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Establishing the Propensity for Dioxin Formation Using a Plume Temperature Model for Medical Waste Incinerator Emissions in Developing Countries

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ABSTRACT

Air pollution control devices (APCDs) are not compulsory for medical waste incinerators (MWIs) in developing countries. In South Africa, combustion gases are usually vented directly to the atmosphere at temperatures greater than the formation temperature of dioxin. The possibility of dioxin formation outside the incinerator stack has been hypothesized. A plume model has been developed and tested in the wind tunnel with a scale model of an incinerator stack. The plume temperature and trajectory predictions of the plume model were verified within a ±3% experimental accuracy. Using South African data, the plume model predicts that the residence time of gases in the temperature range of 150–450 ºC in a plume is 1.3 sec on average for 5% of a year (18 days) at meteorological conditions resulting in wind speeds of less than 1 m/sec. Two published dioxin formation models were used to assess the probability of dioxin formation in the plume. The formation models predict that the average polychlorinated dibenzodioxins/furans (PCDD/Fs) formed in the plume will exceed the stack emission regulations in South Africa of 0.2 ng/Nm^3 toxic equivalent quotient (TEQ) by between 2 and 40 times. The calculated concentrations do not include additional gaseous PCDD/F compounds that may be formed at high-temperature post-combustion zones through pyrosynthesis mechanisms.

IMPLICATIONS

At present, waste managers in developing countries assume that direct venting to the atmosphere acts as an adequate quenching process to prevent the formation of dioxin compounds in the plumes of MWIs. The results indicate that the temperatures and residence times in plumes above an incinerator can be similar to those in the post-combustion zone of incinerators where dioxin compounds have been measured. When these temperatures and residence times are used in the most recent dioxin formation models, the predicted amounts of dioxins exceed the emission concentration guidelines of the South African government.

INTRODUCTION

Regulatory guidelines[1] for the incineration of medical waste are not strictly enforced by the South African authorities, because of ongoing changes in the current legislation and national waste management strategies.[2] Air pollution control devices (APCD) are not compulsory, and combustion gases may be emitted directly to atmosphere at high temperatures. For some incineration processes in South Africa, temperatures as high as 900 ºC have been recorded.[3] Although dioxins are formed at temperatures lower than this, there is no measurement data to indicate the amounts formed in the plumes from incinerator stack tips.

A survey of the literature has shown that no calculations are available to estimate dioxins formed within the first section of the plume. Measurements of dioxins present in stacks have been correlated with the concentrations of particulates, inorganic chlorides, metallic species, and organic precursors,[4-9] and with the residence time of the gases within the temperature ranges of 150–450 ºC[7,8] and 250–450 ºC.[9] To determine whether these conditions exist for significant periods, a model for plume behavior close to the tip of the stack is required.

The plume region prior to the establishment of horizontal flow has been described using fluid dynamic principles[10] and by the classical empirical equations derived by Briggs.[11] At the exit of the stack tip, the plume is assumed

to be a round, perpendicular jet issuing into a horizontal flow of ambient air. The physical conditions of the plume are described by dividing the plume[12] into a zone of laminar flow [i.e., the zone of flow establishment (ZFE)], and a zone of cyclonic flow [i.e., the zone of established flow (ZEF)]. The ZFE has the characteristic parameters of a jet.[10] It has been found that inside the ZFE, the flow distribution does not follow a Gaussian profile because of eddy exchange coefficients.[13] The ZEF takes into account the conditions above the jet caused by turbulence of both the jet and the ambient flowing medium, where the plume bends over and a Gaussian profile occurs.[14]

Studies on a medical waste incinerator (MWI) in South Africa[15,16] indicate that the temperature range of 150–450 ºC, where dioxins may be formed, occurs in the transition from the ZFE to the ZEF after the gases have left the stack tip. The MWI is a simple retort-type multiple-chamber design[17] without APCD, and is a semi-batch operation.[15,16] The importance of dioxin formation was emphasized as the result of work carried out by the CSIR for a multi-pathway health risk assessment (MPHRA) of this MWI[15] during which conditions in the stack of the incinerator were extensively measured.[16] However, dioxins and furans could not be sampled, because the gas temperature in the stack is greater than the 450 ºC temperature during normal operation.[16] Because dioxin was the key risk driver in the MPHRA, a scientific basis for obtaining an upper estimate of the dioxin emissions was required.

