DIOXIN EMISSIONS AND CEMENT KILN OPERATIONS

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INTRODUCTION

A series of dioxin emissions tests were conducted during the week of December 5, 1994 under a variety of operating conditions. In addition to stack gas sampling, process samples including the slurry and CKD were collected for analysis. A brief description of each day's testing is provided below.

Test Day One

Test Day One was conducted under "normal" kiln operating conditions. The fuels were coal, liquid waste fuel and solid waste fuel. The gas temperature in the stack was approximately 520°F. Test Day One represented typical operations of the kiln near the end of its cycle. A scheduled maintenance period was to follow.

Test Day Two

During Test Day Two, activated carbon was injected at a rate of approximately 100 pounds per hour in the ductwork between the kiln exit and the ESP. The feedrate of the activated carbon was determined based upon information provided by the USEPA on carbon injection rates at other types of combustors. The fuels were coal, liquid waste fuel and solid waste fuel. The gas temperature in the stack was approximately 520°F.

Test Day Three

For Test Day Three, atomized water was injected at a rate of approximately 30 gallons per minute into the back of the kiln to cool the exit gas stream temperature. The fuels were coal, liquid waste fuel and solid waste fuel. The gas temperature in the stack was approximately 480°F.

Test Day Four

During Test Day Four, atomized water was again injected into the kiln but, in addition, the insufflation dust rate was set at zero. Normal insufflation dust rates range from about six to ten tons per hour. Fuels were coal, liquid waste fuel and solid waste fuel. The gas temperature in the stack was approximately 460°F.

Test Day Five
For Test Day Five, powdered sulfur was added to the raw mill and ground into the slurry. Typical SO_x emissions are less than 20 ppm. For Test Day Five, SO_x emissions were increased to above 300 ppm. The fuels were coal, liquid waste fuel and solid waste fuel. The gas temperature in the stack was approximately 530°F.

DISCUSSION

The various kiln conditions were carefully selected to determine the effects on dioxin formation.

Activated carbon has been theorized to be an acceptable add-on control for reducing dioxin emissions. The activated carbon is believed to adsorb the dioxins within the carbon pores. Studies at a variety of combustors have indicated that activated carbon does seem to reduce dioxin emissions within a given temperature range.

The injection of atomized water spray into the back end of the kiln resulted in a reduced gas stream temperature into the ESP. The temperature of the gas into the ESP has been shown to be a factor in the formation of dioxins.

Insufflation dust is an internal recycle loop. As such, the dust carries metals and particularly chlorine in a loop back into the kiln. By not insufflating any dust, the theory is that the chlorine necessary for the reaction will be reduced.

The addition of sulfur to the system is believed to cause competing reactions. The exact mechanism of the competing reactions is not fully understood, but theories do exist whereby sulfonation occurs as opposed to chlorination. It is also theorized that sulfur compounds may react with Cl_2 which is required to form dioxins.

RESULTS

Table 1 summarizes the average stack dioxin emissions for the five test days.

Based upon a 95% confidence interval for 2-sided tests, the data are not significantly different when comparing the normal run to the other conditions. Although the data are not statistically different, they do show an interesting trend. The lowest dioxin results were obtained when additional sulfur was added to the system. Testing with water spray and no insufflation dust also resulted in lower dioxin emissions.

Concurrent with the stack testing, Continental collected process samples of the slurry and the waste CKD and tested each for dioxins. The date from the process sample testing indicated some interesting results.

Table 2 summarizes the average dioxin concentrations in the CKD over the five day test period.

On Test Day 2, the dioxin concentration in the CKD approximately 2 orders of magnitude higher than on the baseline Test Day 1. The addition of activated carbon between the kiln and the ESP at an operating temperature in excess of 500° F resulted in a dramatic increase in dioxins in the CKD. Table 1 shows that for the same test periods, the stack gas dioxin emissions were not significantly different.

Table 3 summarizes the dioxin concentrations found in the slurry over the five day test period.

The table shows that dioxins do exist in the raw materials. A mass balance calculation around the back end of the kiln may be conducted to compare the dioxin input in the raw material to the dioxin output found in the stack gas and CKD. For total dioxins and furans, the mass balance indicates that more dioxins are inputted than can be shown in the output streams with the exception of Test Day Two. The mass balance calculation indicates that the addition of activated carbon resulted in less dioxins being inputted that emitted.

Continental has looked at the composite data from the dioxin testing history since the change to fire clay. The data have been compared to the proposed limit of 0.12 ng/dscm. Conducting a Method of Paired Differences test using the difference between 0.12 and the test data results in a calculated student-t value of 0.130 as compared to the critical t of 2.021 from the tables. This indicates that with a 95% confidence interval, the data are not significantly different from the standard of 0.12 ng/dscm. In addition, an individual and moving range process control chart has been generated that indicates an upper control limit of 0.75 ng/dscm TEQ for the same composite data.

CONCLUSIONS

Continental Cement Company has conducted an extensive amount of dioxin testing over the past several years. Their focus has been on learning what operating conditions may affect dioxin emissions and how to control those conditions. Some of the factors found that may reduce dioxin emissions include the following:

- Reducing the gas stream temperature into the ESP;
- Adding an alkali material, Na_2CO_3, to the hot end of the kiln;
- Adding sulfur to the raw material feed; and
- Setting the insufflation dust rate to zero.

Recent testing has demonstrated two very important issues.

- The addition of activated carbon as an add-on control technology at normal operating temperatures **does not reduce dioxin emissions.** In fact, activated carbon injection resulted in much higher dioxin concentrations in the CKD.
- The naturally occurring dioxins found in the raw materials constitute a majority of all of the dioxins emitted from the system. The amount of dioxins attributed to combustion is very much in question.

A statistical analysis of the historical data has indicated that stack emissions at Continental **do not differ significantly from 0.12 ng/dscm.**

Although a substantial amount of testing has already been conducted, additional testing is required to verify the above trends. It is also important to determine the operational feasibility of some of these options and how they may affect the stability of the kiln and the production of clinker.

Table 1

Test Day	TEQ (ng/dscm)	Total D/F (ng/dscm)
1	0.301	20.8
2[1]	0.319	12.3
3	0.407	15.5
4	0.265	11.4
5[1]	0.119	5.8

[1] Averages consist of 2 runs only due to operational conditions during one of the test runs.

Table 2

Test Day	TEQ (ppt)	Total D/F (ppt)
1	0.52	25.27
2	34.61	1341.7
3	0.77	57.37
4	6.90	191.57
5	1.46	40.38

Table 3

Test Day	TEQ (ppt)	Total D/F (ppt)
1	0.72	130.20
2	0.41	46.93
3	0.65	137.25
4	1.18	92.85
5	0.62	48.18