was developed to speciate mercury accurately in flue gas. The Ontario Hydro Method is the appropriate wet chemistry method if mercury speciation measurements are needed.

4.1.2.1 Operating Principles and Sensitivity

Figure 1 gives a schematic of Method 101A. A probe is inserted into the flue gas with a nozzle designed for isokinetic sampling of the flue gas. A pitot probe and a thermocouple are also inserted into the duct. The size of the nozzle is matched to the gas velocity in the flue gas. The probe is traversed in the flue gas during the test in order to collect a representative sample. The sample is withdrawn through the probe and into a heated filter. The filter collects the particulate matter. After the filter, the sample gas is pulled through a series of four glass impingers. The first three impingers contain a solution of 4% $KMnO_4$-10% H_2SO_4. The fourth impinger contains silica gel to dry the gas. Following the impingers there is a pump and dry gas meter.
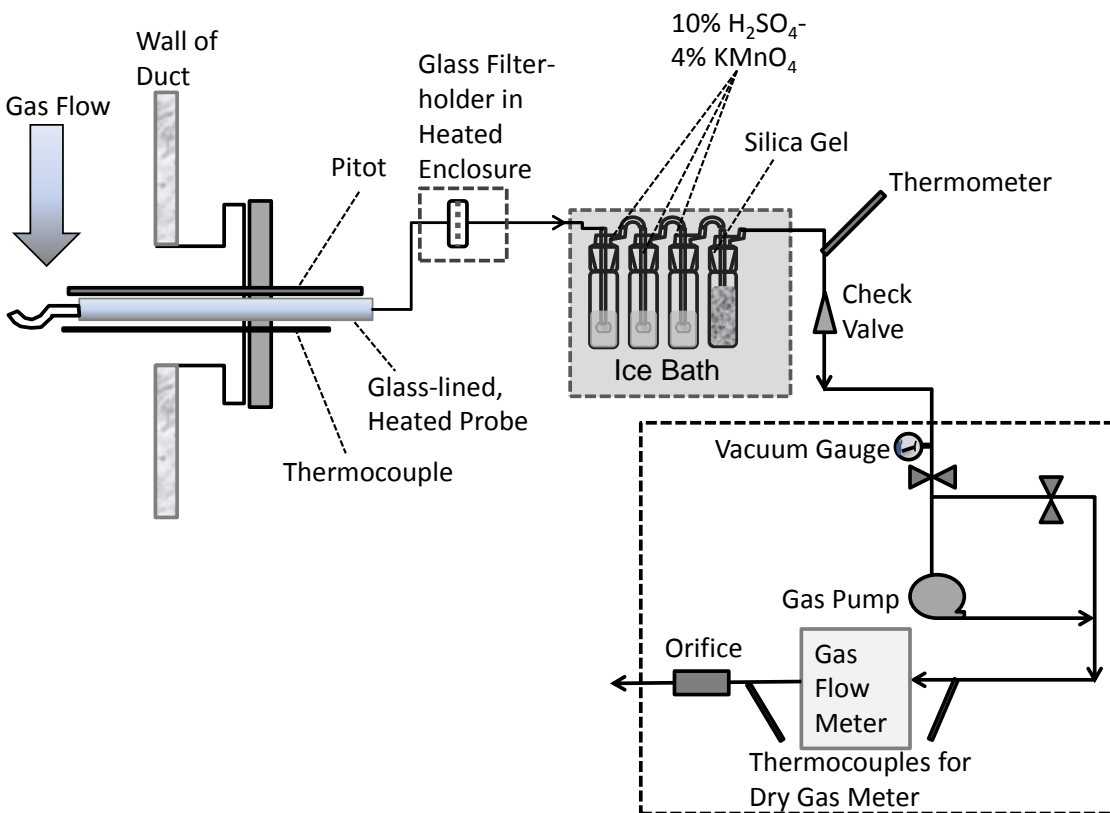
FIGURE 1. SCHEMATIC OF EPA METHOD 101A.

EPA Method 29 is designed to measure the particulate and gaseous emissions of mercury and 16 other trace elements (antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, nickel, phosphorus, selenium, silver, thallium, and zinc). The equipment and sampling train are similar to that for Method 101A, with the exception of the contents of the impingers. In Method 29, gaseous metals and mercury are collected in two impingers in series containing an acidified peroxide solution (5% HNO_3/10% H_2O_2). An empty impinger follows the first two impingers in the train. Elemental mercury that passes through the first two impingers is collected in two impingers in series containing acidified permanganate (10% H_2SO_4/4% $KMnO_4$). A final impinger containing silica gel is used to dry the sample gas. After the measurement, the

contents of the peroxide impingers are saved separately from the contents of the permanganate impingers.

A minimum sampling time of two hours is recommended for Method 101A. Similar sampling time is usually used for Method 29. In Method 101A, if there is a too much oxidizable organic matter in the gas stream, it may be impossible to sample for the minimum time. This problem will be indicated by the loss of the purple color of the $KMnO_4$ solution. The limits of detection of the methods can be improved by increasing the sample time.

In the Ontario Hydro Method, three aqueous 1 N potassium chloride (KCl) impinger solutions are substituted for one of the HNO_3-H_2O_2 solutions. To avoid bias resulting from SO_2 in the flue gas, an impinger of acidified peroxide solution is used directly after the KCl impingers in order to absorb the SO_2. It is assumed that any mercury collected in the acidified peroxide solution was Hg^0, since the KCl solutions would collect all of the Hg^{2+}. Acidified $KMnO_4$ impingers follow the acidified peroxide impingers to collect the rest of the elemental mercury.

All the impinger-based methods require leak-checking before and after the test. Post-test, the glassware, including the glass-lined probe, must be rinsed, and the rinsate saved for analysis. The method also requires the use of blanks for the impinger solutions and the filter in the field. After the test, the filter, collected solutions, and blanks are analyzed in a commercial laboratory.

Three replicate measurements are usually conducted for these methods. These can be done in one day, but are more often completed over two days. The methods require considerable time to set up and recover samples from each measurement. A high level of quality assurance/quality control (QA/QC) and well-trained personnel are needed for these wet chemistry methods.

4.1.2.2 Operating Considerations of Wet Chemistry Methods

The precision of measurement of particulate, oxidized, and elemental mercury is influenced by many factors: flue gas concentration, source, procedural, and equipment variables. To ensure that precise results are achieved, the sampling system must be leak-free, system components must be accurately calibrated, the proper sampling locations must be selected, glassware must be thoroughly cleaned, and prescribed sample recovery, preparation, and analysis procedures must be followed.

These methods are intended to be used after a plant's particulate control device. In many cases (for research or survey purposes), these wet methods are used before the particulate control device, when there is a lot of particulate matter present in the flue gas. In these situations, reactive particulate matter can bias the speciation. This bias can be either shown as artificially high oxidized mercury or high particulate mercury. All the sample gas must pass through the filter. Gaseous mercury species in flue gases can interact with fly ash particles collected on the filter and can produce a positive particulate mercury bias. In some cases, particulate mercury collected on the filter can vaporize because of continued exposure to the flue gas sample and be collected in the impingers. Such vaporization would result in a negative particle-bound mercury bias.

