Mercury Monitoring in a Cement Kiln

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Introduction

The Thermo Scientific Mercury Freedom System was originally designed to meet the requirements of the Clear Air Mercury Rule (CAMR). Several hundred Mercury Freedom Systems were installed in coal-fired power plants across the United States, passing stringent Relative Accuracy Test Audits (RATAs) under varying plant conditions. When the CAMR was vacated in 2009, many plants continued to operate the systems as required by their state or local agencies or to monitor vapor phase mercury emissions. The U.S. EPA Portland Cement Maximum Achievable Control Technology (MACT) rule requires all cement plants in the United States to continuously monitor mercury. With requirements to comply by September 9, 2015 the need to select a mercury monitoring solution is becoming increasingly urgent.

Sources of Variation in Mercury Emissions

There are multiple potential sources of mercury emissions from cement kilns. The primary source is limestone, the main constituent of the raw material. Coal, which is often used to heat the raw material, also 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 a harsh operating environment for stack monitoring, with high temperatures, moisture and dust in the flue gas. Sudden changes in the process can cause large variations in mercury emissions. The Mercury Freedom System is ideal for capturing these dramatic variations in emissions output because it uses a direct measurement method.

Figure 1: View of the Model 83i Probe at southeastern cement kiln.

Raw Mill

In-line kiln/raw mills are used to route the kiln exhaust gases to the raw mill to dry the raw meal. When the raw mill is on, a large portion of the mercury exhausted from the kiln is fed back into the raw mill. A number of studies show that a majority of mercury in particulate dust is recaptured at the raw mill, resulting in lower levels of mercury at the stack when the raw mill is on.[2] With the raw mill 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 on mercury concentrations.

Dust Management

Kiln dust is often reused to augment the raw feed and increase production of cement. This recirculation creates complexities in the measurement and control of mercury.

A fast response mercury continuous emission monitoring system (CEMS) can be used as a process indicator to trigger a plant manager to shuttle dust in the bag house to a different location, such as a finish mill. A CEMS can provide a more accurate picture of the variations in a plant's mercury emissions caused by feedback processes.

One Mercury Freedom System user 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. Figure 1 presents a view of the Mercury Freedom System probe installed in their southeastern cement kiln. By studying changes in mercury levels, the user assessed the immediate impact of process changes and adjusted their strategy of shuttling dust to a finish mill.

Use of Multiple Fuels

Most cement plants use coal to heat the cement kiln. The distribution of mercury varies heavily by the type of coal. According to the U.S. Geological Society COALQUAL database, 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]

Most cement plants use various types of coal and petroleum coke as a main fuel. Secondary fuels include various solid and liquid wastes, plastics and biomass fuels.[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 for economic reasons. The levels and species of mercury can vary greatly depending upon the nature of fuel used.

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 SO_2 scrubber, commonly used with atomic absorption systems, or an expensive carrier gas (e.g., Argon). The system provides true continuous measurement as opposed to batch collection by pre-concentration of mercury on a gold amalgamation trap.

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

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, permeation source 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.

The system extracts the sample using an inertial probe. The probe contains a fast loop with a glass-coated inertial filter that prevents particulate clogging and requires less frequent maintenance. The sample is diluted with instrument-generated zero air or nitrogen before it is transported to the Thermo Scientific Model 80i analyzer, which detects elemental mercury (Hg0), not oxidized mercury (Hg2+). 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 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. Converting the oxidized mercury at the stack minimizes the loss of mercury in the sample line, and consequently removes the need for high temperature in the umbilical line.

The Model 80i analyzer, Model 81i calibrator, Model 82i probe controller and Model 84i permeation source all reside in the rack. The diluted sample from the probe is transported through the optical chamber, where is it subjected to a high intensity UV light source. Mercury in the sample is excited by 253.7 nm wavelength light, which causes it to fluoresce; the fluorescent intensity is directly proportional to the amount of mercury in the sample. The fluorescence is measured by a photomultiplier tube (PMT). Because only mercury is excited by the chosen wavelength, interference from other pollutants is eliminated.

The Model 82i probe controller controls probe parameters such as pressure and temperature, and also controls automated blowback and secondary valve functions. When used 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 and the CEMS. It 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. The analyzer is totally self-contained, linear through all ranges and uses atomic fluorescence detection technology for fast response time and high sensitivity.

The Model 84i Permeation Source uses a permeation assembly to generate a specific and consistent concentration of mercury. The generated mercury concentration, as measured by the model 80i analyzer, is used to confirm the reliability of the model 81i calibrator output in accordance with U.S. EPA Interim Elemental Mercury Traceability Protocol requirements.

