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POLYCHLORINATED DIBENZO-P-DIOXIN AND POLYCHLORINATED DIBENZOFURAN FORMATION AND EMISSION IN THE THERMAL DESORPTION WASTE TREATMENT PROCESS

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**POLYCHLORINATED DIBENZO-P-DIOXIN AND POLYCHLORINATED
DIBENZOFURAN FORMATION AND EMISSION IN THE
THERMAL DESORPTION WASTE TREATMENT PROCESS**

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SUMMARY

It is extremely unlikely that significant amounts (from a regulatory standpoint) of polychlorinated dibenzo-p-dioxins (PCDDs) or polychlorinated dibenzofurans (PCDFs) will be emitted in the off-gas stream from the thermal desorption process, or the treated waste, particularly if the baseline design and anticipated operating conditions of the enhanced bench-scale (EBS) system are used. However, because of the acute toxicity of these compounds and because most of the data on their formation have been extrapolated from studies more related to incineration and fire conditions than thermal desorption, specific laboratory tests and specific EBS runs should be performed to monitor the rate of emission of PCDDs and PCDFs under thermal desorption conditions.

In general, the following four conditions need to exist for significant amounts of PCDD or PCDF (referred to collectively in this report as PCDD/F) to be formed: 1. the presence of fly ash; 2. the presence of an oxidizing source (usually oxygen, but possibly steam or an agent in the waste stream itself); 3. a suitable temperature, and; 4. the presence of a suitable precursor [chlorobenzenes (CB), chlorophenols (CP), or polychlorinated biphenyls (PCBs)]. Although the EBS system provides some of these conditions, it is unlikely that enough fly ash will be produced in the system (because of the low flow rate of the purge gas) to allow a significant amount of PCDD or PCDF formation. Additionally, particulate matter controls will be used to remove air borne particulates from the gas phase.

If PCDD/Fs are present in a waste stream being evaluated in the EBS, they will likely volatilize in the kiln and subsequently condense in the venturi scrubber system.

INTRODUCTION

PCDD/Fs are classes of aromatic chemical compounds considered to be toxic materials and, as such, are regulated with regard to both air emissions¹ and Resource Conservation Recovery Act (RCRA) land disposal restrictions² (LDR). The LDR are poorly defined, but in general indicate that no more than 1 wppb of several classes of PCDD/Fs may be present in certain solids disposed of in Subtitle C landfills. The air-emissions standards are also not well defined, and instead of an absolute concentration or rate standard, emission standards based on the details of a particular operation are specified. For at least one large-scale thermal desorption "Superfund Site" operation³, an air emission performance standard of 30 ng/m³ was specified. State standards for permissible exposure limits in air vary from 0.001 ng/m³ in Massachusetts to 450,000 ng/m³ in Indiana⁴. For permitted thermal desorption operations in the state of Tennessee, it can be expected that the performance standard for PCDD/F emissions will be on the order of 1 ng/m³.

The thermal desorption process is being considered by Martin Marietta Energy Systems (MMES) as a means to thermally treat a variety of waste streams, some of which contain PCBs. For the reasons discussed in this report and because of regulatory considerations, it is prudent to examine in as much detail as reasonably possible, the likely role of PCDD/Fs in thermal desorption. The EBS system is being designed and constructed in order to evaluate thermal desorption as a treatment method for waste streams of interest to MMES. Figure 1 shows a block flow diagram of this system, emphasizing the thermal desorption kiln and off-gassing treatment system. The EBS is expected to be somewhat neutral with respect to PCDD/F production. That is, it is anticipated that PCDD/Fs will neither be created nor destroyed to a significant extent. This system is designed to operate at a kiln temperature at from 350°C to 600°C and use a carrier gas of nitrogen or steam flowing counter current to the waste stream feed. The off-gases pass sequentially through a liquids trap, venturi-jet scrubber, HEPA filter, and sulfur impregnated activated carbon bed, before passing to the stack. The design is somewhat modular so that other off-gassing treatment operations can be installed and used for evaluation.

The general strategy of thermal desorption, using the EBS, is to volatilize hazardous components, such as mercury, PCBs, and other volatile organic compounds (VOCs) which may be present in the waste stream being treated. These volatile components are then condensed in the off-gas treatment system. The intent is that hazardous waste processed in this manner will produce a treated waste stream that is no longer hazardous, and a concentrated collection of condensed hazardous components. If PCDD/Fs are present in the waste stream being treated, they will likely volatilize and condense in the venturi scrubber operation. This condensation process will likely concentrate a number of hazardous components from the waste stream and will be further treated by incineration, cementation, or other appropriate means, in a separate facility.

