FACTORS AFFECTING DIOXIN FORMATION AND CONTROL IN CEMENT KILNS – LESSONS LEARNED

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Introduction

One of the anthropogenic sources of dioxin and dioxin-like compounds is the partial oxidation and fractionation of organics from the raw materials in the cement kiln process. To control dioxins, it is necessary to determine the mechanisms of their formation in the thermal process, both from the standpoint of organic material generation and partial oxidation, and also the chlorination of the organics and the temperature profile where that occurs.

Many studies have been performed demonstrating that dioxin in a cement kiln is not a product of the combustion of fuels. The United States Environmental Protection Agency (US EPA) asserts that the dioxin formation mechanism is associated with the raw material feed end of the manufacturing process, believed to be a function of the residence time and temperature in the air pollution control device.[1] It is generally accepted that the inlet temperature to the air pollution control device (APCD) is the main controlling factor in dioxin formation along with residence time and turbulence in the APCD system; however several other factors can contribute to the increase or decrease in dioxin emissions from cement production (see Figure 3).

Numerous issues have arisen since the onset of dioxin emissions testing in cement kilns for demonstrating compliance with the standards. One of these issues involves some kilns having demonstrated compliance a number of times and having been significantly below the standards, yet upon performance of the required 30-month compliance test they are surprised that their dioxin emissions have increased for no apparent reason.

In the last 5 years, many factors other than APCD temperature have been identified as having a significant effect on dioxin emissions. For instance, spray tower location in the downcomer and temperature control from the top of the tower to the air pollution control device in a preheater kiln can increase residence time at the optimal dioxin formation temperature window, and therefore increase dioxin formation.

In addition, certain operating factors can produce false data which could lead a cement manufacturer to believe that a dioxin emission problem is unlikely. Air inleakage at the top of the tower in a preheater, or after the kiln seals in a long kiln, can cause measured temperatures to be lower than those required for optimal dioxin formation when in fact the actual temperature of the gas stream is ideal for dioxin formation. Also, stratification in the stack can produce incorrect temperature readings, indicating lower temperatures and the potential for lower dioxin emissions than actual.

After investigating the issues associated with kilns that once complied under certain conditions and evaluating the potential changes which caused the emissions to increase while maintaining the same inlet temperature to the baghouse, certain evaluations and parameters have been shown to consistently yield promising results to make changes to bring the kiln system back into compliance, though there is no one solution that fixes the problem of dioxin emissions in its entirety.

Materials and methods

Various data from a number of cement kilns were used to find relationships between dioxin formation and several kiln system operating factors.

Results and discussion

<u>Effect of post-combustion temperature on dioxin formation</u>

In order to produce clinker (the product from a cement kiln), the kiln must combust fuel (fossil fuels such as coal or coke, alternative fuels such as municipal or industrial waste, tires, etc.; or hazardous waste fuel) at temperatures of 1,650°C to 1,925°C, which destroys all organic compounds that may be contained in the fuel. During testing of a number of kilns, operating conditions were varied, and dioxin emissions were measured at the outlet of the APCD. Despite variations in the other operating conditions, it is clear that stack dioxin emissions correlate to baghouse inlet temperature. The highest baghouse inlet temperatures produced the highest dioxin emissions, and low baghouse inlet temperatures generated the lowest dioxin emissions. Figure 1 clearly shows the effect of baghouse inlet temperature on dioxin formation.

Data from the same cement kiln separated by 10 years (Figures 1 and 2) shows that even when the raw material feed is varied, dioxin formation is directly proportional to the temperature at the inlet of the APDC. In Figure 3, the U.S. EPA gathered dioxin emissions data from a number of cement kilns and separated the data based on total hydrocarbon (THC) emission values.[7] This data also verified that while raw feed may have an overall effect on the level of dioxin emissions, APCD inlet temperature is still the major controlling factor in dioxin formation.

