

THE EFFECT OF METAL CATALYSTS ON THE FORMATION OF POLYCHLORINATED DIBENZO-p-DIOXIN  
AND POLYCHLORINATED DIBENZOFURAN PRECURSORS

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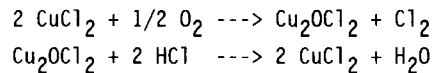
ABSTRACT

The catalytic effects of copper and iron compounds were examined for their behavior in promoting formation of chlorine ( $Cl_2$ ), the major chlorinating agent of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), in an environment simulating that of municipal waste fly ash. Formation of  $Cl_2$  occurred as a result of a metal-catalyzed reaction of HCl with  $O_2$ . Catalytic activity was greatest at a temperature of approximately 400 °C, supporting a theory of de novo synthesis of PCDDs and PCDFs on fly ash particles downstream of waste combustion.

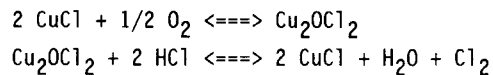
INTRODUCTION

The synthesis of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) has been associated with experiments on municipal waste fly ash particles. Experiments in which fly ash was heated in a flowing air or simulated flue gas atmosphere have noted significant levels of PCDD and PCDF formation (Vogg et al., 1987). These tests support a theory suggesting de novo synthesis of PCDD and PCDF compounds by condensed inorganic and organic precursors on fly ash particles at temperatures around 350 °C (Hagenmaier et al., 1987a). The ability of gas phase/fly ash reactions to produce PCDDs/PCDFs has been further supported by Dickson and Karasek (1987), Rghei and Eiceman (1982, 1984, 1985), Eiceman and Rghei (1982), Vogg and Stieglitz (1986), and Stieglitz and Vogg (1987, 1988).

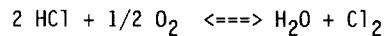
The chlorine source for organic chlorination was determined by gas phase testing to be  $\text{Cl}_2$  rather than  $\text{HCl}$  (Gullett et al., 1989). The Deacon process of chlorine production (Tilly, 1981) with  $\text{CuCl}_2$ :



or  $\text{CuCl}$ :



leading to:



was proposed (Griffin, 1986) and tested (Hagenmaier et al., 1987a) for the role of fly ash-borne metal chlorides in catalytically producing  $\text{Cl}_2$  from  $\text{HCl}$  for the subsequent organic chlorination reaction. Under  $\text{O}_2$ -present conditions, the formation of  $\text{Cl}_2$  was detected with  $\text{CuCl}_2$  (Hagenmaier et al., 1987a). The presence of  $\text{HCl}$  increased the formation of PCDD and PCDF, supporting the proposed mechanism for production of the organic chlorinating agent,  $\text{Cl}_2$ .

Various testing has been done with  $\text{CuCl}_2$  catalysts to verify this mechanism. Stieglitz et al. (1987) have related PCDD and PCDF yield to reaction time, carbon concentration, catalyst amount, and the presence of water vapor. Other +2 charge metals tested included Mg, Zn, Fe, Mn, Hg, Cd, Ni, Sn, and Pb; however, with these other cations, PCDD and PCDF concentrations remained below detection limits, emphasizing the role of Cu noted by Vogg et al. (1987) and Hagenmaier et al. (1987b).

In this work, the role of Cu- and Fe-based catalysts in the formation of  $\text{Cl}_2$ , the major chlorinating agent of PCDDs and PCDFs, was examined through testing in a simulated flue gas atmosphere at temperatures ranging from 300 to 450 °C.

### Materials and Methods

Experiments were run in a concentric quartz tube reactor described in an earlier work (Gullett et al., 1989). Figure 1 illustrates the reactor system and inorganic sampling train.

A number of Cu and Fe compounds ( $\text{Cu}$ ,  $\text{CuO}$ ,  $\text{Cu}_2\text{O}$ ,  $\text{CuCl}$ ,  $\text{Fe}$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ) were tested for catalytic activity. The catalyst (1 g) was embedded in a quartz wool plug, placed in the center of the inner tube of the quartz reactor, and heated to the test temperature. Baseline gas flows were set to give 1500 ppm  $\text{HCl}$ , 10%  $\text{O}_2$  with a  $\text{N}_2$  balance for a total flow rate of 1 l/min. Depending on the catalytic activity, tests lasted from

15 to 30 minutes. Parameters investigated included residence time, temperature,  $O_2$  concentration, and HCl concentration.

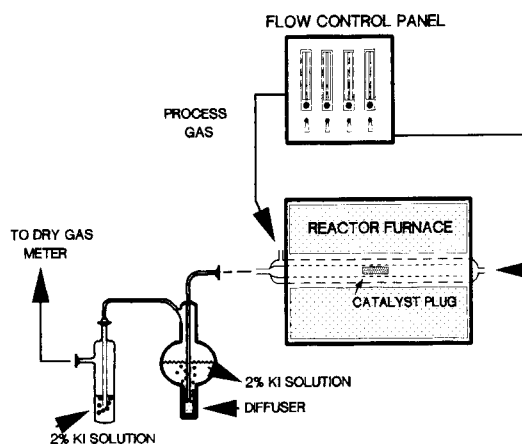


Figure 1. Reactor system and sampling train.

