NATIONAL LIME ASSOCIATION

Protocol to Characterize Mercury Emissions from Lime Manufacturing

Solids Sampling and Stack Testing

Emission Monitoring Inc.

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INTRODUCTION

The National Lime Association sponsored the production of this document and associated Excel workbook to characterize mercury emissions from lime production activities. Contributions to this document were also obtained from Western Lime Corporation and Platt Environmental Services.

This protocol consists of two phases: solids sampling and analyses, and stack emission testing from lime kilns equipped with a baghouse or ESP. Depending on the outcome of the solids analyses for Hg content, stack sampling may be warranted to further determine the fate of Hg in the lime producing facility. The criteria for conducting a stack test is whether estimated emissions exceed 15 lb Hg/MM ton lime, which is the emission factor commonly used by the lime industry to estimate emissions for TRI reporting.

1. Solids Collection

Ideally, solids sampling and analyses should be conducted several weeks before any contemplated stack testing so that the stack testers can determine the suitable concentration for the Method 30B spiked traps.

Lime plant personnel should collect, process, and store samples for four weeks, excluding weekends. However, samples should not be obtained/retained when the kiln system is not operating or where emissions are not representative due to startup, shut down or malfunction. For each solids sample described below, label the container as to date acquired, company name (if analyzed off-site), facility location, kiln ID and contents.

Daily Samples

Limestone. Collect representative samples of limestone from the conveyor belt feeding the kilns each weekday. Reduce raw samples to ¼" using a hammer mill (small mill with 3/8" bar gap). Samples may need to be run through mill repeatedly to achieve ¼ inch size.

Lime Kiln Dust. Collect representative samples of LKD from each baghouse and ESP (and other dry APCDs, especially those where a temperature drop is expected to occur). Take the sample from the same location (e.g., where it's blowing into the bin, from the same port on the baghouse, etc.). Pick a spot where the dust is well mixed.

Fuel. Collect representative fuel samples. Determine a sampling location that will provide consistent samples of the fuel being fed to the kiln during the day that the sample represents. If samples are collected from the coal belt, be sure to collect a sample from the full width of the belt. Reduce the sample to ¼" diameter using hammer mill as described above. Samples may need to be run through the mill repeatedly to achieve the proper size.

Lime (Optional). If the estimated Hg concentration is less than 2 ppb by weight, this step may be of limited value because of the product's negligible contribution to the Hg retained by the kiln system. However, if the company wants to confirm that Hg levels are indeed negligible, collect representative samples from the belt after the cooler, and reduce them to ¼ inch as described above.

Weekly Composite

"Cone and quarter" (Section 9 of ASTM C-50) daily samples and place an identical amount from each daily sample into the container. A total of 1 lb. minimum for the composite sample will be needed for additional analyses. Repeat for each day during the week when samples are acquired. Mix thoroughly.

2. Solids Preparation & Handling

On-site Grinding & Drying of Solid Samples. The stone, lime, and fuel samples should be further processed by grinding each type of sample in a coffee grinder, then sieving the sample to 50 mesh. After sieving, dry the samples in an oven for two hours at a temperature of 180^{o}F, further refine samples in a desiccator for a minimum of two hours. Weigh samples (approximately 1.0g for stone, 0.5g for lime and LKD, and 0.2g for fuel).

A minimum of three samples of each daily and composite sample should be prepared.

Sequence of Solids Grinding. Grind the stone feed samples (and lime, if part of the study scope) before grinding the fuel. Segregate the stone feed (and lime) from the LKD and fuel because LKD and fuel typically have a much higher Hg content than the stone/lime. After each type of sample is ground, the grinding equipment should be cleaned with a paint brush and Kim Wipes.

Sending Solids Off-Site for Grinding, Drying & Analyses. If the samples are to be analyzed off-site for mercury, they should be sent in approximately 100 ml glass or Nalgene bottles with the lid sealed tightly. Ship samples in separate containers to avoid contamination. The lab should grind and dry the samples as described above.

