Investigation of Mechanism of Formation of PCDD/F in Cement Kilns

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The continued perception of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) as highly toxic and ubiquitous by-products of combustion processes has led the US-EPA to propose tougher new regulations and control of their emission[1]. Although PCDD/F have been the subject of more study than any organic pollutant, the state of the scientific literature on their origin might still be considered to be in a state of chaos[2,3]. This is particularly true for their mechanism of formation in combustion processes which has led to many proposed control strategies, the study of which have been time-consuming, costly, and often unfruitful. In order to place the development of control strategies on a firmer scientific basis, the mechanism of formation for a combustion process must first be determined on a case-by-case basis. This paper is concerned with the mechanism of formation and destruction of PCDD/F in both fossil fuel-fired and waste co-fired cement kilns.

Formation in cement kilns also may add extra complexity due to the number of temperature zones; the number of sources of reactants (i.e. the fuel, the raw meal, and chlorinated hydrocarbon (CHC) for co-fired kilns); the alkaline environment; the counter current flow of solids (raw material) and gases; and the high surface area to volume ratio caused by the presence of raw meal and cement kiln dust (CKD).

The Effect of Temperature /Time History

The process-gas temperature profiles of a typical wet and dry process kiln are depicted in figure 1. It is well documented that no organic compound can survive oxidation at temperatures above 1500 K[4]. Thus for the gas-phase PCDD/F formation pathway, we only need concern ourselves with the pre-heating zones of wet and dry process kilns, with the majority of the chemistry occurring in the 700 to 1000 K range. At these temperatures, chlorinated hydrocarbon molecules decompose and can react to form higher molecular weight species that can act as PCDD/F precursors[4]. 700 to 1000 K is also the optimum temperature range for gas-phase chlorination reactions to occur. The time-scale for gas phase reactions is typically 1-6 s, which is within the exposure times expected for cement kilns.

Lower temperatures are required for the heterogeneous PCDD/F formation pathways (catalytic condensation and *de novo*) to be significant. It is well documented in the literature that surface catalyzed formation only occurs in the 400 to 700 K range[3]. Thus we need only concern ourselves with the first preheater stages of dry-process kilns, the analogus chain zone of wet-process kilns, and the air pollution control device (APCD) zone. The time-scale for heterogeneous reactions is usually reported as minutes to hours with time scales of seconds only being recently reported[5]. However, we are now concerned with the residence time of the solids at temperature. (assuming a constant flow of any required gas-phase reactants). The exact time required for the heterogeneous
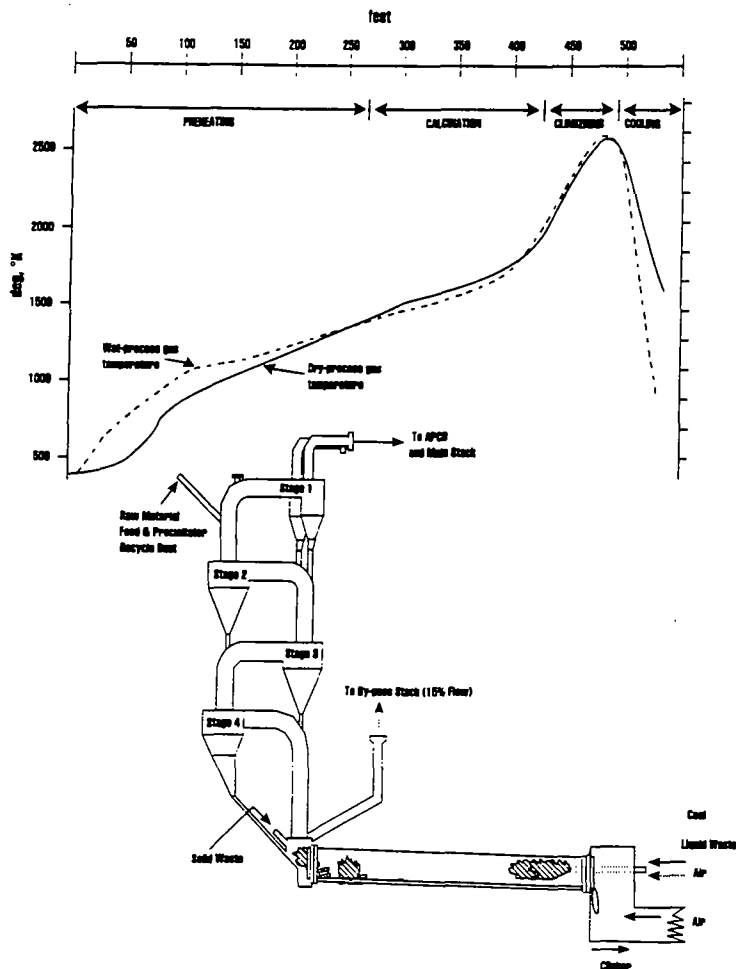
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Figure 1. Schematic diagram of a dry-process cement kiln co-fired with liquid and solid
waste derived fuel. The gas-phase temperature profile of the dry-process
kiln is shown (solid line) along with that of a typical long wet-process kiln
(dotted line). All of the preheating in the dry-process kiln occurs in the
vertical, 4-stage preheated tower which is designed for efficient energy
transfer from the hot kiln gases to the raw meal feed. Preheating in the wet-
process kiln occurs in an additional 260 ft. of kiln known as the chain zone
because it contains metal chains to improve heat transfer.

