NBSIR 84-2872

Containment of Dioxin Emissions from Refuse Fired Thermal Processing Units - Prospects and Technical Issues

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
National Engineering Laboratory
Center for Fire Research
Washington, DC 20234

February 1984

Issued May 1984

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, ***Secretary***
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, ***Director***

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1. EXECUTIVE SUMMARY

There are reports [1-5] that dioxins are emitted from some refuse-fired thermal processing units. The extent to which such emissions occur and the conditions that lead to such emissions have not been clearly defined at the present time. If it is determined that dioxin emissions should be contained or minimized, then it will be necessary to examine strategies for achieving goals of containment or minimization of these emissions.

This report addresses the prospects for and technical issues concerned with the utilization of chemisorption as a technique for containment of dioxin emissions from refuse fired thermal processing units. The results developed in this report suggest that containment, through chemisorption of dioxin emissions from refuse fired thermal processing units, may be technically feasible. Suggestions for research objectives and full scale tests are outlined. Refuse fired thermal processing units equipped for energy recovery may be more preferable than those units which are not equipped for energy recovery, if chemisorption occurs more efficiently at temperatures which are substantially lower than furnace gas exit temperatures.

2. GOALS OF THIS REPORT

- Achieve an understanding of a possible strategy for containment of dioxin emissions from thermal processing units.
- Delineate technical uncertainties which should be addressed to refine the above strategy for containment of dioxin emissions from thermal processing units.
- Delineate experiments to resolve technical uncertainties which may be carried out in laboratories and in full scale thermal processing units.
- Provide a simple model for engineers to use to estimate potential dioxin containment by chemisorption.

3. OBJECTIVES OF THIS REPORT

- Review literature reports of dioxin emissions from thermal processing units and assess long term dioxin containment possibilities.
- Construct an analytical model for chemisorption of dioxins in thermal processing units.
- Utilize literature reports to estimate numerical values of input parameters for the model.
- Utilize the model and input parameters to suggest the feasibility of dioxin containment by chemisorption.
- Evaluate the model test results to suggest technical uncertainties for application of chemisorption containment methods.
- Suggest laboratory-scale and full-scale tests to resolve technical uncertainties for application of chemisorption containment methods.

4. BACKGROUND

There are reports [1-5] that dioxins (in this report "dioxins" means any of the various chlorinated dibenzo-p-dioxins) and related compounds, e.g. furans (in this report "furans" means any of the various chlorinated dibenzofurans) are emitted from some refuse-fired thermal processing units (in this report "thermal processing units" means incinerators and incinerators equipped for energy recovery, i.e. boilers). The extent to which such emissions occur and the conditions that lead to such emissions have not been clearly defined at the present time. If it is determined that dioxin or furan emissions from refuse-fired thermal processing units should be contained or minimized, then it will be necessary to examine strategies for achieving goals of containment or minimization of these emissions.

This report addresses the prospects for and technical issues concerned with the utilization of chemisorption as a technique for containment of dioxin or furan emissions from refuse-fired thermal processing units. There is some preliminary evidence [6] that desorption energies of chemisorbed dioxins on fly ash are large. Values for desorption energies, E_D, of dioxins may be as large as 40-50+ $\mathrm{kcal \cdot mol^{-1}}$[6]. Furans, being in some respects chemically similar to dioxins (see Figure 1) may have comparable desorption energies. As shown in Figure 1. it is assumed that unoccupied adsorption sites on the fly ash are either hydroxyl groups or oxygen atoms. The basis for this suggestion is indicated in the APPENDICES and references contained therein. If it is true that desorption energies are substantial for these compounds, then successful chemisorption of these compounds on some inexpensive adsorbent, e.g. fly ash, may provide a basis for containment of these materials. If fly ash containing chemisorbed dioxins or furans is disposed of into the environment at an ambient temperature of 25 °C and if the rate constant, k_D, for thermal desorption of dioxins or furans is estimated to be [6]

$$k_D < 10^{13} e^{-40000/(RT)} \sec^{-1} \qquad (1)$$

then the time required for one percent of the dioxins or furans to leach from the fly ash due to thermal desorption is about 6.9 million years. Thus, unless it can be demonstrated that chemisorbed dioxins can be leached in the environment by other than ambient thermal stresses, the above construct implies that chemisorbed dioxins on fly ash may remain chemically bound for extremely long periods of time. If this is demonstrated to be a valid finding, then chemisorption may offer a means for safe containment of dioxins or furans, if such a containment is determined to be desirable.

This report provides a feasibility analysis for dioxin or furan containment by chemisorption on a suitable adsorbent. In the following discussion, chemisorption of dioxins on fly ash is modelled under conditions which may be achieved in thermal processing units. The possibilities for examining and testing adsorbents other than fly ash are discussed in the SUMMARY AND CONCLUSIONS section. It is suggested that furans may be considered (see Figure 1) as being amenable to an analysis similar to that presented in this report for dioxins. Therefore an analysis of furan chemisorption is not explicitly presented.

Research objectives and field testing of concepts outlined in this report are recommended in the SUMMARY AND CONCLUSIONS section of this report. It is suggested that the recommended research, development and testing may help optimize understanding of chemisorption of dioxins and furans as a containment technology.

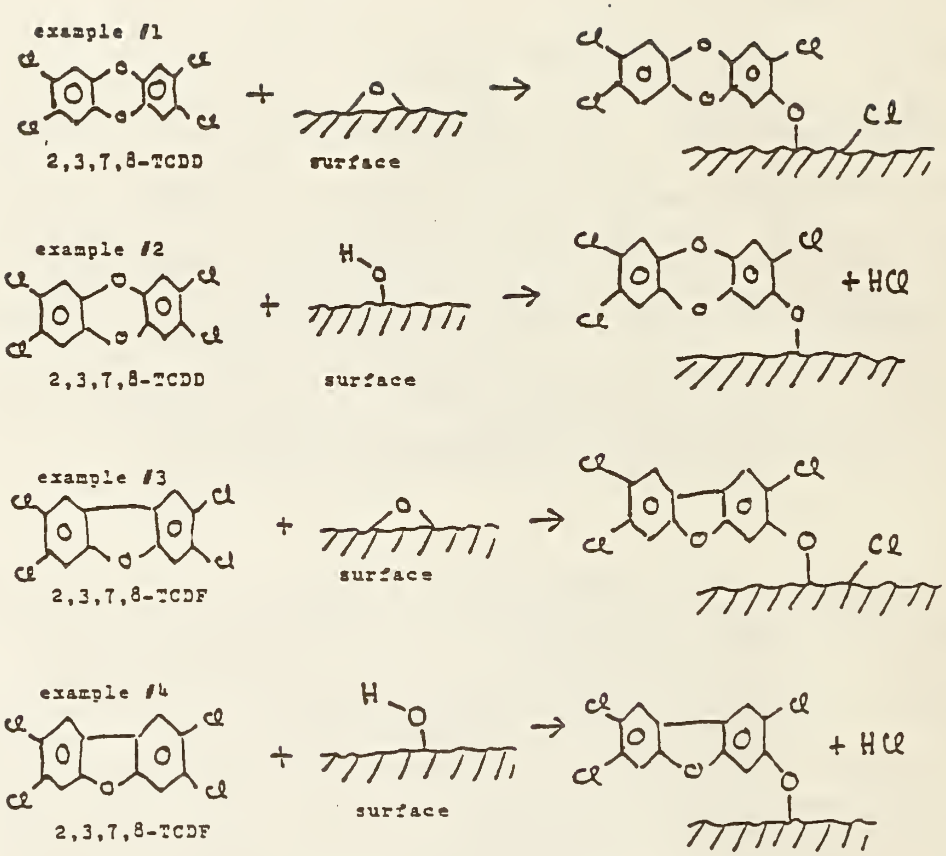

Figure 1. Possible Mechanism(s) for Dioxin (Furan also shown) Chemisorption on Fly Ash.

The examples shown above include reaction of 2,3,7,8-TCDD or 2,3,7,8-TCDF with surfaces which are either sparsely or largely covered with hydroxyl groups. The reader is referred to the APPENDICES for more details.

Some useful background documents are provided in the APPENDICES. These reports are intended to provide a basis for supporting the models for chemisorption that will be developed and to provide a basis for understanding physical chemical aspects of dioxin emissions from thermal processing units.

In the discussions which follow, numerous assumptions and approximations are utilized. Most of these are described in detail in APPENDIX C. Since the intent of this report is only to suggest concept feasibility, the assumptions and approximations should be acceptable. The reader can refine calculations as desired. However, in view of many technical uncertainties, substantial further refinements are probably not warranted until some of the research, development and testing, which is recommended in the SUMMARY AND CONCLUSIONS section of this report, is carried out.

5. MODEL DEVELOPMENT

In the following discussion, it is assumed that chemisorption of competitively adsorbed species is to be modeled in which the chemisorption is described by a Langmuir isotherm [7]. The model is constructed to describe the process of competitive chemisorption in thermal processing units. It is assumed that chemisorption of dioxins and other gaseous species onto entrained fly ash in a hot flowing gas stream may be modeled by treating all species other than dioxins in the gas stream as being approximately equivalent in terms of chemisorption properties. The purpose of this assumption is to simplify calculations and demonstrate the effect of a difference in the adsorption energy, E_A, between dioxins and other species, upon the chemisorption properties of the gas/fly ash mixture. Another advantage of this approximation (and other approximations discussed below) is that a closed-form analytic solution may be developed which may permit the reader to easily use the model to test input parameter variations with a pocket calculator. It is left to the reader to construct whatever refinements are desired, using the model to be developed, as a starting basis.

The reader is instructed to review the material presented in APPENDIX C, particularly the material which deals with modelling catalytic dioxin formation, prior to reading the following discussion. The material presented in the APPENDIX provides a basis for the terminology, assumptions and discussions which are incorporated into the discussion and model development which follows. Where possible, the symbols used in the report which is presented in the APPENDIX, are also used in the discussion which follows.

Dioxins are denoted by the symbol, d. All other competitively chemisorbed species are denoted by the symbol, a. If the dioxins and other species are denoted as being in the gas phase, their respective symbols are not subscripted. If the dioxins and other species are denoted as being chemisorbed, they are symbolized respectively as d_s and a_s, i.e. the symbols are subscripted to denote chemisorption. Adsorption sites for chemisorption are denoted by the symbol, S. For simplicity all adsorption sites are considered to be identical.

Competitive chemisorption can be described by the following representation:

$$d + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} d_s \qquad (2)$$

$$a + S \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} a_s \qquad (3)$$

The time dependent rates of chemisorption of d and a respectively can then be represented by the following equations (notations follow APPENDIX C and Laidler, in reference [7]:

$$\dot{d}_s \equiv \frac{d}{dt}(d) = k_1\, d\, (1- \theta_a - \theta_d) - k_{-1}\, d_s \qquad (4)$$

$$\dot{a}_s \equiv \frac{d}{dt}(a) = k_2\, a\, (1 - \theta_a - \theta_d) - k_{-2}\, a_s \qquad (5)$$

The following definitions and assumptions are made (refer to APPENDIX C for details and an explanation of variables):

$$d = d_o - d_s \qquad (6)$$

$$a = a_o - a_s \qquad (7)$$

$$\Theta_a \equiv \frac{1}{4N_p} \left(\frac{\sigma_a}{\sigma_p}\right)^2 a_s \tag{8}$$

$$\Theta_d \equiv \frac{1}{4N_p} \left(\frac{\sigma_d}{\sigma_p}\right)^2 d_s \tag{9}$$

$$\Theta_a >> \Theta_d \tag{10}$$

The subscript, o, used in equations (6) and (7) above denotes initial values of the concentrations of a and d prior to the onset of chemisorption. If the following additional definitions are made:

$$a_1 \equiv k_2 a_o \tag{11}$$

$$a_2 \equiv - \left\{ \frac{k_2 a_o}{4N_p} \left(\frac{\sigma_a}{\sigma_p}\right)^2 + k_2 + k_{-2} \right\} \tag{12}$$

$$a_3 \equiv \frac{k_2}{4N_p} \left(\frac{\sigma_a}{\sigma_p}\right)^2 \tag{13}$$

Equations (6) through (13) can be used to write equation (5) in the form

$$\dot{a}_s \cong a_1 + a_2 a_s + a_3 a_s^2 \tag{14}$$

The physically meaningful solution to this equation can be shown to be [8]:

$$a_s = \frac{C_1}{C_o} \frac{\left[1 - e^{-t_a j}\right]}{\left[e^{-t_a j} - \frac{C_1}{C_2}\right]} \tag{15}$$

Below, j, C_o, C_1 and C_2 are defined. The symbol, t_a, denotes time for chemisorption of a.

$$j \equiv (a_2^2 - 4a_1a_3)^{\frac{1}{2}} \tag{16}$$

$$C_o \equiv 2a_3 \tag{17}$$

$$C_1 \equiv a_2 - j \tag{18}$$

$$C_2 \equiv a_2 + j \tag{19}$$

At equilibrium ($t_a \rightarrow + \infty$), equation (15) has the solution:

$$(a_s)_{EQ} = - \frac{C_2}{C_o} \tag{20}$$

At equilibrium the forward and reverse rate components of the R.H.S. of equation (4) can be equated to each other, and it follows from equation (10) that the following equilibrium expression can be developed:

$$\left(\frac{d_s}{d}\right)_{EQ} \cong \left(\frac{k_1}{k_{-1}}\right)\left[1- \left(\Theta_a\right)_{EQ}\right] \tag{21}$$

This can also be written as:

$$\left(\frac{d_s}{d}\right)_{EQ} \cong \left(\frac{k_1}{k_{-1}}\right) \left[1- \frac{1}{4N_p} \left(\frac{\sigma_a}{\sigma_p}\right)^2 \left(a_s\right)_{EQ}\right] \tag{22}$$

Rearrangement of equation (15) provides the following solution:

$$t_a = \frac{1}{j} \ln \left[\frac{1 + a_s\left(\frac{C_o}{C_1}\right)}{1 + a_s\left(\frac{C_o}{C_2}\right)}\right] \tag{23}$$

The time required to achieve 99% of the equilibrium value of chemisorbed a_s is found from use of equations (20) and (24) shown below to be:

$$a_s = 0.99\ (a_s)_{EQ} \tag{24}$$

$$t_a(99\%) = \frac{1}{j}\ \ell n\ \left[10 \left\{ 1 - 0.99\ \frac{C_2}{C_1} \right\}\right] \tag{25}$$

using the definition:

$$y \equiv \frac{1}{4N_p}\left(\frac{\sigma_a}{\sigma_p}\right)^2 \tag{26}$$

The expressions which have been developed above can be used to show that

$$\dot{d}_s \cong k_1 d_o\ (1 - ya_s) - [k_{-1} + k_1\ (1 - ya_s)] d_s \tag{27}$$

Near equilibrium,

$$a_s \cong (a_s)_{EQ} \tag{28}$$

If the time required for a_s to reach an equilibrium value is significantly shorter than the time required for d_s to reach an equilibrium value, equation (28) above may be regarded to be exact.

Defining

$$Q \equiv k_1 d_o\ [1 - y(a_s)_{EQ}] \tag{29}$$

$$P \equiv [k_{-1} + k_1\ \{1 - y(a_s)_{EQ}\}] \tag{30}$$

It can be shown that near the equilibrium value of d_s that:

$$d_s \cong \frac{Q}{P}\ (1 - e^{-Pt}) \tag{31}$$

This equation can be rearranged to show that near the equilibrium value of d_s:

$$t \cong - \frac{1}{P} \ln \left(1 - \frac{P}{Q} d_s\right) \qquad (32)$$

To determine the time required to achieve 99% of the equilibrium value of chemisorbed d_s, proceed as follows. First calculate a value for $(a_s)_{EQ}$. Use this value for $(a_s)_{EQ}$ and equations (6) and (22) to calculate a value for $(d_s)_{EQ}$. Set:

$$d_s = 0.99 \, (d_s)_{EQ} \qquad (33)$$

Then use this value of d_s to calculate t_d (99%) in equation (32).

A more approximate value for t_d (99%) may be developed using equation (41) of the report presented in APPENDIX C. Then if the activation energy for chemisorption, E_A of d_s is non-zero [6,9], it follows that

$$t_d^{\text{approx}}(99\%) \cong - \frac{4N_p}{Z_p^d a_o} \left(\frac{\sigma_p}{\sigma_a}\right)^2 \ln \left[1 - \frac{0.99 \left(d_s\right)_{EQ}}{4N_p} \left(\frac{a_o}{d_o}\right)\left(\frac{\sigma_a}{\sigma_p}\right)^2\right] e^{+E_A/(RT)} \qquad (34)$$

The utility of this equation is that it explicitly illustrates the dependence of the time to achieve near-equilibrium chemisorption upon the activation energy for adsorption.

In performing calculations of $(a_s)_{EQ}$ and $(d_s)_{EQ}$ utilizing the above equations, it is important to determine that in spite of approximations used, the results obtained are physically meaningful.

For example, since the available number of surface adsorption sites is limited, the <u>calculated</u> values for $(a_s)_{EQ}$ and $(d_s)_{EQ}$ should be reset to the values $(a_s)_{max}$ and $(d_s)_{max}$ (these are <u>upper limit</u> values for a_s and d_s) respectively, if:

$$(a_s)_{EQ} > (a_s)_{max} \tag{35}$$

$$(d_s)_{EQ} > (d_s)_{max} \tag{36}$$

The values for $(a_s)_{max}$ and $(d_s)_{max}$ may be calculated from the following relationships which are valid assuming equilibrium chemisorption [7] and $a_o \overset{-}{>} (a_s)_{max}$ and $d_o \overset{-}{>} (d_s)_{max}$:

$$\left(\frac{\Theta_d}{\Theta_a}\right)_{max} \cong \left(\frac{\Theta_d}{\Theta_a}\right)_{EQ} = \frac{K_d}{K_a}\frac{P_d}{P_a} = \frac{k_1 k_{-2} d_o m_a}{k_{-1} k_2 a_o m_d} \equiv h \tag{37}$$

$$\left(\Theta_d\right)_{max} + \left(\Theta_a\right)_{max} = 1 \tag{38}$$

Equations (37) and (38) yield the results:

$$(\Theta_d)_{max} \cong h(1+h)^{-1} \tag{39}$$

$$(\Theta_a)_{max} \cong 1 - (\Theta_d)_{max} \tag{40}$$

These equations can be used with equations (8) and (9) to show that

$$(d_s)_{max} \cong 4N_p \left(\frac{\sigma_p}{\sigma_d}\right)^2 \left(\Theta_d\right)_{max} \tag{41}$$

$$(a_s)_{max} \cong 4N_p \left(\frac{\sigma_p}{\sigma_a}\right)^2 (\Theta_a)_{max} \tag{42}$$

In equation (37) above, p_d, p_a, m_d and m_a are respectively the initial (prior to chemisorption) partial pressures of d and a and the molecular weights of d and a.

In addition, if there are more adsorption sites for a and d than initial gas phase species, i.e., if

$$(d_s)_{max} > d_o \tag{43}$$

$$(a_s)_{max} > a_o \tag{44}$$

Then if $(a_s)_{EQ} > a_o$ and $(d_s)_{EQ} > d_o$, the calculated values for $(a_s)_{EQ}$ and $(d_s)_{EQ}$ should be reset to a_o and d_o respectively, instead of to $(a_s)_{max}$ and $(d_s)_{max}$ respectively.

The rate constants for adsorption and desorption of dioxins and other competitively adsorbed species are determined as described in APPENDIX C. However, note that the calculations which will be described in the following section are based on the presumption that there is a non-zero activation energy E_1, for adsorption of dioxins on fly ash. Therefore k_1 is represented by the analytic form:

$$k_1 = Z_p^d \; e^{-E_1/(RT)} \tag{45}$$

The superscript, d, denotes collisions of dioxins with particulates.

6. MODEL INPUT PARAMETERS

Values for input parameters have been assigned to test the model that has been constructed. The values are reported either in Table I of this report, or in APPENDIX C. The reader is referred to APPENDIX C for a discussion of how the values assigned to parameters which appear in equations presented there have been established.

The values assigned to parameters reported in Table I have been chosen based upon information inferred from recent literature and to illustrate the dependence of the adsorption process upon key variables. Some comments pertaining to parameter assignment are presented in Table I. Other comments are presented below.

In general, it should be understood that the assigned values for parameters are approximations, just as the model itself is an approximation. As mentioned previously, the reader can refine the model as desired and can test other input values on this or a refined model. Notwithstanding approximations that are made, the model serves to illustrate how the employment of chemisorption methods may be used to contain dioxin emissions.

E_1, the activation energy for chemisorption of a dioxin molecule, has been assigned a value of 10 $\mathrm{kcal \cdot mol^{-1}}$. This value is assigned based on the observation reported in the literature [9] that significant chemisorption of dioxins on fly ash occurs at temperatures above about 100 °C. In the same literature, it is reported that thermal desorption of dioxins is apparently irreversible even at temperatures up to about 300 °C. Additionally, estimates of the activation energy for thermal desorption of dioxins from fly ash based upon models for catalytic dioxin formation have been suggested [6]. It appears that the activation energy for thermal desorption of chemisorbed dioxins may be large, perhaps in excess of 40 $\text{kcal}\cdot\text{mol}^{-1}$. The value $E_{-1} = 40$ $\text{kcal}\cdot\text{mol}^{-1}$ is used in calculations presented in this report.

Other species besides dioxins are known to be present in the hot gas streams of thermal processing units [1-6]. Many of these species may be capable of being chemisorbed on fly ash [1-9]. In the calculations presented in this report, it is assumed that all chemical species undergoing competitive chemisorption have the same molecular diameter. This is equivalent to stating that the total number of adsorption sites is fixed and that adsorption at any site is non-specific to species identity. The reader can test other assumptions. This assumption also implies the mathematical simplification of grouping all competitively adsorbed species together and treating them as one species with an arbitrarily assigned molecular weight. In this report, the molecular weight for the competitively adsorbed species is assigned a value typical of a three-ringed polycyclic aromatic. Inspection of the model equations suggests that molecular weight dependence is slight in modeling competitive chemisorption. The relative ratio of chemisorbed species to dioxins is assigned a value of one hundred. Other values may be tested by the reader. The dependence of competitive chemisorption of dioxins upon this ratio is intuitively obvious from an inspection of the model equations.