There are practical limitations to the impinger-based methods arising from the complex sample trains, which are composed of relatively large amounts of glassware and tubing. Furthermore, the glass impingers contain strongly oxidizing and acidic reagents requiring complex sample recovery and analytical procedures. Usually, these solutions must be shipped to a laboratory quickly. In some cases, testing contractors have brought complete analytical laboratories on-site for analysis. This reduces the turnaround time for obtaining results, but can substantially increase the cost of the measurements.

4.1.3. Sorbent Trap Methods

The sorbent trap method is an approach to measure mercury emissions over a period of time. In principle, the method draws a measured volume of gas through sorbent traps, which collect the mercury. The traps are then analyzed for the amount of mercury captured. The mass of mercury and the gas volume determine the concentration of mercury in the gas. If there are particles in the gas, the mercury in the particulate will be measured as well.

4.1.3.1 Operating Principles and Sensitivity

Method 30B is a reference method for RATAs of vapor-phase Hg CEMS. Operation of EPA Method 30B is included in 40 CFR Part 60, Appendix A. Under MATS, EPA allows both H CEMS and sorbent trap monitoring systems as continuous monitoring systems. The Sorbent Trap Monitoring Systems (STMS) differ from EPA Method 30B in that they are designed to provide a record of ongoing emissions and have different QA/QC criteria. EPA specifies Performance Standard 12B (PS12B) for sorbent trap monitoring systems installed at coal-fired boilers as continuous monitoring systems for compliance. Sorbent trap methods are intended for use only under relatively low particulate loading (i.e., sampling after particulate control devices); in cases where significant amounts of particle-bound Hg may be present, an isokinetic sampling method for Hg should be used.

A sketch of the sorbent trap method is shown in Figure 2. Gas is drawn through two separate traps concurrently. The sorbent traps must be installed in the probe such that gas is pulled directly into the traps. If there is a significant concentration of particulate-bound Hg expected such that some Hg might be in the particulate form at the measurement point, then the sample must be taken isokinetically. However, sorbent traps are not usually designed to handle high concentrations of particulate matter and will rapidly plug. A common trap sorbent material is activated carbon impregnated with iodine or another halogen like bromine.

The Method 30B traps each have two sections, which are tested independently. The first section is for primary mercury collection. The second section is to provide an indication of mercury breakthrough. If there is too much breakthrough, the sample fails QA. For QA/QC purposes, the first trap of one of a pair of sorbent traps can be spiked with a known amount of mercury before the measurement. Specific QA requirements are included in 40 CFR Part 60, Appendix A.
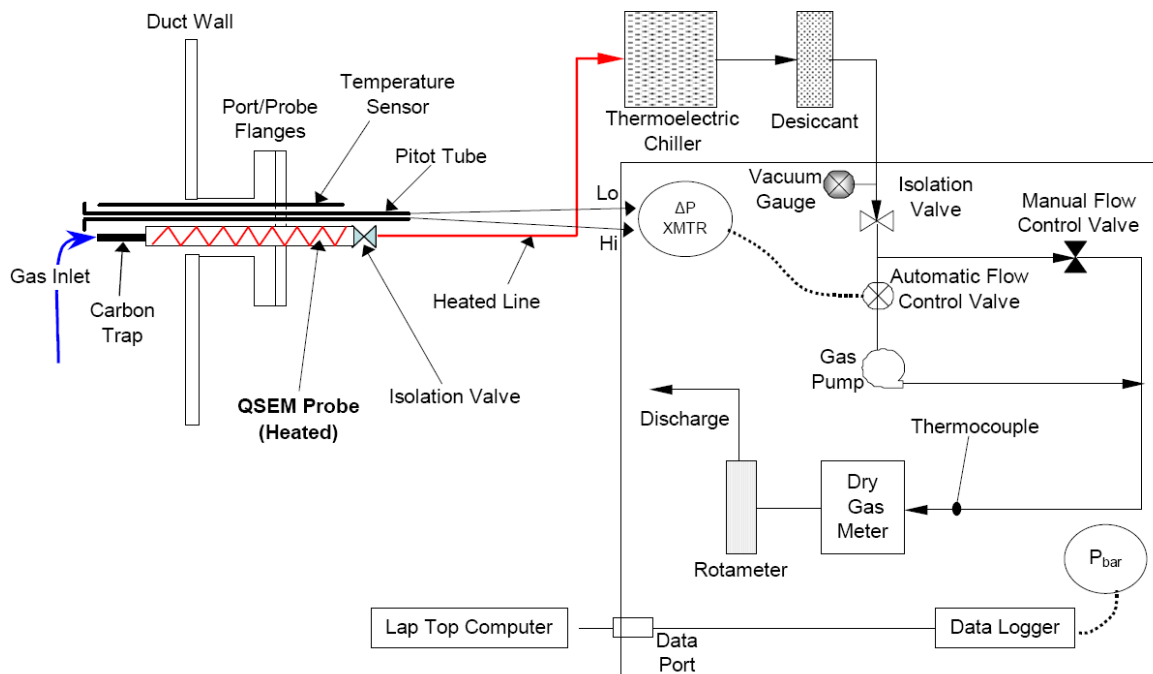
FIGURE 2. SCHEMATIC SORBENT TRAP SYSTEM.[2]

For STMS, PS12B requires that each trap have the sorbent configured into three sections that can be tested independently. As with Method 30B, the first section is for mercury collection and the second section is to quantify breakthrough. The third section is for spike recovery testing. The spike trap is prepared in advance, using a spiked mercury sample gas.

Speciation traps have been developed as an alternative to the Ontario Hydro Method for speciation of mercury in flue gas. The most widely used speciation sorbent trap method is based on Method 30B, although speciation traps are not EPA-approved methods. They can be used for research purposes. In the speciation trap method, there is a particulate collection section, followed by two sections to collect oxidized mercury (primary and breakthrough), which contain KCl on quartz chips, and two sections to collect elemental mercury (primary and breakthrough), which contain iodated or brominated carbon. An acid-gas scrubbing trap may also be used to remove acid gases like SO_2. In some implementations of speciation traps, the particulate collection section of the trap is at the temperature of the flue gas being sampled, and in other implementations, a quartz wool plug is used upstream of the first trap. In any case, the other sections of the traps are controlled to prevent breakthrough of mercury on the KCl sections at high temperatures. Speciation sorbent traps use the same sampling apparatus as that for the total mercury methods, with the exception of a special probe to control the temperature of the sections intended to collect gaseous mercury.

The balance of the Method 30B and STMS sampling systems include a moisture removal system, a dry gas flow pump and dry gas flow meter (or other equivalent mass flow equipment), and related instrumentation. The STMS must have a flow meter with variable flow control to maintain sample flow rate in proportion with load.

After a period of sampling, the traps are removed and analyzed individually to measure the total amount of mercury in the traps. The mercury found in the traps divided by the total gas flow over the period of the sampling indicates mercury concentration in the gas.

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[2] Prestbo, E., Sjostrom, S., Dene, C., Drennan, S., Chu, P., Hawkins, L., Glesman, S., Brunette, B., "EPA Method 324", EPRI Users Group Meeting, Pittsburgh, July 2004.

