FORMATION AND EMISSION OF DIOXIN AND FURAN FROM CEMENT KILNS

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Introduction

Dioxins (PCDDs) and furan (PCDFs) are a group of chlorinated, planar, aromatic compounds considered as environmental toxic pollutants resulting from both natural and anthropogenic activities. Among all the dioxins and dioxin-like compounds the US EPA identified, 17 congeners that possesses chlorine atoms at their 2, 3, 7 & 8 positions, are more toxic than the others. Dioxins and furans have received a great deal of attention due to their long residence time in the environment and carcinogenic effects to human health. One of the anthropogenic sources of dioxins and dioxins-like compounds is from the incomplete combustion of hydrocarbons from the raw materials fed into the cement kiln process. The MACT standard[1] for dioxins for cement kilns is 0.2 ng TEQ/dscm at 7% O_2 with an air pollution control device (APCD) inlet temperature greater than 204.4°C or 0.4 ng TEQ/dscm at 7% O_2 with an APCD inlet temperature less than or equal to 204.4°C. To control dioxins and furans, it is necessary to determine the mechanisms of their formation in the thermal processes.

Several studies reported that the formation of dioxins and furans follows the pathways of pyrosynthesis and de novo synthesis reaction mechanisms based primarily on the temperature range in the kiln systems [2, 3]. However, the de novo synthesis that involves a catalytic reaction at lower temperature ranges in the post combustion process appears to be the most dominant mechanism for final dioxin and furan formation [4]. Numerous researches have been carried out based on the parameters including temperature, carbon, chlorine, oxygen, and catalysts to identify the root cause of dioxin and furan formation in the kiln systems [5]. However, the mechanism behind the formation of dioxin and furan in the cement kiln is not precisely known due to the complexity of their formation reaction. It is generally accepted that the temperature profile is the critical parameter for the formation of dioxin and furan in the cement kiln systems. The objective of this work is to investigate the effect of total hydrocarbon production from the raw material, and product of incomplete combustion (PICs) from the raw material on the dioxin and furan formation in the cement kiln. The relationship between the formation of dioxins and the kiln operating parameters is also discussed.

Materials and methods

The experimental data were collected from 18 cement manufacturing plants that are operating in the United States. All analyses were performed using standard US EPA modified Method 23 and modified Method 1613, respectively. These data were submitted to US EPA as part of data generated demonstrating compliance with the regulations for the combustion of hazardous waste in the United States.

Results and discussion

Effect of total hydrocarbons and product of incomplete combustion on dioxin formation

In general, some cement manufacturing facilities use hazardous waste along with the coal/petroleum coke as fuel in the kiln. Because of the regulations in the United States, these kilns have been required to perform risk assessments to demonstrate the emissions are protective of human health and the environment. Part of the demonstration required testing the organic emissions from the kiln, which have been demonstrated to be coming from the organics in the raw material. These data for both total hydrocarbon (THC) content of the gas stream and the identified products of incomplete combustion of the raw materials were used to evaluate the potential contribution these compounds may have had in the formation mechanism of dioxin and furan. The higher hydrocarbon emission from the cement kiln stack is directly related to the organic loading in the raw feed of cement kiln. In this attempt, the amount of dioxin and total hydrocarbon present in the stack emission was monitored for 18 different cement manufacturing facilities, which was the universe of kilns burning hazardous waste in the United States at the time the regulations were developed. Figure 1 shows the relationship between the dioxin formation and the presence of total hydrocarbons in the emissions. It was observed that there is no correlation between the formation of dioxin and total hydrocarbon presence in the stack emissions. The correlation between the PICs and dioxin formation was also studied (Figure 2). Figure 2 shows that the formation of dioxins does not depend on the amount of PICs generated in the kiln system.