The particulate mass loading values and particle sizes which have been assumed for the fly ash are representative of the range of values for these parameters during thermal processing. Unique rather than distributed values for these parameters, have been assumed to avoid mathematical complications. These approximations make it easier to recognize the dependence of chemisorption of dioxins upon parametric variations of these variables.

The values of the activation energies for chemisorption and desorption of competitively adsorbed species have been assigned corresponding closely to values that have been assigned to polycyclic organic molecules, as reported in the literature [8]. In particular, the zero value assigned to the chemisorption activation energy provides strong contrast to the value of 10 $\mathrm{kcal \cdot mol^{-1}}$ assigned to the chemisorption energy for dioxins. This provides a useful test of the dependence of competitive chemisorption of dioxins upon differences in chemisorption activation energies between dioxins and other chemisorbed species.

Table I - Summary of Assigned Input Values[(a)]

Variable	Units	Values assigned	Comments
T	°C °K	50;150;250;350;450 323;423;523;623;723	The assigned values span the range over which effects on adsorption of activation energy, mass loading, adsorption time, etc. can be demonstrated.
E_1	$kcal \cdot mol^{-1}$	10	See discussion, this section.
E_{-1}	$kcal \cdot mol^{-1}$	40	See APPENDIX C and discussion, this section.
E_2	$kcal \cdot mol^{-1}$	0	See discussion, this section.
E_{-2}	$kcal \cdot mol^{-1}$	30	See discussion, this section.
σ_p	cm	$5x10^{-5}$,$5x10^{-4}$, $5x10^{-3}$	Corresponds to particle diameters of 1,10, and 100 micrometers.
M_p	$g \cdot cm^{-3}$	10^{-7};10^{-6};10^{-5}	Corresponds to fly ash mass loadings of 0.1,1, and 10 grams per cubic meter.
d_o	$g \cdot M^{-3}$	10^{-5}	Must be converted to units of molecules per cubic centimeter for use in equations appearing in this report.
a_o	$g \cdot M^{-3}$	$10^2 d_o$	See discussion, this section.
σ_d	cm	$\cong 4.24x10^{-8}$ cm	See APPENDIX C.
σ_a	cm	σ_d	Arbitrary assignment; see discussion, this section.
m_d	g	321.8	See APPENDIX C.
m_a	g	178.2	See discussion, this section.

(a) All other variables requiring assignment of input values, are assigned values in APPENDIX C and are assigned the same values in this report.

7. RESULTS OF MODEL CALCULATIONS

Calculations, based on the model which has been constructed and the input data presented in this report and in APPENDIX C, have been made to test the dependence of chemisorption upon variations in several of the input parameters. The results of these calculations are presented in Figures 2a through 2c and in Table II.

In Figures 2a through 2c, the y-axis variable is the base ten logarithm of the ratio of chemisorbed dioxins to dioxins which are present in the gas phase. The larger the numerical value of this y-axis variable, the greater the amount of dioxins which are adsorbed on the fly ash compared to the amount of dioxins which are present in the gas phase. To assure successful containment of dioxins by chemisorption of dioxins on fly ash, it is necessary to determine conditions which will maximize the value of this y-axis parameter. Since it is presumed that it may be desirable to collect particulates laden with chemisorbed dioxins, no modeling of chemisorption onto particles smaller in size than one micrometer is carried out. Particles smaller in size than this are more difficult to contain with air pollution control equipment than are larger particles.

All of the results presented in Figures 2a through 2c are based on the assumption of passage of sufficient time for development of dynamic equilibrium partitioning of dioxins between the gas and entrained fly ash. Table II suggests approximate transit times required for development of dynamic equilibrium between gas and fly ash at typical load conditions. The reader may test other load conditions. If the configuration of the flow in a thermal processing unit is insufficient to allow time for development of dynamic equilibrium, the reader can recalculate the partitioning using the time dependent equations which have been presented in the model development section of this report. If the existing gas flow configuration is found insufficient to achieve substantial dioxin containment by entrained fly ash chemisorption, an alternative may be to attempt reconfiguring the flow stream to allow for packed bed chemisorption, as discussed in this report. However, the reader is cautioned that uncertainties in approximations made in this report dictate necessary testing to select materials, configurations and operating conditions for optimal chemisorption.

Figures 3a through 3d illustrate possible configurations for operational control of dioxin chemisorption on fly ash (or other adsorbing materials on which dioxins may be chemisorbed). Figure 3a suggests that mass loading of entrained fly ash may be controlled through variation of gas flow velocities in the thermal processing unit furnace (combustor). If the thermal processing unit is equipped for energy recovery, this may be undesirable if significant fouling or slagging on the energy recovery components is likely to occur. Figures 3b through 3d suggest alternatives if this is a problem. Respectively, these include: (a) injection of supplemental fly ash ahead of air pollution control equipment; (b) use of a packed bed of fly ash or other material or material mixtures; and (c) re-injection of fly ash from the air pollution control eqipment. The temperature of the adsorbing medium may be controlled by variation of gas flow rates, supplemental heating, energy recovery equipment operating conditions or other means.

The effectiveness of chemisorption and thermal destruction processes for containment of dioxin emissions from a thermal processing unit can be considered in terms of (adjustable) thermal processing unit operating parameters - the excess air level and the waste mass feed rate to the unit. Consider the following two cases:

(i) maintenance of a constant excess air level in the thermal processing unit while increasing the mass feed rate, and

(ii) maintenance of a constant feed rate in a thermal processing unit while increasing the excess air level.

Dioxin emissions from thermal processing units may be related to these two operating parameters according to the curves suggested in Figures 4 and 5. The reasons for suggesting this behavior are discussed below for each of the above two cases.

Case (i): The maintenance of a constant excess air level requires that the air flow rate should be increased when the mass feed rate is increased. Increasing the air flow rate (at constant volume) results in a higher flow velocity. This may result in increased particulate (fly ash) entrainment in the flow stream. Increased particulate entrainment may provide a greater surface area for dioxin chemisorption and also (if there is vapor depletion of the dioxin precursors) may drop the size of Θ_a. These results may suppress the extent of dioxin formation. This is suggested in region "A" of Figure 4.

Since the volume of the thermal processing unit is constant, increasing the air flow rate can decrease the process gas residence time. This may shorten the time for effective chemisorption of dioxins (particularly if there is a non-zero activation energy for chemisorption of dioxins) and may reduce the mixing efficiency of air and fuel (due to a decreased mixing time). Mixing problems are discussed in APPENDIX B. When the mass feed rate exceeds some particular value, these effects, which may tend to promote dioxin emissions, may dominate over the effects which are suggested in region "A" of Figure 4. This dominating promotion of dioxin emissions is suggested in region "B" of Figure 4.

Case (ii): The maintenance of a constant feed rate while increasing the excess air level in a thermal processing unit may result in an increased destruction of dioxin precursor species due to an enhancement of oxidation reactions. This is discussed in APPENDIX B. In addition, below some value, increasing the amount of excess air at a constant feed rate may also raise the thermal processing unit operating temperature(s), which also may promote more efficient destruction of dioxins and precursors (see APPENDICES B and C). These effects are suggested in region "A" of Figure 5.

Increasing the excess air can result in an increase in the gas flow rate in a constant volume thermal processing unit. This may result in reduced gas residence times in the thermal processing unit. This shortened residence time may result in poorer mixing efficiencies (see APPENDIX B) and may reduce the extent of effective chemisorption of dioxins, which can be time dependent if the activation energy for dioxin chemisorption is non-zero. Both of these effects may tend to raise the dioxin emission level from the thermal processing unit. In addition, beyond some upper limit of the excess air level, the temperatures in the thermal processing unit may decrease (e.g., due to air dilution effects) and this may decrease the efficiency of thermal destruction of dioxins and precursors (see APPENDICES B and C). When the excess air level exceeds some particular value, these effects which tend to promote dioxin emissions, may dominate over the effects which are suggested in region "A" of Figure 5. This dominating promotion of dioxin emissions is suggested in region "B" of Figure 5.

The inference of the preceding discussion is that regardless of whether or not chemisorption is employed as a dioxin emission control technology in thermal processing units, there may, as evident from a consideration of Figures 4 and 5, be an operating parameter window for assuring effective minimization of dioxin emissions. This implies that fine tuning of operating parameters may be required to ensure that thermal processing units are operating within this suggested dioxin emission minimization window. If it is not possible to operate the unit under these dioxin emission minimization window operating conditions, it may be necessary to employ a chemisorption technology such as illustrated in Figure 3. It is suggested that careful research, testing and development may lead to a definition of thermal processing unit dioxin emission minimization window operating conditions. This may enhance our understanding of how to minimize dioxin emissions from thermal processing units and perhaps result in improvements of thermal processing unit designs. Further discussions of the implications of the results presented in this report are to be found in the SUMMARY AND CONCLUSIONS section.

Table II - Chemisorption Times for Dioxins and Other Species[a]

T °C	t_a (99%) seconds	t_d(99%) seconds
50	2.04×10^{-2}	$7.06\times10^{+4}$
150	1.99×10^{-2}	$1.69\times10^{+3}$
250	1.20×10^{-2}	$1.59\times10^{+2}$
350	5.82×10^{-3}	$4.00\times10^{+1}$
450	4.77×10^{-4}	8.90×10^{-1}

---

[a] Pocket calculator results based on equations in the text and using the values: $\sigma_p = 5\times10^{-4}$ cm, $M_p = 10^{-5}$ g·cm^{-3}.

These results illustrate the sensitivity of adsorption times to activation energies for chemisorption.

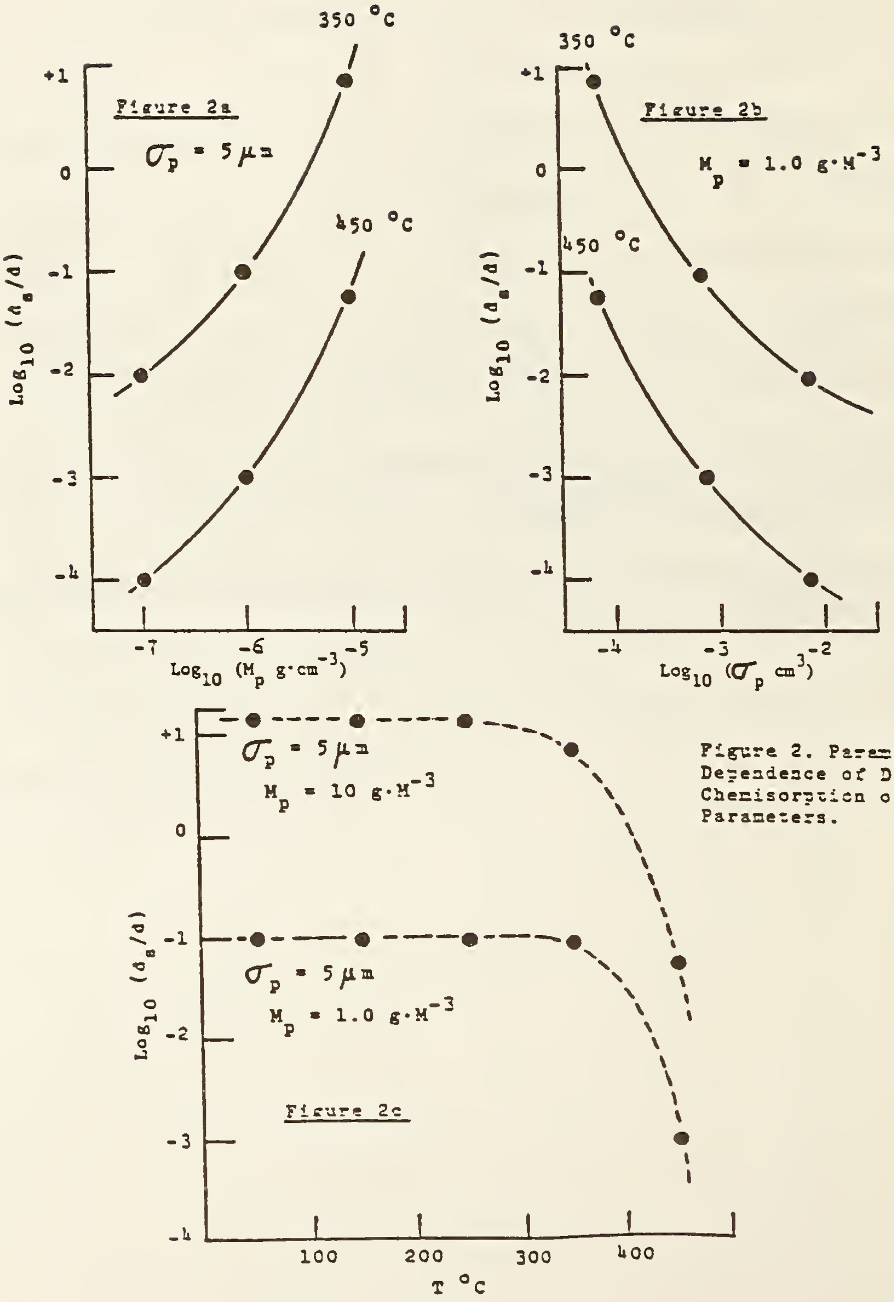

Figure 2. Parametric Dependence of Dioxin Chemisorption on Input Parameters.

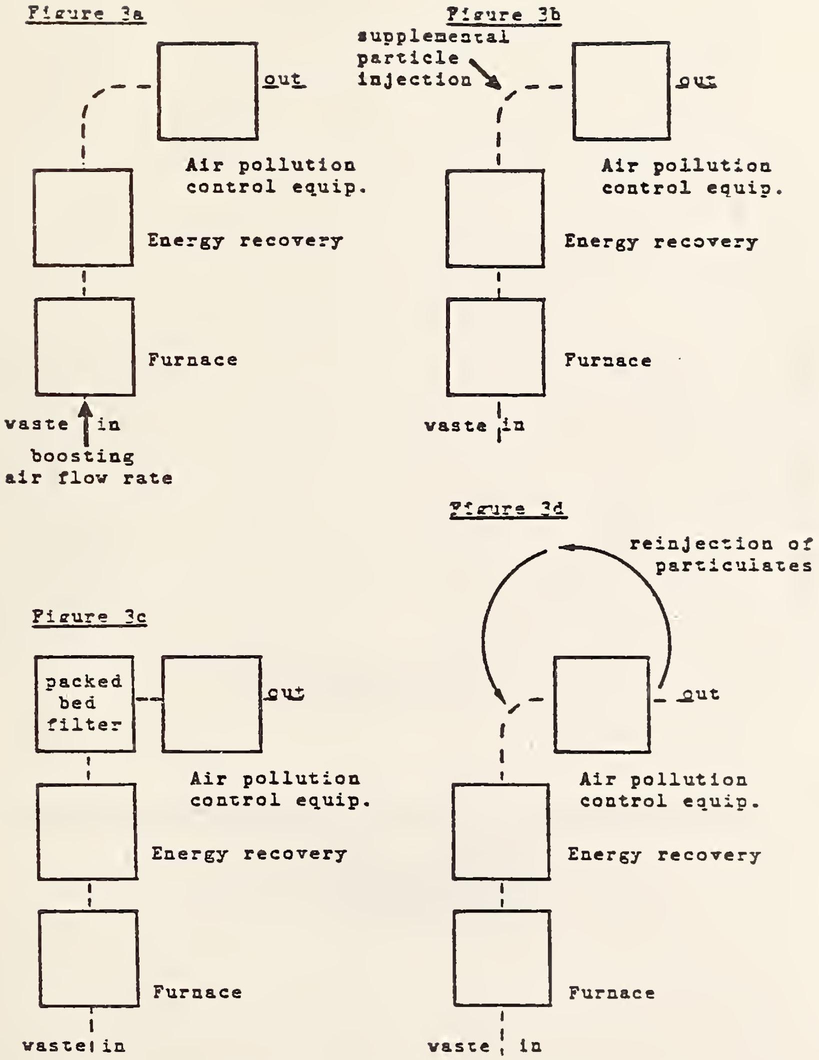

Figure 3. Schematics of Chemisorption Control Technologies.

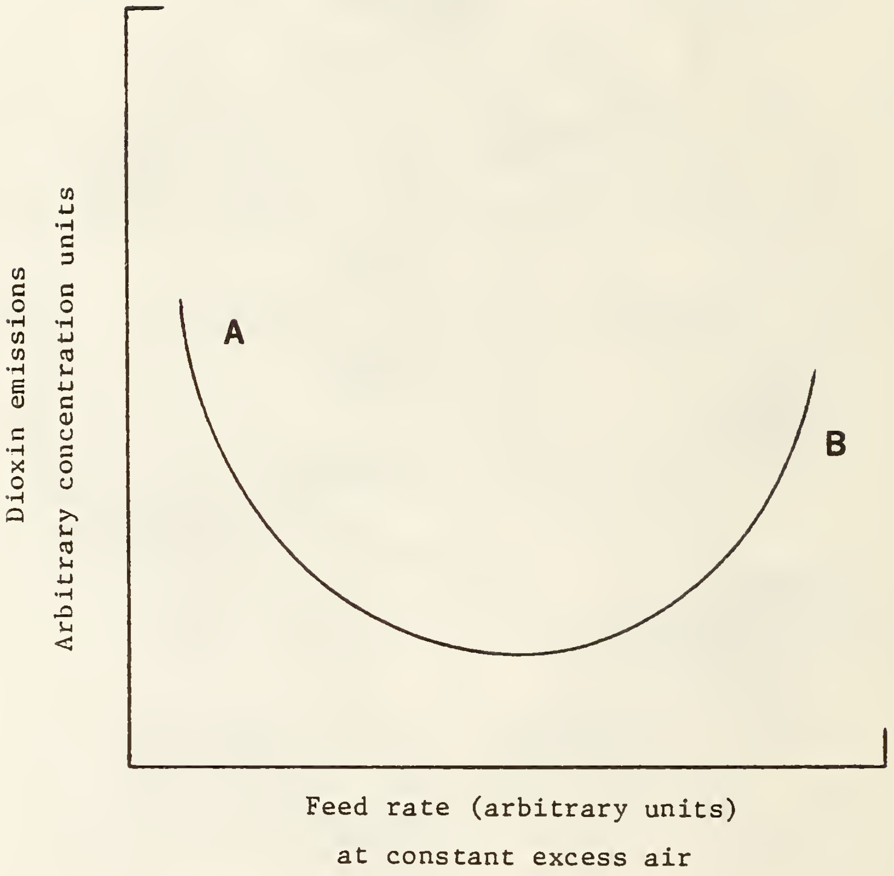

Figure 4. Suggested Dependence of Dioxin Emissions on Feed Rate at Constant Excess Air.

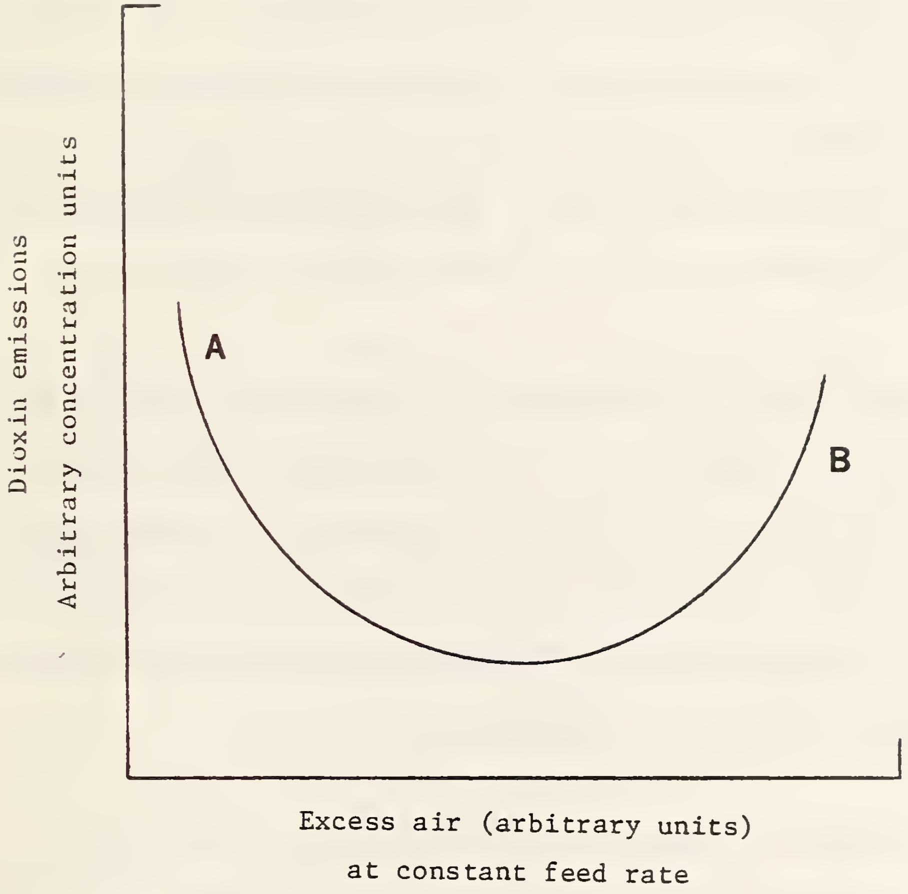

Figure 5. Suggested Dependence of Dioxin Emissions on Excess Air at Constant Feed Rate.

8. CATALYTIC FORMATION OF DIOXINS

Recent literature reports have suggested that dioxin formation in thermal processing units may occur due to chemical mechanisms which involve condensed phase reaction steps [6,10,11], (these references are also respectively APPENDICES C, B and A of this report). Detailed mechanisms which may characterize condensed phase dioxin formation processes have not been tested. The origins of such processes, e.g., condensed phase chemical reactions on grate beds, or chemical reactions in or on fly ash (catalytic or non-catalytic), etc., have not clearly been determined. Carefully designed experiments are necessary to resolve these technical uncertainties.

The methodology proposed in this report for containment of dioxin emissions may involve the use of materials which either themselves may contain dioxin precursors or which may provide reactive surfaces which promote catalytic processes. In view of the brief discussion presented in the paragraph above, it is instructive to consider if the proposed dioxin containment methodology may enhance dioxin formation in thermal processing units.