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The two most widely used approaches to analyze the traps for mercury are: 1) a wet digestion method using atomic fluorescence analysis; and 2) thermal release with atomic absorption analysis. The latter approach can be done on site with the proper equipment. However, it has the disadvantage that the sample is destroyed, so that if there is a problem with the analysis it cannot be checked again and that the sensitivity is less than atomic fluorescence, requiring a larger gas sample volume.

The sorbent trap method for measuring mercury generally has good measurement accuracy down to relatively low mercury concentrations under 0.1 µg/m^3. This can be influenced by sample time, trap size, the analytical method, the skill of the analyst and other parameters that the user can control depending upon their needs. Sensitivity to lower mercury concentrations is achieved by increasing the sample volume, which will also require an increase in trap size. By increasing trap size, sample volume and sample extraction rate, it is possible to reduce the sampling time while measuring lower concentrations of mercury in the flue gas. This may be necessary when testing mercury emission control systems where maintaining test conditions for long periods may not be possible. Another important factor is the analysis method for analyzing the mercury level in the trap. The direct thermal method and the digestion followed by cold vapor atomic fluorescence analysis have different analytical sensitivities (with atomic fluorescence generally sensitive to lower concentrations), which need to be factored into the determination of sample volume.

Before using sorbent traps as a mercury measurement method, it is important to understand the characteristics of the flue gas. Flue gas characteristics that can result in inaccurate mercury measurements include:

- High flue gas temperature, which might cause the captured mercury in the first section of the trap to desorb;
- High particulate loading in the flue gas, when sampling upstream of a baghouse or ESP, which can plug the quartz fiber filter on the trap;
- High bromine content, which might cause interference with accurate mercury capture or oxidation within the trap.

4.1.3.2 Calibration, QA/QC

The flow meter and associated instrumentation (barometer and temperature indication) must be regularly calibrated to ensure that they are reporting the correct volume of gas.

The analyzers used to measure the mercury in the traps must also be regularly calibrated.

A noted earlier, two separate samples are collected in parallel, with each sample having the sorbent divided into multiple sections for quality assurance.

Two samples in parallel are necessary for the purpose of quality assurance – they must agree within prescribed levels or the sample fails QA. The two traps can be installed within the same probe or in separate probes.

For Method 30B, the spiked amount of mercury recovered must be within ±15% of the expected mass of mercury on the first section. For PS12B, the spiked amount of mercury recovered must be within ±25% of the expected mass of mercury on the third section.

4.1.3.3 Operating Considerations of Sorbent Traps

The advantages of sorbent traps versus Hg CEMS for a _short-term_ performance test are:

- Lower cost to install and easier to set up.

- Simpler system to operate and maintain – Sorbent trap systems are less complex than Hg CEMS and won't require as sophisticated of a technical staff to support. However, the personnel involved in sorbent traps do need training on how to properly handle the traps to avoid

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contamination and other problems that could introduce errors.

- Lower concentrations - In principal, sorbent traps may be able to measure to lower concentrations than Hg CEMS, but this is very methodology dependent. Furthermore, Hg CEMS are improving their ability to measure to low levels.

The disadvantages of sorbent traps versus Hg CEMS for _short-term_ performance testing are:

- No real-time, or near real-time data – This is the principal technical advantage of Hg CEMS over sorbent traps. The Hg CEMS information is available in minutes, which enables the performance of Hg emission control processes to be monitored in near real time and can thereby offer advantages in Hg control. Figures 3a and 3b (data from Coyne et al.[3]) show how Hg CEMS data and sorbent trap data compared at one facility equipped with a wet scrubber over a period of 5 days and over 30 days. As shown, there was a wide variation in Hg emissions that is not captured by the sorbent traps. For testing Hg control systems, short-term, high-volume samples are preferred. On site analysis of traps is possible, but will typically delay measurement data by hours.

- Loss of data – If there is a problem with a sorbent trap sample, it may not be discovered until after the sample is completed, and when sorbent trap samples fail their quality control tests the data is lost for the full sampling period. For this reason, EPA Method 30B and PS12B incorporate quality control procedures to minimize this risk and personnel who handle the samples and perform the analysis of the samples must be trained in proper handling and analytical methods.

- Personnel safety – sorbent traps require that personnel go up to the sampling point to remove and replace sorbent traps. This creates an added concern for personnel safety depending upon the location and access of the traps.

Depending upon the length of the test program, it may be determined that a continuous Hg analyzer is economically more attractive. Very short test programs will often favor sorbent traps, but longer test programs may be better served with a continuous Hg analyzer.

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[3] Coyne, L., Winter, S., Schmid, V., Wright, J., "Challenges and Prospects for Sorbent-Based Mercury Emissions Monitoring and Testing", AWMA Conference, June 28, 2007.

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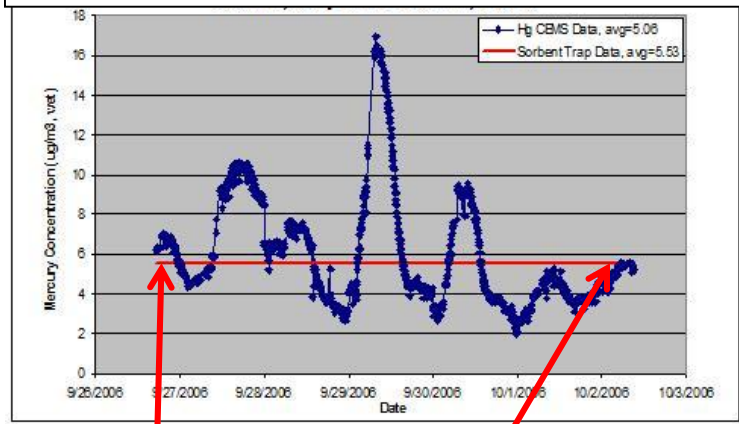**Figure 3a. Five Days of Hg CEMS versus Sorbent Trap data.**

Figure 3b. Thirty Days of Hg CEMS versus Sorbent Trap data.
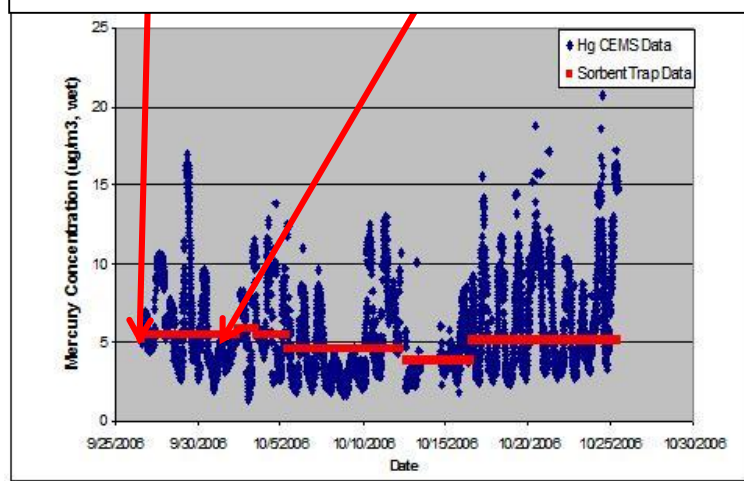
4.2 Choosing Appropriate Measurements

4.2.1 Measurement Locations

Often in a demonstration, there is a desire to measure mercury at more locations in the flue gas path than just the stack. Consider the goals of the test program when determining where to make mercury measurements (or other measurements). Some considerations include the following.