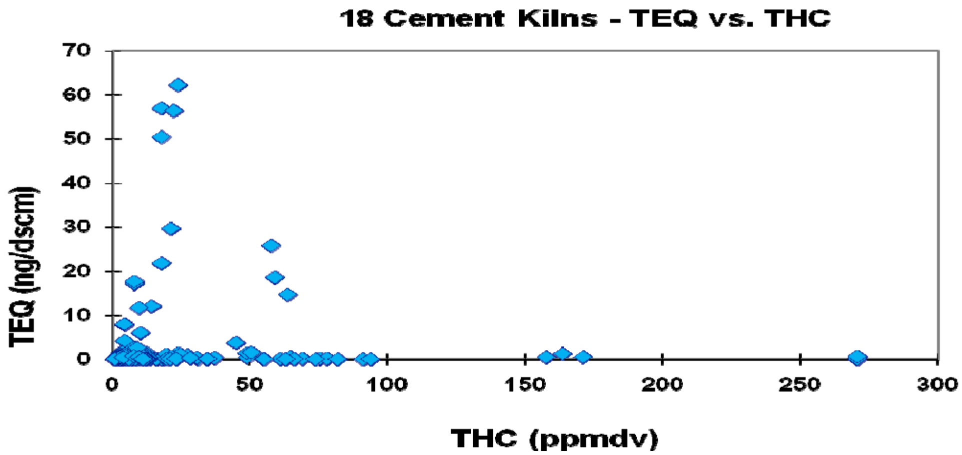

Figure 1: Relationship between the total hydrocarbon and dioxin formation in the cement kiln

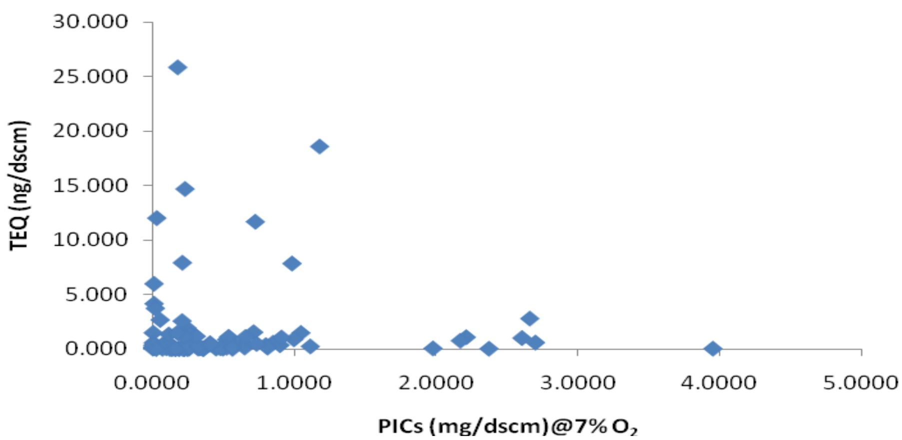

Figure 2: Relationship between the product of incomplete combustion (PICs) and dioxin formation in the cement kiln

Effect of post-combustion temperature on dioxin formation

A study conducted on a typical cement kiln generated data under various operating conditions. Table 1 includes the data resulting from this study. This cement kiln was fired simultaneously with hazardous waste as well as traditional fossil fuels including coal and coke. Note that to produce clinker, the product from a cement kiln, the kiln must combust the fuel (hazardous waste or fossil) at temperatures of 1,650 to 1,925°C, and destroys all organic compounds that may be contained in the fuel. During this study, various kiln operating conditions were varied with emissions of dioxins measured at the inlet and outlet of the APCD, an electrostatic precipitator (ESP). Testing was conducted by both the plant operators as well as US EPA's contractor, Energy and Environmental Research Corporation (EER). Operations of the kiln were conducted under worst-case trial burn conditions as well as under normal conditions. Particulate loading, copper spiking, and temperature conditions were all varied during these tests. With dioxin, the plant's inlet temperatures to the ESP were the key parameters monitored. Despite variations in the other operating conditions, it is clear that the stack dioxin emissions correlate to the ESP inlet temperature. Highest ESP inlet temperatures produced the highest dioxin emissions and low ESP inlet temperatures generated the lowest dioxin emissions. Figure 3 clearly shows the effect of temperature on dioxin formation at the APCD. This data was key to the development of the MACT standards for cement kilns. It was observed that the formation of dioxin can be described as a function of the inlet temperature to the APCD, in this case an electrostatic precipitator (ESP). In addition, the residence time and turbulence in the APCD also influence the formation of dioxins and furans.

Conclusions
Dioxin and furan formation is complex, but can be understood to some degree and has the potential to be controlled. Cement manufacturing facilities that use hazardous waste as a supplement with coal have been a source of information for demonstrating the relationship of the influence of the raw material on the formation mechanism of dioxin for kilns that have not burned hazardous waste. There has not been any data to indicate that the type of fuel combusted has an impact on dioxin formation. The US EPA has also concluded that there is no difference in the dioxin emissions for kilns that burn hazardous waste versus those that do not. There is a general consensus that the high temperature existing in the cement kiln does not allow for product of incomplete combustion to occur from the primary burning zone of a kiln. This has been demonstrated by studies done in the 1990s, which also showed that extreme conditions of very poor combustion are the exception [6,7]. The data obtained from this study have also confirmed that the total hydrocarbon emissions from kilns do not correlate to increases in dioxin formation. In addition, the data also demonstrate that individual PIC emissions also do not correlate to an increase in dioxin formation. The study further indicates that the temperature profile at the back end of the cement manufacturing process continues to be the primary controlling factor for formation of dioxins in the cement kiln system and should be the main focus in trying to solve a dioxin emission problem. Any area downstream of the kiln that is in the optimum dioxin formation temperature of 232.2^oC to 454.4^oC needs to be evaluated to determine if the residence time will contribute to excess dioxin formation. In summary, there is no correlation observed between the dioxin concentration and the presence of high total hydrocarbon and PICs in the stack emission from the cement kiln.

