CEMS Challenges for Cement NESHAP

David M. Rib, Environmental Manager
Keith Shannon, Environmental Specialist
Mitsubishi Cement Corporation

The cement industry has been required to take Continuous Emission Monitoring Systems (CEMS) to a whole new level with the new NESHAP regulations that went into effect in September 2015. Monitors for mercury and hydrochloric acid (HCl) each require a separate rack of laboratory-grade equipment. Particulate monitoring has gone from daily eyeball observation to continuous parametric monitoring. Some of the new limits are in units of mass per unit of production, requiring much more plant data to be recorded into the CEMS DAS. Mitsubishi Cement Corporation (MCC) has implemented these new requirements despite unique additional challenges.

"In the beginning" there was an analyzer for NOx and for O_2 recorded on strip charts. In the 1980s and 1990s you might add analyzers for CO and SOx, but you still had a strip chart, because that was "primary data". Then add a computerized data reporting system to report hourly averages and annual inventories, but you still needed those strip charts in case of a data audit. Initially not all cement plants had CEMS; that was a requirement of some State and local Air Districts.

In 1999 EPA implemented the first cement NESHAP (National Emission Standards for Hazardous Air Pollutants), otherwise known as PC MACT (Portland Cement Maximum Achievable Control Technology) This first cement NESHAP had two emission monitoring areas: exhaust temperature for control of dioxin/furan (D/F) formation, and visible emissions evaluations for dust. These added to reporting requirements, but did not necessarily add to the complexity of a DAS (Data Acquisition System). Exhaust temperatures for D/F were recorded in 3-hour averages, but only exceedances were required to be reported. Visible emissions of the main exhaust could be done by certified observers or by certified COMS (Continuous Opacity Monitoring System), but the many dust emission points from both dust collectors and fugitive points required periodic evaluation by certified eyes.

California added Greenhouse Gas (GHG) inventory reporting in 2009, coming from the AB32 "Global Warming Solutions Act of 2006". California Air Resources Board (CARB) initially allowed calculation of CO_2 emissions based on fuel characteristics. But EPA added GHG inventory reporting in 2010 and required direct measurement of CO_2. So at a minimum, that required adding an analyzer for CO_2 and an exhaust flowrate monitor. The CARB requirements also came with a rigorous auditing requirement by a CARB-certified third party "verifier". This verification requires the DAS to have specific transparency and reporting features.

Now EPA has implemented the new cement NESHAP as of September 2015. This imposed new limits on mercury, chlorides, hydrocarbons and much tighter particulate limits. This required a big jump in the complexity of the CEMS and DAS at each cement plant. The discussions that follow outline the requirements and challenges for our cement plant. The details of the regulations and monitoring equipment would fill many large volumes, so only the basics are addressed to explain what MCC has done to meet the compliance obligations.

<u>Our Special Challenge</u>

MCC had one of the last multi-vent exhaust systems in the country; each of the dust collector's 36 compartments were individually vented to atmosphere. The CEMS had two sample lines, from one vent on the north side and one vent on the south side of the dust collector, drawing sample from each on alternating hours. This worked fine for NOx, SOx and CO, but the new NESHAP monitoring requirements are not so obviously uniform for all the individual vents. The monitors for mercury and hydrochloric acid (HCl), as discussed below, each require their own probe and sample line with no provision for multiple samples, and are prohibitively expensive for multiple units. Both mercury and HCl at low concentrations are very sensitive to changes in temperature and flow. A particulate monitor in one compartment vent can only indicate the condition of the filter bags in that compartment.

The NESHAP preamble promised availability of an "Alternate Monitoring Plan" (AMP) through application for EPA approval. So MCC embarked on a 3-year testing program to gather data on the variations in emissions across the 36 vents. The proposal to EPA showed that although there were variations, the average emission measurements were insignificantly different from the monitored vents. EPA had many issues with the proposal, but counter-offered that at least half of the vents be monitored for all parameters. Given that 18 sets of all monitoring equipment is impractical and prohibitively expensive to purchase, certify and maintain, this amounted to a denial of the AMP.

So MCC installed a new exhaust stack with all the dust collector compartments ducted together. All the CEMS analyzers were moved to a new enclosure and connected to the stack with new sample lines. This also required a conversion of the DAS software (also discussed below). The entire switch was accomplished during a kiln maintenance outage, with almost no CEMS data loss. Certification testing and reporting the new compliance requirements were also challenging, with some tests never before attempted.