Results from Field Installations

The Mercury Freedom system has been installed in more than 20 cement locations worldwide. The first installation was a demonstration installation at a cement plant in the Midwestern U.S. (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”.

Figure 3: View of the Midwestern cement kiln

The Mercury Freedom System was installed in August 2009 and operated for six months. 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 percent of total mercury concentrations were elemental mercury in the absence of an in-line-kiln/raw mill.

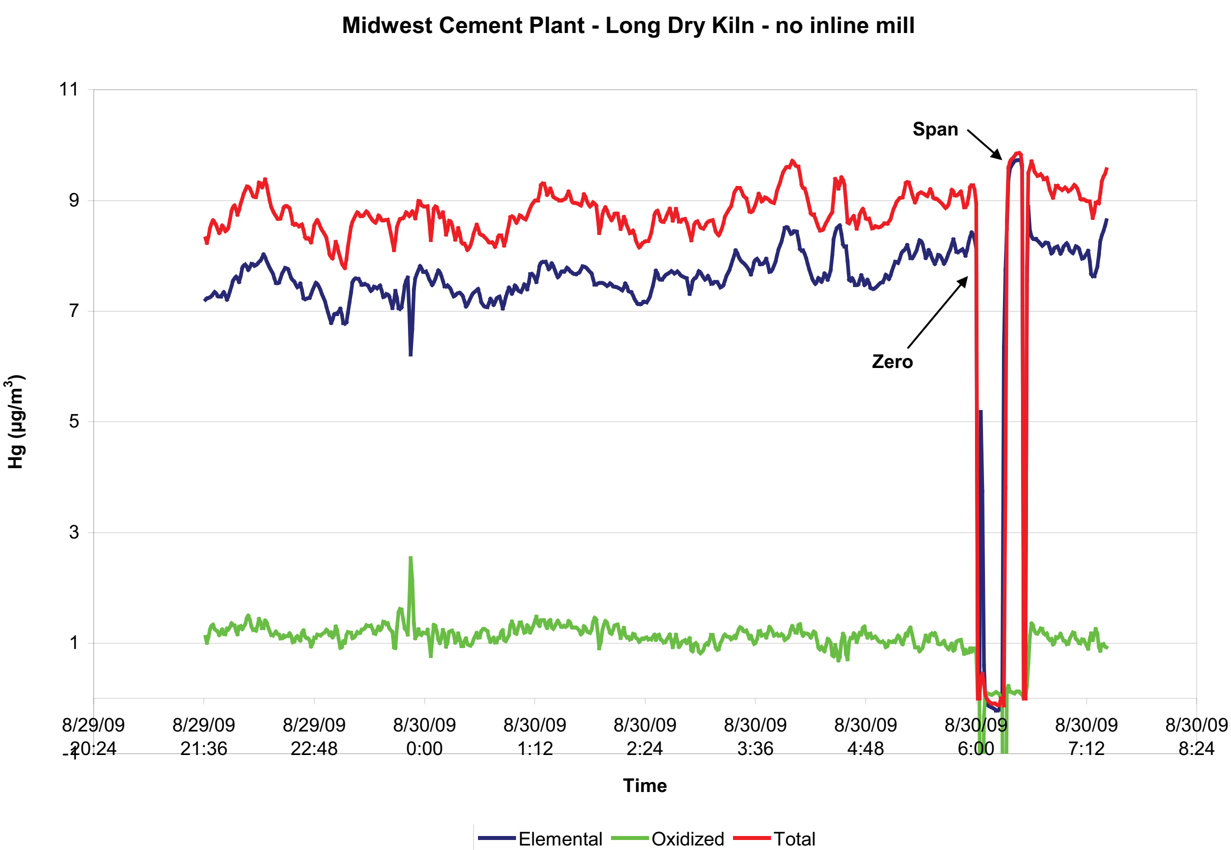

Figure 4: Snapshot of Hg emissions from the Midwestern kiln manufacturing clinker type H.

	Test Run	Date	Start Time	End Time	Reference Method Hg µg/scm	CEM Output HG µg/scm	(RM-CEM) Difference (di)	Difference^2 (di^2)
1	1	09/23/09	0945	1015	12.1	11.7	0.35	0.13
1	2	09/23/09	1053	1123	11.2	11.4	-0.23	0.05
0	3	09/23/09	1148	1218	12.5	11.5	1.01	1.02
1	4	09/23/09	1251	1321	12.1	11.3	0.82	0.67
1	5	09/23/09	1354	1424	10.3	10.8	-0.47	0.22
1	6	09/23/09	1446	1516	11.7	11.8	-0.05	0.00
1	7	09/23/09	1545	1515	12.0	12.0	0.03	0.00
1	8	09/23/09	1638	1708	11.4	12.1	-0.73	0.53
1	9	09/23/09	1730	1800	12.1	11.9	0.19	0.03
1	10	09/23/09	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	di
Mean Differences	-0.004	d avg.
Sum of Differences^2	1.638	di2
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

Table 1: Summary of RATA results from Midwestern cement kiln.

