REDUCING PCDD/PCDF FORMATION AND EMISSION FROM A HAZARDOUS WASTE COMBUSTION FACILITY—TECHNOLOGICAL IDENTIFICATION, IMPLEMENTATION, AND ACHIEVEMENT

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INTRODUCTION

The U. S. Environmental Protection Agency (EPA) has proposed the Maximum Achievable Control Technology (MACT) standards for cement kilns burning hazardous wastes. Within the proposed MACT standards, U.S. EPA requires that the concentration of PCDD/PCDF in stack exit gases be maintained below 0.2 ng/dscm, expressed as toxicity equivalents of tetrachlorinated dibenzo-p-dioxin (TCDD), corrected to 7 percent O_2. For emission sources where the inlet temperature of the electrostatic precipitator (ESP) is maintained at or below 400° F (204 °C), the proposed MACT standard sets the PCDD/PCDF emission at 0.4 ng/dscm at 7 percent O_2.

In order to better position for compliance with the proposed MACT standard for PCDD/PCDF emissions, a cement facility (the facility), which burns hazardous wastes as supplemental fuels, decided to conduct a technological study to identify the best method for reducing the formation/emission of PCDD/PCDF from its facility in central U.S. The facility has performed several tests from 1993 through 1996 to investigate the sources and concentrations of PCDD/PCDF present in the air emissions. During the testing, samples of PCDD/PCDF in the stack gas emissions, raw material slurry, cement kiln dust, and clinker were collected and analyzed for PCDD/PCDF under various operational conditions scenarios. The first task of the study was to understand the mechanisms for PCDD/PCDF formation in the combustion process. This was followed by a broad literature review of available formation/emission control methods that have been tested and applied at various combustion facilities. An in-depth analysis was conducted on previously collected data under various testing conditions at the facility to gain a better understanding of the potential success of individual emission control technologies. Based on these analyses, the authors evaluated the advantages and disadvantages of individual emission control methods for PCDD/PCDF and explored the applicability of the most promising PCDD/PCDF formation/emission control methods to the facility. Then the most promising method was recommended to the facility for consideration and implementation.

The facility has conducted a specific emission test to evaluate the effectiveness of the recommended method. The test results showed that PCDD/PCDF concentrations were controlled below the MACT standard of 0.2 ng/dscm during the emission test. These test results are presented and discussed at the end of the paper.

MECHANISMS FOR PCDD/PCDF FORMATION
The formation and emission of PCDD/PCDF from waste combustion facilities have been subjects of extensive research in the past two decades because of concern over the potential adverse health effect of PCDD/PCDF discharged into the environment. It is important to understand the different pathways in which dioxins can be formed inside a combustion facility (e.g., cement kiln burning hazardous wastes), as these mechanisms can occur in different parts of the kiln, which would dictate potentially different control strategies.

Four major pathways have been identified for the formation of PCDD/PCDF:

1. Emission of unreacted PCDD/PCDF material in the waste.
2. High temperature homogeneous gas-phase formation.
3. Catalytic formation from organic precursors similar in structure to PCDD/PCDF, either on carbon particles in flight, or on ash or carbon particles captured in the air pollution device.
4. Condensed-phase formation from carbonaceous precursors that are chemically and structurally dissimilar to PCDD/PCDF.

REVIEW AND EVALUATION OF PCDD/PCDF FORMATION/EMISSION CONTROL METHODS

The following PCDD/PCDF formation/emission control technologies have been reviewed and evaluated in this study:

- *Control of temperature – time profile in the post-combustion zone*
- Effects on pcdd/pcdf formation/emission through the addition of sulfur
- Injection of alkaline sorbents
- High-temperature separation of fly ashes
- Pcdd/pcdf formation inhibitors
- Role of oxygen and water vapor in pcdd/pcdf formation control
- Catalytic reduction of pcdd/pcdf

EVALUATION OF INFORMATION AND TESTING DATA OF THE FACILITY
In the last several years, the facility has made many efforts to investigate the sources and concentrations of PCDD/PCDF presented in cement kiln air emissions. By using correlation and other techniques, the relations between PCDD/PCDF emissions and individual operating conditions under individual testing scenarios has been investigated. These efforts provided an understanding of the significance of the key operating factors to the formation/emission of PCDD/PCDF in the facility. Based on this understanding, the most effective method for controlling PCDD/PCDF formation/emission are identified for the specific conditions at the facility.