- In order to quantify re-emission of mercury across a wet scrubber, speciated mercury measurements must be made at the inlet and outlet of the scrubber. Optimal quantification of mercury re-emission requires two instruments at two sample locations to accurately and reproducibly measure two mercury species, i.e. elemental and total. The importance of good measurement and historic plant data cannot be overstated. Sampling before and after the wet scrubber also serves to quantify mercury capture efficiency which can be indicative of mechanical and/or operational limitations.
- If it is desirable to quantify mercury reduction during the test program (as opposed to quantifying stack emissions), mercury could be measured in the flue gas upstream of the air preheater or coal samples could be taken (once per day or more frequently) to quantify the mercury input to the boiler.

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Due to higher flue gas temperature and increased particulate loading, any mercury measurement upstream of the air preheater can be difficult to obtain and maintain during a testing period. In some cases, mercury analysis of the coal is a preferred method of determining inlet mercury concentrations.

- In the case of bituminous-fired boilers, it is valuable to measure the concentration of SO_3/H_2SO_4 at the activated carbon injection point because SO_3/H_2SO_4 will vary and can influence mercury capture.
- For any stack measurements, the sampling location must be chosen so that the flue gas is only from the unit being evaluated. For example, if two units feed a single wet scrubber and stack, then the stack measurements may not represent the single unit that is being tested. If a location downstream of the test unit is not available, it may be necessary to test both units simultaneously. If samples are collected downstream of a wet scrubber, any scrubber bypass will affect emissions. Samples collected upstream of the bypass return will not be representative of overall emissions. However, samples collected upstream of the bypass return will provide clearer information on mercury removal across the scrubber.

Measurement locations are also dictated by where ports are available. Mercury CEMS make measurements at a single point. In some cases, it is useful to make temperature or velocity traverses at the measurement locations to determine the homogeneity of the flow field, particularly if there are multiple ports available at a single axial location in the duct. The inlet probe of the Hg CEMS or sorbent trap should be placed at a location that is representative of the average flue gas properties.

4.2.2 Sensitivity Requirements

The goals of the test program influence the required sensitivity of the measurements. Demonstration of MATS compliance levels (on the order of 1 µg/dscm mercury in the stack) can be achieved with commercial Hg CEMS or sorbent traps. If it is desired to achieve considerably lower mercury emissions (less than ~0.2 µg/dscm), Hg CEMS might not be appropriate. STMS can be used, but the sampling time of the sorbent traps should be selected based on the expected mercury concentrations in the stack.

4.2.3 Designing a QA/QC Program for a Demonstration

Ideally, after installing a Hg CEMS, PS12A certification tests should be performed, including:

- Seven day drift check;
- Linearity check;
- Calibration response time check;
- Relative accuracy test audit (RATA) with modified Method 30B as described in Section 4 of Appendix A of Subpart UUUUU in 40 CFR Part 63.

This is typically not practical if a temporary system is being installed for short-term test. In this case, the following is recommended:

- Calibration response time check;
- Abbreviated relative accuracy audit (at least 3 paired samples) with modified Method 30B as described in Section 4 of Appendix A of Subpart UUUUU in 40 CFR Part 63.

On-going quality control requirements for continued use of Hg CEMS are defined in PS12A and include:

- Daily calibration zero and reference gas audits; and
- Periodic relative accuracy test audits with modified Method 30B as described in Section 5 of Appendix A of Subpart UUUUU in 40 CFR Part 63.

For short-term testing periods, it is recommended that EPA Method 30B measurements are conducted periodically throughout the program. It is not practical to conduct a full RATA test.

If a testing contractor is hired to make the measurements, the contractor should provide a QA/QC report for the test period, as well as copies of all data sheets or electronic records.

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4.2.4 Sampling Program

4.2.4.1 Plant Information
Before the testing begins, a list of the plant information requested should be transmitted to the plant. It is important to specify the averaging time for the plant data (one minute, five minutes, etc.). At a minimum, the plant data collected should include:

- Load;
- Total coal flow and/or boiler heat input;
- Excess O_2;
- APH Inlet/Outlet gas temperature;
- Particulate collector gas temperature;
- Concentration of SO_3 at the APH, if measured;
- Total stack gas flow;
- Stack NOx;
- Stack SO_2;
- Stack CO_2;
- Stack CO;
- Stack O_2 (if measured) ;
- Stack temperature;
- Stack opacity;
- ESP secondary current and ESP Secondary Voltage for all fields (if there is concern about the impact of activated carbon on ESP performance) ;
- Baghouse pressure drop (if there is a baghouse) and cleaning frequencies ;
- If there is a wet scrubber: liquid flow rates, pH (if measured), redox potential or ORP (if measured). Scrubber reagent flow, and chloride concentration in the slurry may be important as well.

If coal additives, scrubber additives and/or dry sorbent injection are being used, the type of additives and/or sorbents, the injection locations and injection rates should be noted, including detailed operating parameters of any temporary systems.

4.2.4.2 Solid Samples
Solid samples should be collected, even if stored and not immediately analyzed. Coal samples are needed to confirm the input mercury; the chlorine and sulfur contents of the coal are also useful to measure. If the plant already has a coal sampling system, obtaining splits of the plant's samples is a good way to get samples. At a minimum, daily coal samples should be collected. Be sure to understand how much time there is between the coal sample location and the coal reaching the furnace.

Fly ash samples are the most important ash samples to collect for the sake of measuring its mercury content and/or for concrete testing, if the fly ash is sold for use in concrete manufacturing. Rarely is there any mercury in the bottom ash (dry bottom boilers) or in the slag (wet bottom boilers); therefore, it is a low priority to collect samples of these.

There are two ways to collect a fly ash sample. One way is to take an in-situ (in-duct flue gas) sample using a filter or cyclone. The other way is to collect samples from the hoppers of the baghouse or ESP. In-situ sampling does not provide a large amount of sample, but the sample can be tied to a specific time, which may be useful when relatively short, parametric tests of sorbent injection are being carried out. Fly ash sampling from the hoppers of particulate control devices requires a thoughtful plan, and may include many samples, depending on the complexity of the particulate control device. A sampling plan should include working with Operations personnel to clean out the hoppers before the testing begins in order to have a representative ash sample during the test. It might be helpful in designing a sampling plan to collaborate with a fly ash marketer for tips on how to properly sample ash for the sake of concrete testing.

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4.2.4.3 Scrubber Samples

Scrubber sampling is determined by the scope and goal of the test being conducted. The more samples that are collected and analyzed, the more detailed the final view of the performance of the mercury control strategy as well as the potential impact on operations and by-products will be. However, this comes at a cost. The project manager must define the scope early in order to ensure the necessary samples are taken to provide information aligned with this scope. Remember, once the demonstration has been completed, the opportunity to obtain samples is gone.