Figure 3a illustrates a method for increasing fly ash mass loading by increasing gas flow rates through the furnace of a thermal processing unit. Increased gas flow rates may result in increased entrainment of particulate matter which has only been partially combusted. This results from entrainment of larger diameter particles which may have longer burnout times. This problem would be typical of grate bed burning units. Increased transport of long burning time material may result in increased emissions of unburned, partially burned or chemically transformed organic matter from the thermal processing unit. If dioxins were produced by condensed phase reactions, higher mass flow rates of organic emissions could be promoting higher emissions of dioxins, if other operating conditions remained unchanged. One way to avoid this problem would be to use the methodology suggested in Figures 3b through 3d. These approaches could permit the use of lower organic content adsorbent material or the use of material having a more precisely known organic content. These approaches would therefore be less likely to promote increased dioxin emissions through condensed phase reactions. However, the possibility that catalytic dioxin formation could occur on the surfaces of these materials must still be considered. This is discussed below.

One way for catalytic dioxin formation to occur would be through reaction between a gas molecule and an adsorbed molecule. These reaction mechanisms are known as Langmuir-Rideal mechanisms [7]. Such a dioxin formation mechanism involving likely dioxin precursor molecules is discussed in detail in APPENDIX C. The implications of increased mass loading (increased adsorbent surface area) with respect to the possibility that such a dioxin formation mechanism may occur can be developed from arguments based on the model and inputs suggested in this report as follows.

The results of the model calculations in this report suggest that dioxin containment is most efficient at high mass loadings and at temperatures below about 350 °C. Under these conditions, unless there is an activation energy barrier for chemisorption of competitively adsorbed species, the elapsed time for chemisorption will be short, on the order of a millisecond or less. This sets an upper limit on the time window for dioxin formation by a Langmuir-Rideal mechanism, since the gas phase concentration of precursor species falls to zero once this time is exceeded, except in the case that temperatures are sufficiently high to promote thermal desorption. If the competitively adsorbed species are all considered to be dioxin precursors, e.g., chlorophenols, and the rate constant for the reaction

$$a + a_s \xrightarrow{k_3} d_s \qquad (45)$$

is represented by the expression

$$k_3 = Z_p e^{-E_3/(R/T)} \qquad (46)$$

it can be shown using the formalisms developed in this report that the amount of dioxins produced, at a mass particulate loading of 10 grams per cubic meter and a particle diameter of 10 micron-meters, is small and is totally adsorbed on the fly ash at temperatures below about 350 °C. This assumes an activation energy, E_3, comparable in value to that suggested in APPENDIX C.

Alternatively, dioxin formation on a catalytic surface may be postulated to proceed by reaction between two neighboring adsorbed precursor molecules. These reaction mechanisms are known a Langmuir-Hinshelwood mechanisms [7]. A mechanism of this type is illustrated by:

$$a_s + a_s \xrightarrow{k_4} d_s \qquad (47)$$

If such a mechanism were operative, a large value of the rate constant, k_4, would imply significant dioxin production by reactions such as illustrated by equation (47), may be possible. This assumes that the time to achieve equilibrium coverage of an adsorbent by competitively adsorbed species is considerably shorter than typical thermal processing unit transit times, in the absence of significant adsorption activation energies for these species.

However, there is evidence that suggests either the value of k_4 may not be large or there may be a non-zero activation energy for adsorption of dioxin precursors [1-6,10,11]. This evidence is derived from reports which consistently indicate that emissions of potential dioxin precursors from thermal processing units are generally found to be greatly in excess of concurrent dioxin emissions. If the value of k_4 were large, this would not be found.

Therefore, in view of the above observations, it is unlikely that the reaction step shown in equation (47) will produce large amounts of dioxins at high adsorbent mass loading. In addition, increasing the adsorbent mass loading will decrease the fraction of neighboring precursor molecules if vapor depletion takes place, and this will also decrease the rate of dioxin production by Langmuir-Hinshelwood mechanisms. Again, any dioxins which may be produced, would be adsorbed (and therefore contained) at temperatures below about 350 °C based on the model constructed in this report.

9. SUMMARY AND CONCLUSIONS

The results developed in this report suggest that containment, through chemisorption of dioxin emissions from refuse fired thermal processing units, may be technically feasible. Technical issues which may necessitate further research can be identified. This research may require both laboratory scale investigations and full scale tests of concepts developed in this report. Suggestions for research objectives and full scale tests are outlined in the bullets presented below. Refuse fired thermal processing units equipped for energy recovery may be more preferable than those units which are not equipped for energy recovery.

- As determined from the discussions presented in this report, the most critical factor affecting the required contact time for efficient adsorption of dioxins at any temperature is the energy of adsorption, E_A. The lower E_A is, the shorter the required contact time for efficient adsorption. The higher the temperature of the adsorbent, the shorter the contact time required for efficient adsorption. If the value of E_A is greater than zero, the adsorbent must be heated to effect efficient dioxin containment.

- Laboratory investigations should be carried out to determine E_A for candidate adsorbents, e.g. by type (and composition): carbonaceous (carbon black, graphite, charcoal), ferromagnetic, mineral (sand, fly ash, Zeolites), etc. Mixtures of adsorbents should be similarly tested.

- Different adsorbents can be field tested. Fly ash may be a desirable adsorbent since it is a by-product of refuse fired thermal processing operations and is therefore readily available on site.

- There may be a thermal "window" for efficient chemisorption of dioxins, which is principally defined by the energy of desorption, E_D on the high temperature side and by E_A on the low temperature side. The larger E_D is, the higher the upper limit cutoff temperature for efficient dioxin adsorption will be. The smaller E_A is, the smaller the lower limit cutoff temperature for efficient adsorption of dioxins will be.

- Since adsorption is likely to be inefficient at furnace gas exit temperatures, it will be necessary to drop the gas temperature after the gas exits from the furnace of the thermal processing unit. In the example presented in this report, the temperature should be dropped to below about 350 °C. This implies that incinerators equipped for energy recovery may be desirable, since the process of energy recovery can be used to control the gas temperature and assure that the required gas temperature drop is achieved.

- Increasing the mass loading of fly ash or other adsorbent with which the thermal processing unit gas stream is in contact, may significantly increase the amount of dioxins that are irreversibly adsorbed by the adsorbent.

- Decreasing the particle size of a given adsorbent, or replacing low surface area adsorbents with high surface adsorbents may significantly increase the amount of dioxins that are irreversibly adsorbed on the adsorbent.

- If E_A for a given adsorbent is large, the contact time for efficient dioxin adsorption may be long. In some instances, this may necessitate usage of packed bed adsorbers - for providing longer contact times and higher surface area (mass loading of adsorbent) per unit volume. In addition adsorbent beds would likely have greater thermal inertia and therefore may afford more uniform control of the adsorbent temperature. Adsorbent beds may also provide better particle size control.

- Competitive (multicomponent) adsorption may limit the mass of dioxins that is adsorbed. It is suggested that research be conducted to identify adsorbents which are inexpensive and which preferentially (selectively) adsorb dioxins and similar compounds, e.g. furans.

- The logic presented here for potential control of dioxin emissions should also be applicable to control (containment) of other toxic substances. Conditions for optimal containment may be determined by research, development and testing as suggested above.

- The economics of applications of the suggested methodologies for dioxin containment have not been determined. However, sorbent cleanup of polycyclic organic matter emissions through filtering of flue gas at low temperature through a bed of activated charcoal is a common practice in a number of coal fired power plants in the western United States[8].

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APPENDIX A

PHYSICAL AND CHEMICAL PROPERTIES OF DIOXINS IN RELATION TO THEIR DISPOSAL

The physical and chemical properties of polychlorinated dibenzo-p-dioxins have been considered in relation to prospects for their formation and destruction in incinerator environments. Detailed equilibrium and chemical kinetic considerations have been used in performing qualitative assessments. It is concluded that there are no apparent thermodynamic barriers to their destruction and that kinetic control is a dominating factor in practical incinerator environments. This analysis as well as a consideration of some existing experimental data are used to suggest some useful guidelines and to indicate research which should be carried out in the future regarding dioxin disposal.

INTRODUCTION

Although there is inadequate data to explicitly describe the complete destruction or formation mechanisms of polychlorinated dibenzo-p-dioxins (PCDDs) under thermal stress, enough information is known or can be inferred such that important characteristic features of these processes can be elucidated. We focus attention upon this class of chemicals in view of the fact that there have recently been reported several instances in which dioxins have been associated with gaseous and particulate emissions of incinerators. Two extensive reviews are available (Harris et al. 1981, Esposito et al. 1980). There has been a recent suggestion by some scientists (Bumb et al. 1980) that PCDDs may be ubiquitous as a consequence of trace chemical processes that occur during normal combustion. This hypothesis has been questioned (Kriebel 1981). It appears at the present time that this issue has not been resolved. What is known is that several dioxins, particularly 2,3,7,8-tetrachlorodibenzo-p-dioxin, are extremely toxic substances (Poland and Kende 1976). It is therefore desirable to determine what if any conditions for incineration are likely to minimize formation and maximize destruction of these species.

This paper, will begin with a brief review of the molecular processes which are responsible for destruction of a large polyatomic molecule. We next discuss the limitations imposed by equilibrium thermodynamics. This will be followed by an assessment of kinetic control factors. Some considerations regarding the role of non-gas phase and/or heterogeneous processes will be presented. These factors will be utilized to interpret some of the experimental research that has recently been reported in the literature. Recommendations shall be presented regarding future research as well as practical guidelines pertinent to incinerator operation and possibly risk assessment.

The work presented here is in response to a congressional mandate, and as directed under Section 5002 of the Resource Conservation Recovery Act of 1976 [RCRA], and through support of the NBS Office of Recycled Materials, the DOE Office of Energy for Municipal Waste, and the U. S. Air Force Environics Division, Tyndall AFB.

REACTION MECHANISMS

The kinetic processes which control the decomposition of a complex organic molecule such as a PCDD in a practical incinerator environment may be described by the specification of reaction mechanisms. These reaction mechanisms in turn are composed a series of elementary processes. The rates of these elementary steps in combination with appropriate computer programs can describe the temporal evolution of the chemical specie during the combustion process in an incinerator. Regardless of the detailed mechanism, the fate of the molecule is either a stepwise breakdown to smaller, often more oxygenated species or alternatively a transformation in concert with other species to a higher molecular weight material (eg. soot formation).

It is appropriate to first consider those kinetic processes which are operative in the gas phase. Historically, it is these processes which have been studied most and are best understood. Furthermore, we shall show that an understanding of the general features which characterize gas phase decomposition processes provides in turn, insight into the nature of reactions operative in other phases. As we have discussed previously (Tsang and Shaub 1981), the important elementary processes operative in the gas phase in an incinerator environment may be categorized as either unimolecular or bimolecular reaction steps. The former are represented by reactions of the type

$$A \xrightarrow{k_u} P$$

where A represents a complex organic molecule and P denotes a product (or products) which may not necessarily be a stable specie (or species). The rate of destruction of A by this unimolecular reaction step is $dA/dt = -k_u A$. These reactions for the present purposes can be classified as those involving either bond rupture or complex fragmentation. Bimolecular reactions may either involve addition or metathesis.

$$A + R \xrightarrow{k_b} P + (C)$$

where A and P are as previously defined before, R denotes a specie capable of undergoing reaction with A and C is the other product in metathesis reactions. The rate of destruction of A by bimolecular steps is

$$dA/dt = -(\sum_i k_{bi} R_i)A$$

where the summation over the subscript, i, denotes the fact that in a practical incinerator environment, there may be many reactive species capable of undergoing chemical reaction with A.

THERMODYNAMICS CONSTRAINTS

In order to completely describe the gas phase decomposition of a large organic molecule, it would be necessary to specify exactly all of the reaction steps in a mechanism. In practice, this has not been done to date even for so simple a molecule as methane! Approximations are necessary. In particular, thermodynamics imposes important constraints on the system and in view of the lack of knowledge of detailed mechanism, the first step must be an investigation of the consequences if equilibrium is attained.

A complete thermodynamic characterization of the equilibrium distribution of species present in a gas phase mixture is possible providing appropriate hydrodynamic variables, eg., temperature and pressure, thermodynamic data for all pertinent species, and initial fuel/oxidizer equivalence ratios (a measure of the amount of fuel and oxidizer available) are specified. Up to the present time, the fundamental limitation to complete equilibrium characterization of many systems is due to the lack of thermodynamic data for numerous large organic molecules. This has been particularly true in the case of chlorinated hazardous waste chemicals such as benzenes, phenols, biphenyls, biphenyl ethers, dibenzofurans and dibenzo-p-dioxins. Recently we have utilized estimation techniques (Shaub 1981a, 1981b, Tsang and Shaub 1981) to construct a thermodynamic data base for these molecules. Table I for example, summarizes ranges of gas phase heats of formation estimated for polychlorinated biphenyls (PCBs), polychlorinated biphenyl ethers (PCBEs), polychlorinated dibenzofurans (PCDFs), and polychlorinated dibenzo-p-dioxins. In general, heats of formation decrease with increased degree of chlorination and number of oxygen atoms present in the molecule. Variations within each class are attributable to nearest neighbor interactions when utilizing our estimation techniques. The extent to which these estimates are reliable has been discussed previously (Shaub 1981a). These estimated heats of formation as well as estimates of heat capacities and entropies (Shaub 1981b) can be utilized to construct the necessary thermodynamic data input for equilibrium computations. A typical data sheet for a chlorinated dioxin is presented in Table II. We have used this information together with pre-existing thermodynamic data for smaller polyatomic as well as atomic and diatomic species (Stull and Prophet 1971, Cox and Pilcher 1970, Stull and Westrum 1969) to simulate equilibrium chemical thermodynamic distributions of polychlorinated aromatic species for a range of specifications of initial fuel/oxidizer equivalence ratios, temperatures and pressures characteristic of a practical incinerator environment. We are able to conclude that in terms of equilibrium thermodynamics, at temperatures in excess of 500°C, destruction of polychlorinated aromatics is essentially complete. That is, there is no single compound with any special thermodynamic stability characteristics. Within any particular class of chlorinated compounds, eg. dioxins, there is a trend toward greater stability with increased chlorination if there are no other sources of hydrogen available in the waste feedstock. It is often found in practice that temperatures much in excess of 500 C are required to effect complete destruction. For example Duvall and Rubey (1977) report that commercial PCBs and some dioxins undergo decomposition in air between 640-740 C at a residence time of one second. A 99.995% destruction efficiency is reported for some PCBs at a temperature of 1000 C and the same residence time. This is an indication that at least at the lower temperatures, ($T \lesssim 900$ C) reactions may be kinetically controlled. It is important to recognize, however, that while complete gas phase thermodynamic equilibrium may not obtain in an incinerator environment, a bimolecularly controlled local (psuedo) thermodynamic equilibrium may be expected to develop in practical incinerator environments for small inorganic radicals, particularly those associated with hydrogen/oxygen reactions, (e.g. H, O, OH, H_2O) by virtue of the fact that they undergo fast bimolecular reactions with each other. This means that to a good approximation, equilibrium thermodynamic calculations should serve adequately to "track" concentration of these small inorganic species with variations of temperature and pressure over time scales that are characteristic of an incineration process.

Gas Phase Kinetic Control Factors

It is evident that gas phase processes for destruction of chlorinated dioxins in practical incinerators are kinetically controlled. The destruction of chlorinated dioxins may then be described by the relation,

$$-dA/dt = k_u A + (\sum_i k_{bi} R_i)A$$

It is instructive to consider first the situation in which destruction is governed predominantly by a unimolecular mode of decomposition. It can be shown that under this condition, and subject to a requirement of 99.99% destruction efficiency, the minimum transit time required for achievement of this extent of decomposition is related to the unimolecular rate constant by the expression

$$t(99.99\%) = 9.212\ k_u^{-1}$$

Similarly, for 99.9999% destruction efficiency,

$$t(99.9999\%) \approx 1.5t(99.99\%.)$$

The unimolecular rate constant, k_u, may be written as (pressure dependence is assumed negligible under conditions of incineration)

$$k_u = A_\infty \exp(-E_\infty/RT).$$

Above, R has the value 1.987 cal/(mol•deg K). Values for the pre-exponential factor (units of $\sec^{-1}$) and the activation energy (units of cal/mol) may be conveniently estimated for a dioxin molecule undergoing decomposition via simple bond rupture - a process which sets an upper limit range upon the decomposition time. A reasonable <u>range</u> for the value of the pre-exponential factor is $\approx 10^{15.5 \pm 0.5}$ $\sec^{-1}$ (Tsang and Shaub 1981). Substituent chlorine atom effects (increasing degree of chlorination) should not be expected to result in A_∞ values outside of this spectrum of values. The activation energy for unimolecular decomposition of a dioxin molecule via simple bond rupture should have a value approximately equal to the bond dissociation energy of the weakest bond. Carbon-carbon bond rupture in the aromatic rings is ruled out as being prohibitive due to resonance stabilization in the aromatic rings. The C-H bonds and the C-Cl bonds in benzene and benzyl chloride have dissociation energies of 111 $\mathrm{kcal \cdot mol^{-1}}$ and 95 $\mathrm{kcal \cdot mol^{-1}}$ respectively. An estimate of the bond dissociation energy of the CO bond in dioxins is obtained as follows. The heat of formation of $C_6H_5O\cdot$ (phenoxy radical) is $\Delta H_f^o(g,298) = 11.9\ \mathrm{kcal \cdot mol^{-1}}$ as determined from the reported heat of formation of phenol, $\Delta H_f^o(g,298) = -23.0\ \mathrm{kcal \cdot mol^{-1}}$ (Cox and Pilcher 1970), the bond dissociation energy of the C_6H_5O-H bond, 87 $\mathrm{kcal \cdot mol^{-1}}$ (Colussi et al. 1977), and the heat of formation of atomic hydrogen, $\Delta H_f^o(g,298) = 52.1\ \mathrm{kcal \cdot mol^{-1}}$ (Stull and Prophet 1971). An estimate of the C-O bond dissociation energy in dioxins is that it should be comparable to the C-O bond dissociation energy in diphenyl ether. Since the heat of formation of the phenyl radical is $\Delta H_f^o(g,298) = 78.5\ \mathrm{kcal \cdot mol^{-1}}$ (Benson 1976), and the heat of formation of diphenyl ether is $\Delta H_f^o(g, 298) = 11.94\ \mathrm{kcal \cdot mol^{-1}}$ (Cox and Pilcher 1970), it follows that the bond dissociation energy of the C-O bond in diphenyl ether is

$$\begin{aligned} \mathrm{BDE} &\approx \Delta H_f^o(g, 298)_{C_6H_5\cdot} + \Delta H_f^o(g, 298)_{C_6H_5O\cdot} - \Delta H_f^o(g,298)_{C_{12}H_{10}O} \\ &\approx 78.5\ \mathrm{kcal \cdot mol^{-1}} \end{aligned}$$

It is unlikely that there is any significant resonance energy associated with the central ring in dioxin. In fact, an examination of the central rings in dibenzopyran and 9,10-dihydroanthracene utilizing thermochemical estimates (Benson 1976) and reported values for the heats of formation of these compounds (Cox and Pilcher 1970), leads to the conclusions that there is no significant resonance strengthening of the bonds to the central ring bridge atoms in these compounds and that further, there is a slight central ring destabilization of about 1-4 kcal mol^{-1} due to ring strain. Thus by analogy, it is reasonable to assume that it is unlikely that the bond dissociation energy of the C-O bond in dioxin exceeds 80 kcal mol^{-1}. In fact, it may be lower if partial resonance stabilization of the resulting phenoxy-like radical structure occurs during the bond breaking process.

It follows from the above discussion that in the case of unimolecular dissociation of dioxins, a reasonable estimate for the unimolecular rate constant is

$$k_u \approx 10^{15.5 \pm 0.5} \exp(-80000/RT)\text{sec}^{-1}$$

This value for k_u can be utilized in the expression for t(99.99%) to determine the time required for efficient destruction at various temperatures. In Table III we present a summary of these times for $A_\infty = 10^{15}$ and also $A_\infty = 10^{16}$ to indicate the effect of the variation of this parameter. Clearly, effective removal of dioxins over short periods of time can only occur at <u>elevated</u> temperatures, under conditions of unimolecular kinetic control.

The contribution of bimolecular reactions to the destruction of dioxins may be considered as follows. As mentioned previously, the significance of the existence of local thermodynamic equilibrium in an incinerator evironment is that we can, via computer simulation, determine the concentrations of small inorganic radicals. We have concluded from our equilibrium thermodynamics analysis (Tsang and Shaub 1981) that with respect to bimolecular removal, the major reactive species in the case of fuel rich combustion are hydrogen atoms, and in the case of stoichiometric combustion or excess air combustion, hydroxyl radicals (OH) and to a lesser extent, oxygen atoms. Larger radicals, at elevated temperatures characteristic of an incinerator combustion environment are generally present at lower concentrations due to their instability. In most cases they are also less reactive. Consider stoichiometric or excess air combustion of dioxins. We have determined from our previous analysis of kinetic rate constant data for the rates of attack of OH upon organic substrates that at incinerator conditions bimolecular rate constants will be of the order of $k_b \sim 10^{9 \pm 1}$ $L \cdot mol^{-1} \cdot sec^{-1}$ (Tsang and Shaub 1981). We have estimated the concentration of OH radicals as a function of temperature under the assumption of local thermodynamic equilibrium of small inorganic radicals. The validity of this assumption has been demonstrated (Ernst et al. 1978, Muller et al. 1980, Creighton 1980). It is therefore possible to infer that a residence time of about 1 second and a temperature of the order of 1230 K(957 C) would be required to insure 99.99% destruction efficiency of dioxins via attack of OH. Thus, it can be seen by comparison with Table III, both unimolecular and bimolecular reactions may contribute significantly to dioxin removal at the temperatures where 99.99% removal occurs over time scales typical of incinerator operation.

As we have mentioned previously, OH attack upon unsaturates tends to be electrophilic in nature, leading us to expect a lowering of the rates of bimolecular attack upon chlorinated dioxins and other such as chlorinated biphenyls with increasing degrees of chlorination. Thus, effluent emissions from incinerators should tend to contain predominantly more highly chlorinated dioxins if in fact they do contain dioxins at all. In the case of PCBs, this effect should be more marked as C-Cl bonds are the weakest bonds in these molecules and therefore effects associated with bimolecular attack should be significantly enhanced as under these circumstances (ie high bond energies) unimolecular reactions would be less predominant. These predicitions are supported by experimental results reported in recent literature (Harrison et al. 1980, Duvall and Rubey 1977). In the case of fuel rich systems, H atom concentrations tend to be lower than the corresponding OH concentrations in stoichiometric or excess air combustion. This means that since rate constants for H atom attack at incineration temperatures are comparable to k_b for OH attack, unimolecular decomposition of dioxins may tend to be more important in fuel rich combustion.