Even if the waste stream does not initially contain PCDD/Fs, they can still be a concern in the thermal desorption process if chlorobenzenes, chlorophenols, polychlorinated biphenyls, or other chlorinated aromatics are present in the stream. All of these are potential precursors to PCDD/F formation at elevated temperature, particularly if fly ash is present in the system. Once formed, the

Figure 1. Block flow diagram of the EBS thermal desorption system showing off-gassing control operations.

PCDD/Fs may either remain with the solid waste, with the fly ash, or desorb to the gas phase. If they are present on the surface of the fly ash, they will deposit in the off-gas treatment system at the same place as the fly ash. If the fly ash particles are large enough, this would be in the venturi scrubber system or possibly the high efficiency particulate air (HEPA) filter system. Otherwise they may deposit in the activated carbon bed. If the PCDD/Fs are in the gas phase, they would likely condense in the venturi scrubber.

For waste streams being evaluated for treatment by the EBS, the most obviously identified PCDD/F precursors are PCBs, although since CBs and particularly CPs are generally better PCDD/F precursors than PCBs, the presence of smaller amount of CBs and CPs needs to be evaluated as a possible initiator for PCDD/F formation during thermal desorption. Additionally, low levels (about 1 wppb) of PCDD/Fs have been identified in at least one of the candidate waste streams⁵.

This report describes the chemical processes in the thermal desorption process, particularly as they apply to the EBS, which are important to the fate of PCDD/Fs. Recommendations are made concerning needed experiments in this area and operating conditions which will reduce the likelihood of PCDD/F formation during the thermal desorption process. Due to the large number of acronyms used to this report, an alphabetized list of them is included in Appendix B.

THERMAL DESORPTION OF PCDD/Fs IN THE WASTE FEED

PCDD/Fs are multi-ring aromatic compounds having the general formulae $C_{12}H_{8-x}O_2Cl_x$ and $C_{12}H_{8-x}O_1Cl_x$ respectively. They have molecular weights in the range from 202 to 459 g/mol, have low vapor pressures, and are considered to be quite stable thermodynamically. There are a total of 135 different PCDFs and 75 different PCDDs. Despite their low vapor pressures, they are expected to readily volatilize under thermal desorption conditions above 350°C. Figure 2 is a plot of the predicted vapor pressure as a function of temperature for 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD). Based on a simplified model of the thermal desorption and flow process in the kiln of the EBS (Appendix A gives a brief description of this model), it is expected that 1 ppm of this species in the feed would be reduced to 0.1 ppb at 400°C and a flow rate of 2 L/min in about 15 minutes.

Once in the gas phase, the 2,3,7,8-TCDD molecule would then adhere to any fly ash present or be transported directly from the kiln in the vapor phase. It would then most likely condense in the venturi scrubber and be collected there for further treatment in a separate waste treatment facility.

It is expected that other PCDD/Fs would behave similarly. In general, as the number of chlorine atoms on a particular PCDD/F increase, the thermodynamic stability increases and the vapor pressure at a given temperature decreases. Thus, the residence time required for complete vaporization at a given temperature will increase.

Figure 2. Plot of natural logarithm of vapor pressure of 2,3,7,8-tetrachlorodibenzo-p-dioxin as a function of temperature. This plot was generated by fitting the data in Reference 6 to the Clausius-Clapeyron Equation and extrapolating to higher temperatures.

FORMATION OF PCDD/Fs DURING TREATMENT

As might be expected, the formation from chemical precursors and subsequent transport of PCDD/Fs is much more complicated than their simple vaporization or desorption. This section discusses the thermodynamic stability of PCDDs and PCDFs, likely precursors to their formation, and the role of fly ash in their formation.