pathway is very important since the expected residence time of raw meal solids at the appropriate temperature is only expected to be 5-10 seconds. However, in APCD zone residence time of non-entrained particles may be minutes or longer.

Sources of Reactants

Organic Precursors

Organic precursors may originate from three sources: 1) combustion of the fuel, 2) combustion of any co-fired waste, and 3) organics adsorbed on the raw meal. The nature of the reactants from each source can differ greatly and significantly effect the rate of formation.

The burnout of the fuel which is fired at the discharge end of the kiln is expected to be very efficient, with only minimal organic products surviving. They are almost entirely hydrocarbons with any chlorine in the coal or oil fuel entering the PCDD/F formation zones as HCl and Cl_2 (25:1)[6]. Destruction of CHCs co-fired as liquid wastes at the discharge-end of the kiln is also expected to be highly efficient. Solid waste fired at mid-kiln have a greater chance of producing chlorinated by-products that can act as PCDD/F precursors.

It has been hypothesized that organics present in the raw meal are the major source of organic emissions from cement kilns not burning hazardous waste. To verify this hypothesis, eight raw meal samples were collected from different process points (before and after each preheater cyclone, bag house, grinding mill, and silo) of a local preheater cement kiln not burning waste-derived fuel. This was done to determine the total organic content of the raw meal at various process points. This would help in determining the process point(s) at which the maximum amount of organics evolve and the fate of these evolved organics.

Thermal desorption experiments (in helium and in $7\%O_2$) were conducted on all eight raw meal samples. These experiments were conducted on a high temperature flow reactor system referred to as the System for Thermal Diagnostic Studies (STDS). The detailed design of STDS has been published elsewhere[7]. A packed bed configuration was used to thermally desorb raw meal samples. The results of these experiments showed that cement kiln raw meal contains a wide range of organics including benzene, toluene, naphthalene, alkanes, C_{14}-C_{18} carboxylic acids, phthalates and their derivatives and natural products such as cholesterol. Results of these thermal desorption experiments also showed that long chain carboxylic acids and natural products are evolved in both the 22-250°C and the 250°C-500°C temperature intervals, and that their abundancies decrease with increasing temperature. On the other hand compounds including benzene, naphthalene, and various alkanes are not detected in the 22-250°C temperature interval; however, they are evolved in the higher temperature intervals in approximately the same amounts. From these result it can hypothesized that perhaps all the organics in raw meal are present in the form of long chain carboxylic acids and natural products, and the aromatics and aliphatic organics observed are their dissociation products. This hypothesis was strengthened experiments in which phthalates were spiked on to the raw meal and it was observed that phthalate dissociated into benzene, biphenyl and other products.