It is useful to make another observation regarding the incineration of hazardous materials such as dioxins. A distinction should be made between <u>mean</u> furnace operating temperatures which may tend to be low relative to destruction of dioxins (750 C is not atypical in municipal incinerators), and the much higher temperatures which are obtained in the flame regions of the furnace. Thermal profiles in the region of flames are commonly in the range 1250 C to 1750 C over a distance in excess of 15-20 cm with peak temperatures (1750 C and higher) extending over distances of 5-10 millimeters or more (McDonald 1980, Bechtel 1980, Switzer et al. 1980, Oran et al 1980, Dibble et al. 1980). In a practical incinerator environment, these distances may be greatly extended. As is evident from Table III, it is these high temperature regions which are primarily responsible for destruction of dioxins and other similar hazardous waste stream materials. At flow velocities of 10-50 ft$\cdot$s^{-1}, 99.99% (or even 99.9999%) gas phase destruction is to be expected if all the dioxin material is successfully heated to these temperatures. Thus while average furnace temperatures may be lower than what is required for dioxin disposal, local flame temperatures if felt by all molecules in the system can provide the impetus for successful decomposition.

With regards to the formation of chlorinated dioxins in the gas phase once temperatures for destruction of chlorinated dioxins are achieved, the same driving forces which are available to destroy dioxins will also lead to decomposition of dioxin precursors such as chlorinated phenols. Additionally, in a municipal incinerator, concentrations of hazardous wastes tend to be low relative to the bulk of the waste stream. Formation of dioxins in the gas phase would require a minimum occurence of a bimolecular step, characterized by a very slow rate relative to the overall process of decomposition, due to low values associated with bimolecular rate constants for highly sterically hindered reactions (Gardiner 1972). There are reports of a few dioxin precursors (predioxins - eg. polychlorinated 2-phenoxyphenols) apparently directly producing high yields of chlorinated dioxins under mild (ca. 275 C) thermal stress (Esposito et al. 1980, Nilsson et al. 1974). It should be noted that there is no indication that these materials are especially prevalent in municipal waste streams. In addition, there has been no demonstration that conversion of these predioxins to dioxins occurs in the gas phase. Such a reaction would be expected to be highly sterically hindered and possibly retarded by resonance stabilization of an intermediate phenoxy radical structure.

The previous discussion has assumed an model in which all hazardous waste materials such as chlorinated dioxins are in a homogenous gas phase mixture, ie. pre-mixed burning, and that further, all of the gas is successfully elevated to the high flame temperatures required for successful decomposition. In practical incineration this is not the case. Fuel and air are not pre-mixed, although a highly efficient spray injection liquid hazardous waste incinerator may approach this ideal. When improper mixing occurs, extremely fuel rich or fuel lean pockets of gas may pass through some parts of the incinerator and may possibly escape from the furnace area particularly if loading is excessive. If the mixture is exceedingly fuel rich or fuel lean the gas pockets may not support ignition, and consequently material destruction may not occur due to formation of local cold spots or lack of reactive species. Additionally, extremely fuel rich combustion may promote undesirable condensation reactions and lead to soot formation which can perturb energy transport to an from regions in the incinerator in addition to other undesirable effects. Recently, liquid injection incinerators were utilized onboard the M/T VULCANUS incinerator ship to destroy organochlorine wastes containing 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) as an impurity to the extent of an average 2 ppm (Ackerman et al. 1978). The flame temperature in the liquid injection incinerators was maintained at all times above 1250 C during the incineration of organochlorine wastes. Residence times normally ranged from 0.5 to 2 seconds. Combined TCDD destruction efficiencies of > 99.93% were reported for three burns. An efficiency > 99.99% was reported for one burn. It is clear from these results that the predicted efficient destruction of dioxins in the gas phase is realizable in practical excess air incineration. Slight departures from expected theoretical efficiencies may have been due to some of the problems discussed previously.

Non Gas Phase Effects

In the last few years, there have been several reports of dioxin emissions from full-scale combustion facilities (Olie et al. 1977, Buser and Bosshardt 1978, Buser et al. 1978, Eiceman et al. 1979, 1980). In general emissions from municipal waste incinerators have been consistently lower than those reported for industrial waste incinerator facilities (Harris et al. 1980). The majority of reports of dioxin emissions have been concerned with analysis of fly ash samples, particularly those collected from electrostatic precipitators. Although there are problems with the analytical methodology these observations make necessary the consideration of non gas phase effects.

In a typical incinerator equipped with an electrostatic precipitator the principal areas for loss of solid which are of concern are the following:

a) Fly ash and other particulates $\lesssim$ 10 µm in diameter may pass through the settling chambers and centrifugal separators into the electrostatic precipitator. Here, assuming efficient operation, particles as small as 0.1 µm to 0.01 µm will be collected. This material is highly oxidized, with carbon or soot contents (organic fraction) commonly as low as 5% by weight and ranging up to 40% by weight (Domino 1979) in poorly designed or inefficiently operated incinerators. (It is possible that real time optical probing for soot deposited on fly ash may prove to be a useful indicator of efficient incinerator operation). Glassy particulates may be harder to trap due to the difficulty associated with ionization of this material. Fly ash in hoppers from electrostatic precipitators is subject to management by containment. However, due to the size of this particulate matter great care in handling may be essential, particularly with dry fly ash, to avoid raising a cloud of this material.

b) Particles smaller in size than 0.01 µm will readily escape through an electrostatic precipitator and pass out the stacks. This fly ash is highly oxidized and has been thoroughly thermally stressed. This material is not subject to management by containment and represents a direct emission into the environment. Dioxin transport, if it occurs to an appreciable extent on this material could be particularly serious as deposition efficiencies for inhaled particles of this size range strongly favor pulmonary and tracheobronchial regions as opposed to nasopharyngeal regions of the respiratory tract (Natusch and Wallace 1974). In this respect, it is also particularly important to control soot emissions (organics) as for example, benzo [a] pyrene, a common soot constituent, has been found to predominate in small pulmonary depositing particles (Natusch and Wallace 1974).

The inorganic content of fly ash is present as metal oxides. The relative amounts of the metal oxides present in fly ash vary widely from one sample to another in different incinerators. On the average SiO_2 is the principle inorganic oxide ($\approx$ 55%). Fly ash from municipal incinerators tends to also have significantly higher ratios (Domino 1979, Cheremisinoff and Morresi 1976, Hardesty and Pahl 1979) of SiO_2/Al_2O_3 and CaO/Fe_2O_3 than fly ash from lignite coal. The Al_2O_3 fraction in municipal incinerator fly ash is often low due to aluminum can recycling. Generally, fly ash will be basic when there are high amounts of calcium and/or magnesium and low amounts of irons and/or aluminum. Quartz (SiO_2) and many types of glass also tend to be basic. That is, there may be many hydroxyl (OH) groups on the surface of these materials. The ash fusion temperatures (Domino 1979) of most municipal incinerator fly ash are comparable to those reported for fly ash from various coals (Hardesty and Pohl 1979), and typically range from about 2000 F (1093 C, 1366 K) to about 2500 F (1371 C, 1644 K). Thermal conductivities of fly ash tend to be somewhat larger than those for most coals.

The above information about fly ash is helpful towards development of an understanding of the conditions under which one might expect dioxins would be present in this material. That this is so, may be seen from the discussion presented below. At one atmosphere pressure and a temperature of 600 C, energy transport from the surface of a 1000 μm diameter particle of coal to its center takes place during a time scale of the order of one second. Under similar conditions, a 100 μm coal particle will be heated during a time scale of ∿ 10 ms (Russel et al. 1979). These figures are approximate time scales, but nonetheless they serve to bring out the point that sub-micron size coal particles will heat to the core in times much shorter than a millisecond. Since fly ash particles have similar thermal conductivities, it is reasonable to expect that during incineration submicron size particles should be uniformly heated to high temperatures on time scales that are short relative to transit times through high temperature zones. Fusion, which is known to commonly occur, may further promote heating of particle cores if the particles are transformed to a liquid state due to convective transport of heat and oxidants. Under these conditions, dioxins present inside sub-micron size fly ash particles may be subject to the same unimolecular processes as in the gas phase. Additionally, oxidative attack of hydroxyl or other small radicals on particles may also contribute towards decomposition. For example it has recently been demonstrated that OH radicals rapidly attack the surface of carbonaceous materials even at room temperatures to produce approximately equal amounts of CO and CO_2 (Mulcahy and Young 1975). Since the surface of fly ash in incinerators may be basic, surface bound hydroxyl radicals may also play a role. Other surface effects may also be operative. The implication of this discussion is that providing these particles are subjected to the same high temperature oxidative conditions as is the gas in an incinerator, high destruction efficiencies are to be expected. In fact, the completeness of oxidation of inorganic material in submicron size fly ash may imply that dioxin and other organic component levels in these particles should be lower than in the gas phase under conditions of fuel lean, high temperature incineration.

Ash which collects in hoppers in the region of the electrostatic precipitator may commonly range in size up to about 10 µm. The uncertainties regarding time scales for heating could be as large as an order of magnitude. This does not affect the nature of our analysis regarding submicron sized particles. However, as regards particles with diameters on the order of 10 mµ, if particle heating time scales due to uncertainties were actually higher by an order of magnitude, the time to heat the core of these particles could be a significant fraction of the particle transit times through the highest temperature zones. In this respect more experimental work in determining actual particle heating times would be very helpful. As can be determined from reports of fly ash collected from some electrostatic precipitators, levels of dioxins have been found to be in the ppb range. Note that if the input waste stream contained ppm levels of dioxins, or of material that may be converted to dioxins (to the extent of ppm dioxin levels during time scales similar to those in incinerators), a 99.99% combustion destruction efficiency due to rapid particle heat up relative to transit times would imply ppt to ppb levels of dioxins will be present in electrostatic precipitator fly ash consistent with what has been reported in some instances.

This would imply electrostatic precipitator fly ash has probably been uniformly heated. Whether or not this analysis has validity in an actual incinerator requires statistically representative information about input feed streams that has not presently been reported. This information would also provide in part, a useful guide in determining the effectiveness of varying furnace flame temperatures and residence times.

Recently, formation of polychlorinated dibenzofurans (PCDFs) at levels approaching 1% has been reported from the pyrolysis of polychlorinated biphenyls (PCBs) in sealed quartz mini-ampoules at temperatures of 550-850 C (Buser et al. 1978b). Molar ratios of PCB to oxygen in an ampoule were varied from 1:7.5 to about 1:7.5. The maximum amounts of PCDFs reported were found at 550 C. At 850 C levels found are reported as < 0.01%. The important point associated with this work, although not brought out by these authors, is the fact that at the lower temperatures (550 C) where highest formations occurred, their results clearly show the reaction to be self inhibiting. That is, decreasing the amount of PCBs in a quartz ampoule by a factor of ten actually results in more than a six-fold increase in decomposition. Since gas phase reactions involving oxygen are not important at these temperatures, the self inhibiting nature of this reaction clearly rules out any chain branching mechanism and suggests that the reactions are taking place on the surface of the quartz ampoules.

Synthesis of chlorinated dioxins and PCDFs have also been reported under similar conditions in quartz ampoules from chlorinated benzenes

(Buser 1979) and chlorophenates (Rappe and Marklund 1978). It is highly likely that again, surface effects are also operative here as no kinetically plausible gas phase processes are conceivable at these temperatures for formation of these compounds. Additionally, it should be noted that there is a long history of problems due to surface effects in quartz and glass vessels that have been encountered in the study of gas phase reactions of halogen containing organic compounds. As quartz tends to be basic, it is possible that hydroxyl groups on the surface of the quartz ampoules may be a reactant source for promoting formation of dioxins from PCBs and other precursors. As mentioned previously, fly ash may also tend to be basic and usually has a high SiO_2 content. Thus, in a manner similar to quartz, fly ash may possibly act as a promoter for surface reactions leading to formation of dioxins and similar materials in an incinerator environment. The relative surface of glass ampoules compared to that of fly ash in an incinerator has not been established. Thus the validity of extrpolating the latter results is uncertain. However, the observation of similar distribution patterns in chromatograms of dioxins obtained from municipal incinerator, and controlled experiments involving chlorophenates in quartz ampoules (Buser et al. 1978) and on leaves or wood (Rappe et al.) supports this suggestion. It is important to note that in a study of production of PCDFs from specific PCBs that was carried out in quartz ampoules (Buser et al. 1978b), the PCBs were destroyed with an efficiency > 99.99% at a temperature of 850 C. Since PCBs are kinetically more stable than dioxins, comparable destruction efficiencies are to be expected for the latter. Thus, while fly ash may possibly promote dioxins formation at lower temperatures around 550 C, high destruction efficiencies still appear to be possible if the fly ash is subsequently subjected to elevated temperatures for times comparable to those required for gas phase destruction at elevated temperatures, providing the ash is uniformly stressed. This latter point is important, since if dioxins or precursors are trapped inside particles and the cores of particles are not thermally stressed, destruction efficiencies may be lower than expected, due to a thermal insulating effect.

CONCLUSIONS AND SUGGESTION FOR FUTURE RESEARCH

Below, we enumerate a number of tentative conclusions which may be drawn from the above discussions, in the hope that they will provide some useful guidance to enable persons concerned with the disposal of dioxins and similar materials to understand to some extent what is possible via incineration. It seems reasonable to us to expect that 99.99% or higher destruction efficiencies are well within the capabilities of modern municipal waste and hazardous waste incinerators. Our basic conclusion is that destruction efficiencies are not likely to be limited by thermodynamic or kinetic control factors at high enough temperatures and sufficient residence times. However, in light of our discussions above, the following points should be considered:

a) Mixing is very important and should be monitored closely, especially to avoid cold spots which may result in insufficient thermal stressing.

b) As particle size increases, core heating time scales may be lengthened. This must be considered an important factor in terms of particle transit times through the furnace and in fly ash disposal.

c) A careful statistically representative characterization of the input waste feed stream is necessary to properly further assess actual destruction efficiencies.

d) Providing stack (uncontained) emissions of dioxins and related materials are reduced to acceptable levels, incineration of dioxins should in principle be a manageable problem since ash in hoppers is contained ash and therefore subject to further treatment if needed.

As regards future research, it would be most helpful if physical properties of various fly ash, eg. thermal conductivities, fusion temperature, alkalinity, surface reactivity, porosity, etc. were more thoroughly determined. Rate processes of chemical reactions are readily subject to scientific scrutiny, and more carefully designed experiments are needed in the future, particularly with regards to kinetics of reactions involving materials such as dioxins and precursors on various surfaces. It should also be noted that since dioxins and similar chemical substances may be found in some fly ash, the prior history of disposal practices of fly ash would dictate that there may exist a need to investigate the chemical, photochemical and biological fate of these substances as they may exist in some ash dump sites. Certainly, some monitoring of historical sites would be instructive.

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Table I

Gas Phase Heat of Formation for Chlorinated Hazardous Waste Compounds

Class	ΔH_f^o(g, 298 K) kcal·mole^{-1}
Polychlorinated Biphenyls	+ 35.93 → + 0.07
Polychlorinated Biphenyl Ethers	+ 10.3 → - 54.25
Polychlorinated Dibenzofurans	+ 18.26 → - 48.12
Polychlorinated Dibenzo-p-dioxins	- 22.7 → -100.2

Table II

octachlorodibenzo-p-dioxin $C_{12}O_2Cl_8$ (Ideal Gas State) Mol. Wt. 459.744

		cal mol^{-1} K^{-1}			kcal mol^{-1}		
T^oK	C_p^o	S_T^o	$-(G_T^o-H_0^o)/T)$	$H_T^o-H_0^o$	ΔH_f^o	ΔG_f^o	Log K_p
200	54.54	111.60	81.45	6.03	-100.72	-71.94	78.602
298	70.86	136.58	95.58	12.23	-100.21	-57.93	42.454
300	71.12	137.02	95.84	12.36	-100.20	-57.65	41.989
400	83.45	159.25	108.97	20.11	-99.44	-43.57	23.799
500	92.81	178.93	121.03	28.95	-98.57	-29.70	12.979
600	99.88	196.50	132.17	38.60	-97.68	-16.01	5.829
700	105.20	212.32	142.51	48.86	-96.79	-2.46	0.768
800	109.23	226.64	152.15	59.60	-95.87	10.95	-2.992
900	112.32	239.69	161.16	70.68	-95.06	24.26	-5.890
1000	114.72	251.66	169.62	82.04	-94.17	37.46	8.186
1100	116.61	262.68	177.59	93.61	-93.78	50.58	-10.047
1200	118.11	272.90	185.11	105.35	-92.39	63.62	-11.584
1300	119.33	282.40	192.23	117.22	-91.59	76.59	-12.874
1400	120.32	291.28	198.99	129.20	-90.83	89.50	-13.969
1500	121.14	299.61	205.43	141.28	-90.09	102.34	-14.908

Table III 99.99%

Dioxin Decomposition Times, Gas Phase

$k_u = 10^{+15} e^{-80000/RT}$			$k_u = 10^{+16} e^{-80000/RT}$
τ =	°C	°K	τ =
2 billion years	227	500	200 million years
6 years	477	750	0.6 years
46.5 minutes	727	1000	4.65 minutes
1 second	977	1250	1/10 second
1/2 second	1000	1273	5/100 second
4 milliseconds	1227	1500	400 microseconds
5 microseconds	1727	2000	1/2 microsecond

APPENDIX B

DIOXIN FORMATION IN INCINERATORS

Abstract

Processes which may contribute to the formation of polychlorinated dibenzo-p-dioxins (PCDDs) in incinerators are examined. A model mechanism has been constructed to investigate the possibility of homogeneous gas phase formation of PCDDs from chlorophenols in an incinerator environment. Numerical calculations have been made. The results lead to the conclusion that the probability of gas phase formation of PCDDs is likely to be very low at high temperatures, $\gtrsim$ 1200 K, if mixing between fuel and air is efficient. In addition, production of PCDDs from chlorophenols is found to depend upon the square of the chlorophenol concentration. Probable sources of non-idealities in practical incinerators are examined. Effects of use of auxiliary hydrocarbon fuel and excess air are examined. The potential role of non-gas phase effects is considered. A discussion of some of the significant problems which complicate a further understanding of PCDD formation processes in incinerators has been presented in a manner that highlights future research needs.

Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) have been reported to have been found in incinerator emissions and other combustion sources [1, 2]. It has been suggested that these chemicals may be ubiquitous as a consequence of trace chemical processes that occur during combustion [3]. This is a controversial question (4a, b). With respect to their formation in municipal incinerators, it has been suggested that likely major routes of formation are from chemically related compounds such as chlorobenzenes, chlorophenols and PCBs [5]. There appears to be uncertainty as to the relative importance of formation from non-chlorinated precursors and inorganic forms of chlorine or from chemically unrelated chloro-organic compounds such as polyvinyl chlorides [5]. Laboratory experiments which deal with the formation of PCDDs and PCDFs from chlorophenols, chlorophenates, chlorobenzenes and PCBs have been reported [1, 2, 4b, 6, 7]. Most observations concerning the formation of hazardous waste compounds such as PCDDs during thermal incineration are fundamentally qualitative in nature in the sense that they do not provide detailed answers which can lead to process modifications that may minimize the formation of PCDDs. None of the experiments [1,2,6,7] which have been reported to date can be considered to be adequate to demonstrate that the compounds (PCDDs, PCDFs, etc.) which have been observed to form are attributable to gas phase processes [8,9]. In addition, it has previously been suggested that in some instances there seems to be evidence that formations reported in some laboratory experiments may in fact be due at least in part to surface reactions [10,11]. There is a substantial body of literature in which it has been explicitly demonstrated that reactions involving chlorinated organic species are frequently affected or controlled in whole or in part by the presence of reactive surfaces [8, 12-27].

In the following discussion some aspects of these problems are examined by first considering the potential for gas phase formation of PCDDs under strictly homogeneous conditions in order to establish a frame of reference. Existing information about gas phase reaction processes is drawn upon to develop a reasonable mechanism for gas phase formation of PCDDs from a suggested precursor, chlorophenols [2]. Next, some possible gas phase non-idealities which may develop during thermal incineration are examined. This will be followed by a consideration of potential non-gas phase contributions. Some general conclusions will be drawn regarding the problem of understanding PCDD formation in incinerators.

Mechanism Construction

The reaction steps which make up the proposed gas phase mechanism, discussed below, are shown in Table I. The species denoted by P, P•, PD and D respectively represent polychlorinated phenols, polychlorinated phenoxy radicals, polychlorinated 2-phenoxyphenols (dioxin precursor [2]) and PCDDs. These compounds are shown in Figure 1, where Cl_x and Cl_y denote the varying extent of chlorination of the compounds. In Table I, the species denoted by the symbol, R, represent any other organic fuel compounds in the gas phase mixture. R• and Pr denote a fuel molecule from which a hydrogen atom has been abstracted and unspecified products respectively. In Figure 2, the pathways of the proposed mechanism are shown schematically.

The rate constants assigned to the steps in the mechanism have been given values similar to rate constants which have been reported in the literature for analogous reactions. However, where there are uncertainties, the numerical values have been adjusted somewhat to bias the mechanism in favor of PCDD formation i.e., worse case modeling.

As constructed below, the mechanism is of a general nature. That is, isomer specific kinetic rate constants are not estimated. In this regard note the following points. Unimolecular rate constants, except for resonance stabilization effects, are not sensitive to substitutions to the bond being broken at positions greater than those corresponding to α (adjacent) substition (30). In addition it is expected that an increasing degree of chlorine substitution of the precursor chlorophenols will result in markedly slower rates of hydroxyl radical attack by addition reactions (30). Worse case modeling implicitly accounts for these effects in determining the overall (worse case) upper limit probability for PCDD formation as a class of molecules. The latter observation with respect to hydroxyl radical attack implies qualitatively that for gas phase processes, increasingly chlorinated PCDDs should be increasingly recalcitrant to bimolecular decomposition. That is, isomer distributions should be skewed toward higher chlorinated species. More quantitative statements regarding isomer specific reactions requires further experiments and more refined theoretical calculations. As the intent of this report is to examine the overall importance of gas phase mechanisms for PCDD formation rather than isomer specific differences, further refinements are not necessary here.