Thermodynamic Considerations

Thermodynamic considerations suggest that many combinations of carbon (C), hydrogen (H), oxygen (O), and chlorine (Cl), under thermal desorption conditions, can potentially lead to PCDD/F formation. A few example thermodynamic calculations follow using materials which might be found in waste streams. Care needs to be used in interpreting the results of these and other thermodynamic calculations on the free energy change (driving force) for chemical reactions. The more negative the free energy change for a particular reaction, the larger the thermodynamic driving force. However, this type of calculation merely indicates that whether a reaction is possible, and says nothing about how fast the reaction will occur, or whether or not other reactions are also possible. Generally, the presence or absence of plausible reaction mechanisms takes precedence over the magnitude of the free energy change.

Although very little experimental data exists on the thermodynamic properties of PCDD/Fs a number of theoretical calculations have recently been performed which allow free energy change for reactions to be estimated. The thermodynamic data and the source of the data as well as the designators used in the following equations are summarized in Table 1 at the end of the thermodynamic sections. Most of the enthalpy data was generated by additive interaction effect schemes, while the entropy data was calculated from both interaction effect schemes and molecular parameters. Since different additivity schemes were used by different authors, the results sometimes differed. When the results differed, care was taken to use consistent reactant and product data in an attempt to provide the best possible estimate of the free energy change for a given reaction.

Chlorinated Benzenes to PCDDs

For the reactions forming some chlorinated dioxins from 1,2-dichlorobenzene,

and

Table I. Thermodynamic data used in free energy calculations.

Species	Designator	$\Delta H_f(298)$ (kcal mol ⁻¹)	S_{298} (cal mol ⁻¹ K ⁻¹)	Ref- erence
chlorine (g)	Cl ₂	0	53.3	C
hydrogen (g)	H ₂	0	31.1	C
oxygen (g)	O ₂	0	49.0	C
hydrochloric acid (g)	HCl	-22.1	44.7	C
carbon dioxide (g)	CO ₂	-94.0	51.1	C
water (g)	H ₂ O	-57.8	45.1	C
1,1,2 trichloro- ethane (g)	C ₂ H ₃ Cl ₃	-34.6	80.6	C
dibenzo-p-dioxin (g)	DD	-15	92.6	A
1-chlorodibenzo-p-dioxin (g)	1-CDD	-21.9	82.2	E
2,3,7,8-tetrachlorodibenzo-p- dioxin (g)	2,3,7,8-TCDD	-82.5	114.3	A
2-chlorobiphenyl (g)	2-CBP	36	88	B
2,3,4'-trichlorobiphenyl (g)	2,3,4'-TCBP	23	98	B
2,3,6,2',4',5'-hexachloro- biphenyl (g)	2,3,6,2',4',5'-HCBP	8	113	B
benzene	B	19.8	64.3	C
1-chlorobenzene (g)	CB	12.2	72	D
1,2-dichlorobenzene (g)	1,2-DCB	7.1	80	D
1,2,3-trichlorobenzene (g)	1,2,3-TCB	2.2	88.7	A
2,3,5-trichlorophenol (g)	2,3,5-TCP	-52	99.2	B
1-chlorodibenzofuran (g)	1-CDF	6.4	109.8	E

A - Reference 7

B - Reference 8 used for enthalpy of formation. Entropies estimated by adding entropy for biphenyl plus 5 cal/mol for each chlorine atom

C - Reference 10

D - Reference 9 used for enthalpy of formation. Entropies estimated by adding entropy for benzene plus 8 cal/mol K for each chlorine atom

E - Reference 11

the standard Gibb's free energy changes, in kcal/mol (of PCDD formed), as a function of temperature can be respectively approximated by the expressions

$$\Delta G_1^\circ = -96.7 + 0.0325T, \quad (5)$$

$$\Delta G_2^\circ = -212.3 + 0.0535T, \quad (6)$$

$$\Delta G_3^\circ = 18.9 + 0.0115T, \quad (7)$$

and

$$\Delta G_4^\circ = -2.0 - 0.0212T, \quad (8)$$

where ΔG° is the standard free energy change of the reaction and T is the temperature of the reaction in Kelvin.