HCl concentrations were measured by gas phase measurements with a Thermoelectron model No. 15 analyzer.  $Cl_2$  concentrations were determined by bubbling the reactor effluent through two impingers containing a potassium iodide (KI) solution buffered with 1 M sodium hydroxide (NaOH) and 1 M potassium dihydrogen phosphate ( $KH_2PO_4$ ). This method is described fully in Fisher et al. (1987).

X-ray diffraction (XRD) analyses for compound identification were performed on a Siemens model D-500 diffractometer with a copper target source running at 50 kV and 40 mA. The entrance aperture was 1.0 degree and the detector slit was 0.05 degree. A scintillation detector with a graphite monochromator was used. Spectra were identified by computer comparison with the Joint Committee for Powder Diffraction Spectra (JCPDS) spectral files.

X-ray fluorescence (XRF) analyses for element identification were performed on a Siemens SRS-101 using chromium radiation at 50 kV and 40 mA. A lithium fluoride 202 analysis crystal was used for dispersion. The Cu peak and background were counted for 1 min.

### Results and Discussion

Testing with Cu-based catalysts (Cu, CuO,  $Cu_2O$ ) embedded in the quartz wool plug indicated the production of  $Cl_2$  through 1) HCl depletion as recorded by the Thermoelectron HCl analyzer and 2) positive KI tests. These results validated the likelihood of the Deacon process occurring, indicating catalytic activity. Tests show that all three catalysts were nearly equal in terms of  $Cl_2$  production. XRD analyses of the quartz

wool/catalyst plugs from all three catalysts after testing were conducted to determine the compounds present. Testing with CuO catalyst resulted in a black catalyst plug followed by green crystals toward the tube reactor exit. The black substance was identified as CuO (Tenorite, JCPDS No. 5-661). The deliquescent green crystals were identified as  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (Eriochalcite, JCPDS No. 33-451). Analysis of the  $\text{Cu}_2\text{O}$  plug gave identical results. The Cu plug also left a CuO core, but the outer crystals were found to be CuCl (Nantokite, JCPDS No. 6-344). As described previously, CuCl and  $\text{CuCl}_2$  are the active Deacon process catalysts, explaining the production of  $\text{Cl}_2$  in the presence of the compounds tested. Catalytic activity was found to be stable over a period of several hours after which it declined as the active catalyst slowly migrated with gas flow down the reactor tube and out of the high temperature zone.

The  $\text{Cu}_2\text{O}$  was further tested to elucidate the effect on  $\text{Cl}_2$  production of reaction time (about 2 to 10 s), temperature (300 to 450 °C), HCl concentration (0 to 1500 ppm), and  $\text{O}_2$  concentration (0 to 10%). Baseline conditions of 10 s gas residence time, 400 °C, 1500 ppm HCl, 10%  $\text{O}_2$ , and balance  $\text{N}_2$  were used unless otherwise indicated.

The effect of gas residence time upon the catalytic conversion of HCl to  $\text{Cl}_2$  is illustrated in Figure 2. The conversion to  $\text{Cl}_2$  is independent of time over the range (2.7 to 8.2 s) of this testing effort, indicating that the reaction forming  $\text{Cl}_2$  takes place rapidly. Conversion of HCl between 35 and 45% resulted under baseline conditions.

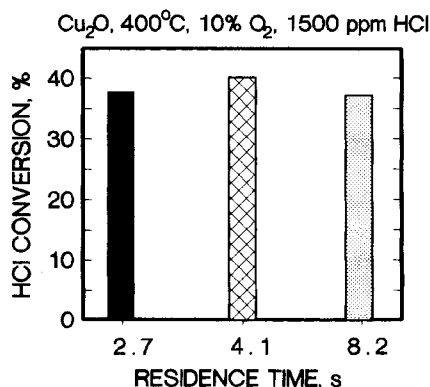


Figure 2. Effect of residence time on the Deacon process.

The results of testing  $\text{Cu}_2\text{O}$  under baseline conditions for HCl depletion ( $\text{Cl}_2$  production) show that catalytic activity is greatest at about 430 °C over the tested range of 300 to 500 °C. Figure 3 illustrates maximum HCl conversion between 50 and 60% formation. Tests at 300 °C gave no  $\text{Cl}_2$  production.

The influence of  $O_2$  concentration upon the Deacon process was examined by variation of the baseline test conditions (400 °C, 1500 ppm HCl) from 0 to 10%  $O_2$ . Figure 4 shows an extreme effect of  $O_2$  concentration from 0 to 3%, after which HCl conversion ( $Cl_2$  production) stabilized at about 45%. Above 3%  $O_2$ , the reaction may be considered to be zero order in  $O_2$ .

