

Mercury Monitoring in a Cement Kiln

Anand Mamidipudi, Product Line Manager

Thermo Fisher Scientific, 27 Forge Parkway, Franklin, MA 02038

Key Words:

- Mercury
- Hg
- Cement
- Kiln
- Raw Mill
- In-line Kiln
- Baghouse
- Dust Shuttling
- Particulate
- CVAF

Introduction

The Thermo Scientific Mercury Freedom system was originally designed to meet the requirements of the Clear Air Mercury Rule (CAMR), which was promulgated in 2005 for the U.S. Coal-fired Utility industry. Subsequently several hundred Mercury Freedom Systems were installed and operating in coal-fired power plants across the United States, passing stringent Relative Accuracy Test Audits (RATAs) under varying plant conditions. The CAMR was vacated in 2009, however many plants continue to operate the systems as required by their state or local agencies or, in some cases, to monitor vapor phase mercury emissions for effective process control. On September 9, 2010, the U.S. EPA promulgated the Portland Cement MACT rule, which requires all cement plants in the United States to monitor mercury on a continuous basis at the cement kiln.

This application note discusses the adaptability of the Mercury Freedom System to the unique conditions in a cement plant. Results of the Mercury Freedom System from a series of early installations in cement plants are discussed in relation to the new regulatory requirements and changing process flow conditions. Further, this application note shall examine the suitability of the current design of the Mercury Freedom System to the cement application and identify potential areas of improvement, if required.

Sources of Variation in Mercury Emissions

There are potentially multiple sources of mercury emissions from cement kilns due to the large variety of fuels and raw materials



used in the process. The primary source of mercury emissions is limestone, the main constituent of the raw material that is used to produce cement. Coal, which is often used as the primary fuel to heat the raw material, contains mercury which becomes a part of the plant's emissions.¹ Mercury is also a part of dust captured in the Air Pollution Control Device, which is reintroduced to the cement kiln. Other smaller sources of mercury emissions include sand and iron ore.

The cement process is known to be a harsh operating environment for stack monitoring on account of high temperatures, moisture and dust in the flue gas. Furthermore, sudden changes in the process can cause large variations in mercury emissions. The Mercury Freedom System is ideal for capturing such dramatic variations in emissions output because it uses a direct measurement method (discussed later) unlike a sorbent trap or batch amalgamation. Some of the conditions affecting mercury output in a cement kiln are discussed in the coming paragraphs.

Raw Mill

In-line kiln/raw mills are used to route the kiln exhaust gases to the

raw mill in order to dry the raw meal. This allows a more efficient use of the plant's energy. When the raw mill is on, a large portion of the mercury that is exhausted from the kiln is fed back into the raw mill; the mercury is either attached to particulate dust that is recycled or is a constituent of the drying gases. A number of studies show that a majority of mercury in the particulate dust is recaptured at the raw mill, which results in lower levels of mercury at the stack when the raw mill is on.² When the raw mill is turned off, accumulated mercury is released and emitted through the stack. The drying gases are also bypassed through the main bag house, which can cause additional spikes of mercury. Numerous studies, including one of our own presented in this document, illustrate the impact of the raw mill condition on the concentrations of mercury.

Dust Management

Kiln dust is often reused to augment the raw feed and increase production of cement. This recirculation of kiln dust to the raw feed creates complexities in the measurement and control of mercury in the cement process. A fast response mercury continuous emission monitoring system or

CEMS can be used as an effective process indicator to trigger a plant manager to shuttle dust in the bag house to a different location such as a finish mill. Also given the sudden variations in levels of mercury due to the dynamic conditions caused by the feedback processes, a continuous monitoring system can provide a more accurate picture of the plant's mercury emissions in relation to changes in the process.

One user of the Mercury Freedom System at a cement kiln in the southeastern U.S. conveyed that the system was an effective tool in determining mercury levels in the bag house. This modern kiln is located in Northern Florida with a five-stage preheater, pre-calciner, and an in-line raw mill. Figure 1 presents a view of the probe (part of the Mercury Freedom System) installed in the southeastern cement kiln. By studying the changes in mercury levels, the user was able to assess the immediate impact of process changes and accordingly adjust their strategy of shuttling dust to a finish mill.