Temperatures Range--The temperature from the exit of the kiln to the stack typically decreases as a result of (1) heat losses, (2) air leakage, and (3) water injection. The temperature at the inlet to the ESP, T_i , is therefore expected to be greater than that at the stack, T_s. The average temperature difference between the APCD inlet and the stack is 36.7 °F (20.4 °C) and the standard deviation is 10.8 °F (6 °C). In the data correlation, temperatures that are more than two standard deviations outside the mean, i.e. those below 15 °F (8.3 °C) and above 59 °F (32.8 °C), might deserve special scrutiny when analyzing the temperature dependence of the emissions. There is only one occurrence of a delta T higher than 58.3 °F (32.4 °C); however, there are several occurrences of temperature differences less than the lower limit of 15.1 °F (8.4 °C) (in addition to the negative values).

Role of Air Infiltration on Cooling--An energy balance on the flue gas between the APCD inlet and the stack, assuming a flue gas flow rate of m_f, and air infiltration m_a, yields:

$$(m_a + m_f)C_{p,f}(T_s - T_o) = m_f C_{p,f}(T_i - T_o) + m_a C_{p,a}(T_a - T_o) - Q_{loss}$$

where Q_{loss} is the rate of heat loss to the ambient from the ESP inlet to the stack. This equation, neglecting the change in $C_{p,f}$ with composition and temperature, may be rearranged to give:

$$T_i - T_s = \{m_a C_{p,a}(T_i - T_a) + Q_{loss}\}/(m_f C_{p,f}) \qquad (1)$$

A mass balance between the furnace outlet and the stack can be used to determine the relationship between the oxygen concentration at the furnace outlet, C_f, and the concentration at the stack, C_s. For an oxygen concentration of 21 percent in air, and simplifying the equations by neglecting the temperature dependence on volume, one can show that:

$$(m_a/m_f) = (C_s - C_f)/(21 - C_s) \qquad (2)$$

One can use equations (1) and (2) to obtain some insight on the role of air infliltration on cooling of the combustion gases. For many runs among the facility data, the value of C_f was around 2 and C_s around 4. For such values the value of (m_a/m_f) is 0.12, corresponding to an infiltration rate of about 12 percent of the flue gas. For this value of the air infiltration, using representative values of $C_{p,f}$ of 0.30 Btu/(lb)(°F) and $C_{p,a}$ of 0.24, the air infiltration will contribute 44 °F (24.4 °C) to $T_i - T_s$. This is in the range of the observed values suggesting that air infiltration is the major contributor to the cooling between the ESP inlet and the stack.

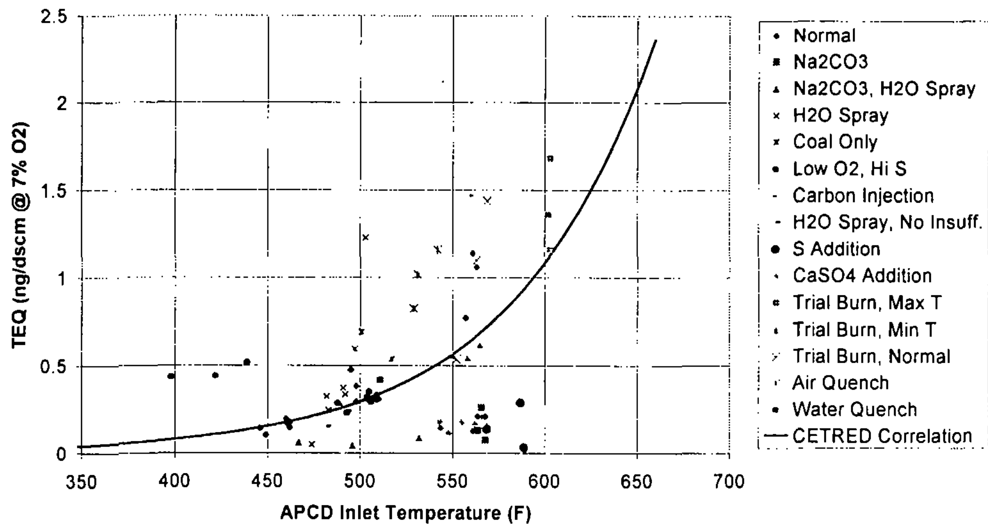
Temperature Dependence--The TEQ results for stack gases are plotted versus ESP inlet temperature in Figure 1. The data show the trend with temperature expected when the dioxin formation is dominated by the low temperature catalytic route. The temperature dependence of the cement kiln data in CETRED was given by the following two correlations:

$\text{Dioxin}_{(\text{at } T)}/\text{Dioxin}_{(\text{at } 350°F)} = \exp[0.014(350 - T)]$ for low CO (approx <100 ppm)

$\text{Dioxin}_{(\text{at } T)}/\text{Dioxin}_{(\text{at } 350°F)} = \exp[0.0117(350 - T)]$ for high CO

The correlation was plotted on Figure 1 using a dioxin value of 0.2 ng/dscm at a temperature of 470 °F (243.3 °C) as a reference. As shown, the majority of the data follow the general trend of the correlation. The outlying points in general represent unusual conditions as discussed below. A review of Figures 1 indicates that most of the uncorrected data follows a negative trend with ESP inlet temperature with the exception of a few points in the temperature range of 550 °F (287.8 °C). If we look closely at this data, it is clear that the majority of these dioxin values that appear abnormally low for the stated ESP inlet temperature represent tests where either sulfur or an alkali metal was added as a dioxin control measure

Figure 1. TEQ dioxin emissions versus ESP inlet temperature for all testing conditions.