3. Solids Analysis Preceding the Stack Test

Mercury

Identify the most complete and representative daily and weekly composite solid sample sets for two weeks. For each sample type, analyze them using an Ohio Lumex analyzer[1]:

Analyze the five daily samples in duplicate for the selected week (i.e., the first week or most representative operating week) and each of the weekly composite samples for the four week period.[2] This will total 9 samples for each of the sample types or a total of 27 samples (36 samples if lime product is analyzed.). Input results into appropriate sheets of the Excel workbook provided by NLA.

Calculate the mean of each set of five daily samples and the mean of the weekly composite samples. Input results into Excel workbook.

Compare the results of the composite samples to the daily samples and decide whether additional analyses are required. The results should be within 10% of the mean or 0.2 ng/g. Input results into Excel workbook.

Calculate the total Hg inputs for feed and fuel and calculate LKD retention using the stack test considerations spreadsheet in the Excel workbook.

Determine whether stack testing is warranted by examining potential to emit. If potential to emit is greater than 15 lb/ton lime, then complete the dust retention of Hg section of the spreadsheet[3] If the potential to emit considering LKD retention is still greater than 15 lb/ton lime, then stack testing is likely warranted.

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[1] NLA has arranged a special price of $50/sample for NLA members who send their samples off-site for analysis, provided certain procedures are followed.

[2] For each daily sample and weekly composite, two samples should be analyzed. The average of the two samples should be treated as the Hg concentration for that sample and date unless the data between the first two samples varies by greater than 10% (or +/- 0.2 ng/g if Hg concentration is below 1ppb). If so, a third sample should be analyzed and data evaluated to determine if more samples need to be prepped and analyzed.

[3] This calculation calls for each kiln's dust generation rate, which should be available from the company's GHG report.

Chlorine, Unburned Carbon, and Sulfur[4]

For each kiln to be tested, after setting aside a sufficient amount of each solids sample to conduct the mercury testing described above, arrange for the remainder of the weekly composite samples[5] to be analyzed prior to the test as follows:

	% Moisture	% Sulfur	Chlorine ppm	% Unburned Carbon
Limestone	ASTM D3302	ASTM C25	ASTM D6721	NA
LKD		NA	NA	ASTM D6316*
Coal/coke		ASTM D4239	ASTM D6721	NA

* Determination of Total, Combustible and Carbonate Carbon in Solid Residues from Coal and Coke

4. Stack Testing

If the results from the solid phase testing reveal that stack testing is warranted (i.e., estimated emissions exceed15 lb Hg/MM ton lime), plant personnel should coordinate with testers in advance to ensure proper preparations are in place. These include inspection of ladders and platforms and stack structure to ensure safe access and safe working conditions. Additional considerations are: removal of port closures (or replacement), provision of adequate electrical power, and assurance that testers conform with plant/company safety requirements.

The following tests should be performed using methods from 40 CFR Part 60, Appendix A:

1. Method 1 and Method 2 –Stack gas flow rate
2. Method 3, or 3A – Stack gas molecular weight
3. Method 4, or Alternate 4 – Stack gas moisture content
4. Method 30B – Total mercury using Ohio Lumex total Hg traps. Duplicate "paired" samples, and spike recovery runs, as specified by method.
5. Modified Method 30B -- Elemental and Oxidized Hg using Ohio Lumex speciated Hg traps. Single traps for each run.

[4] Typical costs are: $65/sample for chlorine, $125/sample for unburned carbon, and $45/sample for sulfur, along with a prep fee of $60/sample.

[5] Whether all weekly composite samples need to be analyzed is a matter of judgment. For example, if the Hg content of each weekly composite of LKD is negligible, then probably all four weekly composites need not be tested for unburned carbon. Contact Arline Seeger at aseeger@lime.org or 703 243-5488 if you'd like to discuss your plant-specific Hg results and number of weekly composite samples that should be tested for sulfur, chlorine and unburned carbon.