Figure 1: View of Model 83i probe at southeastern cement kiln

Use of Multiple Fuels

As mentioned earlier, most cement plants use coal as a primary fuel to heat the cement kiln. The distribution of mercury in coal can vary heavily by the type of coal that is being used. According to the COALQUAL database compiled by the U.S. Geological Society, different geographical regions show great variation in the amount and mode of occurrence of coal. The mode of occurrence plays a major role in the species of mercury created during cleaning, combustion and leaching.³

Cement plants use various types of coal and petroleum coke as their primary fuels, either alone or as mixed fuels. On rare occasions oil and natural gas are also used as main fuels. Secondary fuels include scrap tires, various solid and liquid wastes, plastics and many biomass fuels, such as wood waste, sewage sludge, animal meal and fat.⁴ The operations of the cement plant are hugely cost-sensitive, so it is not uncommon to see fuels being switched or combined during cement production due to economic drivers. As a result, the levels and species of mercury can vary greatly depending upon the nature of fuel used and their combustion efficiencies.

Description of the Thermo Scientific Mercury Freedom System

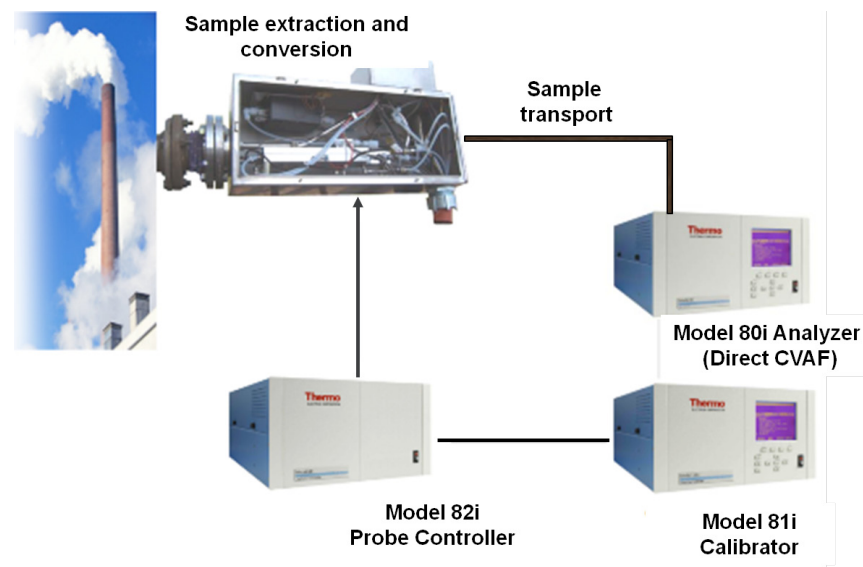
The Mercury Freedom System offers high measurement sensitivity, fast response times and robust operation in harsh environments through a simple design that closely resembles a traditional wet-basis dilution extractive CEMS. The system is capable of measuring elemental, ionic and total mercury in exhaust stacks through the use of Cold Vapor Atomic Fluorescence technology. This design also eliminates the need for an SO₂ scrubber, commonly used with atomic absorption systems, or an expensive carrier gas (e.g. Argon) and provides true continuous measurement as opposed to batch collection by pre-concentration of mercury on a gold amalgamation trap.

The Mercury Freedom System consists of a sampling probe at the stack, a heated umbilical line for sample transport, and a rack of instruments that include the analyzer, calibrator and probe controller. The rack, which is placed in an accessible temperature-controlled location, also contains a zero-air generator and a sample pump. A working diagram of the Mercury Freedom System is shown in Figure 2.

As shown in the figure, the system extracts the sample using an inertial probe at the stack. The probe contains a fast loop that prevents particulate clogging and requires less frequent maintenance by using a glass-coated inertial filter. The sample is diluted with instrument-generated zero air or Nitrogen (for greater sensitivity) before it is transported to the measuring instrument, the Thermo Scientific Model 80i analyzer. The Model 80i Analyzer detects elemental mercury (Hg₀), not oxidized mercury (Hg₂₊). Therefore, in order to detect all (total) mercury, oxidized mercury needs to be converted into elemental mercury.

The probe splits the sample into two flow paths, one of which uses a dry converter to convert the oxidized mercury into elemental mercury. This way, one of the sample tubes carries elemental mercury and the other tube carries total mercury, which includes the converted oxidized mercury.

Figure 2: High-level view of the Mercury Freedom System



Converting the more reactive oxidized mercury at the stack will minimize the loss of mercury in the sample line, or consequently remove the need for a high temperature in the umbilical line.