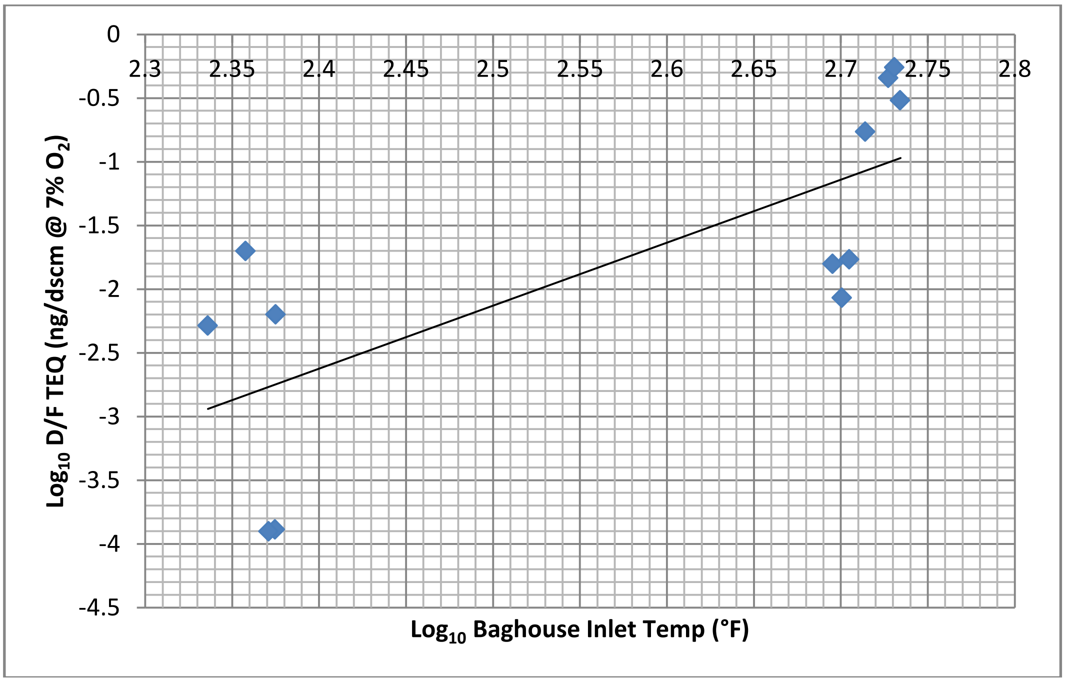

Figure 1: Log dioxin vs. log baghouse (APCD) inlet temperature, year 2000

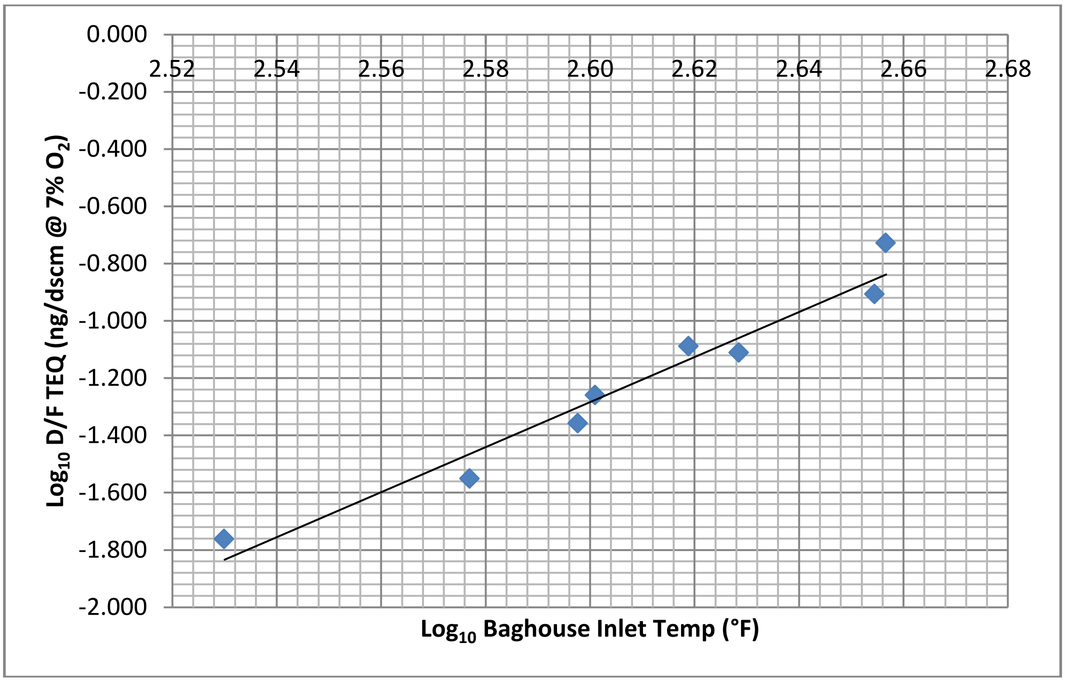

Figure 2: Log dioxin vs. log baghouse (APCD) inlet temperature, year 2010

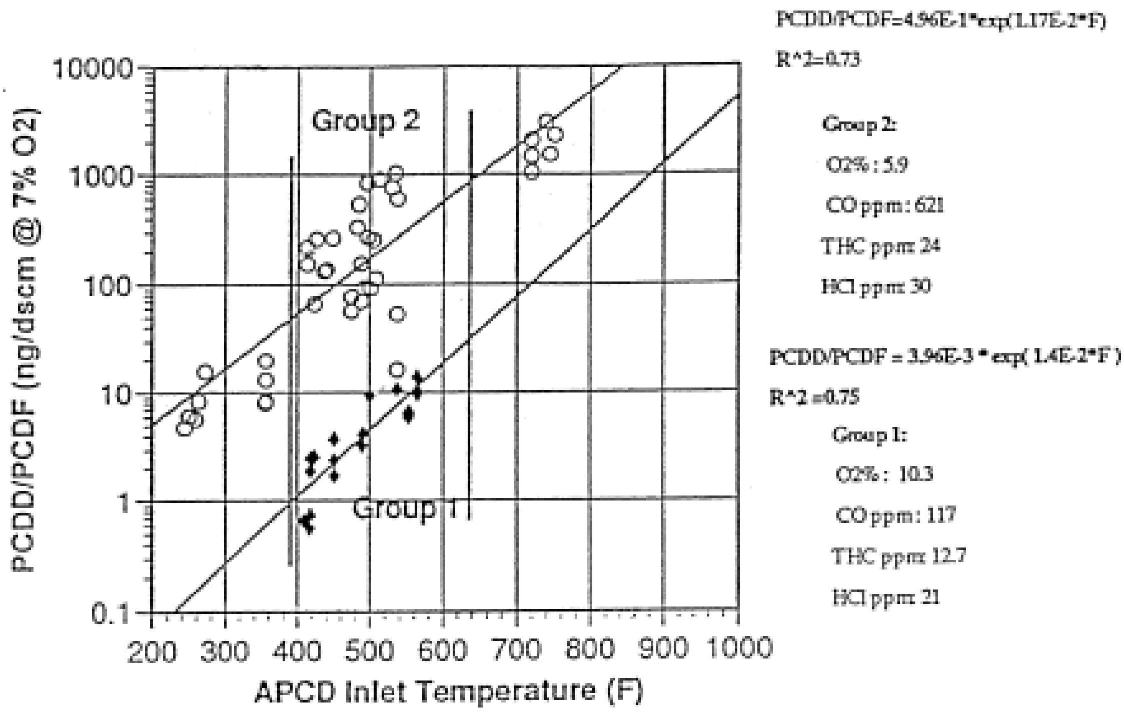

Figure 3: Dioxin vs. APCD inlet temperature for differing raw materials

In addition to APCD inlet temperature, the residence time and turbulence in the APCD influence the formation of dioxin. Factors such as location of the spray tower in the downcomer and different temperature control mechanism available to plant personnel can change the residence time and temperature at the critical dioxin formation temperature window, whereas air inleakage may produce artificially low APCD inlet temperatures. Improper location of the conditioning tower can lead to insufficient cooling or shortening of the residence time at the critical dioxin formation temperatures.

Investigation parameters

First, we must evaluate the temperature profile in the kiln where the gasses are at the 450-750 °F range, and the residence time at those temperatures to determine how it can be shortened. Then, we must review the location of the conditioning tower to determine if it is attacking the temperature profile and residence time appropriately. An inherent problem with cement kilns is that the specific design of kilns is not consistent and will determine the temperature profile and residence time at specific temperatures, thus each kiln must be evaluated on an individual basis.

