

# IS THERE A MEANINGFUL DIOXIN: CHLORINE LINK IN COMMERCIAL SCALE SYSTEM FLUE GASES?

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## Discussion by

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If dioxin starts forming in significant quantities in the temperature range of 600-700°F, why not rapidly quench the gas stream from 800°F to 120°F with water?

## AUTHOR'S INTRODUCTION

The authors wish to thank the discussors for raising their questions. This provides us an opportunity to eliminate any confusion and hopefully advance the state of knowledge regarding dioxin emissions from commercial scale systems. Most importantly, by exposing the falsity of the implicit assumption in the title of the paper -- that there is a meaningful link between feed stream chlorine content and dioxin emissions -- regulatory policy can focus on areas that are likely to make a difference.

## AUTHOR'S REPLY

Rapid quench systems are not needed to minimize dioxin emissions from waste-to-energy systems. The majority of the dioxins are formed across the air pollution control system if the gas is above 425-450°F. Field measurements indicate that dioxins are quite low at the economizer outlet where flue gas temperatures are typically around 425°F. When a spray dryer is used, the flue gas temperature is

dropped below 350°F and dioxin levels approach the method detection limit for 2-hour samples. Consequently, a rapid quench to saturation temperatures is not really needed.

The WTE industry evolved along power plant design lines. This meant that energy recovery was important. Unfortunately quenching from 800°F throws away about 25 percent of the available energy. This, in turn, loses the potential to sell the same 25 percent of the steam or electricity that a WTE system could generate.

Since municipal waste combustors [MWCs] have historically complied with particulate emissions limitations and not HCl limits like hazardous waste incinerators, wet emissions control systems were not needed to meet regulatory requirements. Also, early experience with wet scrubbers was generally poor at these facilities. As a result, dry systems came to predominate the industry. We now know that the performance of spray dryer absorbers followed by an electrostatic precipitator or fabric filter can emit negligible dioxin concentrations.

## Discussion by

Stephen Boppart  
Senior Applications Specialist Norit  
Americas, Inc.

You have identified that temperature and catalysts seem to have a significant effect on dioxin formation. Could you elaborate in what temperature range in which this occurs and what catalyst plays a role?

#### AUTHOR'S REPLY

Mr. Boppert's question is really out of scope for the investigation. We have looked at much of the data and offer the following remarks as observations rather than definitive answers. Formation seems to occur in APCS with elevated temperatures. The most spectacular increases are seen across high-temperature ESPs, ones operating at 500-650°F window before an air heater. The specific catalysts have not been identified, but MWC flyash which has an extended, porous surface area with higher carbon levels (RDF fired and massburning systems characterized by char in the flyash) seems to be associated with higher dioxin levels. Note, however, that higher is a relative term. Dioxins have been measured in gas fired home furnace emissions as well as coal and oil fired boilers. The exact mechanisms have not yet been defined, but it is safe to say that chlorine feed rate is not a predominant factor in commercial scale systems.

#### Discussion by

Anthony Licata  
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There has been considerable speculation throughout the industry that there was no correlation between the chloride content of MSW and dioxin emissions. The publication of this paper and ASME's report should resolve this issue and allow us to get on to solving other issues.

The authors have also provided an additional service by providing a data base for fingerprinting various sources of dioxin emissions. With this method testers will be able to verify their data and, maybe in the future, we will be able to correlate ambient readings to sources.

Since the authors have indicated that the salt in ambient air can produce dioxins, I was wondering if they could identify the source of fluorine for furans?

I would like the authors to speculate on the question that if the ambient salt could cause dioxin emissions in MWCs, why don't we see the same relationship in coal- and oil-fired boilers?

#### AUTHOR'S REPLY

We apparently need to clarify our comment that there is sufficient chlorine in ambient air to make 2,500 ng/dsm<sup>3</sup> @ 7% O<sub>2</sub>, 2,3,7,8 TCDD. This statement was offered as an explanation of why reducing the chlorine content of waste feeds in commercial scale systems was not particularly productive. Even with chlorine free feed stocks, there is enough chlorine in ambient air to make more dioxin than is observed in commercial scale stack gas.

Okita, T., K. Kaneda, T. Yanaka and R. Sugai ("Determination of Gaseous and Particulate chloride and Fluoride in the Atmosphere," Atmospheric Environment, Vol. 8, pp. 927, 1974) indicate that the levels of atmospheric HCl are probably in the low-ppb range and the HCl is produced from the reaction of sea salts with acids and perhaps NO<sub>x</sub>. We are not aware of the source or concentration of ambient HF, although this would be an interesting thing to find out if fluorinated dioxins become a real issue.

Regarding dioxin from fossil fuel combustion, we are aware that Battelle measured dioxins in coal fired utility boiler stack emissions in the United States and by ETSU in English coal fired spreader stoker equipped boilers. While still speculation, perhaps with implementation of the NO<sub>x</sub> RACT Rule, which encourages coal fired utilities to "mess-up" their combustion and produce a high carbon fly ash instead of fused, glassy spheres, coal fired utility boiler dioxin emissions increased since the flyash conditions have been changed to become more like those that characterize spreader stokers. Ladesanstalt fur Immissionsschutz, Nordrhein-Westfalen found dioxins in the emissions from oil and natural gas fired home heating systems.