The Model 80i analyzer resides in the rack along with the Thermo Scientific Model 82i Probe Controller and the Model 81i Calibrator. The diluted sample from the probe is transported through the optical chamber, where it is subjected to a high intensity UV light source (mercury vapor lamp). Mercury in the sample is excited at a certain wavelength of light, 253.7 nm, which causes it to fluoresce at the same wavelength. The intensity of fluorescence is directly proportional to the amount of mercury in the sample. The amount of fluorescence is captured by a photomultiplier tube (PMT) and ultimately converted to a digital reading. The method of analysis eliminates the possibility of interference with other pollutants because only mercury is excited at the chosen wavelength.

The Model 82i Probe Controller monitors and controls various probe parameters such as pressure and temperature, and also controls automated blowback and secondary valve functions. When used in conjunction with the Thermo Scientific Zero Air Supply, the Model 82i delivers clean dilution gas to both the Model 81i calibrator and the probe.

The Model 81i Calibrator generates mercury vapor used to calibrate the Model 80i Analyzer. The CEMS, as a system, is also calibrated with mercury vapor generated by the Model 81i Calibrator. The Calibrator uses a Peltier Cooler and mass flow controllers to generate precise amounts of elemental mercury. Mercury span gas is transported through the sample line to the probe. During a calibration cycle, the calibration gas floods the probe and is drawn through the inertial filter back into the analyzer for measurement.

The Model 80i Analyzer displays Elemental Hg, Oxidized Hg, and Total Hg concentrations on a front panel display. The Model 80i Analyzer is totally self-contained, linear through all ranges and uses proven pulsed fluorescence detection technology giving fast response time and high sensitivity.

Results from Field Installations

We have installed the Mercury Freedom system in several cement locations worldwide. Some are demo installations for the purpose of studying the characteristics of mercury emissions in cement plants and also for evaluating the performance of the Mercury Freedom System under varying conditions of the process with and without the presence of an in-line kiln/raw mill.

Our first installation was at a cement plant in the Midwestern U.S. (see Figure 3). The Midwest installation in KY/IL area was an older, long, dry, horizontal kiln without an inline raw mill. This kiln was primarily making Clinker type “H”, according to the company.

The Mercury Freedom System was installed in August 2009 and operated for six months while

plant personnel were becoming familiar with the instruments and accessories. During this time a number of tests were run to determine the system’s performance. Figure 4 offers a snapshot of these results, showing that nearly 90% of total mercury concentrations were elemental mercury in the absence of an in-line-kiln/raw mill. We observed later from another study (discussed below) that an in-line kiln/raw mill dramatically reversed this scenario.

Towards the end of the study, a RATA was performed. This test is the major part of any certification process done on any type of CEMS for regulatory compliance. Table 1 describes the results of the RATA, where the output of the Mercury Freedom System was measured against the 30B reference method. The Mercury Freedom System performed with great distinction in this test, showing a strong Relative Accuracy (3.1%) in comparison to the reference method. In a following test, the Mercury Freedom System also showed strong correlation against speciated traps, a significant achievement given the lack of precedence for such testing.

Figure 3: View of the Midwestern Cement Kiln



Figure 4: Snapshot of Hg Emissions from the Midwest kiln manufacturing Clinker type H.