The free energy expressions, Equations 5-8, assume the enthalpy change and entropy change of the reactions are independent of temperature. Additionally, the standard free energy change is strictly applicable to forming pure components at 1 atmosphere partial pressure, instead of gas mixtures with various partial pressures. While neither of these assumptions is completely correct in this instance (particularly the pure components at 1 atmosphere pressure assertion), the free energy of reaction calculations do provide reasonably good approximations to the spontaneity of the reactions. The fact that ΔG_1° and ΔG_2° are negative at all temperatures below 2500 K, indicates that Reactions 1 and 2 are thermodynamically favorable at these temperatures and that the reactants are thermodynamically unstable under these conditions. Reaction 3, however, is never thermodynamically favored, and Reaction 4 is always favored. While all 4 of these reactions use 1,2-dichlorobenzene as the dioxin precursor, the thermodynamic predictions are similar for a wide variety of chlorobenzene to dioxin reactions. The general thermodynamic trends for this class of reactions can be summarized as follows:

- the reaction with molecular oxygen is always favored thermodynamically below about 1500 K,
- the reaction with water vapor (or steam) is never favored thermodynamically if no dechlorination occurs, and
- the reaction with water vapor (or steam) is sometimes favored thermodynamically if some dechlorination occurs (as in Reaction 4).

As stated above, just because these reactions are favored thermodynamically, there is no reason to expect that they will occur to any appreciable rate at any temperature, it merely indicates that the reaction is possible. It is clear from the bonding in chlorobenzenes, for example, that several elementary steps are required before PCDD/F formation is possible (See the discussion in the mechanisms section of this report). It should be noted that the reaction of chlorobenzenes with

oxygen to form carbon dioxide, water vapor, and chlorine gas is also favored thermodynamically.

Chlorinated Phenols to PCDDs

For the reaction forming 2,3,7,8-TCDD from 2,3,5-trichlorophenol,

the standard Gibbs free energy change, in kcal/mol, as a function of temperature can be approximated by the expression,

$$\Delta G^\circ = -22.7 + 0.0053T. \quad (10)$$

Despite the fact that the free energy change of Equation 9 is less negative than the free energy change for Equations 1 or 2, chlorophenols are much better PCDD precursors than chlorobenzenes. This is because no external supply of oxygen atoms is necessary for the PCDD formation. Additionally, if the chlorophenol has ortho-substituted groups as does 2,3,5-TCP, reactive sites are already present in the correct ring position for the formation of the ether linkages necessary for PCDD/F formation.

Polychlorinated Biphenyls to PCDDs

For the reactions forming some chlorinated dioxins from chlorinated biphenyls,

and

the standard Gibbs free energy change, in kcal/mol, as a function of temperature can be respectively approximated by the expressions

$$\Delta G_{11}^\circ = -57.9 + 0.0236T, \quad (14)$$

$$\Delta G_{12}^\circ = 57.7 + 0.0027T, \quad (15)$$

and

$$\Delta G_{13}^\circ = -19.1 - 0.0927T. \quad (16)$$

The trend for PCB reactions is the same as for the CB reactions, namely, the reaction with molecular

oxygen is thermodynamically favored, but the reaction with water is favored only for some cases when some dechlorination occurs.

This fact is important for the EBS system, which will be used to evaluate the relative merits of using nitrogen versus steam as the purge gas.

Chlorinated Aliphatics to PCDDs

For the reaction forming 2,3,7,8-tetrachlorodioxin from 1,1,2-trichloroethane and steam,

the approximate free energy expression is,

$$\Delta G_{17}^\circ = -68.7 - 0.229 T. \quad (18)$$

Again, the large negative value of the free energy at all temperatures indicates the reaction is thermodynamically favorable (as are other reactions between steam and 1,1,2-trichloroethane). While few would suggest that this reaction is likely to occur during thermal desorption, it illustrates that the formation of PCDDs is thermodynamically favorable from a wide variety of substances which might potentially be found in waste streams.

Polychlorinated Biphenyls to PCDFs

The PCDF forming analog to Reaction 11 is,

with a corresponding free energy expression of,

$$\Delta G_{19}^\circ = -29.6 - 0.0285T. \quad (20)$$

Note that at room temperature, Reaction 19 has a standard free energy change of -38.1 kcal/mol, while Reaction 11 has a standard free energy change of -50.9 kcal/mol. In other words, at room temperature Reaction 11 is strongly favored thermodynamically over Reaction 19. This is generally true for the formation of PCDDs and PCDFs due to the increased stability of PCDDs over PCDFs at low temperatures. Reactions analogous to the other PCDD forming reactions are possible, but are not presented in this report.

Oxygen Dependence of Reactions

It is worth considering the predicted oxygen dependence of the PCDD and PCDF forming reactions. The equilibrium constant, K , is related to the standard free energy change for a reaction by the expression,

$$K = \exp(-\Delta G^\circ/RT), \quad (21)$$

where R is the gas constant.