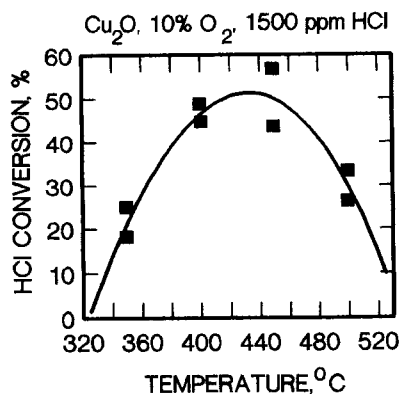


Figure 3. Temperature dependency of the Deacon process.

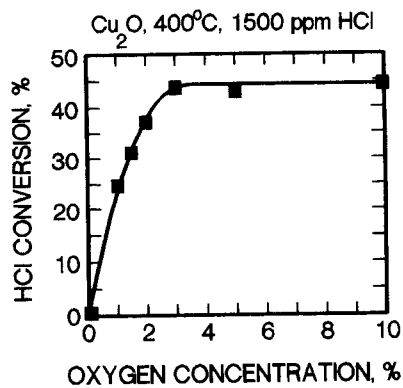


Figure 4. Effect of oxygen concentration on the Deacon process.

Variation of HCl concentration from 250 to 1500 ppm exhibits no significant change in conversion levels for each of the catalysts tested as shown in Figure 5. This clearly demonstrates a first order dependency on HCl for the reaction. Figure 6 shows a plot of reaction rate as a function of HCl concentration for the reaction with Cu as the catalyst, with the first order dependency illustrated by the linearity of the plotted points. As a result of this relationship, a decrease in HCl supplied to the catalyst surface will result in a decrease in production of  $Cl_2$ .

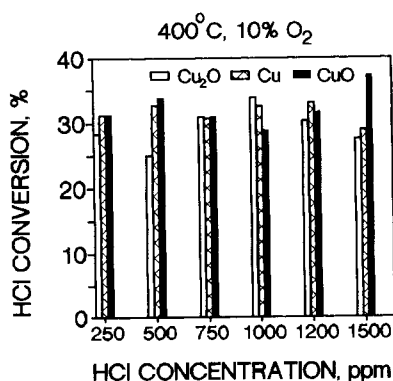


Figure 5. Effect of HCl concentration on the Deacon process.

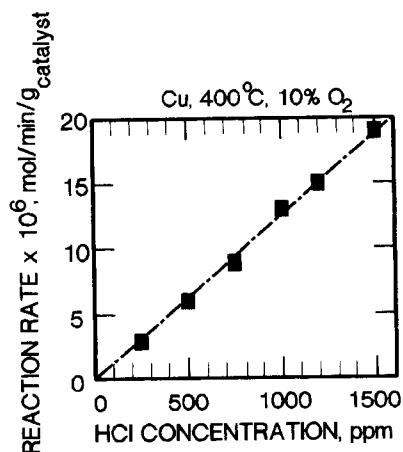


Figure 6. Effect of HCl concentration on the Deacon process reaction rate.

The role of other catalysts in the production of PCDDs and PCDFs was analyzed for their ability to produce  $\text{Cl}_2$ . Three Fe-based catalysts (Fe,  $\text{Fe}_2\text{O}_3$ , and  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ) were tested using the baseline conditions and found not to be active for the Deacon process (no  $\text{Cl}_2$  production); however, thermal breakdown of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ , resulting in  $\text{Cl}_2$  production, was noted at temperatures around and above 300 °C.

A sample of municipal waste fly ash provided by Environment Canada from the Quebec City plant was analyzed by XRD and XRF for the presence of Cu compounds. Preliminary XRF results indicated the amount of elemental Cu to be 0.3 wt %. XRD analysis for individual Cu compound identification was impossible due to the small amount of Cu present and the large number and type of other phases present. Initial spectra showed considerable amounts of sodium chloride (NaCl), potassium chloride (KCl), and other water soluble phases. Testing in the tube reactor with a 2.7 g plug of the fly ash (0.008 g Cu) under baseline conditions resulted in production of trace  $\text{Cl}_2$  (1.3% conversion of HCl).

#### CONCLUSIONS

The experimental results indicate that the presence of Cu compounds in municipal waste combustion fly ash will lead to the conversion of HCl to  $\text{Cl}_2$  via the Deacon process. This process readily takes place at temperature and  $\text{O}_2$  conditions similar to those shown by other researchers to be favorable to the formation of PCDDs/PCDFs. Furthermore, thermal breakdown of other metal chlorides may contribute  $\text{Cl}_2$ . Previous experiments have shown that  $\text{Cl}_2$  is the predominant chlorinating specie in formation of chlorinated precursors to PCDDs and PCDFs. Therefore, reducing the amount of  $\text{Cl}_2$  present in the PCDD/PCDF formation region should decrease the levels of these highly toxic compounds found in municipal waste combustors.

#### ACKNOWLEDGMENTS

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