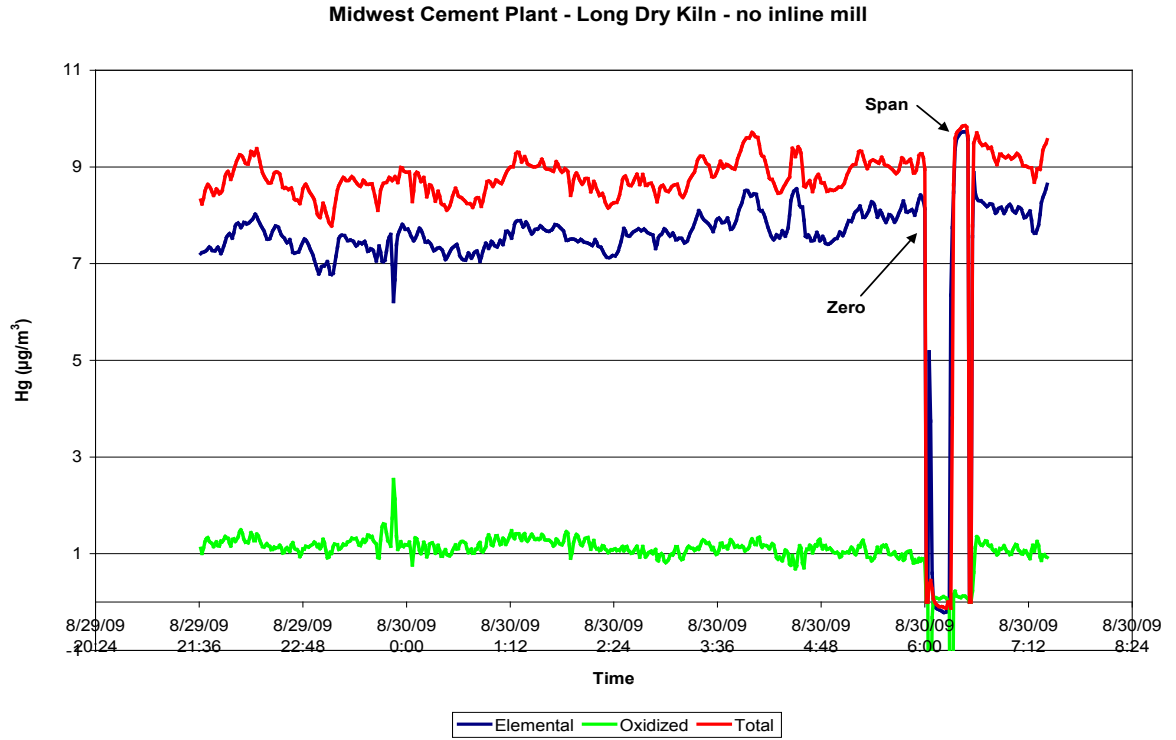


Table 1: Summary of RATA results from Midwest Cement kiln

	Test Run	Date	Start Time	End Time	Reference Method Hg $\mu\text{g}/\text{scm}$	CEM Output Hg $\mu\text{g}/\text{scm}$	(RM-CEM) Difference (d)	Difference ² (d ²)
1	1	09/22/09	0945	1015	12.1	11.7	0.35	0.13
1	2	09/22/09	1053	1123	11.2	11.4	-0.23	0.05
0	3	09/22/09	1148	1218	12.5	11.5	1.01	1.02
1	4	09/22/09	1251	1321	12.1	11.3	0.82	0.67
1	5	09/22/09	1354	1424	10.3	10.8	-0.47	0.22
1	6	09/22/09	1446	1516	11.7	11.8	-0.05	0.00
1	7	09/22/09	1545	1615	12.0	12.0	0.03	0.00
1	8	09/22/09	1638	1708	11.4	12.1	-0.73	0.53
1	9	09/22/09	1730	1800	12.1	11.9	0.19	0.03
1	10	9/23/2009	0855	0925	9.7	9.6	0.06	0.00

n	9	
t(0.025)	2.306	
Mean RM Value	11.396	RM
Mean CEM Value	11.400	CEM avg
Sum of Differences	-0.035	d
Mean Difference	-0.004	d avg
Sum of Differences ²	1.638	d ²
Standard Deviation	0.452	sd
Confidence Coefficient	0.348	CC
Relative Accuracy based on % of RM Value	3.1	%
Relative Accuracy based on difference	0.0	Mean Difference

We also tested the Mercury Freedom System in a Southeast Cement plant (shown earlier in Figure 1). The main goal of this test was to observe the changes in mercury emissions under raw mill on/off conditions.

The Southeast site easily connected the Mercury Freedom System into their plant's Allen Bradley PLC using Modbus TCP over Ethernet. They were able to log all health parameters of the system, in addition to the concentrations reported by the monitor. Two main conclusions can be drawn from the tests at this cement kiln. First, as seen in Figure 5, there was a noticeable increase in mercury concentrations, from less than $5 \mu\text{g}/\text{m}^3$ to greater than $50 \mu\text{g}/\text{m}^3$ when the raw mill was turned off. The observed concentrations return to extremely low levels when the raw mill is turned back on. Secondly, it can be seen that the presence of an in-line kiln/raw mill has a significant effect on the speciation of mercury. Unlike the Midwest plant, this Southeast kiln showed that oxidized mercury formed a greater percentage of the total mercury concentration.

Given that both kilns were being fired by similar fuels, it is likely that the in-line kiln/raw mill contributed to the change in speciation between these two studies.