Towards the end of the study a RATA was performed (Table 1) where the output of the Mercury Freedom System was measured against the 30B reference method.

The Mercury Freedom System showed a strong Relative Accuracy (3.1%) in comparison to the reference method.

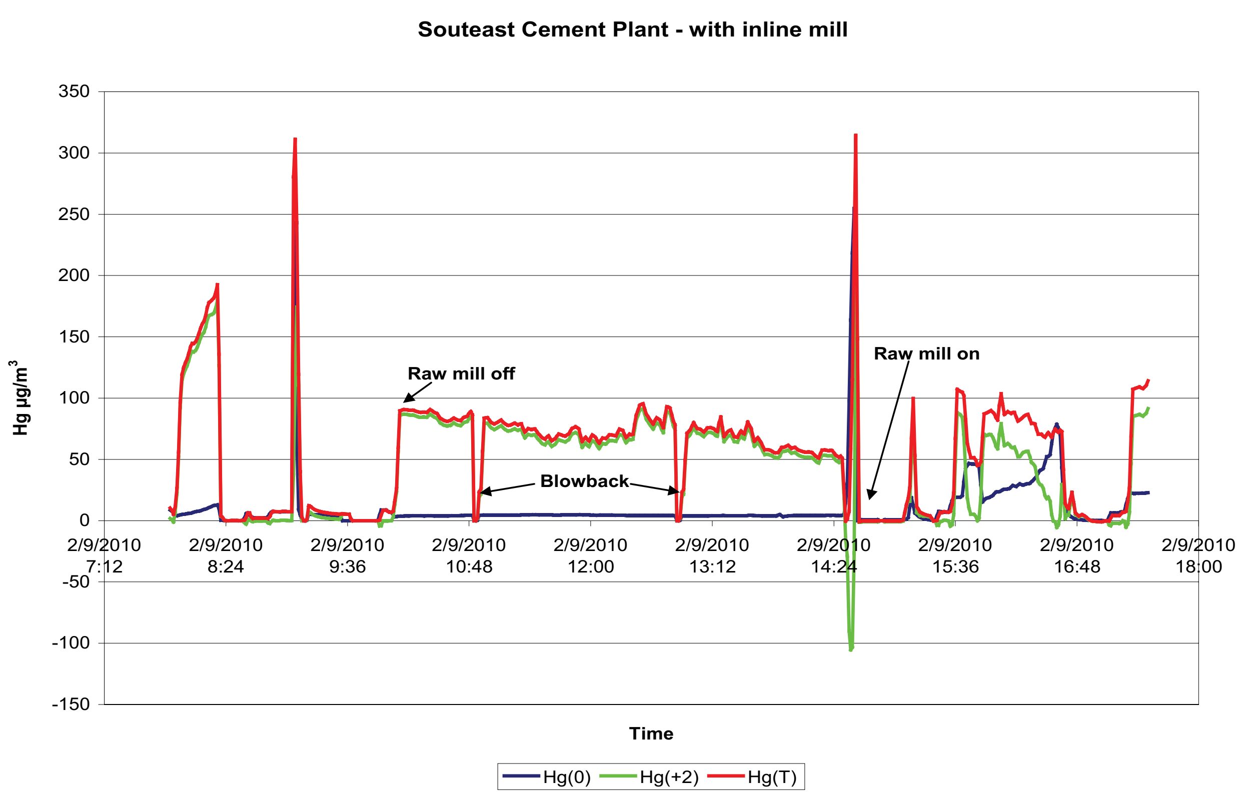

Figure 5: We also tested the Mercury Freedom System in a Southeast Cement plant (shown earlier in Figure 1). The main goal of this test was to observe the changes in mercury emissions under raw mill on/off conditions. It can be seen that the presence of an in-line kiln/raw mill has a significant effect on the speciation of mercury.

Conclusion

The Mercury Freedom System has been successfully tested and installed in multiple cement plants. 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 μg/m^3 — when the raw mill is off, mercury levels can excede 300 μg/m^3, as shown in Figure 5. 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 regulatory monitoring requirements of the cement industry. We will continue to focus on enhancing the range and sensitivity of the instruments to meet more stringent needs.

References:

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