Reasons for taking scrubber samples include the following:

- To determine impact of mercury capture strategy on scrubber liquor and by-product composition;
- To determine if a scrubber liquor composition favors the reduction of ionic (Hg^{2+}) mercury in solution to elemental mercury; in this case, known as mercury re-emission, the scrubber is operating at lower mercury capture efficiencies and limits the ability of the unit to control mercury emissions;
- To determine where the mercury that is scrubbed from the combustion gases ends up and in what form;
- To characterize scrubber water and the by-product circuit for mercury and other species of interest including the final form and process stream in which it exits the unit.

Conditions during which samples should be collected include:

- *Baseline* - Pre-testing timeframe while unit is operating at steady-state condition. It is suggested that this be during full-load condition.
- *Testing*- Samples should be taken minimally once per day from the first day of testing until the last day of testing, more is better. The test service provider should be able to provide direction on sampling, preparations and storage.
- *Post-test samples* - Taken over a period of time as the unit returns to pre-test operational conditions.

Depending on the volume and operation of the scrubber, consideration must be given to account for the residence time of the absorber slurry. It may take a week for a large scrubber to come to a new steady-state condition as operating conditions change. For short-term test programs, the FGD will often not have achieved steady state with the Hg control in operation.

Scrubber liquor should be sampled during the three periods outlined above. Replicate samples for a given condition are recommended. In addition to "typical" operational characterization such as pH, temperature, ORP and concentration of chloride, it is recommended to separate the liquid phase from the solid phase. The liquid phase can be analyzed for anions, cations, and soluble mercury content. The solid phase can also be analyzed for mercury content and trace metals. The analytes each have a specific sample storage, preparation, and shelf-life to consider. This information can be obtained from the testing service or analytical laboratories familiar with the scrubber liquor matrix.

Other samples that could be taken include hydroclone samples (i.e. light and heavy fractions), gypsum, gypsum filter press filtrate, limestone, limestone feed, recycle water, and any other addition stream entering the wet scrubber. A detailed material flow diagram around the scrubber ultimately serves to highlight sampling points useful in obtaining information consistent with the project scope. Wastewater treatment influent and effluent should also be considered in order to complete the picture regarding mercury's strategic impact.

5. MERCURY CONTROL TECHNOLOGIES

5.1   Background

This section briefly covers the various technologies that might be considered as solutions to controlling mercury emissions from a coal-fired electricity generating unit (EGU). The information is organized according to the application point within the EGU. This is not intended to be an exhaustive list as technology

is changing rapidly.

5.2   Mercury Control - A Technology Approach

Mercury and other hazardous air pollutants are generated during the combustion of coal to generate electricity. The removal of mercury from flue gas generally consists of Speciation Control, Capture, and Removal from the system. The potential solutions for each of these steps or combination is provided below based on the EGU's air quality control device (AQCD) configuration. A brief description of available technologies for each AQCD configuration is provided but is not meant to be an exhaustive list. The reader is encouraged to research potential mercury control strategies applicable to the specific EGU and its operational goals as part of setting the test plan scope.

5.2.1 Flue Gas Mercury Speciation Management

5.2.1.1 Background

The combustion of coal results in the release of mercury into the flue gas in the form of particulate, gaseous elemental and gaseous oxidized mercury. Particulate mercury is removed via existing particulate control devices. Oxidized mercury can be efficiently captured by current technologies for scrubbing acid gases, but re-emission control and removal of the mercury from the scrubber liquor need to be tested.

Elemental mercury is more problematic and generally needs to be oxidized in order to be collected. The higher the elemental mercury level in comparison with the target emission rate, the more difficult it will be to meet the emission limit. Many technologies are being tested with a good degree of success to convert the elemental mercury to the oxidized form to enhance capture. The application of these different technologies requires the EGU to consider many balance-of-plant factors, process and equipment parameters and desired compliance outcomes versus costs and reliable, consistent operability.

5.2.1.2 Fuel Blending

Generally, the fraction of oxidized mercury present in coal combustion gas is correlated with the halogen content of the fuel. For example, subbituminous coal from the Powder River Basin (PRB) typically has lower halogen content (less than 100 μg/g), resulting in lower fractions of oxidized mercury in the flue gas and hence the lower native mercury captured across existing AQCDs. Eastern bituminous coals typically have higher halogen contents (100-2,000 μg/g) leading to a higher fraction of oxidized mercury in the flue gas and hence, typically, higher native mercury capture. In addition, the combustion of Eastern bituminous coals often results in a high fraction of unburned carbon (measured as loss-on-ignition or LOI) in the fly ash, which can increase native capture of mercury. However, the higher sulfur content of Eastern bituminous coals can result in high concentrations of sulfuric acid vapor in the flue gas. Sulfuric acid vapor interferes with the adsorption of mercury on carbon. Even with high LOI in the fly ash, native capture of mercury can be low.

Augmenting the halogen content of the fuel by mixing fuels with low and high halogen contents is a potential approach to increasing the oxidized mercury fraction in the combustion gas. Such a strategy requires fuel supply control and adequate mixing of the combined fuels. Not all plants have the ability to receive and blend coals from two different sources.

5.2.1.3 Boiler Additives

Boiler additives are chemicals that are added to the fuel or injected into the flame zone. These additives increase the oxidized fraction of mercury in the combustion gas with little to no impact on the total mercury concentration. The most widely used additives are halogen-containing salts. Bromine-based additives result in better performance than chlorine-based additives on an equal mass basis. The application of these technologies can be as simple as applying a liquid to the solid fuel prior to the combustion zone of the boiler. Equipment requirements are minimal and temporary installation for test purposes exhibit small footprints, low power consumption and are minimally invasive. Typically, boiler additives are liquids to facilitate application onto the fuel. The presence of excess or free halogens in the flue gas could lead to enhanced equipment

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corrosion and downstream water contamination issues. A holistic balance-of-plant approach needs to be taken to ensure that solving an issue in a particular place in the flue gas path does not create issues in downstream processes.

5.2.1.4 Post-Boiler Additives
Post-boiler additives are halogen-containing materials that are injected into the combustion gases either prior to the air preheater or after the air preheater. As above, the highest performing additives, i.e. low dose to reach high mercury oxidation, are based on bromine.

5.2.1.5 Mercury Oxidation across SCRs

The presence of a selective catalytic reduction (SCR) system post-boiler has a positive impact on mercury oxidation, and when used in conjunction with WFGD, is an effective and common control technology for Hg removal. While the SCR is installed primarily for NO_x emission control, the catalyst will oxidize mercury in the combustion gas; the degree of oxidation depends on the catalyst composition, the amount of halogen in the flue gas, and the temperature of the catalyst.

In addition, catalyst manufacturers are developing new catalysts or recommending an additional catalyst layer to increase mercury oxidation without increasing SO_2 oxidation to SO_3 while delivering consistent NO_x reduction. The presence of an SCR can also significantly reduce the amount of halogen that is needed in the flue gas to oxidize mercury. In addition, the ammonia injected into the SCR for NOx control can impact the oxidation of mercury. It is important to understand the need for NOx control versus mercury oxidation. Other recent developments include boiler additives that both facilitate mercury oxidation, and prolong the catalyst activity and lifetime when burning a high phosphorous fuel.