Three test runs of one-hour duration should ordinarily be performed, but additional runs should be conducted if substantial variation in the three runs is observed. As a guideline, results should be within 20% of the mean or +/-0.2 ug/m^3 absolute difference.

Paired Method 30B samples and single speciated Hg sample traps are to be acquired simultaneously. Method 30B for total Hg is to be conducted as per the Method using paired traps and all QA/QC activities shall be performed and documented. Method 30B, modified for speciated traps, is to be conducted simultaneously using specially prepared traps from the Ohio Lumex Company. Therefore, three runs are to be conducted with three traps being operated simultaneously; two total Hg and one speciated Hg. Volumetric flow rates are to be performed after each Hg sample run.

Trap temperature for the speciated mercury train must be maintained at 212^{o}F throughout testing in order for oxidized Hg to be collected on the trap. For stack temperature in excess of 212^{o}F, an air cooled probe must be utilized in order to cool the traps to the proper temperature. For stacks cooler than 212^{o}F, the Hg probe must be heated to maintain trap temperature.

Results are to be reported as shown below. In addition, QA results are to be reported, including all Hg calibration data, and spike recoveries (for standard 30B traps only).

STACK TESTING MATRIX

Test Analyte	Test Method	Reporting Units
Effluent Flow Rate	1-4	acfm, dscfm O_2, CO_2, and Moisture
Hg^T	Method 30B	Hg^T µg/m^{3*}, lb/hr, lb Hg/ton Lime
Hg^0, Hg^{+2}, Hg^T	Modified M. 30B	Hg^T µg/$m^{3,}$ lb/hr, lb Hg/ton Lime Hg^0 µg/m^3, lb/hr, lb Hg/ton Lime Hg^{+2} µg/m^3, lb/hr, lb Hg/ton Lime

* Concentration results (ug/m^3) are to be corrected to 7% O_2.

5. Plant Operational Data & Hg Analysis of Solids Obtained on the Stack Test Day

Plant Operational Data. The plant should determine and record kiln stone feed rate (and calcination factor), fuel(s) feed rates and LKD generation rates, and baghouse/ESP inlet temperature. Hours of kiln operation for each day should also be noted. Feed rates may be estimated based on lime production measurements and reliable feed/product ratios or vice versa and other factors can be used to estimate LKD generation. Unusual conditions or circumstances should be noted, as well as salient APCD parameters (e.g., air-to-cloth ratio, bag type), and other

system features that may affect Hg in the system (e.g., dampers or other temperature reduction measures preceding the inlet to the APCD).

Solids Sampling & Hg Analysis. The plant should collect and process daily samples of limestone, (lime), LKD, and fuel during each day of the test in the same locations as the pre-test samples were acquired. A minimum of three samples of each solid should be prepared.

Two samples of each solid (stone, LKD and fuel) should be analyzed for mercury during the stack testing day while on-site with the Ohio Lumex analyzer. If the data between the first two samples varies by greater than 10% of the mean (or +/- 0.2 ng/g if Hg concentration is below 1 ppb), a third sample should be analyzed and the data evaluated to determine if more samples need to be prepped and analyzed.

6. Chlorine, Unburned Carbon & Sulfur Analysis of Solids Obtained on Stack Test Day

After setting aside a sufficient amount of each solids sample to conduct the mercury testing described above, arrange for the remainder of each sample to be analyzed as follows:

	% Moisture	% Sulfur	Chlorine ppm	% Unburned Carbon
Limestone	ASTM D3302	ASTM C25	ASTM D6721	NA
LKD		NA	NA	ASTM D6316*
Coal/coke		ASTM D4239	ASTM D6721	NA

* Determination of Total, Combustible and Carbonate Carbon in Solid Residues from Coal and Coke

7. Mercury System Balance

While the stack testers are on-site, calculate total Hg inputs for feed and fuel, calculate LKD (and lime) Hg retention. Use the stack test considerations spreadsheet in the workbook for this exercise. Compare with mercury stack emissions during source test. Investigate and resolve implausible results.