MCC was prepared to meet all the NESHAP emission limits for the September 2015 compliance date, except for the conversion to the new exhaust stack. EPA allowed extension to the cement industry because of remaining problems with low concentration HCl calibration gas and mercury calibrator units for higher mercury levels. MCC was not impacted by either of those issues, but obtained an extension for installation of the new single stack and conversion to standard EPA monitoring methods.

The MCC clinker cooler also exhausted through a multi-compartment, multi-vent dust collector. Those vents were ducted together into two new vent stacks, each with a particulate monitor. Previously, there had only been visual opacity monitoring of that exhaust, so the new monitors required new routing to get the data to the CEMS DAS.

Mercury monitoring

Mercury monitors had been done mostly by sorbent tubes in the past. Sorbent tubes is an option for the continuous monitoring, requiring a semi-automated system to collect sorbents periodically and do the de-sorption analysis and back calculate to an emission rate. The CEMS analyzers are just barely "out of the laboratory" and are more complex than most CEMS. The detector sees only elemental mercury, so a converter is necessary to change ionic mercury to elemental. Calibration gas is impossible at the extremely low concentrations, so a calibration generator vaporizes the correct amount of mercury. The calibrator is certified by a primary source every two years. In between certification, it is checked weekly by a second calibrator, called a permeation source (permeator). When the calibrator is sent out for its certification, either a loaner calibrator is needed, or a second calibrator must be purchased. MCC has a Mercury CEMS from Thermo Fisher Scientific (Thermo), with the converter probe, two calibrators and a permeater.

The analyzer output is in µg/m^3 (micro grams per normal cubic meter), which translate to about 0.1 ppb, so the concentrations are extremely low. The EPA limit for mercury emissions is in units of pounds of mercury per million tons for cement clinker production, on a 30-day rolling average. So the DAS must get a signal from the plant data system for clinker production and incorporate that into the calculations. That could be from a weigh feeder that actually handles clinker or the kiln feed. MCC uses the kiln weigh-feeder (calibrated quarterly) and a conversion factor (typical clinker/feed ratio) for clinker production. That is collected by the DAS as a “raw clinker” amount for each hour. An adjustment factor is added monthly based on a physical inventory of clinker production.

NESHAP does not specify a substitution methodology for any missing mercury data, but instead specifies calculation of the 30-day averages using each hour of valid data. That is different than other CEMS where EPA procedures in Part 75 specify substitution to fill in missing data.

It is impractical to have a full back-up to the mercury CEMS. Each component is very expensive: the converter probe, sample line, analyzer, calibrator and permeater. One option is to have a complete sorbent collection system in place, and send those out for analysis; which is very expensive and introduces another layer of equipment and data collection challenges. MCC has instead stocks spares of all the key components. A second calibrator unit was purchased to address the periods when the primary unit is away for re-certification.

Hydrochloric Acid monitoring

The NESHAP requirement is to limit chloride emissions in the form of hydrochloric acid (HCl) to 3 ppm, corrected to 7% O_2. That is difficult to monitor because HCl is so easily lost into any moisture condensation, so the sample must be maintained hot. There are wet chemistry methods that require long sampling times, so it can’t be continuous. The only detection with potential for accuracy is FTIR (Fourier Transform Infra-Red), which is another “barely out of the lab” technology. Calibration gases are only recently available with some stability. Annual certification testing requires accuracy compared to both a reference analyzer and to spiked calibration gases.

EPA NESHAP offers a few options for HCl monitoring. An FTIR may measure HCl directly, and may be certified annually with one of three methods (PS-15, PS-18, or CPMS criteria). Sulfur Oxides may be monitored as a surrogate, with a SOx limit set annually to correspond to the HCl limit conditions. Or parameters of a scrubbing system (wet or dry) may be established periodically. MCC uses hydrated lime injection to limit HCl, and reports that injection rate through the CEMS DAS to show compliance.

It is impractical to have a backup FTIR for HCl, with the expensive probe, sample line and analyzer. MCC has not yet succeeded in certification of the FTIR for HCl (the quest continues). When that is accomplished, the lime injection rate with annual re-certification will be the backup for CEMS FTIR monitoring.