Each of the reaction steps as given in Table I is discussed below. The assigned rate constants have been biased to favor PCDD formation. Therefore the reader is strongly cautioned not to use these estimates out of the context of this paper, as actual values for these rates will be quite different in some cases.

The reaction,

$P \rightarrow P\cdot + H$ (R1)

represents the simple unimolecular bond rupture of the weakest bond in a polychlorinated phenol. The activation energy for this step is taken as the O-H bond energy in phenol, which has been determined experimentally [28]. Chlorine substitution is not expected to affect substantially this value [10]. The pre-exponential factor is assigned a value comparable to that associated with the formation of benzyl radical from dissociation of toluene [29] as a reasonable estimate. Thus, $k(R1) \approx 10^{15.5} \exp(-86000/RT)\ s^{-1}$ is assigned.

The reaction,

$OH + P \rightarrow P\cdot + H_2O$ (R2)

represents the process of hydrogen atom abstraction by hydroxyl radicals. In high temperature combustion such as incineration, the hydroxyl radical is the most important small inorganic radical present under typical incinerator operating conditions [10, 11, 30-34]. Furthermore, there is evidence that a <u>local</u> thermodynamic equilibrium between small inorganic radicals rapidly develops in the combustion flame zone [10, 11, 34]. A temperature dependent hydroxyl radical concentration can therefore be estimated from the local equilibrium assumption. In addition, a bimolecular rate constant of $\approx 10^9\ L\cdot mol^{-1}\cdot s^{-1}$ for hydroxyl radical attack on PCDDs has been estimated [10]. The mechanism uses the value of $\approx 10^9\ L\cdot mol^{-1}\cdot s^{-1}$ for this reaction, and is biased in favor of PCDD formation by ignoring the addition reaction of OH to polychlorinated phenols, even though OH addition to aromatic compounds is known to occur [30, 36-38]. The adduct from OH addition may simply decompose back to the original reactants, or undergo further reaction with molecular oxygen or other species present in the combustion system, leading eventually to ring opening [10, 28, 35, 36], a process which would not be expected to favor PCDD formation. Note also that the electrophilic nature of OH attack in addition reactions leads to a drastic lowering of the rates with increasing halogenation and that addition reactions usually decrease in rate as the temperature is increased [30].

The reaction,

$$P\cdot \rightarrow Pr \qquad \text{(R3)}$$

represents the decomposition of the phenoxy radical, resulting in elimination of CO, which has been observed to occur [28, 39]. The assigned rate constant, $k(R3) \approx 10^{13.6} \exp(-57654/RT)\ L\cdot mol^{-1}\cdot s^{-1}$ follows from analogy to the results of Colussi, Zabel and Benson [28].

The reaction,

$$P + P\cdot \rightarrow PD + Cl \qquad \text{(R4)}$$

represents the formation of a PCDD precursor, a polychlorinated 2-phenoxyphenol. In order to bias the mechanism in favor of PCDD formation, the possibility of reaction at other than the 2 position is ignored. Reaction at other than the 2 position has been reported, although not explicitly for the gas phase [40, 41] and may ultimately lead to polymerization in some instances. The rate of this bimolecular reaction, (R4), is probably very slow with a very small steric factor and possibly a negative temperature dependence [10, 42]. It is probably slower than the hydrogen abstraction reaction, (R7),

$$P\cdot + R \rightarrow P + R\cdot \qquad \text{(R7)}$$

Mulcahy and co-workers [43] have reported (for the unsubstituted phenol) that the reaction

$CH_3 + P \rightarrow CH_4 + P\cdot$

has an activation energy barrier of $E_A \approx 8 \pm 2$ kcal·mol^{-1}. Since $\Delta H^\circ_{298} = 17.8$ kcal·mol^{-1} for the reverse of this reaction [10, 44, 45], the activation energy for the reverse of this reaction may be estimated to be about 26 kcal·mol^{-1}. Therefore, by analogy, to bias the mechanism in favor of PCDD formation, a value of $k(R7) \approx 10^8 \exp(-26000/RT)$ L·mol^{-1}·s^{-1} is assigned to the rate constant for reaction (R7). (In all rate equations that appear in this paper the gas constant, R, has the value 1.987 cal·mol^{-1}·K^{-1}). A value of $k(R4) \approx 10 \times k(R7)$ is assigned to the rate constant for the reaction, (R4).

Reaction, (R5),

$$PD \rightarrow D + HCl \qquad (R5)$$

is a molecular elimination reaction leading to PCDD formation. Rate expressions for the molecular elimination of HCl from alkyl chlorides have been reported [29, 46], with pre-exponential factors in the range typically $\approx 10^{13.5 \pm 0.5}$ and activation energies of typically $E_A \approx 50 \pm 5$ kcal mol^{-1}. Reaction rates for gas phase molecular elimination of HCl from aromatics are not reported in the literature. However, the reaction is not likely to be faster than above, due to geometric requirements on the orientation of the hydrogen and chlorine atoms on the two rings and the strengths of the bonds involved [10, 20]. The closest analogue for reaction (R5) that is reported in the literature [47a, b] is the unimolecular elimination of HCl from 1-(1-chloroethyl)-2-methylbenzene for which a rate constant of $k = 3.55 \times 10^{13} \exp(-44{,}830/RT)$ s^{-1} is reported [47a]. The value $k(R5) \approx 10^{14} \exp(-45000/RT)$ s^{-1} is asssigned to the rate constant for reaction, (R5) in order to bias the mechanism in favor of PCDD formation. In fact, by analogy to other aromatic systems [48, 49] there is reason to suspect a substantially higher activation energy as well as possible competition between this molecular elimination channel and other simple unimolecular bond fission reactions. It is also likely that there is a small steric factor to be associated with reaction, (R5) [10].

Reaction (R6),

$$PD + OH \rightarrow D + H_2O \qquad \text{(R6)}$$

is similar to reaction (R2), for which we have previously estimated a bimolecular rate constant of $k(R2) \approx 10^9$ L•mol^{-1}•s^{-1}. Here reaction, R(6), is actually a combination of a rate limiting abstraction reaction

$$PD + OH \rightarrow PD\cdot + H_2O \qquad \text{(R6)'}$$

leading to production of a polychlorinated 2-phenoxyphenoxy radical which then rapidly reacts unimolecularly to form a PCDD (although not explicity noted, the fast reaction also results in elimination of either a Cl or an H atom)

$$PD\cdot \rightarrow D \qquad \text{(fast)}$$

and ignore the possibility of decomposition, in order to bias the mechanism in favor of PCDD formation. For the same reason, the addition reaction of OH is ignored.

Reaction (R8),

$$P\cdot + OH \rightarrow Pr \qquad \text{(R8)}$$

is expected to be faster than reaction (R2), since both reactants are radicals. However, to bias the mechanism in favor of PCDD formation, the rates are assumed comparable and set $k(R8) = k(R2)$.

Reaction (R9),

$$D \rightarrow Pr \qquad \text{(R9)}$$

represents the unimolecular dissociation of a PCDD to form products which will, at the temperatures where reaction (R9) becomes important, subsequently undergo further decomposition. A rate constant of

$k(R9) \approx 10^{15.5} \exp(-80000/RT)\ s^{-1}$ [10] has previously been estimated for this reaction.

Reaction (R10),

$$OH + D \rightarrow Pr \qquad (R10)$$

is the bimolecular reaction of a PCDD with a hydroxyl radical. A value $k(R10) \approx 10^9\ L{\cdot}mol^{-1}{\cdot}s^{-1}$ has previously been estimated for this reaction [10,11]. The mechanism is biased in favor of PCDD accumulation by reducing this value to $k(R10) \approx 10^8\ L{\cdot}mol^{-1}{\cdot}s^{-1}$.

Reaction (R11),

$$O_2 + P{\cdot} \rightarrow Pr \qquad (R11)$$

is the bimolecular reaction of a polychlorinated phenoxy radical with molecular oxygen. The reaction of the unsubstituted phenoxy radical with molecular oxygen has been estimated to have a rate constant of $\approx 10^8\ L{\cdot}mol^{-1}{\cdot}s^{-1}$ [48-51], and this value has been assigned here.

Reaction (R12),

$$R + OH \rightarrow R{\cdot} + H_2O \qquad (R12)$$

is expected to be slower in general than reaction (R8). However, to bias the mechanism in favor of PCDD formation, $k(R12) \approx 10^9\ L{\cdot}mol^{-1}{\cdot}s^{-1}$ is assigned, since the availability of the species, R, will decrease the concentration of P· through reaction (R7). The reverse of reaction (R12), is neglected since in combustion typical of incineration, the radical R·, resulting from hydrogen atom abstraction is highly labile and can react further with molecular oxygen, other fuel molecules and hydroxyl radicals, which will be present at substantially higher concentrations than the phenoxy radical [8-10, 30].

Reaction (R13),

$$R \rightarrow Pr \qquad (R13)$$

like reaction (R12), actually represents a broad spectrum of reactions, and a typical value of k(R13) $\approx 10^{16} \exp(-90000/RT)\ s^{-1}$ has been assigned [29, 46]. These reactions are strongly temperature dependent, and will tend to become important at temperatures at which PCDD destruction, as opposed to formation is already strongly favored.

Computer Simulation

The mechanism, as given in Table I has been used to study the possibility of PCDD formation under typical incinerator combustion conditions (below) through computer simulation via a standard Gear type [52] ordinary differential equation system solver. Various initial conditions were tested. A typical trichlorophenol has been considered although this choice is arbitrary in view of the generalities of the mechanism. Initial mole fractions of fuel reactant and oxygen are assigned based upon assumption of stoichiometric combustion (equivalence ratio equal to one) and conversion to carbon dioxide, water and HCl as major products. Atmospheric pressure was assumed and reaction at a range of temperatures from 500 K to 1500 K was investigated. Four cases (i-iv) were examined, for which initial mole fractions are as given in Table II. In all cases, the concentration of hydroxyl radical was defined through the assumption of local equilibrium to be $(OH)_{EQ} \approx 10^{-1.7} \exp(-35000/RT)\ mol \cdot L^{-1}$ [10,30].

Case (i) is used as a base against which to test the role of molecular oxygen and auxilliary hydrocarbon fuel in the destruction of polychlorinated phenols and in the possible formation of PCDDs. In actual stoichiometric or fuel lean combustion, there is (except in the case of mixing inhomogeneities between fuel and air) considerable molecular oxygen available up to the point of substantial fuel conversion. Therefore, this case is actually worse than the true situation and probably greatly exaggerates gas phase PCDD formation beyond what is realistically to be expected in ordinary combustion in the absence of significant mixing inhomogeneities between fuel and air. It is also not representative of a pyrolysis process, where $[OH] << [OH]_{EQ}$. In fact, for pyrolysis the mechanism would have to be developed differently, with inclusion of unimolecular initiation reactions such as reaction, (R1), and exclusion of emphasis on reactions involving hydroxyl radical attack. Note, however, that in the gas phase these reactions are likely to be characterized by large activation energies. Thus gas phase pyrolysis may not necessarily be expected to produce substantial amounts of PCDDs, as initiation reactions may have rate constants comparable to those for decomposition of PCDDs etc. In addition, it is possible that polymerization reactions would have to be included as part of the pyrolysis process [40, 41]. With great care, since the mechanism is biased in favor of PCDD formation, this case may possibly be regarded as suggestive of the situation in which an unburned fuel pocket, due to mixing inhomogeneities, passes into a post combustion zone where oxygen has already been depleted, but the [OH] radical concentration still tracks the local temperature in the incinerator. However, to determine fully the importance of this case one would have to analyze carefully the statistical character of variations of fuel/air inhomogeneities throughout a combustor and in addition develop refined estimates of the rate constants to eliminate the bias. In the case of a well designed incinerator we suspect the importance of fuel/air inhomogeneities is probably small relative to the bulk combustion process. This case in which the fuel is a pure phenol in no way corresponds to municipal incineration where such a chlorinated compound would only be present as a trace substituent in the input feed stream and not as a major component. In any event, note that in fact, if the phenol were present as a nearly pure compound in a waste stream, it would be most likely recovered for further use rather than destroyed thermally.

Case (ii) is more suggestive of combustion of a chlorophenol under hazardous waste incinerator conditions. Normally, most incinerators are run under stoichiometric or excess air conditions. However, to bias the mechanism in favor of PCDD formation we have adjusted the initial mole fraction of molecular oxygen to a level of about 60 percent of its value in stoichiometric combustion. This has the effect of de-emphasizing the rate of loss of the chlorophenoxy radical, P•, via reaction R11.

Case (iii) corresponds to a fuel rich pocket in a post combustion zone environment in the combustion of a mixture of a phenol and an excess of an auxiliary hydrocarbon fuel. This case is intermediate between combustion in a liquid hazardous waste incinerator where the percent of chloro-organic could be higher and the case of municipal incineration where the chloro-organic content would be lower. Again, molecular oxygen is treated as though it were unavailable.

Case (iv) is similar to case (iii) but has molecular oxygen present during the combustion stage. Case (iv) is to be compared to case (iii) as case (ii) is to case (i).

Discussion

The results of modeling these four cases for combustion during an elapsed time period of one second, which is a residence time typical of incineration are presented in Table III. The symbols P, P•, D and PD used in Table III are defined in Figure 1. Below, the results are analyzed. Concentrations for all four cases were computed for a wide range of reaction times other than t = 1 second but are not presented here to save page space.

Under the conditions of case (i) - i.e. post-combustion mixing and reaction of unburned chlorophenol with hydroxyl radicals, some substantial PCDD formation is indicated at intermediate temperatures. This is the only case where that is true. However, this case is not realistic. It assumes the entire initial mole fraction of phenol makes it into the post combustion zone of an incinerator. This is not likely to happen. In fact under normal operating conditions in a well designed incinerator, only a very small amount of unburned fuel would be likely to enter the combustion zone. Therefore, realistically, these mole fractions of PCDD produced under case (i) would have to be weighted by the fraction of fuel which actually makes it to the post combustion zone. On the basis of such a weighting process, one would expect a much lower PCDD formation than indicated in case (i).

In all the other cases it is quite clear that PCDD production is very low. The use of auxiliary fuel, stoichiometric or excess air and high temperatures (all of which are common operating conditions) promote phenol destruction to products other than PCDDs. At flame temperatures, gas phase PCDD formation would be below detection limits. Note also from Table III that in all cases the level of chloro-2-phenoxyphenol formation is predicted by the mechanism which has been utilized, to be much lower than PCDD formation. In part this may possibly explain why chlorophenoxyphenols are not commonly reported as products of combustion.

As can be seen by comparing results in Tables IIIa with IIIc or Table IIIb with IIId, it is significant to note that production of PCDDs from the precursor, chlorophenols, depends upon the square of the precursor concentration.

In actual practice, it is found that PCDD emissions sometimes exceed the levels predicted by the above results. This requires consideration in some detail as to the nature of these circumstances. Some additional possibilities may be:

a) PCDDs were originally present in the input feedstreams and survive thermal destruction in significant amounts.

b) Due to mixing inhomogeneities some unburned chloroorganics survive the main combustion environment and make it into the post-combustion zone.

c) Temperature fluctuations (thermal transients) result in incomplete thermal stressing due to gas entrapment in cold pockets, promoting PCDD production at above ambient but below flame temperature conditions.

d) Molecules other than chlorophenols are being converted to PCDDs in the gas phase.

e) Inorganic chlorine sources in municipal waste input feed streams lead to chlorination of organics and ultimate formation of PCDDs in the gas phase.

f) Non-gas phase, or a combination of gas and non-gas phase reactions are contributing to the production of PCDDs during the combustion process.

With regard to (a), it has been stated that at least for municipal waste streams, PCDDs are not initially present in input feedstreams in significant amounts [5], to the extent that would be required to account for observed levels of emissions. In the case of hazardous waste incineration streams, the situation would depend on the feedstock. By way of a hypothetical example, note that if it were the case that a municipal waste stream contained 1 part per thousand of chlorophenols which in turn contained 100 ppm of a PCDD impurity, then the expected PCDD level in the effluent stream (gas plus fly ash combined) would be on the order of tens of ppb if the PCDD destruction efficiency were zero (due to dilution) and would readily fall to a few parts per trillion once the destruction efficiency exceeds 99% for the PCDDs. We have previously described an estimation procedure for calculating the expected destruction efficiencies if homogeneous mixing is developed in the gas phase of an incinerator [10,11]. This procedure was applied to the case of PCDD destruction. We could conclude from these estimates that the gas phase thermal destruction efficiency for PCDDs is extremely high at flame temperatures typically achieved in an incinerator, $T \gtrsim 1500$ K [10,11].

With regard to (b), further investigation is warranted as there is not much data presently available about statistically representative temporal or spatial frequencies of unburned fuel pockets of varying fuel/air composition in practical incinerators. Mixing inhomogeneities may develop for various reasons, e.g., poor atomization may sometimes be a problem in liquid hazardous waste incinerators. Samuelsen [53] has discussed the formation of eddies or pockets of varying fuel air mixtures in non-premixed flames. Breen [54] has estimated that eddy lifetimes may range anywhere from 10 to 50 milliseconds. Whether or not these eddies will ignite depends significantly upon the fuel/air ratio in an eddy and upon the extent to which an eddy may mix together with other eddies [53]. Appelton and Heywood [55] have discussed how inhomogeneities due to eddies or pockets of varying fuel/air mixtures may affect pollutant formation in continuous flow combustors burning atomized liquid fuels.

In addition, in the case of liquid injection, peculiarities of the liquid mixture being injected may sometimes present problems. Wood and others [56] have demonstrated that during the combustion of a multi-component fuel drop, the composition of the drop and its surrounding vapor change by a process of simple batch distillation. The inference here is that one must sometimes be careful as to which fuels are to be mixed together if fuel properties are such that substantial distillation may be likely to occur. As an example, consider the injection of a mixture consisting of small amounts of chloroform and chlorophenol diluted in an auxilliary hydrocarbon fuel such as n-octane. To begin with, if atomization and/or mixing are poor, the maximum temperature will occur, not at the stoichiometric equivalence point, but at a somewhat lower equivalence ratio (leaner fuel mix than theoretical stoichiometric composition) corresponding to introduction of a substantial amount of excess air [57]. At this maximum temperature point, the mixture will be efficiently thermally decomposed. On movement into the fuel lean and fuel rich sides of this maximum temperature point, temperatures may be increasingly substantially lower and destruction efficiencies may be component specific. In <u>apparent</u> contradiction to expectations based upon a kinetic scale of incinerability [30], one would observe in some off maximum temperature circumstances, due to the batch distillation process, that much more chloroform than chlorophenol could persist through the combustion zone. This is because the selective evaporation of chloroform into the vapor phase rapidly enriches the vapor phase in this component as the droplet begins to evaporate [58]. Depending on the amount of enrichment this can significantly reduce the extent of reaction in the chloroform enriched vapor phase due to the flame inhibiting characteristics of the resulting mixture [59, 60]. If the combustion zone is small, subsequent fluid hydrodynamic processes may remove some of this self inhibiting mixture from the region of the combustion zone before more substantial mixing and enhanced combustion can occur. At the same time, the liquid droplet is becoming enriched in chlorophenol and auxilliary hydrocarbon fuel (increasing mole fraction) by the distillation process. This mixture may have less flame inhibiting character (due to chloroform removal) and as such will subsequently burn more completely on evaporation. Thus more chlorophenol than chloroform is destroyed in these circumstances. It may be the case that as the chlorophenol is mostly contained in a droplet which is burning at or near its boiling point [61], some conversion to secondary products of formation may occur within the droplet prior to complete evaporation. However, this in itself (and similarly for the case of secondary product formation due to pyrolysis reactions which might occur during the short period of warm-up of the escaping vapor to its ignition point [62]) would not necessarily create a hazardous secondary product emission problem if the chlorophenol enriched droplet subsequently totally evaporates within the high temperature combustion zone and providing the off-maximum temperature is still substantially high enough to thermally decompose the resulting gas phase mixture. Similar arguments would apply to the small amounts of chlorophenol lost to the chloroform enriched vapor phase. A complication could arise if flame inhibition occurs to such a substantial extent that it results in flame extinguishment in the region of the chlorophenol enriched drops. This problem could possibly be solved by allowing for a large enough combustion zone such that the droplet could subsequently be re-ignited. In most cases, some approaches to these problems would be to improve atomization, improve mixing, adjust the initial fuel mixture composition to avoid undesirable distillations, provide for a high temperature combustion zone transit time which significantly exceeds the droplet burnout and mixing times, or to employ afterburners (staged combustion).

In any event, predictions of incinerability based upon chemical kinetics [30] are still possible. The problem of the apparent breakdown of a kinetic scale of incinerability is solved by recognizing that the incinerability scale is designed to be applied to homogeneous gas phase mixtures. Thus, once a distillation process occurs the kinetic scale of incinerability must be adjusted to account for formation of enriched and depleted vapor mixtures and their local environment temperatures. In such a case, a weighting must be employed to account for these physical mass transfer and associated effects which are a consequence of the distillation process.

It is possible to design experiments for measuring directly fast transient fuel burning fluctuations [63,64], but these methods have not been commonly applied to the process of incineration. Note that if in fact mixing inhomogeneities are a problem, it is not a problem without possible practical solution for reasons mentioned previously.