High Temperature Route to Dioxin Formation--Dioxins are produced either by a homogeneous path at temperatures around 1600 – 1800 °F (871.1 – 982.2 °C) or catalytically in the temperature window of 450 to 650 °F (232.2 to 343.3 °C). The correlation of the data with ESP inlet temperature in the preceding section suggests that the catalytic path dominates. The few data points that did not follow this trend might be indicative of an alternate pathway for dioxin formation under certain operating conditions. It is also possible that there is some other artifact with respect to the data that is not known at this time. Further analysis of the testing data suggests that the high temperature route was more important for those tests in which the dioxin concentrations were high.

RECOMMENDATION OF THE MOST EFFCETIVE MEASURE FOR PCDD/PCDF FORMATION/EMISSION

Based on the literature review of the available techniques for controlling PCDD/PCDF formation/emission from combustion facilities and the strong correlation of dioxin emissions with ESP inlet temperature among the facility emission data, it is clear that the most effective measure for reducing dioxin emissions at the Hannibal plant would be through the reduction of the ESP inlet temperature. The projection analysis revealed that reducing the ESP inlet temperature to 400 °F (204.4 °C) would be a very effective control measure for PCDD/PCDF formation/emission, reducing the TEQ levels to values meeting the proposed MACT standards.

To prevent the injection of water near the ESP inlet from resulting in significant pluggage and the formation of cementitious deposits, the authors suggest to introduce the water in the chain section of the kiln allowing opportunity for gas/water contacting on the chain surfaces. This would also provide a greater probability for passing through the critical dioxin-formation temperature window prior to entering the ESP.

FACILITY TESTING RESULTS

In order to determine PCDD/PCDF concentrations in the stack emission after facility's revision inside its kiln and to validate the effectiveness of recommended most effective measure for reducing PCDD/PCDF emissions, The facility conducted a stack emission test during the week of June 6, 2000. Three non-consecutive test days were concluded with a one-day kiln equilibration period between each test day. The testing was performed within 30 days after a scheduled kiln maintenance period where additional chain was added to the chain section for increased heat transfer and temperature control capabilities. A spray system that directly impacted the chain zone was operated during the test to further decrease process gas temperatures prior to entering the ESP. Specific temperature ranges were maintained at the inlet to the ESP through the duration of each test day. EPA Method 23 was used to determine the PCDD/PCDF concentration of the stack gas.

Results for all of the three testing days are shown in Figure 2. Each data point represents the average temperature and corresponding PCDD/PCDF TEQ concentration for individual 3-hour test runs. A strong correlation between ESP inlet temperature and PCDD/PCDF concentration is evident. The average of the three 3-hour test runs for each test day suggests that the facility will comply with the MACT standard of 0.2 ng/dscm for PCDD/PCDF if the temperature at the inlet to the ESP is maintained below 430^0-440^0 F. The results also proved that recommended most optimistic measure for reducing PCDD/PCDF formation/emissions was effective.

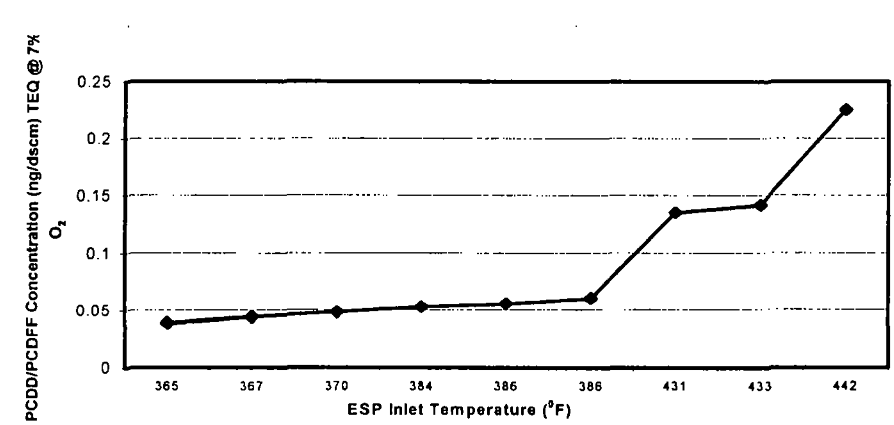


Figure 2: PCDD/PCDF Concentration vs. Temperature Measured at the ESP Inlet

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