A two-stage model (PlumeDIOX) was developed by the CSIR to provide estimates of the concentration of dioxin compounds formed in the MWI plume. PlumeDIOX combines a hot plume model, describing the physical characteristics of the plume during the cool-down to ambient temperatures, with published dioxin formation models.[7-9]

DEVELOPMENT OF A HOT PLUME MODEL

Empirical equations derived by Briggs[11] are applicable only to determine the final plume height and cannot be used to estimate the plume characteristics close to the stack exit. In addition, the Lagrangian velocity correlation coefficient indicates that a Gaussian model is not applicable very close to the source, where diffusion is rapid.[18] A similarity or Gaussian model can, however, be used when the plume is in the established flow region.

In the ZFE, the necessary equations were derived from the properties of a deflected turbulent jet.[10,11,14,19] In the ZEF, the physical characteristics of the plume were determined from the conservation of mass, momentum, and energy.[12,13,20,21] Appendix A summarizes the equations used to describe these two zones of the hot plume.

Assumptions Used in the Development of the Plume Model

The following assumptions simplify the mathematical description of the model:

- The ZFE corresponds to calculations of a deflected jet,[10] and viscous effects can be neglected. However, some corrections are made for the density and velocity changes caused by buoyancy.[19] The bend-over of the plume that does occur in this zone is calculated from a modification to the Briggs equation for a bent-over buoyant plume;[11]
- In the ZEF, the mean flow velocity perpendicular to the main flow along the length of the plume is small in comparison with the main flow velocity. The secondary flows perpendicular to the plume axis caused by bend-over of the plume are consequently ignored;
- In the ZEF, the turbulence is uniform, giving a Gaussian concentration distribution profile;[22]
- Molecular transports are considered negligible in comparison with turbulent transports;
- Once released into the atmosphere, the plume is an isobaric system;[23]
- Aerodynamic effects such as down-wash of the plume caused by surrounding structures are neglected;
- Linear mixing occurs after the stack exit (i.e., the density of the mixture is a volume-weighted average of the densities of the components);[21]
- The molecular weight and specific heat of the exit gases are approximately the same as those of the surrounding air; and
- The model is formulated as a steady-state model in which time derivatives are set equal to zero.

Plume Coordinates Used in the Model Calculations

The equations are based on the system illustrated[12] in Figure 1. The system can briefly be described as follows:

- The ambient wind velocity is uniform and horizontal over the whole height of the plume and is given by the term U_a;
- The first part of the plume is already known as the ZFE. Its length is given by the term δ. The characteristics of the plume at the end of this zone will describe the origin of the coordinate system for the ZEF;
- The ZEF is treated as an axis-symmetric turbulent plume with a temperature gradient only in the vertical direction. Consequently, only a two-dimensional coordinate system is considered, with y being the distance above the origin and x the approximate distance from the origin; and

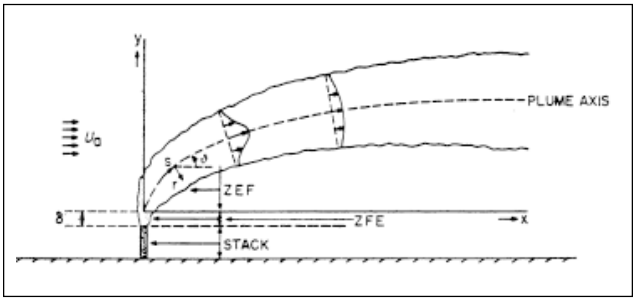

Figure 1. Plume coordinates used for mathematical formulation.

- *s*, *r*, and φ are taken as the plume coordinates in the ZEF, as shown in Figure 1.

Hot Plume Model Verification

An experimental study was conducted at the wind tunnel facilities of the Division of Aeronautical Science and Technology (Aerotek) of the CSIR, South Africa.[24] The experimental design consisted of a hot plume ejected into a steady horizontal cross flow. The stack was 0.2 m in diameter and 1.2 m high, and was insulated to prevent excess heat loss. Cyclonic flow in the stack was prevented by a flow distributor system at the bottom of the stack. The stack was placed close (~0.5 m) to the inlet of the wind tunnel. The total flow height of the tunnel is 1.5 m, with 1 m above ground level. The stack therefore extended into the horizontal flow region by 0.2 m. An average cross flow of between 1.3 and 1.6 m/sec was maintained in the wind tunnel. Further stability could not be attained because of the influence of ambient conditions outside the inlet and outlet of the tunnel at these low velocities.