Using Reaction 11 as an example, the temperature dependence of K can be written as,

$$K_{11} = \exp(-11.93 + 29,139/T), \quad (22)$$

while the equilibrium expression is,

$$K_{11} = P_D P_{H_2} / P_B P_{O_2}, \quad (23)$$

where P_D is the partial pressure of 1-CDD, P_{H_2} is the partial pressure of hydrogen, P_B is the partial pressure of 2-CBP, and P_{O_2} is the partial pressure of oxygen. Assuming a partial pressure of 10^{-6} atm for 2-CBP (approximately its vapor pressure at 100°C) and a conversion of 0.1% of 2-CBP to 1-CDD, Equations 22 and 23 can be combined to give the expression,

$$P_{O_2} = 10^{-12} \exp(11.93 - 29,139/T), \quad (24)$$

where P_{O_2} is the equilibrium amount of oxygen in atmospheres as a function of temperature and the hydrogen partial pressure is assumed to be the same as 1-CDD (no other sources or sinks of hydrogen). Figure 3 shows a plot of the logarithm of P_{O_2} as a function of temperature. As shown in the plot, at all reasonable thermal desorption temperatures, P_{O_2} is exceedingly small. This means that for any practical thermal desorption system operating under these conditions, the oxygen concentration will always be such as to favor the formation of at least 0.1% of 1-CDD from 2-CBP. It should be emphasized that other products, such as carbon dioxide, are favored even more at high temperatures and high oxygen levels.

Figure 3. Equilibrium pressure of oxygen versus temperature as predicted by Equation 24 for Reaction 11. The area above the curve represents the region where 1-CDD is thermodynamically favored, while the area below the curve represents the region where 2-CBP is favored.

Of course hydrogen can be added to the carrier gas to increase the equilibrium oxygen partial pressure. It would take, however, an impractical hydrogen partial pressure (several thousand atmospheres) to have a significant effect on the thermodynamic predictions.

Comparative PCDD and PCDF Stability

It is also instructive to consider the relative stability of PCDDs and PCDFs as a function of temperature and oxygen content. This might be of interest where PCDDs are formed during the heat-up phase of thermal desorption. Consider, for example, the following PCDD to PCDF conversion reaction,

The standard free energy expression approximation for Reaction 25 is

$$\Delta G_{25}^{\circ} = 28.3 - 0.0521T, \quad (26)$$

and the expression for the equilibrium constant is

$$K = P_F P_{\text{O}_2}^{1/2} / P_D . \quad (27)$$

Assuming that $P_F/P_D = 100$, combining Equations 26 and 27, and solving for P_{O_2} gives,

$$P_{\text{O}_2} = 10^{-4} \exp(52.4 - 28,485/T) , \quad (28)$$

Figure 4 shows a plot of the logarithm of P_{O_2} versus temperature. At oxygen partial pressures below the line on the graph, the conversion from 1-CDD to 1-CDF is predicted to be nearly complete. As the temperature increases, the relative stability of 1-CDF to 1-CDD increases and the equilibrium partial pressure of oxygen increases. For example, at 400°C, 7 atm. of oxygen would be in equilibrium with a 100:1 ratio of 1-CDF to 1-CDD. In other words, under thermal desorption conditions, the thermodynamics predicts nearly complete conversion of PCDDs to PCDFs, if the temperature is over 400°C. Of course, it is necessary that the residence time at elevated temperature be sufficient for the required molecular rearrangement to occur.

Qualitatively, this thermodynamic behavior is expected due to the dominance of the entropy term in the free energy expression at high temperatures. Because the PCDD to PCDF conversion has a net increase of 1/2 mole of gas, it is expected that the entropy change for general PCDD to PCDF conversions will always be positive.

Figure 4. Relative stability of 1-CDD and 1-CDF as a function of temperature and equilibrium oxygen content. Based on thermodynamic considerations, below the curve on the graph there is insufficient oxygen in the system to prevent the formation of 1-CDF from 1-CDD.

PCDD and PCDF Formation Mechanisms

Most of the information on the formation mechanisms of PCDD/Fs is speculative and little quantitative kinetics data exists on the reaction rates. This section describes two classes of formation mechanisms and the evidence for each.