The possibility (c), is to an extent, related to the degree of mixing, although other parameters are also operative in controlling thermal fluctuations [65-67]. Detection of fast (100 Hz and higher) thermal fluctuations at a point in space in turbocombustors has been made optically [63] and via physical measurement with fast time constant thermocouples [68-70]. Application of optical detection to an incinerator environment will require correction for substantial particulate entrainment in the flow stream. The application of fast time constant thermal measuring devices will require innovative technology such as R. R. Dils new high temperature optical fiber thermometer [71] to avoid large error measurements, since at flow speeds and temperatures typical of an incinerator, convective transport is greatly diminished relative to the situation in a turbocombustor [68-71]. Under incinerator conditions of low flow rates, thermocouple fast transient temperature measurements are substantially based upon radiative transport, and this dependence is the source of the large errors in these thermal measurements when thermal fluctuations are rapid. Numerical simulations of scales of incinerability or formation in the presence of temperature fluctuations are possible [10,11,30,65-67]. It is important to stress that in numerical simulations of destruction or formation of organic species in non ideally mixed reactive flows with temperature fluctuations, one must as a minimum, account for not only the effects of unimolecular but also of bimolecular processes such as those involving hydroxyl radicals [10,11]. If this is not done, results can be misleading. The extent to which a typical thermal destruction process as characterized by the rate constant expression

$$k_{destruction} = k_{bimolecular}[OH] + k_{unimolecular}$$

becomes dominated by the unimolecular character may possibly provide useful information about deviations from the ideal case of well mixed fuel/air combustion at flame temperatures. Another important question for case (c) that will have to be addressed is the question as to what extent or not unburned or partially combusted fuel trapped in a relatively cool pocket can be easily transported to the post combustion zone where PCDD formation might possibly take place. While it is known that transport of unburned or partially combusted fuel does occur in some specific instances, for example in a diffusion flame [53-55], a detailed and quantitative assessment of this problem in practical incinerators has not yet been developed. More work needs to be done in this respect, since at least in the case of turbopropulsion, thermal fluctuations can be enormous [68] and fluctuations in turbulent flames in general have been known sometimes to be substantial [53-55,67,71]. We suspect based on observed combustion efficiencies that the statistical probability for transport of unburned fuel in a cold pocket to the post combustion zone is probably low in a well designed incinerator [10].

The possibility (d), that molecules other than chlorophenols lead to gas phase formation of PCDDs under typical incinerator conditions is amenable to the same type of numerical analysis as presented in this paper. It is reasonable to expect that the fewer the features a precursor molecule has in common with PCDDs or PCDFs (e.g. aromatic character, and chlorine or hydroxyl functional groups), the more complex the mechanism one would have to propose for PCDD or PCDF formation. Under these circumstances, at high temperatures, $T \gtrsim 1200$ K, there will probably be more competitive destruction pathways (vs. formation pathways) than in the mechanism proposed in this report for PCDD formation from chlorophenols (or polychlorinated 2-phenoxyphenols). Thus, the probability for gas phase formation of PCDDs or PCDFs would be expected to decrease under these circumstances. As mentioned previously in this report, the author feel there have been no experiments made to date which unambiguously demonstrate that gas phase formation of PCDDs and PCDFs occurs under typical incinerator combustion conditions [1, 2, 4b]. However, the authors feel confident that such experiments can be designed and used to test for non gas phase and inhomogeneous mixing effects [8,9,63-71].

The possibility, (e), that of de novo synthesis from inorganic sources of chlorine in the gas phase has not been extensively examined [1,2]. The authors have briefly investigated the presence of $FeCl_2$, $FeCl_3$ and NaCl in the gas phase through numerical equilibrium modeling under conditions typical of incineration, for example, as outlined in this paper. This modeling indicates that in incineration, temperatures in excess of 1000 K are required for low levels of NaCl to build up in the gas phase and that temperatures in excess of about 1200 K are required for low levels of iron chlorides to develop in the gas phase. Equilibrium conditions at lower temperatures overwhelmingly favor distribution of these metals among non gas phase species.

The quantitative reactivity of NaCl or iron chlorides as a source of chlorine for gas phase chlorination of organics at high temperatures has not been reported. In addition the time required for these inorganic chloride species to develop to equilibrium concentrations is not reported under typical incinerator combustion conditions. In the event that aluminum recycling is not practiced, aluminum chlorides would also have to be considered in a similar manner. Heavy metal chlorides, e.g. $ZnCl_2$, $CdCl_2$ and $PbCl_2$ are much more volatile at these temperatures [72], but except for fairly specific waste streams the amounts of these metals initially present is usually low.

The above discussion implies that even if these materials are present and reactive in the gas phase at incinerator conditions, there are not likely to be any simple mechanisms in which through only a few steps, the production of PCDDs would occur to any significant extent. This is because the bimolecular rates associated with the reaction steps of any proposed mechanism would be low as a consequence of the low gas phase concentrations of these species at incinerator operating temperatures. As seen from modeling of chlorophenol combustion, at high temperatures PCDD formation involving multistep processes consisting of several reaction steps where reactant concentrations are low to begin with cannot easily compete with other routes which lead to destruction during the combustion process. For these reasons the authors suspect de novo synthesis from inorganic precursors is unimportant in the gas phase. This discussion does not imply, however, that de novo synthesis from inorganic sources of chlorine via non-gas phase processes is to be discounted. Quite the contrary, multiphase reactions involving inorganic chlorides have been reported, including those which produce HCl and Cl_2 from metal chlorides [73] and those which result in the production of PCDDs [74] and other chlorinated organics [75].

The last and most intriguing possibility, (f), is the assumption that non-gas phase or a combination of gas and non gas phase reactions may be contributing to the production of PCDDs during the combustion process. Allusions have previously been made in this paper to the extensive literature which reports the enhanced reaction sensitivity of organic species to the presence of reactive surfaces. Thus, reactions involving suspended fly ash or reactive processes within or on the grate beds of incinerators may have to be considered.

Fly ash itself is principally a mixture of silica and metal oxides [10] and should have many reactive Lewis and Bronsted acid and base sites which could presumably promote reactions [23-25] at temperatures considerably below those at which the previously discussed destruction processes dominate. In fact, chloro-organics formed from reactions in the presence of chlorine and fly ash have recently been reported [21]. The authors have also indicated that there is other research which appears to suggest oxygenation of chloro-organics to form PCDFs may be due to surface reactions [10]. One must also consider the work of Nestrick and co-workers [27] in synthesizing PCDDs from chlorophenates which must be due to surface reactions in view of the low temperatures in which reactions were carried out. The highly polar nature of the metal to oxygen bond in the chlorophenates that were used and the surface reactivity of the silica support they used probably favor ionic reactions on the surface [23-25], possibly involving surface bound hydroxyl groups and other reactive sites. At these temperatures [27] radical reactions in the gas phase cannot compete. Surface reactions and/or reactions inside solids (such as fly ash and other materials) therefore seem to be strong candidates as potential sources for PCDD and PCDF formation. Transport of these compounds into effluent emissions could then possibly be due to insulation inside particles that have not been sufficiently heated to the core. Presumably, vapor emissions of toxics would in part then be associated with particle outgassing in the post combustion zone [10]. In addition, particles, like unburned air/fuel pockets, may possibly also act as transport agents for passage of unburned toxic precursors to the post combustion zone, where formation may be favored. Alternatively, the presence of particulates among unburned air/fuel pockets in the post-combustion zone may promote surface reactions leading to PCDD formation followed by thermal desorption into the gas phase. A correlation of PCDD emissions with particle size may be informative in understanding the relative importance of the above possibilities although care in interpreting results may have to be exercised if data is taken from units equipped with electrostatic precipitators due to differences in the ease of ionization of particles of varying material composition.

Other complicating effects associated with particle emissions may at times potentially be encountered. For example: With respect to fly ash particle size as a function of distance measured moving away from an incinerator point source, fly ash particle size distributions taken from soil samples (surrounding the incinerator point source) may shift to deposition of particles of smaller sizes onto the soil. This is anticipated from differences in the terminal gravitational settling velocity between particles of different sizes [76,77]. If the smaller particles have been more thermally stressed in the incinerator due to the strong dependence of particle heat up times with particle diameter [10,78], then isomer distribution ratios of PCDDs/octa-CDD (e.g. hepta-CDD/octa-CDD) formed on the fly ash particles should be observed to asymptotically shift towards lower ratios as one moves away from the incinerator point source, i.e., particle size and PCDD/octa-DD ratios reflect their thermal history inside the incinerator and should track each other. That the shift should occur in the direction of lower ratios on moving away from the incinerator point source is a reflection of the increasing thermal [30,79] and kinetic [10,11] stability of PCDDs with increasing degree of chlorination, i.e., on the more thermally stressed particles the more kinetically and thermally stable PCDDs should predominate. The asymptotic nature of the shift reflects the fact that below a certain particle size, essentially complete (to the core) thermal heating of all fly ash particles which have been exposed to high temperatures inside the incinerator has occurred. Whether or not this trend could be interpreted to demonstrate that volumetric as opposed to surface formation (or deposits) of PCDDs are occurring in the incinerator requires further analysis, particularly with respect to heat sinking and particle porosity during the lifetime of the fly ash particle's tranversal through the incinerator. This analysis probably applies to municipal waste incineration where there are not likely to be any significant amounts of PCDDs to begin with. In the case of hazardous waste incinerators the analysis may be more complicated depending upon which if any PCDDs are initially present in the input feedstream.

In addition to reactions inside of or on the surfaces of particles, the possibility for liquid phase transformations may have to be considered in some instances. The literature is replete with reports of organic synthesis of PCDDs in various solutions with and without catalysts (see reference [2] and references contained therein). Liquid phase reactions may possibly occur, e.g., in liquid injection hazardous waste incinerators where atomization is poor and droplet evaporation times approach or exceed combustion zone transit times. In these instances it may be worthwhile to investigate alteration of droplet evaporation times, improving atomization, use of afterburners (staging), etc., as mentioned previously.

A further source of precursors may be from compounds entrained in the input combustion air feedstream itself. For example, Junk and co-workers [80-83] have discussed in careful detail the presence of PCBs in combustion air. Therefore, in addition to waste feedstream sources [1-5, 84] additional consideration may have to be given to the history of combustion air as it passes through an incinerator. However, with respect to gas phase formation processes, arguments similar to those presented in this paper probably apply, and PCDD formation from trace organics in input combustion air is therefore probably unimportant at the same conditions and high temperatures that would ordinarily promote PCDD destruction.

Conclusions

Clearly, to more fully understand details of the processes for formation and destruction of toxics such as PCDDs and PCDFs during the process of high temperature combustion, more research is required for reasons and in directions indicated above. On the other hand, it is important to recognize that there is no unique thermal or kinetic stability attributable to these compounds [30] that would prohibit their efficient destruction at high temperatures. As seen from Tables III (a-d), the use of an auxiliary fuel and the availability of molecular oxygen reduces dioxin levels substantially. This can be attributed in part to reaction steps R7 and R11 shown in Table I. Thus, as one possibility, inhomogeneities in a practical sense, may to some extent be compensated for by the use of chlorine free auxiliary fuels in after burners where economically feasible.

As regards gas phase processes, note that the foregoing discussions suggests gas phase PCDD formation is likely to be of low probability if precursors are present only at low concentrations. This is a natural consequence of the bimolecular nature of the formation reaction step, R4. Note, however, that if PCDDs are already present in the gas phase, there is likely to be a high probability of formation of PCDFs from PCDDs in the gas phase, if the reaction is postulated to proceed via radical attack on a central ring oxygen atom of a PCDD molecule resulting in abstraction of the oxygen atom, followed by rapid ring closure. In fact, PCDFs have been reported present in municipal incinerator emissions at high loading levels (1, 2, 4b). The problem is to fully account for the dioxin emission levels.

In order to further understand these problems it is appropriate that several research objectives should be set for the scientific community as enumerated below. This listing is not all inclusive but does serve to highlight some current research needs with respect to understanding the processes by which PCDDs, PCDFs and similar toxic compounds may be formed and destroyed during practical thermal incineration:

(a) Analytical methods should be further developed and applied to quantify types and amounts of specific organic compounds and classes of organic compounds not only as a function of fly ash (or bottom ash, ESP ash, etc.) particle size but also as a function of their distribution on the surface of or inside (volumetric and internal surface due to pores) particles. The same comments should be understood to apply to inorganic species associated with fly ash emissions (or bottom ash, ESP ash, etc.). In addition the distribution of species among the various phases (solid/fly ash, soot; liquid/water aerosol, organic aerosol; gas/evolved gas) needs to be characterized.

(b) Efforts should be made to study and understand <u>fast transient</u> phenomena in incinerators, e.g. cold pockets, pre-ignition pyrolysis, mixing inhomogeneities, etc.

(c) Much more effort should be directed toward understanding the nature of condensed phase reactions (catalyzed and uncatalyzed), e.g., surface reactions, reactions in solids, etc.

(d) Predictive, reactive flow multidimensional fluid hydrodynamic numerical simulations should be performed to study the dynamic character of the incineration process.

(e) Laboratory scale experiments need to be performed as an aid to refining rate constants associated with reaction steps in any proposed mechanisms. These should include both gas phase and condensed phase kinetics. With more refined mechanisms sensitivity analysis should be undertaken. Similarly more thermodynamic data is needed for species such as chlorophenols, PCDDs, PCDFs, etc., which is more reliable than what is currently reported, if predictions of equilibrium isomer distributions are to be made with greater accuracy.

(f) Complicating effects, e.g. selective compound distillations, particle size separations, etc., should be examined in more detail.

(g) Optical methods should be applied to real time detection of transient species in incinerator environments; especially hydroxyl radical due to its importance in the combustion process. Continuous rather than intermittent (e.g. as with a 10 Hz pulsed laser) measurements would be desirable in order to understand perturbations in concentration measurements due to effects such as vortex shedding.

(h) Interferences in analysis, e.g. of organic compounds in fly ash due to naturally occurring particulates [85], should be very carefully assessed.

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TABLE I - PROPOSED PCDD FORMATION MECHANISM(a)

#	Reaction Step	Rate Constant	
R1	$P \rightarrow P\cdot + H$	$10^{15.5}$ exp(-86500/RT)	S^{-1}
R2	$P + OH \rightarrow P\cdot + H_2O$	10^{9}	$L\cdot M^{-1}\cdot S^{-1}$
R3	$P\cdot \rightarrow Pr$	$10^{13.6}$ exp(-57654/RT)	S^{-1}
R4	$P + P\cdot \rightarrow PD + Cl$	10^{9} exp(-26000/RT)	$L\cdot M^{-1}\cdot S^{-1}$
R5	$PD \rightarrow D + HCl$	10^{14} exp(-45000/RT)	S^{-1}
R6	$PD + OH \rightarrow D + H_2O$	10^{9}	$L\cdot M^{-1}\cdot S^{-1}$
R7	$P\cdot + R \rightarrow P + R\cdot$	10^{8} exp(-26000/RT)	$L\cdot M^{-1}\cdot S^{-1}$
R8	$P\cdot + OH \rightarrow Pr$	10^{9}	$L\cdot M^{-1}\cdot S^{-1}$
R9	$D \rightarrow Pr$	$10^{15.5}$ exp(-80000/RT)	S^{-1}
R10	$D + OH \rightarrow Pr$	10^{8}	$L\cdot M^{-1}\cdot S^{-1}$
R11	$P\cdot + O_2 \rightarrow Pr$	10^{8}	$L\cdot M^{-1}\cdot S^{-1}$
R12	$R + OH \rightarrow R\cdot + H_2O$	10^{9}	$L\cdot M^{-1}\cdot S^{-1}$
R13	$R \rightarrow Pr$	10^{16} exp(-90000/RT)	S^{-1}

(a) The rate constants have been biased to favor PCDD formations, therefore, the reader is strongly cautioned not to use these estimates out of the context of this paper, as actual values for these rates will be quite different in some cases.

Table II. Initial Mole Fractions$^{(a)}$

	CASE (i)	CASE (ii)	CASE (iii)	CASE (iv)
$X_{O2}^{(b)}$	0.	0.1	0.	0.1
X_R	0.	0.	$99X_P$	$99X_P$
X_P	3.16×10^{-2}	3.16×10^{-2}	3.16×10^{-4}	3.16×10^{-4}

(a) $(OH) \approx (OH)_{EQ} \approx 10^{-1.7} \exp(-35000/RT)$ [30]. Total pressure = one atmosphere (760 torr). Other species, e.g. N_2, H_2O, HCl, Pr, etc., which do not participate as reactants in the mechanism shown in Table I make up the balance of the mole fractions not explicitly detailed in Table II.

(b) In cases (ii) and (iv), the mole fraction of molecular oxygen has been set to a level of about 60 percent of the stoichiometric combustion value as follows from the discussion presented in the body of this paper.

Table IIIa. Concentration(a) of species after 1 second: case(i)

T(k)	P	P•	D	PD
500	7.70-4	2.31-16	6.58-28	7.10-22
600	6.42-4	2.03-9	2.34-16	2.01-13
700	5.50-4	1.20-7	5.31-11	1.86-10
800	4.79-4	2.41-6	4.21-8	1.83-9
900	4.01-4	1.85-5	1.97-6	3.16-9
1000	2.46-4	1.09-5	7.18-6	1.73-12
1100	4.11-5	6.83-7	1.91-6	1.73-12
1200	6.21-8	4.57-10	3.43-10	8.42-19
1300	9.34-19	4.12-21	5.43-32	1.49-36
1400	5.26-79	<1.00-70	<1.00-70	<1.00-70
1500	<1.00-70	<1.00-70	<1.00-70	<1.00-70

(a) e.g.: The number: 1.53-12 is 1.53 x 10^{-12} moles/liter. The symbols P, P•, D, and PD are defined in Figure 1.

Table IIIb. Concentration of species after 1 second: case(ii)

T(k)	P	P•	D	PD
500	7.70-4	2.79-17	7.95-29	8.58-23
600	6.42-4	1.01-14	3.69-21	2.05-18
700	5.50-4	6.80-13	8.43-16	1.85-15
800	4.79-4	1.59-11	5.64-13	1.23-14
900	4.03-4	1.75-10	3.48-11	3.02-14
1000	2.53-4	8.71-10	6.68-10	3.23-14
1100	4.04-5	7.69-10	2.29-9	1.91-15
1200	5.74-8	4.75-12	3.61-12	8.10-21
1300	2.07-18	6.76-22	7.97-33	2.19-37
1400	3.11-70	<1.00-70	<1.00-70	<1.00-70
1500	<1.00-70	<1.00-70	<1.00-70	<1.00-70

Table IIIc - Concentration of Species After 1 Second: Case (iii)

T(k)	P	P•	D	PD
500	7.70-6	2.31-18	6.58-32	7.10-26
600	6.42-6	2.08-11	2.55-20	2.12-17
700	5.50-6	1.20-9	5.31-15	1.86-14
800	4.79-6	2.45-8	4.26-12	1.86-13
900	4.03-6	2.00-7	2.09-10	3.45-13
1000	2.52-6	1.17-7	7.73-10	4.34-14
1100	4.12-7	6.85-9	1.95-10	1.73-16
1200	6.52-10	4.80-12	3.61-14	9.29-23
1300	9.92-21	4.38-23	2.82-36	7.73-41
1400	<1.00-70	<1.00-70	<1.00-70	<1.00-70
1500	<1.00-70	<1.00-70	<1.00-70	<1.00-70

Table IIId - Concentration of Species After 1 Second: Case (iv)

T(k)	P	P·	D	PD
500	7.70-6	2.79-19	7.93-33	8.57-27
600	6.42-6	1.01-16	3.70-25	2.06-22
700	5.50-6	6.80-15	8.46-20	1.86-19
800	4.79-6	1.59-13	5.64-17	1.23-18
900	4.03-6	1.75-12	3.49-15	3.02-18
1000	2.52-6	8.68-12	6.71-14	3.21-18
1100	3.16-7	7.92-12	2.31-13	2.02-19
1200	6.29-10	5.21-14	3.95-16	9.74-25
1300	9.03-21	2.96-24	1.57-37	4.31-42
1400	<1.00-70	<1.00-70	<1.00-70	<1.00-70
1500	<1.00-70	<1.00-70	<1.00-70	<1.00-70

Legends for Figures

Figure 1. Species contained in the model mechanism.

Figure 2. Biased mechanism schematic.

