Field Sampling Procedure for Sampling Cement Kiln Dust and Clinker from Portland Cement Plants Burning Hazardous Waste

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On December 2, 1992 Rachel's Hazardous Waste News No. 314 printed headlines entitled "Cement and Kiln Dust Contain Dioxins" This publication was the result of a leak of a briefing document dated Oct. 8, 1992 from EPA to the Director of Solid Waste and it indicated that dioxins and furans were detected in all of the fifteen samples of clinker and all of the six samples of kiln dust from cement kilns burning hazardous waste. These particular allegations were of significant concern to the cement industry and efforts were immediately undertaken to determine the validity of the statements and the scientific acceptability of the reported data.

In investigation of the situation, there was some support for the idea that dioxins may be generated in the exhaust section of the kiln system where the air pollution control devices (APCD) are located due to the potential for naturally occurring organics forming in the raw material to react when temperatures range between 450°F and 750°F. However, it was with great disbelief that the industry viewed the contention that dioxins were coming out of the burning end of the kiln where temperatures are typically in excess of 2500°F; temperatures at which no organics would be present that could possibly form dioxin compounds. A preliminary review of the data indicated that dioxin formation on the surface of cement kiln dust particles (CKD) may be a possibility with significant numbers of TCDD congeners being identified in a few dust samples. A review of the data for the clinker quickly indicated that the TCDD hits in the analytical procedures were at or below the detection levels and were also subsequently found in the blanks or could be found in the blanks at levels that were being reported in the

Rachel's Waste News article.

It became apparent to the industry that further sampling needed to be done and it would not be prudent to wait for the United States Environmental Protection Agency (USEPA) to perform another round of samples. The industry then proceeded to develop their own sampling procedure to improve upon the procedure used by USEPA. A grab sample was used to perform the analyses that were completed during 1992 by EPA. Data from the cement industry indicated that grab sampling may not be adequate for obtaining a representative sample while performing organic analyses on CKD.

The Boiler and Industrial Furnace (BIF) Rule, which became effective August 21, 1991, mandated that hazardous waste burning kilns must sample their CKD and determine if there was any significant difference between their CKD while burning vs. not burning hazardous waste. The levels of contaminants outlined in 40 CFR 266 Appendix VII had concentration limits that were extremely low and, in some cases, actually below achievable detection limits. The only alternative for making the Bevill determination as required by BIF was to document whether or not that particular compound was detected in the CKD at the minimum achievable detection level. While trying to analyze CKD at or below the minimum detection level it became quite apparent in the review of data from the four plants that false positives were occurring. This occurrence was due to either sample contamination or laboratory cross-contamination while the analyses were being performed. The data was then submitted for quantitative analysis, qualitative analysis and statistical evaluations to determine an appropriate sampling procedure and also to determine what detection levels would be applicable for avoiding false positives. The results indicated that the current sampling procedures (grab samples with limited quality control in the laboratory), in addition to the minimum detection level-based decision, yielded the possibility of approximately 70% false positives.

The results of the statistical evaluation indicated that the required CKD determination could be performed with an upper tolerance level (UTL) raised by a factor of 2 above the minimum detection level. Using this procedure, the probability of a false positive would be minimized and revised sampling procedures would allow for an increase in the precision and accuracy of the results. The sampling procedure was expanded to develop a composite sample of 25 individual subsamples instead of the single grab sample that was typically performed by taking 25 individual grab samples that were

obtained 8 hours apart, a better representation of the time period during which the kiln was operating was developed with a sampling procedure that was indicative of a six-month time period. During the course of that 4 1/2 day sampling period, procedures were utilized that would provide a high degree of accuracy and precision associated with the samples taken and was much more representative than an individual grab sample.

Subsequent to the statistical evaluation, the following sampling protocol was developed and is currently in use in the U.S. by the cement industry for performing the dioxin/furan analysis on CKD and clinker.

SAMPLING PLAN FOR CEMENT KILN DUST - The sampling method for cement kiln dust must provide accuracy and precision of the measured parameters such that concentrations under varying operating conditions can be meaningfully compared.

1.0 SAMPLING DESCRIPTION - Duplicate composite samples will be obtained from the cement kiln dust sampling point. The sampling point should be located prior to the dust arriving in a storage or retention area. Duplicate composite samples are two samples, each composed of the same number of paired subsamples. The cement kiln dust will be sampled during twenty-five (25) consecutive shifts (or hours). At the sample point, two grabs will be made, one for composite sample #1 and the other for composite sample #2. This procedure will result in two composite samples comprised of twenty-five (25) subsamples gathered from twenty-five (25) consecutive sampling periods (every 4 hours or every hour). Compositing will be performed at the laboratory. If a sampling time is missed, sampling will extend into the twenty-sixth (26th) shift (or hour) in order to obtain the twenty-five (25 necessary subsamples. A trip blank, obtained from the laboratory, and a field blank, collected in the field, will be analyzed as quality control measures. the blanks will be collected during the final sampling period.

2.0 SAMPLING EQUIPMENT - The following materials will be required for the sampling programs: a stainless steel, precleaned "scoop" for catching cement kiln dust; two (2) labeled, clean receptacles (glass jars) with lids to transport subsamples from cement kiln dust sampling point to compositing canisters; waterproof, rubproof marker for labeling; one (1) labeled, closed trip blank and one (1) labeled field blank containing XAD resin obtained from the laboratory to be used for quality control. The stainless steel scoop will be used to obtain the two grab subsamples at the sample point. Each

sampling jar should be labeled independently and sequentially.

3.0 SAMPLING PROCEDURE - Samples should be taken at approximately the same time during each sampling period so that there is a four hour (± 1.0 hour) (or sixty-minute) interval between samples. the trip blank should be transported to the sampling location unopened. They should be retained in the central location where all samples will be protected until shipping. At the appropriate time, the sampler(s) will proceed to the sample point and will sample according to the following protocol: 1. don NEW surgical gloves; 2. uncover sample collection jars; 3. remove sampling "scoop" form #1 storage; 4. fill the "scoop" with cement kiln dust and place it in first jar; 5. wait approximately 30 seconds; 6. fill sampling "scoop" again with cement kiln dust and place it in second jar; 7. cover both jars; and 8. wash "scoop" again with DI water and return it to its storage area. During the final sampling period, a field blank will be collected according to the following procedure: 9. don NEW surgical gloves; 10. uncover sample collection jars including blank; 11. allow filed blank to remain open while steps 4, 5 and 6 are repeated; 12. cover sample collection jars; and 13. return samples and field blank to compositing location.

4.0 COMPOSITING THE SUBSAMPLES - Subsample receptacles (jars) will be provided by the laboratory. The glass jars containing samples will be forwarded to the laboratory where composite samples will be prepared. The 25 sub-samples will be combined at the laboratory to produce each composite.

5.0 SPLITTING SAMPLES FOR ANALYSIS (OPTIONAL) - Each sub-sample should be split after being homogenized prior to sending out for analysis. Each split sample should be labeled. The split samples should be retained on-site until further notice. The trip blank and field blank samples should also be shipped with the samples for identical analyses.

6.0 RECORDKEEPING - Documentation of problems encountered or any deviation from approved procedures and operating conditions should be made throughout the sampling period by operations management at the facility.

Environmental Research Foundation. Cement and kiln dust contain dioxins. Rachel's Hazardous Waste News. Washington, D.C. December 2, 1992;314.
Croom, J. Organic compound concentrations and the method detection limit for cement kiln dust. 1993.