Fly Ash Catalyzed Formation

Although formation of PCDD/Fs may be thermodynamically favored when processing some waste streams, it is unlikely that the rate of formation will be significant unless fly ash is formed during the process. This is because fly ash acts as a catalyst in the PCDD/F formation process¹². The following mechanism, while it has little theoretical basis, has been used successfully¹³ to predict the dioxin content in the off-gas stream from two incinerators^{14,15}. While the thermal desorption process has clear differences from the incineration process, this mechanism provides a starting point for evaluating the dioxin off-gas process in thermal desorption.

The process initially assumes a bimolecular reaction step between two reactive precursor molecules and is most readily associated with the precursors being chlorinated benzene and/or chlorinated phenol molecules, one of which is condensed on a fly ash particle and the other of which is in the gas phase. This can be represented by the equation,

where P_s represents the precursor adsorbed on the surface of fly ash, P_g is the species in the gas phase precursor, and D_s is the PCDD/F species formed on the fly ash.

The PCDD/F can then either desorb from the fly ash, dechlorinate, or decompose. These processes are represented by the equations,

and

where D_g is the gas phase PCDD/F species, Pro is the dechlorination product, and Dpro is the decomposition product.

Thus, if the fly ash is quenched after step 1 occurs, but before steps 2, 3, or 4 occur, the dioxin species will be present on the surface of the fly ash. If step 2 occurs before steps 3 or 4 occur, the dioxin will be present in the gas phase.

Using incinerator data from References 11 and 12, rate constants as a function of temperature have been determined for the 4 steps in the process. Because of the difficulty relating fly ash concentrations, and the likelihood that PCBs are more likely to be the precursors in waste streams

evaluated by the EBS, the numerical values and temperature dependence of the rate constants for each of the 4 steps are not presented here. Instead, the following observations about the mechanism and incinerator data are made.

- The PCDD/F content of the off-gas stream for the incinerator that was examined ranged from 5 to 100 ng/m³.
- The incinerator data indicated a ratio of 10 ng/m³ of PCDD/F (gas phase plus fly ash surface) in the off-gas stream for every 10¹⁰ molecules/cm³ of precursor in the gas phase.
- The model predicts that with increasing temperature, the PCDD/F content of the gas phase will increase relative to the concentration on the fly ash surface, but that at the temperature of the off-gas from the EBS, almost no PCDD/F should be present which is not on the surface of fly ash particles (if they exist).

Other Formation Mechanism Considerations

In addition to both the fly ash catalyzed formation of PCDD/Fs and thermodynamic considerations, other factors are important to the kinetics of the formation of PCDD/Fs from chlorinated aromatics. For example, it is well known that under most circumstances, PCBs will more likely form PCDFs than PCDDs, even though the overall thermodynamic free energy change sometimes favors the formation of PCDDs. The reason for this is clear from the geometry of the reactants. Consider the PCDF formation analog to Equation 13,

This reaction requires replacement of one of the ortho-chlorines with a hydroxyl group, followed by splitting out of HCl between the hydroxyl group and the adjacent ortho-chlorine on the other ring. In addition to the bonds which are formed in Equation 33, Equation 13 requires the biphenyl bond to be broken and an addition ether linkage to be formed. Thus, it is clear why Equation 13 would rarely be observed.

For direct reaction between two molecules to lead to a PCDD, two conditions need to be met¹⁶:

- the compound must be an ortho-substituted benzene ring in which one of the substituents includes an oxygen directly attached to the ring, and
- it must be possible for the two substituents to react with each other to form an independent compound.

It should be noted, that in a reactive system such as a thermal desorption kiln, it is conceivable that several steps could occur to lead to PCDDs, and thus the initial reactant need not meet the above two conditions.

THERMAL DESORPTION EMISSION DATA

Although there is an abundance of information available on PCDD/F emissions from incineration operations, very little has been published on thermal desorption operation emissions. Reference 3 describes a large-scale thermal desorption operation which was used to treat soil contaminated with VOCs, polynuclear aromatic hydrocarbons, metals, and sulfur. Treatment temperature was about 650°C with a feed rate of 10 tons/hr and an unknown residence time. The off-gas treatment system consisted of a series of vapor cyclones, a baghouse, and an activated carbon adsorption bed. Stack analysis results indicated a total PCDD/F emission concentration of 0.26 ng/m³. This was well below the target value of 30 ng/m³, but not completely insignificant. This trend of low, but not unmeasurable PCDD/F emissions from thermal treatment systems, appears to be general.