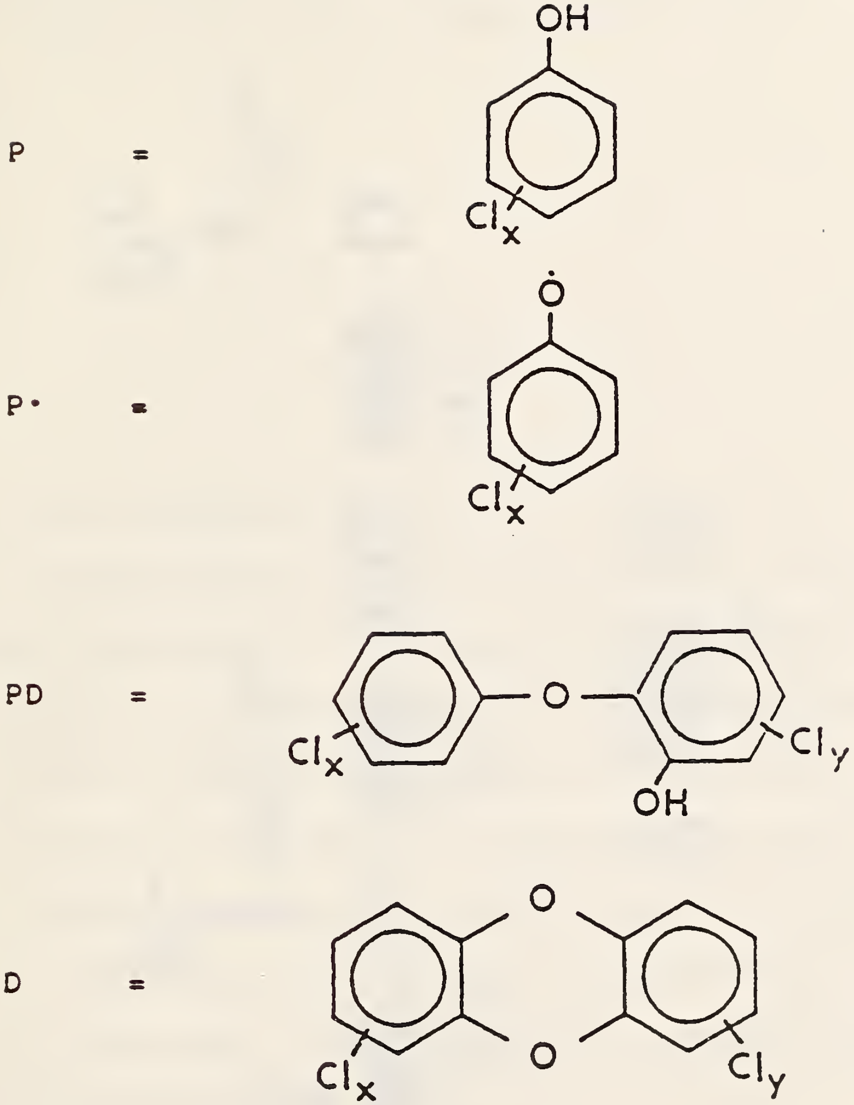
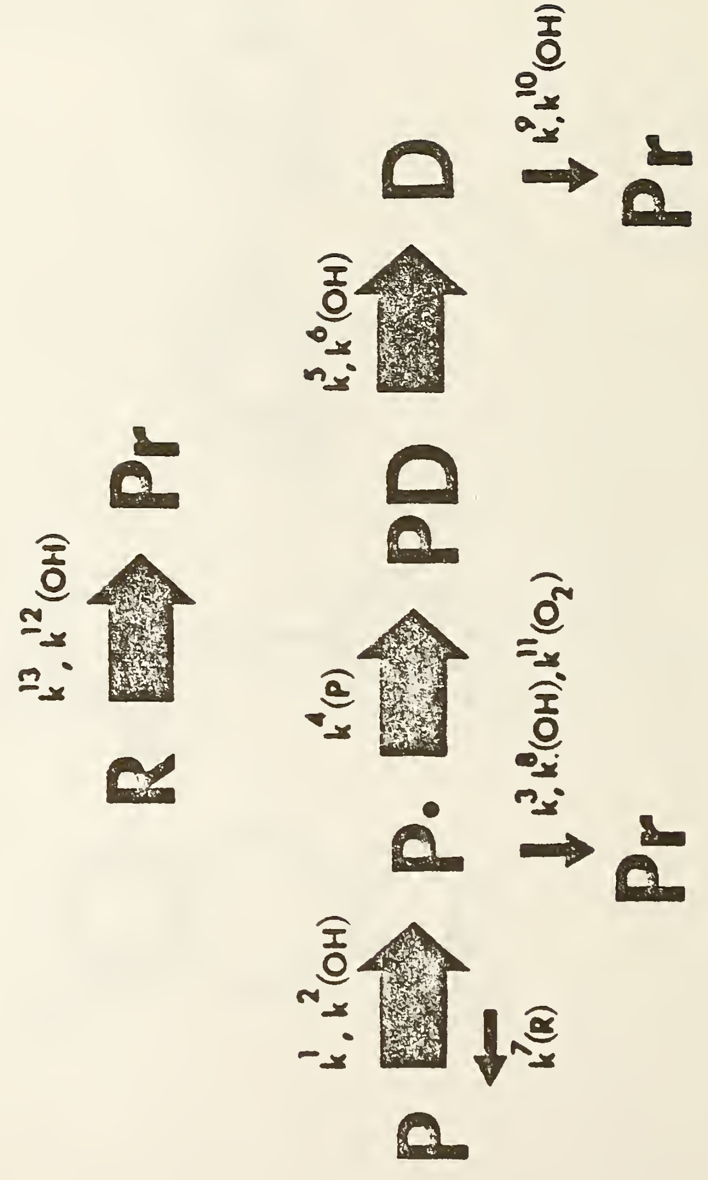


Figure 1. Symbolic representation of species in proposed mechanism.


P
$k^{1}, k^{2}(OH)$
$k^{7}(R)$
P•
$k^{4}(P)$
PD
$k^{5}, k^{6}(OH)$
D
$k^{3}, k^{8}(OH), k^{11}(O_2)$
Pr
$k^{9}, k^{10}(OH)$
Pr
R
$k^{13}, k^{12}(OH)$
Pr

APPENDIX C

OVERVIEW OF DIOXIN FORMATION IN GAS AND SOLID PHASES UNDER MUNICIPAL INCINERATOR CONDITIONS

ABSTRACT

Mechanisms for the formation of dioxins during incineration via gas and gas-fly ash interactions are presented and discussed. On the basis of simplifying assumptions analytical expressions which relate dioxin formation with elementary reactions are derived. Based on a postulated mechanism, it is concluded that gas phase formation proceses do not account for observed dioxin emissions from municipal incinerators. For gas-fly ash interactions, observations are used to develop a model for catalytic dioxin formation. It is concluded that catalytic and other non gas phase processes need to be considered in order to account for observed dioxin emissions from municipal incinerators.

INTRODUCTION

The results of quantitative analyses of effluent emissions (gas and particulate fly ash) from municipal incinerators suggest that levels ranging from parts per trillion to parts per million of polychlorinated dibenzo-p-dioxins (hereafter referred to in this paper as, dioxin[s]) may sometimes be emitted to the environment [1-4].

It has been shown that [5,6] dioxins cannot be formed at the reported levels on the basis of gas phase formation processes. Instead it has been suggested that [5,6] dioxin formation may be associated with catalytic processes involving suspended fly ash in the hot flowing gas stream and/or via some other condensed phase processes. The purpose of this report is to develop a simple model for gas-solid dioxin formation from fly ash. First, some concepts dealing with gas phase dioxin formation and destruction mechanisms will be reviewed. Through simplifying assumptions, an analytical form for a previously proposed mechanism will be derived to explicitly demonstrate the chemical processes which limit dioxin formation in the gas phase. Second, it will be shown that a mechanism for dioxin formation from fly ash catalysis can be constructed. When calibrated against reported observations this leads to prediction of the expected range of rate parameters for reactive catalytic processes.

GAS PHASE PROCESSES FOR DIOXIN FORMATION

It has been shown [6] through construction of a "worse" case model, that it is unlikely dioxin formation may be occurring via gas phase processes. This was demonstrated through a computer solution of coupled rate relations assumming typical incinerator operating conditions.

However, in developing the computer based numeric solution for predicted levels of dioxin formation certain significant features were not brought out. To rectify this problem an analytic solution of the previously proposed dioxin formation model under certain simplifying conditions is presented. The outline in a previous report is followed [6]. The pertinent chemical species are symbolically noted in Figure 1. The proposed "worse" case (i.e. biased towards dioxin formation beyond what is realistically likely to occur) mechanism for dioxin formation is shown in Table I. The species denoted by the symbol, R, denotes all other hydrocarbon fuel molecules. R• is the corresponding radical. Use of the reported rate constants beyond the intent of these reports is not advised. They are biased away from likely actual numerical values one would expect to determine experimentally.

On the basis of the "worse" case hypothesis it is assumed that $P \sim P_o$ and $R \sim R_o$, i.e., constant levels of precursor and hydrocarbon fuel molecules are maintained. The mechanism is further based in favor of dioxin formation by assuming no free molecular oxygen is present in the post-flame combustion zone. This is equivalent to stating that reaction step R11 shown in Table I may be ignored. It is then possible to apply a steady state treatment to determine the concentration of P• and PD from the proposed mechanism. For $(P\cdot)_{ss}$

$$(P\cdot)_{ss} \approx \frac{[k_1 + k_2\,(OH)_{EQ}]P_o}{k_3 + k_8\,(OH)_{EQ} + k_4P_o + k_7R_o} \qquad C(1)$$

Inspection of the assigned rate constants in Table I, for the temperature range of interest in the post-flame combustion zone, leads to the result that

$$(P\cdot)_{ss} \approx \frac{k_2(OH)_{EQ}}{k_3 + k_8(OH)_{EQ}} \qquad C(2)$$

In this and subsequent expressions, the hydroxyl radical concentration is determined by a local equilibrium assumption [6]. Similarly,

$$(PD)_{ss} \approx \frac{k_4P_o}{k_5 + k_6\ (OH)_{EQ}}\ (P\cdot)_{ss} \approx \frac{k_4k_2(OH)_{EQ}}{k_5(k_3 + k_8(OH)_{EQ})}\ P_o^{\ 2} \qquad C(3)$$

It follows that,

$$d(D)/dt \approx [k_5 + k_6(OH)_{EQ}]\ (PD)_{ss} - [k_9 + k_{10}(OH)_{EQ}]D \qquad C(4)$$

For post-flame combustion zone temperatures, this reduces to,

$$d(D)/dt \approx k_5(PD)_{ss} - k_{10}(OH)_{EQ}D \qquad C(5)$$

From the boundary condition that at t = 0, the dioxin level D(t = 0) = 0, it follows that,

$$D \approx \frac{k_5(PD)_{ss}}{k_{10}(OH)_{EQ}}\ [1 - \exp(-k_{10}(OH)_{EQ}t)] \qquad C(6)$$

and using equation (3), this may be written as,

$$D \approx \frac{k_4k_2(OH)_{EQ}}{k_{10}(OH)_{EQ}[k_3 + k_8(OH)_{EQ}]}\ (1 - \exp\ [-k_{10}(OH)_{EQ}t])\ P_o^{\ 2} \qquad C(7)$$

In equation (7) the dependence of dioxin formation upon the square of the precursor polychlorinated phenol molecule concentration is demonstrated.

It has previously been shown that at flame combustion temperatures, dioxin production cannot compete with dioxin destruction [5,6]. Therefore it is of interest to consider the production of dioxin in the post-flame combustion zone where temperatures are considerably below flame combustion temperatures.

Consider <u>municipal</u> solid waste burning which results in the production of post-flame combustion zone levels of $\sim$ 300 $\mu g \cdot M^{-3}$ of polychlorinated phenols. This corresponds to a level of $\sim$ 0.01% (the actual value depends upon fuel composition and fuel air stoichiometry) of initial fuel being polychlorinated phenols that are subsequently destroyed at a destruction efficiency of $\sim$ 99% on passage through the flame combustion zone. The other 1% is transported to the post-flame combustion zone due to mixing heterogeneities. <u>Alternatively</u>, this could be thought of as corresponding to conversion of $\sim$ 0.01% of fuel on the grate bed of a municipal incinerator to polychlorinated phenols which are then as in the former case transported with a comparable destruction efficiency through the flame combustion zone to the post-flame combustion zone.

Assume all polychlorinated phenols are present as a trichlorophenol. This assumption has no serious bearing upon any of the conclusions which will be drawn. It is made in order to simplify the analysis by enabling assumption of a specific molecular weight for the polychlorinated phenols. The municipal incinerator is assumed to be operating at one atmosphere total pressure. A post-flame combustion zone transit time of one second [5,6,9] is assumed. Several solutions are summarized for a range of post-flame combustion zone temperatures in Table IIa, using equation (7). It is clear from these results that even for a "worse" case model, if dioxins are presumed formed by gas phase processes alone, predicted dioxin emission levels cannot account for those which have been reported for comparable loading levels of polychlorinated phenols in municipal incinerators [1-4]. This is due to the dependence of the dioxin emission level upon the square of the polychlorinated phenol loading level.

It is not possible to account for observed dioxin emission levels based upon a presumption that precursors of less complexity than polychlorinated phenols are involved in a gas phase formation process. The minimum number of critical bimolecular reaction steps is greater than one. Consider the case in which the mechanism to produce dioxins involves a polychlorinated benzene and polychlorinated phenol. The critical bimolecular reaction steps will be two in number: e.g., i) either a polychlorophenoxy radical must attack a polychlorobenzene molecule or a polychlorophenyl radical must attack a polychlorophenol molecule, and ii) a hydroxyl radical must attack the resulting product. Alternatively, in the case of dioxin production from polychlorinated benzenes alone, there will be at least three critical bimolecular reaction steps in any proposed gas phase mechanism. This increased dependence upon bimolecular reaction steps renders gas phase production of dioxins from other precursors than polychlorinated phenols less likely than their production from polychlorinated phenol precursors.

GAS-FLY ASH REACTION MECHANISMS

Assumptions

In practical MUNICIPAL incineration, the situation with respect to multiple phase (gas plus fly ash) post-flame combustion zone processes is complicated. It is necessary to impose simplifying assumptions in order to develop an approximate model for these complex processes.

The assumptions used in this paper are as follows:

1) Assume the post-flame combustion zone in a municipal incinerator is characterized by an average temperature of 700 °C [7,8]. In an actual incinerator there are both spatial and temporal thermal fluctuations in the post-flame combustion zone. Since the intent of this report is only to demonstrate that there may be a basis to suspect catalytic dioxin formation, the assumption is not critical. Once a model has been developed it may be tested at other temperatures as a check for sensitivity to substantial temperature variations.

2) Assume, due to mixing heterogeneities, that polychlorinated phenols are present in the post-flame combustion zone gas phase at a level of 300 $\mu g \cdot M^{-3}$. This is a typical loading level to assume based upon reported field observations [9]. Higher and lower loading levels will also be examined.

3) Assume that the gas and fly ash both travel with the same average flow velocity, and that the residence time of the material in the post-flame combustion zone is one second. A residence time of this order is representative of municipal incinerators [5,6,10].

4) Assume a fly ash loading of 3.5×10^{-6} $g \cdot cm^{-3}$ (about 0.1 $g \cdot ft^{-3}$) in the post-flame combustion zone. This would be deduced, e.g., from a stack emission of 0.175×10^{-6} $g \cdot cm^{-3}$ from pollution control equipment operating at 95% efficiency with respect to particles of this size. Fly ash loading has been reported [11] to range from 2.8×10^{-7} $g \cdot cm^{-3}$ to 1.15×10^{-5} $g \cdot cm^{-3}$ in some coal fired power plants.

5) Assume the average radius of fly ash particles in the post-flame combustion zone is $\sigma_p \approx 5 \times 10^{-4}$ cm (10 μm diameter). It is known that there is a particle size distribution [12-15]. Since surface catalysis

is being tested, larger particles having lower surface area are ignored. Smaller particles are ignored. In coal fired power plants it has been reported that maximal surface area is associated with particles having a diameter comparable to that assumed here [12a]. Differences in particle composition, (e.g., mineral, carbonaceous, ferromagnetic), while potentially significant [12b, c] are not considered in this report.

6) Assume the fly ash is approximately spherical in shape and has low porosity with respect to high molecular weight organics (i.e., it is treated as a solid). Field observations [16] have shown that most fly ash is essentially spherical for small particulates due to fusion and surface tension effects. It frequently appears to be approximately solid throughout when examined by microprobe techniques [16c]. The presence of cenospheres [17] and a consideration of their potential role as microreactors for dioxin and other compound formation or destruction is not discussed. Cenosphere production is correlated to slag viscosity [17]. The variability of cenosphere concentration in municipal incinerators is not quantified at the present time. Similarly, particle porosity [18] has not been quantified with respect to organic compound formation and destruction in municipal incinerators.

7) Assume an approximate surrogate for fly ash in terms of catalytic effects is silica. This assumption is based upon reports [19-20] that there are similarities between distribution patterns of chloroaromatic species produced in quartz ampoule experiments and those which have been reported in municipal incinerator emissions. Each particle will be assigned a density approximately that of glass [21], about 2.5 $g \cdot cm^{-3}$.

8) Assume the effective area of a surface site per adsorbed trichlorophenol molecule (including excluded adjacent space) on a fly ash particle is equivalent to an area described by a circle having a radius of $\sigma \approx 3 \times 10^{-8}$ cm. This is equivalent to having $3 \times 10^{+14}$ sites$\cdot$cm^{-2} of surface area. This value compares well with a previously assumed value [22]. This assumption does not imply that a molecule (plus excluded area) actually occupies an area described by a circle having a radius of 3×10^{-8} cm. Rather, the radius is assigned in order to effectively limit the number of available reactive sites to about $3 \times 10^{+14}$ sites$\cdot$cm^{-2}.

The assumption of 3×10^{14} sites$\cdot$cm^{-2} of fly ash surface area is equivalent to assuming there are 3×10^{12} sites$\cdot$cm^{-3} of gas volume in the post-flame combustion zone. This compares favorably with an estimate of 7×10^{12} adsorption sites$\cdot$cm^{-3} reported for polycyclic aromatic hydrocarbons on fly ash in a coal fired power plant [12a]. In addition, in comparison to estimated molecular surface areas for polycyclic aromatic molecules [23], the assumed effective surface area for a trichlorophenol molecule implies that the molecule does not lie flat on the surface of the fly ash. The nature of the surface bonding remains to be determined. This requires a consideration of the types of reactive sites [24] which may be present under municipal incinerator combustion conditions.

9) Assume the total gas pressure in the post-flame combustion zone is one standard atmosphere at the specified operating temperature.

10) Assume the molar ratio of polychlorinated phenols to other molecules capable of undergoing competitive surface adsorption (chemisorption), is 10^{-2} in the post-flame combustion zone. While an assumed mass loading of 300 μg$\cdot$M^{-3} of polychlorinated phenols in the post-flame combustion zone implies the ratio in the input waste feed stream is much lower than

this, the assumption is made here that the kinetic incinerability characteristics of polychlorinated phenols boosts the ratio on passage through the flame combustion zone. Alternatively, one can consider that not all molecular species will successfully compete with polychlorinated phenols for available adsorption sites [12a,b] at post-flame combustion zone temperatures.

11) Assume molecular species in the post-flame combustion zone that do compete with polychlorinated phenols for adsorption (chemisorption) sites on the surrogate fly ash have adsorption and desorption rates [12a] approximately comparable to those for polychlorinated phenols. This implies the relative fractional surface area coverage at any given time will be proportional to the mole fraction ratio of adsorbing species present.

12) Langmuir adsorption isotherms for the adsorbing (chemisorption) species are assumed.

Mechanism for Catalytic Dioxin Formation

On the basis of the above assumptions, models for catalytic dioxin formation via gas-fly ash interactions may be hypothesized. As an example, one particular model involves the following reaction steps .

$$g + s \xrightarrow{k_a} g_s \qquad C(8)$$

$$g + g_s \xrightarrow{k_1} d_s \qquad C(9)$$

$$d_s \xrightarrow{k_2} d \qquad C(10)$$

Above, s represents a surface site for chemisorption; g and g_s respectively represent gas phase and chemisorbed polychlorinated phenols; and d and d_s respectively represent gas phase and chemisorbed dioxins. Molecular species other than polychlorinated phenols which may also be adsorbed are represented by the symbol, "a". The equivalent adsorption for species "a" analogous to reaction step (8) above is represented as

$$a + s \longrightarrow a_s \tag{C(11)}$$

Calculation of Input Parameters for the Model

If the fly ash mass loading in the post-flame combustion zone is $M_p \approx 3.5 \times 10^{-6}$ g·cm^{-3}, with an average particle radius of $\sigma_p \approx 5 \times 10^{-4}$ cm, and an average particle density of $\rho_p \approx 2.5$ g·cm^{-3}, the number of particles per cm^3 will be

$$N_p = \frac{M_p}{(4/3)\pi\sigma_p{}^3\rho_p} \approx 2.7 \times 10^2 \text{ particles}\cdot\text{cm}^{-3} \tag{C(12)}$$

If the fly ash particles are assumed uniformly distributed, (more likely, they are randomly distributed, however, the distinction is not critical) the average distance between particles is

$$d_p \approx (N_p)^{-1/3} - 2\sigma_p \approx 7.1 \times 10^{-2} \text{ cm} \tag{C(13)}$$

This implies that if the particles are uniformly distributed and move with about the same average flow velocity as the gas in the post-flame combustion zone (a valid assumption for 10 μm diameter particles), time scales for diffusion of gas species to the fly ash particles will be short compared to post-flame combustion zone transit times. This is a consequence of short distances between fly ash particles. This means that with respect to gas-particulate reactions, it is possible, as an approximation, to ignore spatial mixing heterogeneities except when mixing scales are very large and the fly ash particles cannot be treated as though uniformly distributed.

The average mass per particle, m_p, is

$$m_p = (4/3)\pi\sigma_p^3 \ \rho_p \approx 1.3 \times 10^{-9} g \qquad C(14)$$

At P = 1 atmosphere total operating pressure and a temperature of 700 C (973 K), the total number of molecules per cm^3 is

$$N_T \approx N_o(PV)/(RT) \approx 7.5 \times 10^{18} \text{ molec}\cdot\text{cm}^{-3} \qquad C(15)$$

In equation (15), P = 1 atmosphere, V = 1 cm^3, T = 973 K, R is the universal gas constant in units of $cm^3\cdot atm\cdot mol^{-1}\cdot K^{-1}$, and N_o is Avogadro's number, 6.02×10^{23} molecules per mol.

Compared to molecular velocities (as distinguished from average gas flow velocities) the fly ash particles can be treated as being stationary. Therefore the relative velocity, u, can be computed from the gas molecular velocity alone [25]

$$u \approx 1.46 \times 10^4 \left(\frac{T}{MW_g}\right)^{1/2} \approx 3.24 \times 10^4 \text{ cm}\cdot\text{s}^{-1} \qquad C(16)$$

In equation (16), MW_g is taken as the molecular weight of a trichlorophenol molecule, 197.35 $g\cdot mol^{-1}$ and T = 973 K (700 C). Assume the competitively adsorbed species have the same molecular weight and therefore move at the same molecular velocity. This assumption has no serious effect upon the model development.

