CHLORINE VERSUS DIOXINS - CONTROL METHODS TO MINIMIZE EMISSIONS

Joseph J. Santoleri, P.E.
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Discussion by

Floyd Hasselriis
Hasselriis Associates
New York, New York

The author has presented an excellent and needed summary of what is known regarding the combustion of wastes containing chlorinated hydrocarbons, especially emphasizing the formation of free chlorine in the combustion zoned, and the importance of chlorine in the formation of PCDD/PCDFs.

At the outset, it should be emphasized that the author has focussed on combustion of hazardous wastes in incinerators regulated by RCRA, and under the boiler and industrial furnace (BIF) regulations. These wastes and their combustors have been regulated in an entirely different manner than the emissions from municipal wastes. RCRA rules focussed on destruction and removal efficiencies (DREs) and either 99% control of HCl or, for BIFs, ground level concentrations of HCl.

The author emphasizes the importance of chlorine in the flue gases on the generation of dioxins, and the sparsity of test data on free chlorine release due to the lack of a regulatory requirement to measure it in the stack.

He notes that the level of HCl in combustion products or stack gases was not found to correlate with PCDD/F emissions in the cited ASME study by Rigo et al, and suggests that "we may find a better correlation between Cl2 entering the APC and PCDD/Fs emitted." I am concerned about this statement! In my judgement, the fact that the levels of HCl entering the APC has not been found to influence PCDD/F emissions **from facilities having acid gas scrubbers** shows that it is the effectiveness of APCs operating at temperatures less than 300°F which results in removing whatever dioxins and furans which may be present for whatever reason. Lack of production, absorption and condensation, at these temperatures is the reason for this effectiveness.

My question to the author is: is there any reason to believe that in spite of the low emissions from such APCs in spite of high HCl inlet levels, that high chlorine levels would cause formation of PCDD/Fs which would not be removed by the APC?

The author states that rapid quenching of combustion gases results in low dioxin emissions, as demonstrated in hazardous waste incinerators with no heat recovery boilers. By contrast, he cites high dioxin emissions from HWIs employing fabric filters followed by wet scrubbers and ionizing wet scrubbers. Has he given consideration to the possibility that dioxins captured by the scrubber may be emitted in the water vapor leaving the stack? In such a case it does matter whether or not dioxins are generated by poor combustion, or on metallic and flyash surfaces, since they were not effectively prevented from emission by the scrubber. Tests of WTE facilities having wet scrubbers have shown this to happen: there are also remedies to this problem.

AUTHOR'S REPLY

The RCRA regulations on HCI emissions for hazardous waste incinerators did not include chlorine. It was not until the BIF regulations were issued in 1991 that both chlorine and hydrogen chloride were listed as emissions to be controlled. HCI is easily absorbed in a water spray column or a tower using water as the colling and neutralizing media. There had been no requirement to measure chlorine gas. Responsible designers, owners and operators of waste burning combustors added the necessary scrubbers to absorb not only the HCI, but also the chlorine. However, many systems were installed without the chlorine scrubber. If the waste had little or no ash, particulate scrubbers were not required. Without scrubbers for PM or Cl_2 those systems with heat recovery coils or a waste heat boiler could trap any ash that did accumulate on the tube surface at a temperature of 300°C +/.50. This has resulted in PCDD/F reformation even through wet scrubbers were installed downstream of the boiler. Better control of chlorine formation in the combustion zone with a combination of temperature and excess air has the potential of reduced PCDD/F emissions.

Systems that do incorporate rapid quench of the flue gases often had excellent PM scrubbers with emission levels < 0.01 gr/dscf. Some that operated without PM scrubbers or with low efficiency PM scrubbers with the proper conditions upstream allowing the combination of PM, Cl_2, unburnt hydrocarbons at a temperature of 300°C would have emissions of PCDD/Fs. As Hasselriis notes, some wet scrubbers with rapid quenchers at WTE facilities had levels of PCDD/F emissions. One must look carefully at the upstream conditions on those systems with rapid quenchers.

Discussion by

Kim Chaffee
Regional Sales Manager
Wheelabrator Clean Air System, Inc.

Would it be useful to measure Cl_2 continuously to control dioxins & furans? If so, in what range?

AUTHOR'S REPLY

Chlorine should be measured upstream of the APC system to determine if the problem is due to combustion or to other causes such as corrosion reactions. Stack measurements are required to determine if the unit is in compliance. However, if chlorine may be considered as the cause the PCDD/F emissions, it must be measured downstream of the combustion zone or at the exit of the boiler prior to any rapid quench or absorption.