Table 1. Effect of post combustion temperature on dioxin formation

Operating Condition		Plant Run Number	EER Run Number	Inlet PCDD/PCDF Total ng/dscm @7% O_2	Inlet 2,3,7,8-TCDD TEQ ng/dscm @7% O_2	Stack PCDD/PCDF Total ng/dscm @7% O_2	Stack 2,3,7,8-TCDD TEQ ng/dscm @7% O_2	Plant ESP Temp (^oC)	EER ESP Inlet Temp (^oC)
Low Kiln Exit Temp – High Particulate Loading	TRIAL BURN	Run 1				*5.73*	*0.08*	*202.7*	
		Run 2				*105.65*	*0.42*	*221.1*	
Low Kiln Exit Temp – Low Particulate Loading		Run 3				*9.35*	*0.11*	*208.3*	
		Run 4	Run 1	19.94	0.370	*25.93*	*0.32*	*218.3*	230.5
High Kiln Exit Temp		Run 5	Run 2	8.84	0.158	*119.74*	*0.92*	*268.3*	287.2
		Run 6	Run 3	6.26	0.088	*211.86*	*1.41*	*265.5*	289.4
		Run 7	Run 4	8.47	0.097	*445.39*	*4.79*	*271.6*	296.1
High Kiln Exit Temp with Copper Spiking		Run 8	Run 5	9.94	0.199	*342.45*	*4.14*	*269.4*	293.3
High Kiln Exit Temp with Copper Spiking and Water Quench		Run 9	Run 6	14.62	0.218	*64.14*	*0.71*	*240.5*	241.1
		Run 10	Run 7	326.4	3.525	*16.04*	*0.21*	*237.7*	348.3
High Kiln Exit Temp	NORMAL OPERATION		Run 8	9.03	0.132	*87.63*	0.412	*245.5*	272.2
			Run 9	16.77	0.261	*72.142*	0.673	*243.3*	268.3
Low Kiln Exit Temp			Run 10	8.87	0.158	*9.606*	0.131	*195.5*	219.4
			Run 11	7.02	0.158	*7.974*	0.085	*196.1*	217.7

Data in Italics were collected by the plant.
Plant ESP temperature is less than EER inlet temperature. EER inlet temperature was taken at the sample location, approximately 60.96 m from the ESP.

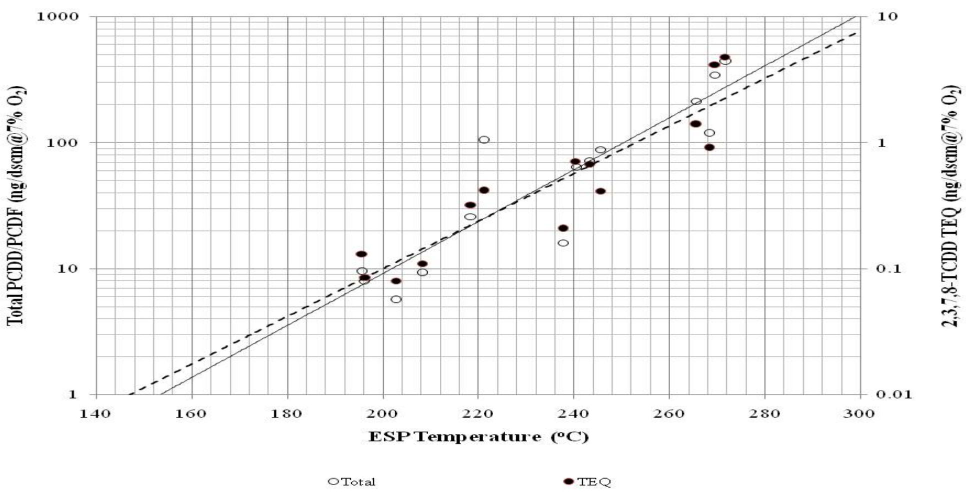

Figure 3: Effect of inlet temperature of APCD on dioxin formation

References

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