From Figure 2, it can be seen that THC present in raw meal decreased sharply after the first two preheater cyclones and stayed the same in the third cyclone. There is a slight increase in THC from raw meal exiting the fourth cyclone; this increase could be because this is the first time hot kiln gases come in contact with the raw meal, therefore some condensation of kiln gas organics is possible due to the temperature difference. A sample collected from the bag house (process point 8) also shows an increase in THC. This increase occurs because, at the lower temperatures of the bag house, some gas phase organics will condense on solids. As shown in Figure 2, there are large deviations between the runs at process point 2. This is because the process point 2 raw meal sample

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contains large and varying amounts of volatiles. Deviations can also be the result of the heterogeneous nature of the sample and also because there is some surface dissociation occurring which is very sensitive to even minor differences in packing. However, enough experiments were performed to obtain a trustworthy trend.
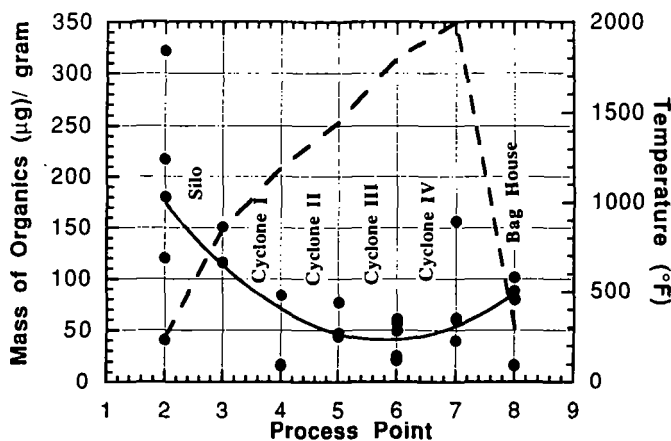

Figure 2. Filled circles represent the mass of organics (μg) evolved per gram of raw meal at each process point. The solid line is the best fit for the organics evolved at each process point. The dashed line represents corresponding process temperature (°F).
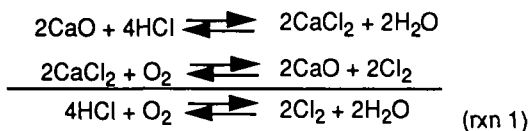
To gain better insight into the thermal desorption of raw meal organics, the total organics thermally desorbed at each process point were divided into different molecular weight ranges and different chemical classes. Most of the organics are in the 200 to 300 amu molecular weight range and are C_{14}-C_{18} carboxylic acids. The second largest group include organics that are natural products and that have molecular weights greater than 400 amu. Aromatics and aliphatics (or the compounds with molecular weight less than 200 amu) form a small fraction of the total organics desorbed from raw meal. These results are again consistent with the previously proposed hypothesis that organics are present in raw meal as long chain carboxylic acids or phthalates, cholesterol, and their derivatives.

The results of oxidative thermal desorption experiments showed that organics might be present as long chain carboxylic acids or as natural product derivatives on the raw meal; however, in the presence of oxygen and at process unit temperature they enter the gas-phase as oxygenated aromatic compounds. A comparison of thermal desorption experiments in helium and 7%O_2, shows that some organics are converted to water and CO_2 while others (e.g., aromatics and aliphatics) are converted to phenolics or organic acids. Some of the long chain carboxylic acids have been converted into benzo di-carboxylic acids; the natural products (cholesterol) are converted into their acetates and esters. This change in the chemical species is very important in understanding the fate of these organics downstream of the preheating zone. Results of these experiments indicate that organics from raw meal enter the cement kiln process at points where temperature, time, and their chemical form is favorable for PCDD/F formation, if a chlorine source is available.

<u>Chlorine Source</u>

Chlorine may be present in the PCDD/F formation zones as organic chlorides (RCl), HCl, Cl_2, alkali and alkaline earth chlorides (AClx), and transition metal chlorides (MeClx). RCl is only expected to be significant when CHCs are co-fired in solid wastes. HCl/Cl_2 concentrations are expected to be higher when large quantities of CHCs are co-fired but are known to still be significant when some coals and fuel-oils are fired. The HCl to Cl_2 ratio is extremely important, as Cl_2 is a much superior chlorinating agent to HCl. The presence of chlorine as AClx/MeClx is due to the occurrence of alkali and metal ions in the raw meal. The chlorine may also be initially present in the raw meal or be captured from the gas-phase by alkali reactions of the raw meal. The interconversion of chlorine containing species is discussed below.