The range of chlorine measurement, will be site specific. Stack test data from 9 sites indicates a stack emission ranging from 0 to 100 ppm. Assuming a 90% scrubbing efficiency the range upstream of the APC system could be 0-1000 ppm. I would use a safety factor of 2 and extend the range to 2000 ppm.

Discussion by

A. John Chandler
A. J. Chandler and Associates Ltd.

In striving to control the release of contaminants from waste management alternatives, one important aspect is that we understand the chemistry and thermodynamics of the process. This paper makes a contribution to our understanding of the potential effects of chlorine in the formation of PCDD/Fs in waste combustion facilities.

While basic understanding is an important part in developing better control systems, the paper raises a number of questions in my mind, particularly in light of the findings of the referenced ASME/Center for Research and Technology Development report on the relationship between chlorine and PCDD/Fs in stack gases. It is very important to note that the ASME study found no practically significant relationship between changing levels of chlorine in the waste feeds to combustion facilities and PCDD/F air emissions. Similarly, no consistent or practically significant relationship was found when the analysis considered the available Cl_2 data and in its absence, used the Deacon reaction described by the author to account for the relative relationship between uncontrolled HCl and Cl_2 concentrations.

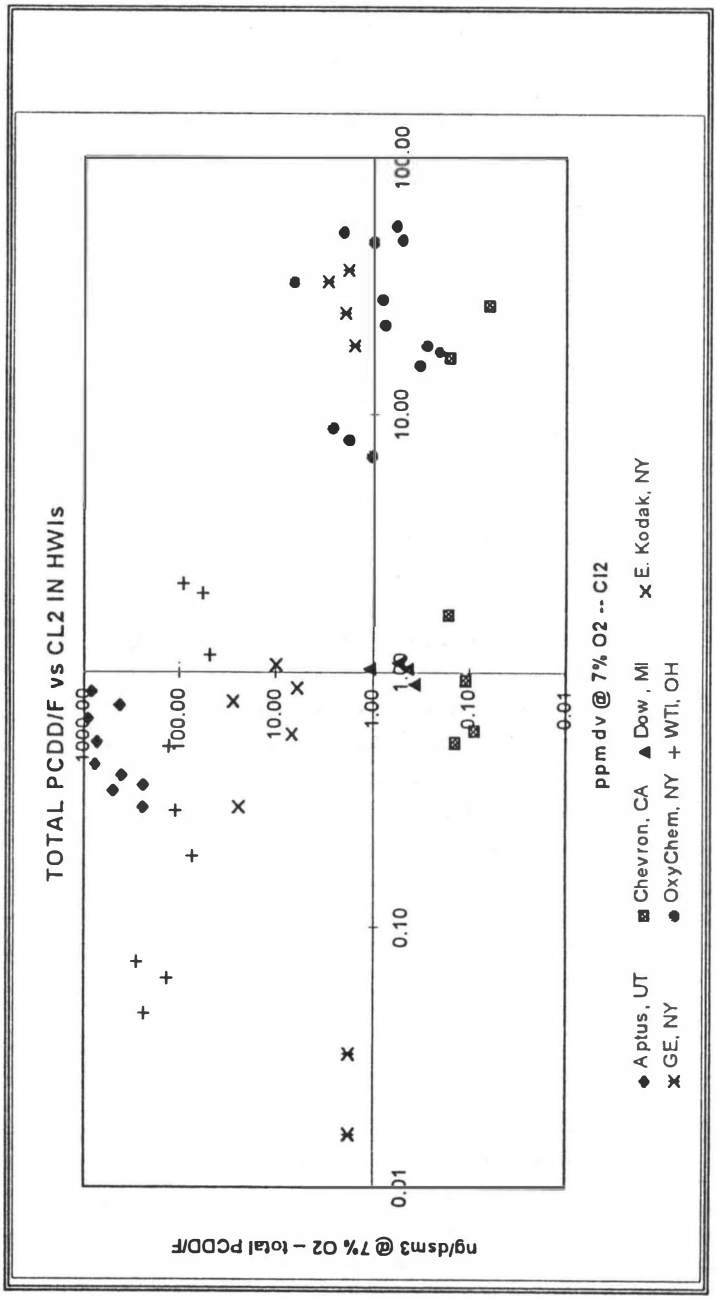
It was my understanding that in-depth reviews of test data and operational parameters on the latest generation of MWCs have shown little if any relationship between CO and PCDD/F. Only when CO levels clearly exhibit combustion deficiencies, i.e. levels well in excess of 200 to 400 ppm_{dv} @ 7% O_2, do we start to see increased PCDD/F emissions. Suggesting an unqualified link between CO and PCDD/F emissions does not promote more universal understanding of the process or when various factors predominate emissions.