RECOMMENDATIONS AND CONCLUSIONS

A review of existing data on the formation of PCDD/Fs under thermal desorption conditions has provided considerable qualitative, but little quantitative information on the process. Thermodynamic calculations have been shown to be only somewhat useful in correlating observed PCDD/F emission levels with thermal desorption operating conditions. It is clear that thermal desorption systems can be operated in a manner that produce PCDD/Fs at a level below that of regulatory concern, but that care must be taken to assure that their formation is controlled.

The following recommendations are made in order to minimize the probability of PCDD/F emissions from the EBS system and to provide a better understanding of PCDD/F formation and vaporization in the thermal desorption process.

- Minimize the formation and emission of fly ash. Two obvious ways to do this are to minimize the purge gas flow rate and to provide adequate particulate matter removal operations in the off-gas treatment system.
- Consider using nitrogen as the purge gas. If the rate of thermal desorption is not impeded by using nitrogen as opposed to air or steam, it has the advantage of reducing the probability of molecular collisions which could lead to the oxygen-phenyl bonds necessary for PCDD/F formation.
- Analyze the waste stream before and after treatment for chlorinated aromatics, as well as sampling the off-gas for the same. This will provide the best material balance data to determine the fate of PCDD/Fs in the system.
- Perform small-scale experiments to determine the rate of formation of PCDD/Fs from precursors likely to be found in the waste streams of interest. This will provide data which can be used to help define the optimum operating conditions for thermal desorption.

APPENDIX A - THERMAL DESORPTION AND FLOW MODELLING

Two forces are perceived to be dominant in the mass transport of the vapor from the thermal desorption process. One force is the gradient of the chemical potential of the vaporizing material normal to the surface of the solid waste and the other force is the pressure gradient which causes the carrier gas to flow longitudinally through the system. These forces are rendered into more suitable form for modeling when it is recognized that the chemical potential gradient of the vapor in this system reduces to a concentration gradient (under most circumstances) and can be described by gas phase diffusion. Additionally, the pressure gradient of the carrier gas results in a carrier gas velocity which can be used directly to model the transport of the vapor in the direction of flow of the carrier gas. Diffusion in this dimension is ignored for the time being as are buoyancy effects and potential pressure gradients in the direction normal to the solid waste. Substitution of the mathematic representation of these forces into the continuity equation yields the partial differential equation to be solved:

$$\partial c / \partial t = D \partial^2 c / \partial y^2 - v \partial c / \partial x, \quad (A-1)$$

where c is the concentration of the vapor, t is time, D is the diffusion coefficient, y is the coordinate normal to the solid waste, v is the convective velocity of the carrier gas, and x is the coordinate parallel to the solid waste.

The appropriate boundary conditions for the EBS are,

$$c = c_0 \exp(-kt) \text{ at } y = 0, \quad (A-2)$$

where c_0 is the initial concentration of the desorbing component in the waste stream, and k is the desorption rate constant at the temperature of the kiln. This boundary conditions changes to,

$$c = 0 \text{ at } y = 0, \quad (A-3)$$

when the desorbing component has been depleted from the condensed phase.

Additional boundary conditions are,

$$\partial c / \partial y = 0 \text{ at } y = L, \quad (A-4)$$

where L is the effective distance from the waste to the kiln wall (no flux through the kiln wall),

$$c = 0 \text{ at } x = 0, \quad (A-5)$$

(purge gas is "clean" when it enters the kiln), and

$$c = 0 \text{ at } t = 0, \quad (A-6)$$

(gas phase in kiln is initially clean).

Because of the complexity of this system of equations, it is best to solve them numerically on a computer, particularly for continuous operation of the kiln. This has been done and is being documented in a separate report in progress.¹⁷ Applying this model to 2,3,7,8-TCDD and extrapolating the data on PCBs in Reference 18 to the conditions described in the "Vaporization of PCDD/Fs in the Waste Feed" section of this report, produces the results described in that section.

