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CHLORINE VS. DIOXINS - CONTROL METHODS TO MINIMIZE EMISSIONS

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ABSTRACT

With the enactment of the Boiler and Industrial Furnace (BIF) regulations in August, 1991, hazardous waste combustors were required to sample and demonstrate compliance with Chlorine (Cl_2) emissions. The Resource Conservation and Recovery Act of 1976 required analysis and control of Hydrogen Chloride (HCl) emissions with no requirements for chlorine emissions from combustion systems burning chlorinated organic and organic waste streams. Previous to the BIF regulations, the levels of chlorine emissions from waste combustion systems had not been measured or their impacts on emissions known. Recent studies have demonstrated that the formation of precursors that create the Products of Incomplete Combustion (PICs) such as PCDD/PCDFs is caused by the free Cl_2, moreso than the HCl. Chlorine may be minimized in the combustion process by control of several parameters. These include temperature, excess Oxygen, Hydrogen to Cl_2 ratio, and Sulfur to Cl_2 ratio.

The effect of ash deposition on metallic surfaces such as boiler tubes, heat exchange surfaces, pollution control devices, ductwork and bag filter supports cause cells of activity between the HCl, Cl_2, iron, and copper which again serve as catalysts for the formation of PCDD/PCDFs. The effect of chlorine concentration in the flue gases, the temperatures of the surfaces allowing the reactions to take place, and the time available for the reaction will be discussed in relationship to the PIC emissions. HCl is easily absorbed in water, whether in a quench tower or spray dryer. Chlorine is much more difficult to neutralize than HCl and requires a basic solution of caustic or lime. Therefore, Cl_2 often persists in those APC systems that are designed for the 99% removal of HCl only.

Emissions of PCDD/PCDFs may be minimized to nondetectable levels with controls applied to combustion zones as well as APC systems knowing the impacts associated with the formation of the precursors and in particular, Chlorine. This paper should allow a better understanding of the conditions which create the problems associated with formation of free chlorine in combustion systems. It should help the designers and operators of these systems understand the potential solutions that can be implemented.

INTRODUCTION

In a 1978 study "Trace Chemistries of Fire", Dow Chemical Company contended that when mythical gods gave man fire, dioxin was thrown into the deal. [Dow Chemical, USA, 1978] Dow theorized that dioxins come primarily from combustion sources, including industrial incinerators, wood burning stoves and cigarette smoke and are omnipresent in the environment. Dr. Christopher Rappe and a number of other dioxin researchers stated the Dow study was scientifically flawed because it failed to discriminate among the different types of dioxins. [Rappe, Buser., C. Et al, 1978]

Combustion systems have been found to form dioxins in circumstances of inefficient combustion of chlorinated hydrocarbons. These are the result of insufficient oxygen (reducing atmosphere), poor mixing of the oxygen with the burning fuel containing chlorine, low temperatures (<800°C) and short residence times. Other mechanisms in the total combustion and APC system which lead to dioxin formation are flame bypassing and carryover, formation from organic precursors, gas phase synthesis in the flame, gas phase synthesis and surface catalyzed formation in the formation temperature window and formation within the bulk of carbonaceous solids. By control of temperature and oxygen, and insuring an adequate ratio of H_2 to Cl_2, it is possible to find and maintain optimum combustion conditions to minimize formation of free chlorine and unburned hydrocarbons and the resultant PCDD/PCDFs.

Hasselriis has shown results of tests at various types of incinerator applications. Comparisons are made to the combustion zone temperature and CO emission vs. total PCDD/PCDF emissions in ng/m^3 [Hasselriis, 1987]. Even in the most efficient combustion systems, reformation will occur in cooler zones downstream of the combustion zones. A great deal of research has taken place since 1989 to better understand this phenomenon. Critical to the formation is the presence of particulates to provide surface for catalytic reactions (copper chloride and iron chloride provide the most rapid reactions), temperatures of 250°C to 350 C, precursors such as chlorophenols, and stable compounds of chlorinated hydrocarbons plus residence time.

In this paper, the role of chlorine in the de Novo formation of PCDD/PCDF will be covered. Its release in the corrosion process between ash and boiler/economizer surfaces will be shown.

The effect of typical temperatures of tube surfaces found in the boiler and economizers as well as that on the quenched zones of APC systems in the formation of PCDD/PCDFs will be discussed.

More research is necessary on the effect of cleaning cycles on boiler tube surfaces as well as precipitator plates and fabric filters. Efforts are being made at this time to study these conditions and their effects on formation of PCDD/Fs.