In cement kilns, the low levels of soot and fly ash suggests that their contributions would be minimal. However, the high levels of alkaline earth oxides and hydroxides (i.e. CaO, $Ca(OH)_2$, MgO, $Mg(OH)_2$) may have a profound effect through catalyzing the Deacon reaction which converts relatively unreactive HCl in to highly reactive Cl_2[8].

$$2CaO + 4HCl \rightleftharpoons 2CaCl_2 + 2H_2O$$
$$2CaCl_2 + O_2 \rightleftharpoons 2CaO + 2Cl_2$$
$$4HCl + O_2 \rightleftharpoons 2Cl_2 + 2H_2O \quad \text{(rxn 1)}$$

The homogeneous gas-phase equilibrium of deacon reaction favors HCl at combustion temperatures, with essentially no Cl_2 existing above 900K. As the temperature of the gas drops, equilibrium begins to favor formation of Cl_2. However, the conversion is too slow kinetically in a purely gas-phase system to be important. The presence of alkaline earths or transition metals is known to sufficiently increase the rate of reaction such that equilibrium can be re-established. The presence of Calcium as a catalyst partially converts HCl to $CaCl_2$ and also results in conversion of HCl to Cl_2 at approximately 2 % levels at all temperatures. The formation of Cl_2 would be expected to increase the yield of CHCs and PCDD/F formed by gas-phase chlorination and $CaCl_2$ may act as a solid state catalyst.

Full -Scale Studies

Stack emissions of PCDD/F from cement kilns have been quite varied with total emission concentrations of a few ng/dscm to thousands of ng/dscm having been reported[1,8]. Due to the small amount of available controlled research data, only limited correlations between kiln type, APCD design, waste feed composition, or combustion variables have been observed. Isolated studies have been reported where emissions correlate inversely with kiln O_2 and chain-zone temperature and directly with APCD temperature[1,6,8,9] The most compelling evidence for the mechanism of PCDD/F formation may be the observations of formation of chlorobenzene in the preheater of dry-process kilns[8,10]. Formation correlates directly with the chlorine content of the process gas and inversely with preheater temperature which suggests a surface catalyzed chlorination of chlorobenzene.

However PCDD/F concentrations have not always correlated with the chlorobenzene concentration in facilities in which chlorobenzene formation has been observed[8]. Furthermore, PCDD congener distributions have maxima at hepta- to octa-chlorination while PCDF congener distributions have maxima at penta- to hepta-chlorination[1,6,8]. This strongly suggests that the origin and mechanism of PCDD and PCDF may be different. Limited studies of the addition of Na_2CO_3 and K_2CO_3 as chlorine scavengers have been conducted[9]. Na_2CO_3 was effective in reducing PCDD/F emissions; however, K_2CO_3 resulted in an increase. This negative results for K_2CO_3 may have important implications in that it suggests a role of chlorine recirculation and buildup

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in the formation of PCDD/F: KCl, being semi-volatile, would be expected to recirculate to the preheat zone in some cement kiln design resulting in increased availability of chlorine to participate in PCDD/F formation.

Full-scale studies in which the APCD temperature and stack emissions have been measured indicate a strong, inverse Arrhenius-type correlation between TEQ and APCD temperature[1,9]. When the ESP is operated below 475 K, TEQs are consistently below 0.1 ng/dscm[9]. This has been interpreted as removal and destruction of PCDD/F on CKD in the APCD. This position issupported by independent studies which indicate that PCDD/F are catalytically destroyed on the surfaces of CKD[9]. However, an Arrhenius-type relationship also exists between temperature and rate of $CuCl_2/KCl$ oxychlorination of phenol, a reaction which is known to produce PCDD/F at temperatures above 475 K[11]. It is important to understand which of the above mentioned processes is really reponsible for reduction in PCDD/F emission. If destruction of PCDD/F on CKD in APCD is responsible for lower PCDD/F emissions, then PCDD/F emissions may be controlled independent of the origin and mechanism of formation. However because limited measurements of the APCD inlet concentrations of PCDD/F have been made, it is not clear how efficient the control in the APCD may actually be.

Conclusions

From the results of laboratory and field studies, we can conclude that organics from raw meal enter the process (i.e., kiln flue gas) in the initial stages of preheating zone (i.e., first two cyclones in preheater kiln) mainly as oxygenated aromatic compounds. Time and temperature downstream of the preheating zone are not sufficient to destroy all the organics that enter the kiln gas during these process points. However, time and temperature conditions are favorable for PCDD/F formation. This finding leads to the conclusion that raw meal organics are not only a major source of stack THC emissions but also serve as organic source for PCDD/F formation reaction.

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