5.2.2 Mercury Sorbents for Particulate Control Devices

5.2.2.1 Background
EGUs with fabric filters (FFs) and/or electrostatic precipitators (ESPs) provide an opportunity to employ mercury sorbents. These sorbents are typically dry materials that are introduced into the flue gas or combustion gas and capture oxidized and elemental mercury. In this way, once the mercury is transferred from the gas phase to the solid phase, it is captured on the sorbent and fly ash in a particulate control device (PCD) in a form that will safely pass leaching and landfill requirements. Mercury sorbents can be loosely categorized as carbon-based and inorganic (non-carbon) sorbents.

Testing of these materials typically requires ports installed in the duct work prior to or after the air preheater and prior to PCDs. Multiple lances are installed in the ports, preferably in an arrangement that allows for good sorbent dispersion and complete coverage of the duct. It is critical to have access to several ports to allow multiple lances to be inserted into the combustion gas at different levels to insure rapid dispersion of the sorbents and maximize sorbent/combustion gas mixing. Depending on the demonstration provider, computational fluid dynamic modeling (CFD) is used prior to the test to insure adequate mixing and sorbent/combustion gas contact time to maximize mercury capture.

Sorbent testing can be done either with an existing silo or with a temporary skid-mounted feeder capable of handling super sacks. The feed system should preferably be gravimetric (as opposed to volumetric) for more accurate feed rates, and will also include, blowers, lines, lances, and injection ports that span the duct being treated. These are necessary to disperse the sorbent into carrier air and convey it to the injection point to insure uniform application during the test.

In all cases, it is important to realize that the added sorbents will add to the particulate loading on the FF and ESP. Prior to and during testing, it is important to determine if the particulate control device can handle the added particulate loading. Particulate measurements and/or opacity monitoring can help assess additional loading.

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A final application point for mercury sorbents is into the combustion gas prior to a wet flue gas desulfurization (WFGD) system. In such a case, the WFGD serves both as a particle and sulfur capture device. In this configuration, the sorbent becomes part of the gypsum or scrubber by-product entering the wastewater treatment system.

5.2.2.2 Activated Carbon

Activated carbon injection (ACI) involves the injection of a powdered form (typically of a particle size range of 10 - 40 microns) of activated carbon into the flue gas to adsorb mercury from the flue gas upstream of a particulate collector. ACI is a mature technology with over 63 GW of commercial bookings as of mid-2012. Extensive commercial experience has shown that ACI can cost-effectively control mercury emissions with a wide variety of coals and plant configurations. The carbon is typically injected either between the economizer and the air preheater (APH), or between the APH and the PCD. The injection location hinges on a number of factors including contact time, port availability, interactions with DSI (Dry Sorbent Injection) chemicals and boiler additives, and vapor-phase sulfuric acid concentration in the flue gas. It should be noted that there are a host of patented technologies that are based on injection location.

There are several grades and types of ACI currently available. For EGUs burning coals with sufficient halogen, adequate mercury oxidation is reached in the combustion gas and different grades of activated carbon are available. Many activated carbons do not perform well in the presence of SO_3. For EGUs burning "high sulfur" fuels, sulfur trioxide-resistant activated carbons are available.

Finally, for EGUs burning low halogen-containing fuels with low or no mercury oxidation in the combustion gas, the use of a brominated activated carbon, or the combination of activated carbon with the use of a bromine-based boiler additive, can often greatly increase the mercury capture performance versus non-brominated activated carbon. For more information on boiler additives, see Section 5.2.1.3. In PRB-fired boilers with ESPs, SO_3 is often injected as a flue gas conditioning agent. For these boilers, an alternative flue gas conditioning agent might be tested with activated carbon or a sulfur trioxide-resistant activated carbon could be tested.

Historical drawbacks to the use of ACI include the potential impact on the particulate control device and its potentially deleterious impact on fly ash quality with respect to its use in concrete. In the latter case, the increased fly ash carbon content can adsorb air entrainment additives that are used in many concrete formulations. However, thanks to continued research and development, great strides have recently been made in addressing both these issues, as well as in advances to significantly improve PAC's mercury capture efficiency. These newer PACs have resulted in reduced PAC injection amounts and achievement of very low mercury residual emissions in the treated flue gas. R&D on the use of fly ash in concrete has resulted in commercial development of concrete-compatible activated carbons (halogenated and non-halogenated).

5.2.2.3 Inorganic Sorbents

Inorganic (non-carbon) mercury sorbents for room temperature sorption have been known for some time in small-scale applications. Only recently have inorganic sorbents been developed with the ability to function at the higher temperatures of the combustion gases. These sorbents are also applied as dry powders in manners and locations similar to activated carbon (See above Section 5.2.2.2). These sorbents have patented proprietary compositions that have met with varying degrees of success. Their advantage is lack of impact on fly ash quality regarding use in concrete. As these are inorganic, color is not an issue as well. Currently, a limitation of this class of mercury sorbents is their limited full-scale experience.

5.2.3 Wet, Semi-Dry and Dry Scrubber Additives

5.2.3.1 Background

The capture of sulfur emissions from coal-fired EGUs has been a focus since 1970 and has renewed emphasis with the passage of the MATS rule. A viable mercury co-reduction strategy utilizes the existing AQCDs

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designed to control sulfur emissions, i.e. WFGD systems, and dry flue gas desulfurization (DFGD) systems. For this strategy to be successful, mercury must exist in the gaseous oxidized form, because it alone is soluble in the water of the liquor. Elemental mercury is not practically soluble in scrubber liquor.

WFGDs utilize a water-intensive process in which an alkaline solution, based on lime or limestone for example, is used to capture and neutralize sulfur dioxide and acid gases. WFGDs can be designed to handle fuel sources with up to 6% sulfur content and achieve greater than 99% removal of SO_2. The process can be designed to operate with inhibited, natural or forced oxidation. Inhibited oxidation yields sodium or calcium sulfite as a by-product. Forced oxidation systems generate potentially sellable by-product gypsum (calcium sulfate). The "scrubber" types include venturi, spray tower, and jet bubbler designs to facilitate intimate contact of the combustion gas with the liquid. The efficiency of mercury capture across any given WFGD is dependent on several design parameters and at least one complicating chemical reaction known as mercury re-emission.

DFGDs consist of semi-dry and dry spray dryer technologies available under a variety of trade names and configurations. Generally, DFGDs utilize significantly less water in the process of capturing acid gases including sulfur dioxide, with dry scrubbers consuming the least amount of water. Typically, these scrubbers are designed for fuels with sulfur contents less than 4.5%. Spray dryer absorbers (SDAs) typically handle fuels with less than 2.5% sulfur. These limitations ensure at least 95% capture of sulfur from the combustion gas. DFGDs, like their counterpart WFGDs, require mercury present in the combustion gas to be oxidized to facilitate capture.