APPENDIX B - ACRONYMS AND CHEMICAL SYMBOLS

B	benzene
C	carbon
C ₂ H ₃ Cl ₃	1,1,2 trichloroethane
CB	chlorobenzene
Cl	chlorine
Cl ₂	chlorine
CO ₂	carbon dioxide
CP	chlorophenol
DD	dibenzo-p-dioxin
EBS	enhanced bench-scale
H	hydrogen
H ₂	hydrogen
H ₂ O	water
HCl	hydrochloric acid
HEPA	high efficiency particulate air
MMES	Martin Marietta Energy Systems
O	oxygen
O ₂	oxygen
PCB	polychlorinated biphenyl
PCDD	polychlorinated dibenzo-p-dioxin
PCDF	polychlorinated dibenzofuran
VOC	volatile organic compounds
1-CDD	1-chlorodibenzo-p-dioxin
1-CDF	1-chlorodibenzofuran
1,2-DCB	1,2-dichlorobenzene
1,2,3-TCB	1,2,3-trichlorobenzene
1,2,6,2',4',5'-HCBP	1,2,6,2',4',5'-hexachlorobiphenyl
2-CBP	2-chlorobiphenyl
2,3,4'-TCBP	2,3,4'-trichlorobiphenyl
2,3,5-TCP	2,3,5-trichlorophenol
2,3,6,2',4',5'-HCBP	2,3,6,2',4',5'-hexachlorobiphenyl
2,3,6,9-TDBF	2,3,6,9-tetrachlorodibenzofuran
2,3,7,8-TCDD	2,3,7,8-tetrachlorodibenzo-p-dioxin

REFERENCES

1. McCoy, D. E., *RCRA Land Disposal Restrictions: A Guide to Compliance*, Vol 12, p.3.13, Elsevier Science, Inc., New York, NY, 1994.
2. Tennessee State Air Pollution Control Regulations, Chapter 1200-3-9, *Construction and Operation Permits*, October, 1989.
3. J. H. Hutton and A. J. Trentine, *Thermal Desorption of Polynuclear Aromatic Hydrocarbons and Pesticides Contaminated Soils at an Ohio Superfund Site: A Case Study*, 94-FA155.05, Porter, IN.
4. Marshall Sittig, *Handbook of Toxic and Hazardous Chemicals and Carcinogens*, Vol 2, p 1519, Noyes Publications, Park Ridge, NJ, 1991.
5. Letter from B. K. Mattie to C. M. Noakes, *Disposal Area Remedial Action (DARA) Soil Sampling and Analysis (S&A)*, February 17, 1994.
6. B. F. Rordorf, *Thermochimica Acta*, 85, 435-438, 1985.
7. W. M. Shaub, *Thermochimica Acta*, 58, 11-44, 1982.
8. W. M. Shaub, *Thermochimica Acta*, 62, 315-323, 1983.
9. W. M. Shaub, *Thermochimica Acta*, 55, 59-73, 1982.
10. D. Thompson, *Chemosphere*, Vol. 29, No. 12, pp. 2583-2595, 1994.
11. D. R. Lide and H. V. Kehiaian, *CRC Handbook of Thermophysical and Thermochemical Data*, CRC Press, Inc., Boca Raton, FL, 1994.
12. Fangmark, I., et. al., *Chemosphere*, Vol 29, Nos., 9-11, pp. 1903-1909, 1994.
13. E. R. Altwicker, et. al., *Chemosphere*, Vol. 20, Nos. 10-12, pp. 1935-1944, 1990.
14. OSWEGO; Draft Final Report, DCN88.233.012.26, prepared for New York State Energy Research and Development Authority, Nov., 30, 1988; *Data analysis results for testing at a two-stage modular MSF-incinerator*. Oswego County ERF, Fulton, NY.
15. New York State Energy Research and Development Authority, Report 87-16, June 1987. *Results of the combustion and emissions research project at the Vicon incinerator facility in Pittsfield, MA*. Final Report, Volume 1.

16. J. Vuceta, et. al., *State-of-the-Art Review: PCDDs and PCDFs in Utility PCB Fluid*, CS-3308, SCS Engineers, Inc., Long Beach CA, 1983.
17. J. H. Leckey, *Chemical Reactions and Numerical Modeling of Vapor Transport in Thermal Desorption Waste Treatment Processes*, Martin Marietta Energy Systems, Inc., Oak Ridge, TN. - In Progress.
18. Uzgiris, E. E., et. al., *Chemosphere*, Vol. 30, No. 2, pp. 377-387, 1995.

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