Total Hydrocarbons

The EPA NESHAP has a limit of 24 ppm for Total Hydrocarbons (THC), measured in hot sample gas. MCC already had a Thermo THC analyzer, using gas from the cooled CEMS sample. This was replaced with the Thermo high-temperature THC analyzer and the gas is taken off the sample line before the CEMS gas chiller. MCC bought a second, identical THC analyzer as a backup.

Particulate monitoring

As previously noted, this used to be either an opacity monitor or daily visual readings. EPA's new NESHAP requires a continuous parametric monitoring sytem (CPMS) with annual comparison to Method 5 testing. The limit is 0.07 pounds of filterable particulate per ton of clinker produced. An annual compliance test measures emissions compared directly to the limit, and also the annual comparison establishes what monitor output corresponds to the emission limit. The DAS only needs to report the monitor output in milliamps or similar units. Some kiln exhaust particulate concentrations are so far below the limit it requires spiking in order to establish a reasonable correlation. MCC purchased a feeder device from Tecweigh to inject particulate into the exhaust during testing. The result is a CPMS correlation that establishes a compliance limit that is well above the typical output of the monitor.

This particulate monitoring is required for both the main kiln exhaust and for the clinker cooler exhaust. The clinker cooler particulate limit is the same as for the main kiln exhaust, 0.07 lb particulate per ton of clinker, with the same annual testing. The three monitors, one for the main exhaust and two for the clinker cooler, are all the same light-scattering model from FilterSense. A spare monitor is kept in stock as a backup.

Standard CEMS

Standard CEMS is a relative term. What began as just NOx and O_2 now includes CO, CO_2, SOx and exhaust flow. MCC has Thermo analyzers for NOx, SOx, CO, CO_2. The FTIR has capability to be the backup for all of these. The O_2 analyzer is an AMI model and the moisture monitor is MAC. Moisture may be a default value set during annual testing for each operating mode (raw mill on and off). Exhaust flow is monitored with two Kurz detectors, a primary and a backup. The NOx limit is in units of pounds NO_2 per ton of clinker produced, on a rolling 30-day average, so the DAS needs flow and clinker data.

Data Acquisition System (DAS)

The DAS (a.k.a. DAHS Data Acquisition & Handling System) had to evolve through the NESHAP compliance process as well. Way back "in the beginning" a few wires carried the signals from a few analyzers directly to the DAS computer. Now there are many methods and pathways for data via multiple PLCS, Modbus and servers, and the DAS reads everything from single mA values to computer software "hand-shakes". Some of these signals come directly from analyzers to the DAS. Others go through PLCs and servers. The plant operational data is sent through servers from the plants own data system.

Only a few years ago, MCC had a custom DAS from an individual programmer. California's Greenhouse Gas reporting regulations necessitated an upgrade to an auditable modern DAS, and MCC contracted with Custom Instrumentation Services Corporation (CiSCO). The original multi-vent exhaust had two CEMS sample points, so CiSCO customized the DAS to fit that situation. All that changed with the new single stack, back to a more typical monitoring. But even so, there were many inputs for the DAS to handle:

- All of the analyzers' measurements, status indication, calibrations
- Flow monitors measurements and daily function checks
- Particulate CPMS outputs
- Clinker production rate
- HCl emission control system lime injection rate
- Process status per NESHAP definition and per GHG definition

There are also many reporting requirements that must be supported with DAS reports:

- Daily calibration checks for all analyzers and monitors
- Weekly converter checks on the mercury monitor
- Quarterly cylinder gas audits for analyzers
- Annual RATA tests. Need 1-minute data during each run.
- Annual particulate CPMS correlation. Need 1-minute data during each run
- Adjustment of concentration values to 7% O_2
- Substitutions for invalid data per Part 75 procedures for NOx, CO2, CO, SOx
- Calculation and periodic reports for criteria pollutants, CO_2 and NESHAP

<u>Challenges Remain</u>

There are a few more issues yet to be resolved for NESHAP compliance. The HCl certification procedure PS-18 was only recently finalized by EPA. MCC has attempted this procedure multiple times and has yet to succeed. There are many detailed requirements, but it mainly is just very difficult to match a reference method at 3 ppm of HCl. EPA's Electronic Reporting Tool (ERT) has been difficult to use and the type of reports to be submitted electronically has been evolving. At this point, most NESHAP reports are uploaded as attached files. Both source testing companies and DAS reports will need to adapt to these new EPA reporting requirements. Achieving NESHAP compliance for the first set of demonstration reports has been quite a journey, and there may yet be more issues encountered in keeping in compliance for longer term.