Conclusion

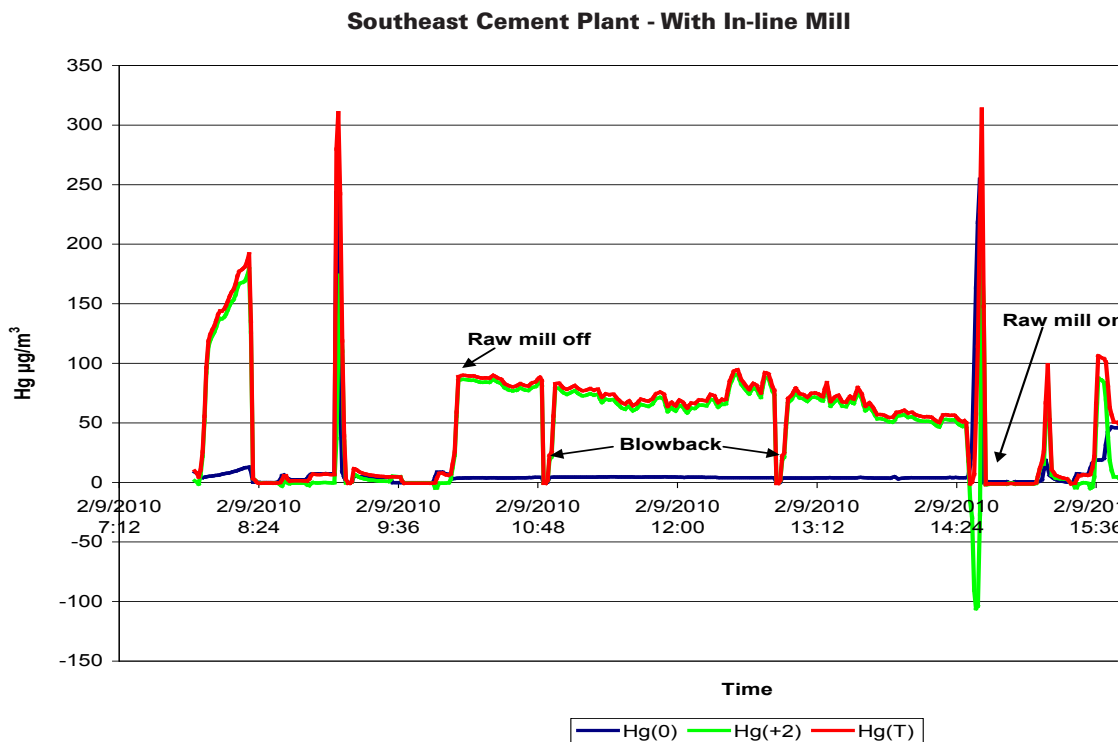
The Mercury Freedom System has been successfully installed and tested in multiple cement plants. A review of early installations makes it apparent that a cement kiln offers significantly different conditions than a coal-fired plant. Mercury levels exhibit large swings due to changes in raw mill condition and dust management procedures within a plant. When the raw mill is on, observed mercury levels can be below $1 \mu\text{g}/\text{m}^3$. Conversely, when the raw mill is turned off, observed mercury levels can be greater than $300 \mu\text{g}/\text{m}^3$. Also it is interesting to note how the portion of oxidized mercury in relation to total mercury increases significantly in the presence of an in-line kiln/raw mill.

In summary, our field tests have proven that the current design of the Mercury Freedom System is fully capable of meeting the requirements of the cement industry and we will continue to focus on enhancing the range and sensitivity of the instruments to meet more stringent needs that may arise in the future.

References:

1. "Fate of Mercury in Cement Kilns", C.L. Senior, A. F. Sarofim and E. Eddings
2. "Precliner Cement Kiln Mercury (Hg) Emissions Control", David Gossman, Gossman Consulting Inc., Vol 12, Number 2, February 2007
3. "Mercury in Coal – Abundance, Distribution and Modes of Occurrence", U.S. Geological Society
4. "Co-utilisation of coal and other fuels in cement kilns", IEA Clean Coal Centre, August 2003

Figure 5: Results from Southeast cement kiln showing effect of Raw Mill condition



In addition to this offices, Thermo Fisher Scientific maintains a network of representative organizations throughout the world.

Air Quality Instruments
27 Forge Parkway
Franklin, MA 02038

North America
+1 866 282 0430
+1 508-553-0430

thermoscientific.com/AQI

© 2011 Thermo Fisher Scientific Inc. All rights reserved.

All other trademarks are the property of Thermo Fisher Scientific Inc. and its subsidiaries.

Specifications, terms and pricing are subject to change. Not all products are available in all countries. Please consult your local sales representative for details.