Since

$$\sigma_g << \sigma_p \qquad C(17)$$

and

$$\sigma_a << \sigma_p \quad , \qquad C(18)$$

the collision frequency, Z_p per gas phase molecule per cm^3 per second in a gas that contains N_p particles per cm^3 is

$$Z_p \approx \pi N_p(2\sigma_p)^2 u \qquad C(19)$$

It follows from equation (16) that for both the trichlorophenol and competitively adsorbed species,

$$Z_p \approx 3.24 \times 10^4 \ \pi N_p(2\sigma_p)^2 \approx 275 \text{ collisions}\cdot cm^{-3}\cdot s^{-1} \qquad C(20)$$

If the fly ash particles are completely covered by polychlorinated phenols and competitively adsorbed species, then under assumptions made previously, maximum fractional coverage, $\Theta_{g_{max}}$ by polychlorinated phenols is found by utilization of the relations

$$\Theta_{g_{max}}/\Theta_{a_{max}} \approx \xi \qquad C(21)$$

$$\Theta_{g_{max}} + \Theta_{a_{max}} \approx 1 \qquad C(22)$$

$$\xi \equiv X_g/X_a \approx 10^{-2} \qquad C(23)$$

In equations (21)-(23), $\Theta_{g_{max}}$ is the maximum fractional coverage by the polychlorinated phenol molecules. $\Theta_{a_{max}}$ is the maximum fractional coverage by the competitively adsorbed gas phase species. X_g and X_a are

respectively the gas phase mole fractions of polychlorinated phenols and competitively adsorbed species. The above relationships are set in terms of the total available number of sites. Contributions to surface coverage by dioxins are ignored assuming the number of molecules of dioxins adsorbed on the fly ash surface is always considerably less than the number of adsorbed polychlorinated phenol molecules. The validity of this assumption will be demonstrated. Implicit in equation (21) is the approximation that equilibrium constants (ratio of adsorption rate constant to desorption rate constant) for polychlorinated phenols and competitively adsorbed species are equivalent. This approximation may affect quantitatively the numerical solution of the model to be developed, but does not affect the substance (conceptualization) of the model.
Using equations (21) - (23)

$$\Theta_{g_{max}} \approx \xi/(1 + \xi) \approx 10^{-2} \qquad \mathrm{C(24)}$$

$$\Theta_{a_{max}} \approx 1-\Theta_{g_{max}} \approx 0.99 \qquad \mathrm{C(25)}$$

If the initial mass loading, M_g, of polychlorinated phenols (as trichlorophenols) in the post-flame combustion zone is 300 $\mu g \cdot M^{-3}$, then the initial molecular number density per cm^3, g_o, of trichlorophenols in the post-flame combustion zone is

$$g_o \approx \frac{M_g N_o}{MW_g} \times 10^{-12} \approx 9.15 \times 10^{11} \text{ molecules} \cdot cm^{-3} \qquad \mathrm{C(26)}$$

In equation (26), N_o is Avogadro's number, 6.02×10^{23} molecules$\cdot$mol^{-1} and MW_g is the molecular weight of trichlorophenol, 197.35 g$\cdot$mol^{-1}. The factor 10^{-12} converts $\mu g \cdot M^{-3}$ to units of $g \cdot cm^{-3}$. Since the ratio of polychlorinated phenols to other competitively adsorbed gas phase species has been taken to be 10^{-2}, the initial molecular number density of competitively adsorbed species, a_o, is

$$a_o \gtrsim 10^2 g_o \gtrsim 9.15 \times 10^{13} \text{ molecules}\cdot\text{cm}^{-3} \qquad C(27)$$

The maximum number density of adsorbed trichlorophenol molecules per N_p particles per cm^3 is

$$g_s^{max} \gtrsim 4N_p \left(\frac{\sigma_p}{\sigma_g}\right)^2 \Theta_{g_{max}} \gtrsim 3 \times 10^{10} \text{molecules}\cdot N_p \text{ particles}^{-1}\cdot\text{cm}^{-3} \qquad C(28)$$

If the adsorbed dioxin molecules are assumed to occupy an effective area twice that of the adsorbed trichlorophenol molecules, then

$$d_s^{max} \gtrsim (1/2) g_s^{max} \gtrsim 1.5 \times 10^{10} \text{ molecules}\cdot N_p \text{ particles}^{-1}\cdot\text{cm}^{-3} \qquad C(29)$$

The maximum number of competitively adsorbed species per N_p particles per cm^3 is

$$a_s^{max} \gtrsim 4N_p \left(\frac{\sigma_p}{\sigma_a}\right)^2 \Theta_{a_{max}} \gtrsim 3 \times 10^{12} \text{ molecules}\cdot N_p \text{ particles}^{-1}\cdot\text{cm}^{-3} \qquad C(30)$$

This means

$$g_s^{max} \gtrsim 0.03\ g_o \qquad C(31)$$

$$a_s^{max} \gtrsim 0.03\ a_o \qquad C(32)$$

The parameters developed above are tabulated in Table 3.

Model Development

The assumptions can be used together with parameters developed above to construct a model consistent with the mechanism symbolically represented by equations (8)-(11).

Assume adsorption occurs for every gas-fly ash collision involving a trichlorophenol molecule or competitively adsorbed molecule. Assume the rate of desorption is much slower than the rate of adsorption. The mechanism of competitive adsorption may be represented by

$$a + s \rightarrow a_s \qquad \text{C(33)}$$

$$g + s \rightarrow g_s \qquad \text{C(34)}$$

From a previous assumption it may be inferred that $\Theta_g << \Theta_a$. Therefore an equation for the reaction step represented by equation (33) may be derived independent of the contribution from the reaction step represented by equation (34). The assumption that every collision of a competitively adsorbed molecule with a fly ash particle results in adsorption can then be used to show that

$$d(a_s)/dt \approx Z_p a(1-\Theta_a) \qquad \text{C(35)}$$

Since $a_s << a_o$ it follows that $a \approx a_o$. From equation (25)

$$\Theta_a \approx [1/(4N_p)](\frac{\sigma_a}{\sigma_p})^2 a_s \qquad \text{C(36)}$$

Subject to the boundary condition that $a_s = 0$ at $t = 0$, (defined as the time at the point of transition from the flame combustion zone to the post-flame combustion zone) equation (35) has the solution

$$a_s \approx 4N_p \left(\frac{\sigma_p}{\sigma_a}\right)^2 [1-\exp\{-\frac{Z_p a_o}{4N_p} \left(\frac{\sigma_a}{\sigma_p}\right)^2 t\}] \qquad C(37)$$

This result may be used to develop a solution for the temporal evolution of the surface coverage, g_s, represented by the reaction step shown by equation (34) for which

$$d(g_s)/dt \approx Z_p g\ (1-\Theta_a-\Theta_g) \qquad C(38)$$

Since $g_s^{max} \approx 0.03\ g_o$ and $\Theta_g << \Theta_a$, it follows, using equations (36) and (37), that

$$d(g_s)/dt \approx Z_p g_o \exp\{-\frac{Z_p a_o}{4N_p} \left(\frac{\sigma_a}{\sigma_p}\right)^2 t\} \qquad C(39)$$

Subject to the boundary condition that $g_s = 0$ at $t = 0$ (with t being defined as before), equation (39) has the solution

$$g_s \approx 4N_p \left(\frac{g_o}{a_o}\right)\left(\frac{\sigma_p}{\sigma_a}\right)^2 [1-\exp\{-\frac{Z_p a_o}{4N_p} \left(\frac{\sigma_a}{\sigma_p}\right)^2 t\}] \qquad C(40)$$

This result may be rewritten as

$$t \approx -\frac{4N_p}{Z_p a_o} \left(\frac{\sigma_p}{\sigma_a}\right)^2 \ln\{1 - \frac{g_s}{4N_p} \left(\frac{a_o}{g_o}\right)\left(\frac{\sigma_a}{\sigma_p}\right)^2\} \qquad C(41)$$

When $g_s \approx 0.99\, g_s^{max}$ and values for parameters that appear in the above equation and as reported in Table 3 are used, it is found that

$$t \approx 5.5 \times 10^{-4} \text{ seconds} \tag{C(42)}$$

This result implies nearly complete coverage of the fly ash will occur in times which are short compared to an assumed post-flame combustion zone transit time of one second. Therefore the model mechanism can be examined in terms of an assumption of steady surface coverage during the post-flame combustion zone transit time. The assumption is made that the number of dioxin molecules adsorbed on the surface is significantly less than the number density of adsorbed trichlorophenol molecules on the surface. The assumption of a steady level of coverage implies further development of the model will require examination of equations (9) and (10) and associated rate constants

$$g + g_s \xrightarrow{k_1} d_s \tag{C(9)}$$

$$d_s \xrightarrow{k_2} d \tag{C(10)}$$

Rate expressions for the reaction steps given by equations (9) and (10) are

$$d(d_s)/dt = k_1 g(\Theta_g - \Theta_d) - k_2 d_s \tag{C(43)}$$

$$d(d)/dt = k_2 d_s \qquad C(44)$$

Equation (43) may be rewritten using

$$\Theta_d \approx \left(\frac{1}{2N_p}\right)\left(\frac{\sigma_g}{\sigma_p}\right)^2 d_s \qquad C(45)$$

as

$$d(d_s)/dt = k_1 g \Theta_g - \left\{\frac{1}{2N_p} \left(\frac{\sigma_g}{\sigma_p}\right)^2 k_1 g + k_2\right\} d_s \qquad C(46)$$

It follows from equation (31) that $g \approx g_o$. If the parameters Q and P are defined as

$$Q \equiv k_1 g_o \Theta_g \qquad C(47)$$

$$P \equiv \left(\frac{1}{2N_p}\right)\left(\frac{\sigma_g}{\sigma_p}\right)^2 k_1 g_o + k_2 \qquad C(48)$$

equation (46) has the solution

$$d_s = (Q/P)\ (1-e^{-Pt}) \qquad C(49)$$

Then equation (44) has the solution

$$d \approx \frac{k_2 Qt}{P} - \frac{k_2 Q}{P^2}\ (1-e^{-Pt}) \qquad C(50)$$

If $e^{-Pt} << 1$, equations (49) and (50) reduce to

$$d_s \approx \frac{Q}{P} \qquad C(51)$$

$$d \approx \frac{k_2 Q}{P} (t - 1/P) \tag{C(52)}$$

The results from some reported field measurements indicate that [26]

$$d \approx 9\ d_s \tag{C(53)}$$

The gas-solid dioxin partition ratio in municipal incinerators is not clearly established at the present time. The location of sampling devices relative to temperature gradients in thermal processing units will affect the outcome of gas-solid organic component partition ratio measurements [27]. Other gas-solid dioxin partition ratios have been reported [28,29]. The development which follows may be generally applied to any reported gas-solid dioxin partition ratios.

When equations (51) - (53) are used, and when $t \approx 1$ second, (the post-flame combustion zone transit time) P may be evaluated from equation (48) to be (at T = 973 K)

$$P \approx 0.61\ k_1 + k_2 \tag{C(54)}$$

If $0.61\ k_1 << k_2$, then

$$k_2 \approx 10 \tag{C(55)}$$

This validates the assumption that for a post-flame combustion zone transit time of one second and an average temperature of 973 K (700 °C)

$$e^{-Pt} << 1$$

If it is assumed that

$$k_2 \approx A_2 e^{-E_2/RT} \qquad C(56)$$

and a preexponential value of

$$A_2 \approx 10^{13}\ \mathrm{sec}^{-1} \qquad C(57)$$

is assigned, it is found that at 973 K (700 °C)

$$E_2 \approx -RT\ln\left(\frac{k_2}{A_2}\right) \approx 53.4\ \mathrm{kcal \cdot mol^{-1}} \qquad C(58)$$

If the average post-flame combustion zone temperature were 773 °K (500 °C), a value of 42.4 $\mathrm{kcal \cdot mol^{-1}}$ would be determined. The value for E_2 is significantly more sensitive to temperature than to municipal incinerator transit time variations over a range of one half to two seconds. If $d \approx d_s$, $E_2 \approx 56.5\ \mathrm{kcal \cdot mol^{-1}}$ at 973 K. If $d \approx 100\ d_s$, $E_2 \approx 49.0\ \mathrm{kcal \cdot mol^{-1}}$ at 973 K.

A representative amount of dioxins associated with fly ash [1-4] (on a weight basis) is

$$d_s \approx 100\ \mathrm{ppb} \qquad C(59)$$

If, for simplicity, it is assumed that the averaged molecular weight of adsorbed dioxins corresponds to that for tetrachlorinated dioxins, $MW_d \approx 321.9\ \mathrm{g \cdot mol^{-1}}$, the molecular number density of adsorbed dioxins per N_p particles of fly ash per cm^3 is

$$d_s \approx 10^{-7} \left(\frac{m_p N_p N_o}{MW_d}\right) \approx 6.6 \times 10^8 \text{ molecules} \cdot N_p \text{ particles}^{-1} \cdot \text{cm}^{-3} \qquad C(60)$$

Equations (47), (48), (51) and (60), the relationship $\Theta_g \approx \Theta_g^{max} \approx 10^{-2}$, a post-flame combustion zone transit time of one second, and the previously determined values for other parameters may be used to show that

$$k_1 \approx 0.73 \text{ (same units as } Z_p) \qquad C(61)$$

The value for k_1 of 0.73 validates the approximation, $0.61\ k_1 << k_2$. If

$$k_1 \approx Z_p e^{-E_1/RT} \qquad C(62)$$

and T = 973 °K (700 °C), it is found that

$$E_1 \approx -RT\ln\left(\frac{k_1}{Z_p}\right) \approx 11{,}500 \text{ cal} \cdot \text{mol}^{-1} \qquad C(63)$$

The low activation energy determined for the reaction represented by equation (9) suggests the chemisorbed molecule is very reactive. Possibly this may be due to removal of a hydrogen or chlorine atom from the surface bound molecule via fast abstraction by gas phase radicals or by neighboring reactive sites on the fly ash particulate.

CONCLUSIONS

Dioxin formation is attributed in this particular model to reaction of gas phase and adsorbed chlorophenols. Desorption of dioxins and other adsorbed species makes new sites available. Competitive adsorption of species other than chlorophenols limits dioxin formation. In addition, dioxin formation is dependent on reaction conditions. The formalism that has been set up can be used to assess other potential scenarios. Carefully designed laboratory experiments can be used to test the models. Possible variations in dioxin formation as a function of chlorophenol loading can be found in Table IIb. The calculations carried out here are based on representative reported results [1-3, 9, 19, 20, 26, 30]. The end results obtained, rate expressions for desorption and catalyzed dioxin formation are reasonable [22,3]. The observation that a substantial activation energy for desorption may be expected is consistent with a report that dioxins are apparently irreversibly adsorbed on fly ash at moderate temperatures [32]. However, unlike the situation in the gas phase, activation energy limits for surface induced processes are rather wide.

The squared dependence upon the precursor concentration with respect to dioxin formation is important. This squared dependence has previously been mentioned in the context of the gas phase process and is apparent in Table 2b for the gas-solid process based on the model examined in this report. This dependence sets strong limits on the extent of dioxin formation and implies that experiments with neat samples or under conditions of high concentration can be extremely deceptive unless properly interpreted.

In addition to the above considerations, there are reports [9, 30] that the degree of chlorination of dioxins is sometimes more extensive than for phenols found in the same municipal waste post-combustion streams. These observations considered jointly with reports of chlorination reactions [30, 33] indicate that it may be necessary to assess the potential role of solid and gas-solid reactions on and in grate beds. Grate bed residence times are considerably longer than flame and post-flame combustion zone transit times in the gas phase in municipal incinerators. In such a case, additional possibilities may have to be considered. The convolution of these processes with mixing inhomogeneities will have to be examined.

The rationale of the present and earlier work [5, 6] is that an understanding of how dioxins can be formed in municipal incinerators may lead to identification of possibilities for process modifications which may minimize emissions.

TABLE I - PROPOSED DIOXIN FORMATION MECHANISM[(a)]

#	Reaction Step	Rate Constant	Units
R1	$P \rightarrow P\cdot + H$	$10^{15.5}$ exp(-86500/RT)	s^{-1}
R2	$P + OH \rightarrow P\cdot + H_2O$	10^{9}	$L\cdot M^{-1}\cdot s^{-1}$
R3	$P\cdot \rightarrow Pr$	$10^{13.6}$ exp(-57654/RT)	s^{-1}
R4	$P + P\cdot \rightarrow PD + Cl$	10^{9} exp(-26000/RT)	$L\cdot M^{-1}\cdot s^{-1}$
R5	$PD \rightarrow D + HCl$	10^{14} exp(-45000/RT)	s^{-1}
R6	$PD + OH \rightarrow D + H_2O$	10^{9}	$L\cdot M^{-1}\cdot s^{-1}$
R7	$P\cdot + R \rightarrow P + R\cdot$	10^{8} exp(-26000/RT)	$L\cdot M^{-1}\cdot s^{-1}$
R8	$P\cdot + OH \rightarrow Pr$	10^{9}	$L\cdot M^{-1}\cdot s^{-1}$
R9	$D \rightarrow Pr$	$10^{15.5}$ exp(-80000/RT)	s^{-1}
R10	$D + OH \rightarrow Pr$	10^{8}	$L\cdot M^{-1}\cdot s^{-1}$
R11	$P\cdot + O_2 \rightarrow Pr$	10^{8}	$L\cdot M^{-1}\cdot s^{-1}$
R12	$R + OH \rightarrow R\cdot + H_2O$	10^{9}	$L\cdot M^{-1}\cdot s^{-1}$
R13	$R \rightarrow Pr$	10^{16} exp(-90000/RT)	s^{-1}

(a) The rate constants have been biased to favor PCDD formations. The reader is strongly cautioned not to use these estimates out of the context of this paper, as actual values for these rates will be quite different in some cases.

TABLE IIa

PREDICTED GAS PHASE DIOXIN LEVELS BASED ON WORSE CASE MODEL

	D ($\mu g \cdot M^{-3}$)			
$P_o (\mu g \cdot M^{-3})$	500^oC	600^oC	700^oC	800^oC
30	$1.85x10^{-7}$	$4.35x10^{-7}$	$6.20x10^{-7}$	$7.06x10^{-7}$
300	$1.85x10^{-5}$	$4.35x10^{-5}$	$6.20x10^{-5}$	$7.06x10^{-5}$
3000	$1.85x10^{-3}$	$4.35x10^{-3}$	$6.20x10^{-3}$	$7.06x10^{-3}$

A residence time of one second is assumed.

TABLE IIb

PREDICTED DIOXIN LEVELS BASED ON GAS-SOLID CATALYSIS MODEL AT 973^{o}K (700^{o}C)

ξ	θ_g	M_p $\mu g \cdot M^{-3}$	d_s $\mu g \cdot kg^{-1}$	$\Sigma(d_s+d)$ $\mu g \cdot M^{-3}$	d/d_s	%	
10^{-3}	10^{-3}	30	1	0.035	8.96	0.023	(a)
10^{-2}	10^{-2}	300	97	3.4	9.06	0.23	
10^{-1}	$9x10^{-2}$	3000	6384	229	9.27	15.3	

"%" is percent conversion of chlorophenols to dioxins in 1 second (a)

TABLE III. TABULATED VALUES FOR PARAMETERS USED IN THE ANALYTICAL METHOD

Variable	Definition and units	value	Equation in text
t	transit time through post-flame combustion zone (second)	1	
ρ_p	density of a fly ash particle ($g \cdot cm^{-3}$)	2.5	
M_g	initial mass loading of polychlorinated phenols in post-flame combustion zone ($\mu g \cdot M^{-3}$)	300	
M_p	mass loading of fly ash particles ($g \cdot cm^{-3}$)	3.5×10^{-6}	
σ_p	radius of fly ash particle (cm)	5×10^{-4}	
σ_g, σ_a	"radius" of polychlorinated phenol, g, and competitively adsorbed species, a (cm)	3×10^{-8}	
σ_d	"radius" of dioxins (cm)	$3\sqrt{2} \times 10^{-8}$	
ξ	gas phase mole fraction ratio of polychlorinated phenols to other competitively adsorbed species	10^{-2}	
P	post-flame combustion zone pressure (atm)	1	
T	post-flame combustion zone temperature (°C or °K)	700 (°C) 973 (°K)	
N_o	Avogadro's number ($molec \cdot mol^{-1}$)	6.02×10^{23}	
MW_g	assumed molecular weight for polychlorinated phenols ($g \cdot mol^{-1}$)	197.35	
MW_d	assumed molecular weight for dioxins ($g \cdot mol^{-1}$)	321.8	
N_p	number density for fly ash particles ($particles \cdot cm^{-3}$)	2.7×10^{3}	(12)

d_p	distance between particles (cm)	7.1×10^{-2}	(13)
m_p	mass per fly ash particle ($g \cdot particle^{-1}$)	1.3×10^{-9}	(14)
N_T	total number of gas molecules per cm^3 at specified (T, P) ($molec \cdot cm^{-3}$)	7.5×10^{18}	(15)
u	average molecular velocity of gas molecules ($cm \cdot sec^{-1}$)	3.24×10^{4}	(16)
Z_p	collision frequency of a gas phase molecule per N_p particles per cm^3 per second ($collision \cdot N_p\ particles^{-1} \cdot cm^{-3} \cdot sec^{-1}$)	275	(20)
$\theta_{g_{max}}$	maximum possible fractional coverage of fly ash by polychlorinated phenols	10^{-2}	(24)
$\theta_{a_{max}}$	maximum possible fractional coverage of other competitively adsorbed species	0.99	(25)
g_0	initial molecular number density in the gas phase of the post-flame combustion zone of polychlorinated phenols ($molec \cdot cm^{-3}$)	9.15×10^{11}	(26)
a_0	initial molecular number density analogous to g_0 but for other competitively adsorbed species	9.15×10^{13}	(27)
g_s^{max}	maximum number density of adsorbed tri-chlorophenol molecules per N_p particles per cm^3 ($molec \cdot N_p\ particles^{-1} \cdot cm^{-3}$)	3×10^{10}	(28)
a_s^{max}	maximum number density of the competitively adsorbed species per N_p particles per cm^{-3} ($molec \cdot N_p\ particles^{-1} \cdot cm^{-3}$)	3×10^{12}	(30)

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NBS-114A (REV. 2-80)

U.S. DEPT. OF COMM. **BIBLIOGRAPHIC DATA SHEET** *(See instructions)*	1. PUBLICATION OR REPORT NO. NBSIR 84-2872	2. Performing Organ. Report No.	3. Publication Date April 1984

4. TITLE AND SUBTITLE

Containment of Dioxin Emissions From Refuse Fired Thermal Processing Units - Prospects and Technical Issues

5. AUTHOR(S)

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6. PERFORMING ORGANIZATION *(If joint or other than NBS, see instructions)*

NATIONAL BUREAU OF STANDARDS
DEPARTMENT OF COMMERCE
WASHINGTON, D.C. 20234

7. Contract/Grant No.

8. Type of Report & Period Covered

9. SPONSORING ORGANIZATION NAME AND COMPLETE ADDRESS *(Street, City, State, ZIP)*

10. SUPPLEMENTARY NOTES

Note to Center and WERB Reviewers: Appendices A,B, and C have already been through the WERB review process, do not review.

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11. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)*

This report reviews and addresses the prospects for and technical issues concerned with the utilization of chemisorption as a technique for containment of dioxin emissions from refuse fired thermal processing units. The results developed in this report suggest that containment, through chemisorption of dioxin emissions from refuse fired thermal processing units, may be technically feasible. Suggestions for research objectives and full scale tests are outlined. Refuse fired thermal processing units equipped for energy recovery may be more preferable than those units which are not equipped for energy recovery, if chemisorption occurs more efficiently at temperatures which are substantially lower than furnace gas exit temperatures.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

boilers, catalysis,chemisorption, containment, dioxins, furans, incinerator emissions, incinerators, thermal processing units

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☒ Order From National Technical Information Service (NTIS), Springfield, VA. 22161

14. NO. OF PRINTED PAGES

150

15. Price

$14.50