A comparison of the author's Table 1 and the data provided in Appendix C of the referenced report shows that only some of the available data have been reproduced in Table 1. There are 40 sets of hazardous waste incinerator data in CRTD-36, including 8 units from 7 HWI with Cl_2 data. While some of these data sets might not meet the author's unstated selection criteria, does inclusion of the balance of the data change the author's conclusion?

When I extracted the data and plotted it in the following figure, I was unable to find any relationship between Cl_2 and PCDD/F within individual facilities. Of course, this may be because the data are all taken at the stack, downstream of the APCS, and the Cl_2 is controlled to some extent by the APCS. Also, since these data were taken at different facilities, it would be incorrect to simply draw a line through all the data points and conclude that increasing Cl_2 decreases PCDD/F emissions. This points out the necessity of considering both what the data are and confounding factors like different facilities and parametric variations in operating conditions when interpreting data.

In the discussion of sulfur effects, the author cites laboratory scale data with doping well outside the ranges normally experienced at MWCs and HWIs. Burning chlorinated plastics with various amounts of high sulfur coal in a fluidized bed boiler in Finland, also reported in CRTD-36, failed to demonstrate any change in PCDD/F air emissions, even at the extreme limits of 100% plastic and 100% coal. The author is asked to speculate on why an effect is found in laboratory scale apparatuses that disappears in at least this full scale installation. There seems to be little doubt that Cl_2 or Cl^- is the active chlorinating agent in various gas-phase and surface catalyzed reactions thought to produce the PCDD/F concentrations we are seeing at commercial facilities. However, since there seems to be little of it around under the temperature and moisture conditions existent in MWCs, the failure to find a significant or consistent relationship in the test data analyzed in CRTD-36 is probably correct. The author's expectation for Cl_2 concentrations seems to bear this out as well. Clearly, as the author suggests, more study would be valuable. This study should, however, be directed towards commercial scale facilities so the practical influences can be assessed. Furthermore, given the complex inter-relationships that occur, data on residue streams could be included in any future studies to eliminate these discharges as sources of significant concern as well.

This paper has made a significant contribution by bringing together information that can be used to address formation questions.



AUTHOR'S REPLY

I do agree with the findings of the ADME/CRTD - Vol. 36 on the relationship between chlorine feed and the PCDD/Fs in the stack gases. As found in the study, there were certain facilities that did show an increase in PCDD/F emissions with an increase in the chlorine content. It would be very interesting to determine if the chlorine levels upstream of the APC system were higher in those systems due to conditions in the combustion zone or due to conditions related to other factors as related in my paper. In reviewing Fig. 1 of your discussion to my paper, I reviewed the date that was presented in the database of the CRTD - Vol. 36. I note that there are cases where the Chlorine levels are higher than the HCI emissions. This is indicative of a problem related either to the combustion process or due to poor scrubbing of chlorine in the APC system. Those with higher chlorine than hydrogen chloride appeared to also have low levels of PCDD/Fs.

I did note however, that there is more direct correlation with PCDD/F emissions to TSP emissions. The scatter of the data is much less than in your Fig. 1 and indicates that the better the particulate removal efficiency, the lower are the emissions of PCDD/Fs. This points to the importance of having both TSP (PM) and acid gas (especially chlorine) scrubbers with high removal efficiencies to minimize formation of PCDD/Fs in the APC system.

Regarding the relationship of sulfur levels in the lab scale vs the full scale systems, this may again be related to the effectiveness of the APC systems installed. The laboratory system was run to show the effectiveness of sulfur in reducing the amount of free chlorine formed. The chlorine gas is converted to the hydrogen chloride acid gas which is easily absorbed in water without the need for costly neutralizing media such as sodium hydroxide. High efficiency PM and acid gas scrubbers as used on the full scale system was not provided in the laboratory test unit. This was included in my paper to point out the importance of using sulfur to reduce the free halogens and insure conversion to the halide which is much easier to absorb in conventional scrubbers.

AUTHOR'S CLOSURE

I appreciate the fact that all discussers realize that there is much more information and research necessary to understand the phenonema that occur in these reactions. It is extremely important that research be continued in these areas under government or private sponsorship.