5.2.3.2 WFGD Additives (Hg Re-emission Control)
WFGDs operating at high sulfur capture rates theoretically should remove 100% of the oxidized mercury from combustion gas. However, in many cases oxidized mercury capture efficiencies are significantly less than theoretical. One demonstrated cause of the limited performance is mercury re-emission. Simply put, mercury re-emission is when elemental mercury concentration in the combustion gas entering the WFGD is lower than that of the stack gas or scrubbed gas. This occurs when oxidized mercury is absorbed into the scrubber liquor, and subsequently reduced in the aqueous phase to elemental mercury, which is then released back into the gas phase. Comparing inlet and outlet mercury concentrations, oxidized mercury concentration decreases across the WFGD (i.e. inlet to outlet) while elemental mercury concentration increases. This can lead to a net higher stack mercury emission. As with all mercury strategy testing, temporal (up to 30 days) variations, such as coal variations and other plant operations, need to be considered in designing a test program, particularly when the WFGD is known to re-emit mercury.

WFGD additives or Scrubber Additives have been developed and demonstrated to reduce or eliminate the occurrence of mercury re-emission. These additives are generated on site or provided as liquids that are added to the scrubber liquor. Application points include the scrubber basin, the suction side of a recirculation pump in spray tower modules, or quench-lines on jet bubbler modules. Generally, any application point which ensures good mixing of the additive into the scrubber liquor will work. Application equipment typically employs an appropriately sized metering pump, storage tank for the additive, and appropriate lines to the injection point. Some suppliers have developed temporary skids, which automatically monitor changes in scrubber liquor chemistry and change the scrubber additive dosage accordingly. Generally, control of the scrubber additive is possible to reduce mercury re-emission to meet total mercury emission limitations, which should be demonstrated on a given unit through a well-designed test program. There are several types of scrubber additives, each with their own unique advantages and some disadvantages.

Besides the liquid scrubber additives discussed above, dry mercury sorbents can be added to WFGDs. This application requires storage and conveying equipment along with dispersing equipment to wet the dry sorbent, such as activated carbon, prior to addition to scrubber liquor. The advantage of this technique is the ability to

sequester the soluble mercury on a sorbent. The disadvantages include additional application equipment, handling of sorbents, and discoloration or contamination of the gypsum byproducts. In order to ensure separation of sorbent solids from the other solid by-products, adjustments to hydroclones might be required.

5.2.3.3 WFGD Blowdown Processing

The strategy of using WFGDs to capture mercury translates to the transfer of oxidized mercury from the gas phase into the aqueous phase of the scrubber. This transfer of mercury can result in an increase in mercury concentration in wastewater effluent from the EGU. There are several additives that can be added to the wastewater treatment system that will insure that effluent discharge from the EGU continues to meet established discharge limits for mercury despite reduced total mercury emissions in the flue gas. However, with stricter effluent guidelines, it may be more difficult to achieve both mercury limits and limits on other species in the effluent, for example, if the bromine content of water has increased beyond permitted levels.

The reader is reminded that consideration of the ultimate disposition of captured mercury and any other accumulated additives or chemicals is important to a successful mercury control strategy.

5.2.3.4 Post-WFGD Solid-Supported Sorbents

Post-WFGD mercury solid-supported sorbents are currently under development. Solid-supported sorbents achieve mercury emissions control without the use of powdered activated carbon, halogens, or re-emissions additives. The sorbent material is installed as a fixed bed above the spray tower nozzles so that the cleaned combustion gas passes through the sorbent as it exits to the stack. Installation of the solid-supported sorbent may require physical alteration to existing WFGDs; the sorbent is designed to last for at least one year, with the sorbent being removed and replaced during a unit outage. Regeneration of the sorbent is a possibility, but has not been demonstrated. Testing of this strategy involves slipstream or sidestream testing of full-scale flue gas.

5.2.3.5 Spray Dryer Absorbers and Circulating Dry Scrubbers

DFGDs such as SDAs and CDSs are gaining popularity within the industry as they can handle "medium" sulfur containing fuels, present a small capital footprint, use less water than the corresponding WFGDs, and produce no liquid discharge. For details on the operation and various designs available, it is suggested that the reader search SDAs, CDSs and NIDS as a starting point. DFGDs capture other toxic air pollutants besides sulfur dioxide and trioxide. Mercury and other acid gases (e.g., HCl) are also captured across this AQCD. However, the optimization of mercury capture across DFGD requires a high fraction of the total mercury concentration in combustion gases be in the ionic form. This is accomplished through the application of speciation control additives discussed in Section 5.2.1 above.

In addition, mercury sorbents as discussed in Section 5.2.2 above can be introduced into the combustion gas prior to the DFGD. This strategy utilizes the combination of the DFGD and FF combination to capture the injected sorbents. For EGU units burning low-halogen fuels, halogenated sorbents can be used to further decrease mercury emissions.

A new category of inorganic mercury sorbent has recently been introduced. This is a liquid product that is combined with the lime slurry feed of DFGD units. This new material is a non-halogen containing sorbent that has demonstrated mercury emission compliance on EGUs burning low-halogen coals, i.e. low fractions of oxidized mercury. Test equipment consists of meter pumps, temporary storage, and transfer lines. The application point is addition to trim water or dilution water entering the DFGD scrubber. Being inorganic, it does not add color to the resulting ash.

5.3   Parting Comments

The above summary cannot practically cover every detail of every available technology or combination of technologies that may be necessary for a given EGU to meet mercury emission regulations. It does however

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provide an overview from which to start. Further information can be obtained from ICAC.

6. ECONOMIC CONSIDERATIONS FOR CONTINUOUS, FULL-TIME OPERATION

6.1 Collect Appropriate Data during Testing

A key issue in planning a test program is ensuring that the plan includes thoughtful collection of data such that the full-scale, long-term costs of operation of the control technology can be assessed. We discussed the types of information that should be addressed in the data collection section, and in this section, we present how to use that data.

6.1.1 Unit Load and Operating Information

Section 4.2.4.1 listed minimum parameters to obtain from the plant information system during the test. Typically the plant data historian will have extensive data available, and depending on the test program focus, your list may include many additional parameters to enable examining a specific component more deeply. Obtaining five-minute averages can be useful for graphing trends such as load variations and day-to-night temperature differences. Longer averaging times may be advantageous for longer test periods (to make the data files more manageable), while shorter averaging times should be used for parametric testing so that the length of time required for the system to respond can be observed.

In order to restrict the operating variables and gain the most understanding of the test results, full load operation should be scheduled for the unit as much as possible. It is easier on the System Dispatch if full load is requested during day time and not on weekends. At a minimum, six hours of full load during each week day of a test week, will provide some consistent operations to make comparisons of test conditions.

Plant operating data should be compared between baseline and test conditions. Any conditions that are not sustainable should be flagged and a decision made as to whether longer runs are needed, or whether a change in operation can be made. Any adverse effects should be evaluated over the longest timeframe possible to improve on the cost/economic analysis of the implications.

Tests should provide basics on the effectiveness at high load and also under load-following conditions when possible. The longer the time horizon the better especially for any approach that is cyclical or results in a buildup in concentration. Maximum concentrations, or periodic inconsistencies and how they are resolved, need to be accounted for, and may be unrealized in test runs that are too short.