Regarding system inputs, we must review the raw materials and alternate raw materials to determine if there has been an introduction of organics, which are particularly good precursors for dioxins at the right temperature, as there is typically sufficient chlorine in the gas stream to allow the reaction to proceed. Further, we must evaluate the chlorine content of the spray tower water to determine if that is of additional concern. We also must review the concentration of dioxins in the cement kiln dust which may provide a recirculating load of already formed dioxins into the raw meal, and determine if there is an outlet for the potential build up which may occur over time.

Finally, qualitative factors such as air inleakage and stratification in the stack must be considered to determine if temperatures and dioxin emissions are being accurately monitored. These operating factors can produce false data which could lead a cement manufacturer to believe that a dioxin emission problem is unlikely. Air inleakage at the top of the tower in a preheater, or after the kiln seals in a long kiln, can cause measured temperatures to be lower than those required for optimal dioxin formation when in fact the actual temperature of the gas stream is ideal for dioxin formation. Stratification in the stack can produce incorrect temperature readings, indicating lower temperatures and potentially lower dioxin emissions than actual.

Conclusion

We have determined that there is no single answer that fits every cement kiln, as each kiln is unique in design, input, and operating conditions. The raw materials are dependent on the geology of the formation and the combination of the locally supplied additives, making for a complex input of potential precursors. After looking at dioxin formation in cement kilns from a holistic standpoint, and understanding the chemistry and formation mechanism of dioxin, it is possible to develop a path to compliance and to lowered dioxin emissions.

References:

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