Even when many samples are collected during a test, a mass balance can be elusive. This lack of closure may be attributable to unreliable solids samples where representative sampling is prohibitively complex, or to liquid samples that have not reached a steady-state condition. In any case, the available data should be evaluated to determine whether it is useful towards projecting long-term capital and operating costs. For example, additional sample analyses may be warranted, if a mass balance is necessary to understand the entire envelope of the operating system.

The most accurate cost forecasting will be for technologies that are already commercially implemented at other facilities for mercury compliance. As an example, activated carbon injection, which has been implemented on many coal-fired applications for compliance with permits, consent decrees, and state standards, has a history of operational reliability that provides a good basis for economic analysis. Factors to consider for any technology are discussed below.

6.2 Evaluate Permanent vs. Test Equipment Size, Locations, Support Systems

Test equipment may be fundamentally different from a permanent installation in terms of equipment size, reliability, location, reagent distribution, and plant support required. If the testing establishes and verifies

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equipment operating ranges, then permanent equipment estimates can be obtained from vendors. Ranges or turndown should account for fuel variability, process ranges, and maximum to minimum load ranges. The costs of any specialized equipment can be estimated by the suppliers with accuracies ranging from a budgetary estimate (+/-30%) to a formal bid that will commit to a price. The bid should include plant support systems (balance-of-plant) such as piping, electrical and controls integration. Depending on timeframe and readiness to proceed with contracting, working with known suppliers is an important step in obtaining accurate economics. For reference, ICAC has a white paper titled "Bid Specification and Information Requirements and Bid Evaluation Form for Activated Carbon Injection Systems" (available at www.icac.com).

6.3 Evaluate and Include Various Costs

6.3.1 Analytical and QC Methods and Equipment

Testing should also consider what process or compositional parameters will be monitored during the test and for permanent installations. Considerations for monitoring continuously, semi-continuously or batch-wise will impact the overall cost for compliance. The types and reliability of methods for example in measuring mercury, SO_2, SO_3, HCl, etc. are also important to evaluate. The ultimate choices will impact both capital as well as operational costs.

6.3.2 Chemicals and Sorbents

If testing establishes and verifies injection rates, similar to the equipment requirements, suppliers can then provide full-scale pricing. A range of quantities may be necessary to request based on your operating capacity factor, fuel variability, process ranges and various solutions that you are evaluating for comparison. If multiple chemicals and sorbent technologies are employed, be sure to estimate a total cost of material use.

6.3.3 Power Consumption

These data should be available from the equipment vendor. Make sure to account for additional pressure drop if measurably affected by the option under evaluation (the plant operational data should support this).

6.3.4 Balance-of-Plant Impacts

While the equipment vendor can describe maintenance on the provided equipment, it can be challenging to assess balance-of-plant maintenance requirements. It is important to consider impacts that may occur outside the window of the test program, such as corrosion, increased periodic maintenance, reduced lifecycle of equipment, etc.

6.3.5 Operation and Maintenance

Operations and maintenance labor required to support the continuous operation of the mercury control technology, measurement systems, and EPA reporting requirements should be assessed.

6.3.6 Disposal Impacts

Any solids that are sold from the plant should be evaluated for impacts from the technology. These solids may include fly ash or gypsum. Various options may be worth considering since disposal may shift from a high-value to a lower-value use, or even landfilling. Lost sales, if applicable, as well as changes in disposal costs, need to be accounted for.

6.3.7 Emissions Impacts

The form of capture should be considered here, as well as emissions of other pollutants such as particulate matter, SO_3, gas phase halogens, etc. For technologies that move the mercury downstream without sequestering it, the ultimate fate of the mercury and the cost and type of additional mitigation equipment or technology should be considered. Re-emission phenomena should be addressed. For technologies that increase particulate loading to a baghouse or ESP, any particulate impact needs to be assessed.

6.4.8 Reliability

Test periods are by nature short in duration and the results can be misleading. The longer the period of testing, the more useful the results will be. Consider the potential impacts of the

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technology and whether the data are representative. If it is not practical to extend a test to a more realistic duration, then talking with other power plants that have the technology installed is recommended in your assessment of costs and reliability.

6.4.9 Licensing Fees

Some technologies may incur a licensing fee from the vendor. Make sure any fee is included in the costs under evaluation and that the terms are well understood.

7. ACRONYMS, UNITS AND ABBREVIATIONS

A & E	Architect and Engineering
ACFM	Actual Cubic Feet per Minute
ACI	Activated Carbon Injection
APC	Air Pollution Control
APH	Air Preheater
AQCD	Air Quality Control Device
ASTM	ASTM International
BOP	Balance of Plant
°C	Degrees Celsius
CDS	Circulating Dry Scrubber
CEMS	Continuous Emissions Monitoring System
CFD	Computational Fluid Dynamics
CFR	Code of Federal Regulations
CO	Carbon Monoxide
CO_2	Carbon Dioxide
COHPAC	Compact Hybrid Particulate Collector
CVAAS	Cold Vapor Atomic Absorption Spectroscopy
CVAF	Cold Vapor Atomic Fluorescence
DFGD	Dry Flue Gas Desulfurization
DSI	Dry Sorbent Injection
EDXRF	Energy-Dispersive X-Ray Fluorescence
EGU	Electricity Generating Unit
EPA	Environmental Protection Agency
EPRI	Electric Power Research Institute
ESP	Electrostatic Precipitator
°F	Degrees Fahrenheit
FF	Fabric Filter
HAP	Hazardous Air Pollutant
Hg	Mercury
Hg^0	Elemental Mercury
Hg^{2+}	Oxidized or Ionic Species of Mercury
Hg_p	Particulate-Bound Mercury

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HBr	Hydrogen Bromide
HCl	Hydrochloric Acid
ICAC	Institute of Clean Air Companies
ICR	Information Collection Request
H_2O_2	Hydrogen peroxide
HNO_3	Nitric Acid
H_2SO_4	Sulfuric Acid
KCl	Potassium chloride
$KMnO_4$	Potassium permanganate
LOI	Loss on Ignition (an indication of carbon content in fly ash)
MACT	Maximum Achievable Control Technology
MATS	Mercury and Air Toxics Standards
MW_{net}	Megawatts Net
MW_{gross}	Megawatts Gross
N_2	Nitrogen
NIDS	Novel Integrated Desulfurization System
NIST	National Institute of Standards and Technology
NO_x	Nitrogen Oxides
O & M	Operations and Maintenance
O_2	Oxygen
ORP	Oxidation Reduction Potential
PAC	Powdered Activated Carbon
PCD	Particle Control Device
PM	Particulate Matter
PRB	Powder River Basin
QA	Quality Assurance
QC	Quality Control
RATA	Relative Accuracy Test Audit
SCA	Specific Collection Area
SCR	Selective Catalytic Reduction
SDA	Spray Dryer Absorber
SNCR	Selective Non-Catalytic Reduction
SO_2	Sulfur Dioxide
SO_3	Sulfur Trioxide
STMS	Sorbent Trap Monitoring Systems
UV	Ultra Violet
WFGD	Wet Flue Gas Desulfurization
XRF	X-Ray Fluorescence

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