A liquid petroleum gas (LPG) burner, operating at an LPG-to-air ratio slightly higher than the stoichiometrically requirement, was used to generate the hot plume from the stack. Dilution air was injected at the bottom of the experimental stack to obtain an adequate exit flow rate and also consumed the remaining excess LPG. The LPG gas and burner airflow rates were controlled using calibrated rotameters. The total airflow (burner and dilution) was controlled using a 28-mm orifice plate and water u-tube manometer.[24] The exit velocity of the stack gas was calculated from a mass balance over the burner/stack system and the measured exit temperature. The ambient cross-flow velocity was measured with a hot wire anemometer.

The temperatures along the plume trajectory were measured using five thermocouples, placed in line with the cross wind as indicated in Figure 2. The central thermocouple at the stack exit was taken as the zero reference point in space. The five thermocouples were mounted on a computerized *xyz* table. The linear movement of the plume toward the tunnel exit was confirmed by a smoke releaser. The thermocouples were therefore moved only in the *xy* direction. Random incremental steps were taken

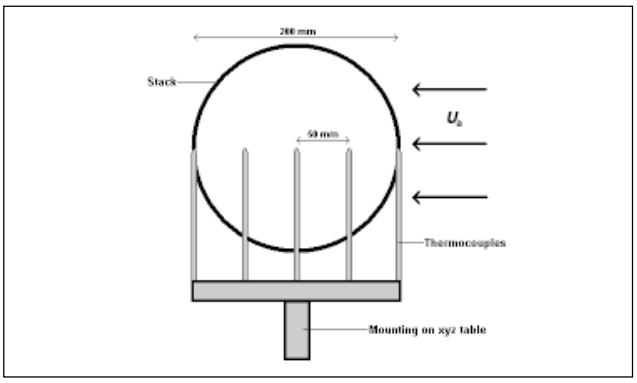

Figure 2. Thermocouple positioning at the stack exit.

until the highest temperature was observed between the five thermocouples. The position of the thermocouples was maintained at this location for ~5 min to reach temperature stability. A third-order polynomial curve was fitted to the data at each measurement location to determine the plume center location and temperature (Figure 3).

Table 1 summarizes the conditions of the exit plume and the ambient conditions generated inside the wind tunnel. In Table 1, the experimental values are compared with those of an industrial incinerator, which the experimental stack simulates. For an accurate simulation, the Reynolds number of the exiting plume and the velocity ratio (U_0/U_a) should be similar[25] for both the scaled-down stack and the industrial process. The values given for the industrial process in the table are typical of conditions that have been measured at some plants in South Africa.[3] The results of one measurement cycle are compared with the model predictions in Figures 4 and 5.

Verification Discussion. The accuracy of the model was estimated from the correlation coefficient between the measured values and the values predicted by the model. This coefficient measures the relationship between two data sets independent of the unit of measurement. The population correlation calculation returns the covariance

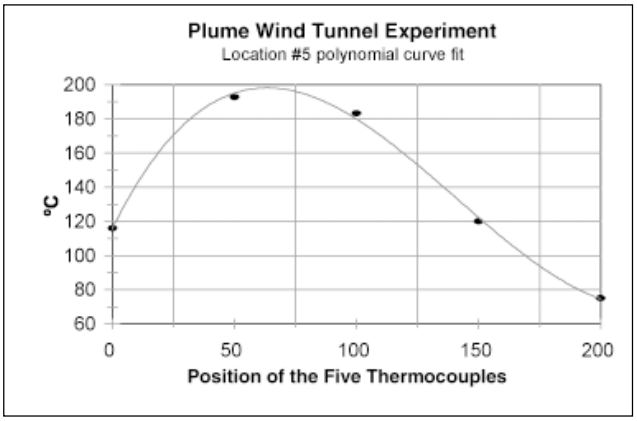

Figure 3. Polynomial curve fitted to the fifth measurement location's data.

Table 1. Conditions of the CSIR wind tunnel experiment.

Property	Units	Experiment	Industrial Process
Temperature	°C	286	900
Velocity	m/sec	1.49	5
Diameter	m	0.2	0.2
Density	kg/m^3	0.56	0.27
Viscosity	kg/m.sec	0.29	0.47
Wind velocity	m/sec	1.42	5
Reynolds number		5740	5731
Velocity ratio		1.05	1.00

of two data sets divided by the root product of their standard deviations[26]

$$\nu = \frac{Cov(\xi, \eta)}{\sqrt{Var\xi \cdot Var\eta}} \quad (1)$$

where ν is the correlation coefficient, η is the model data set, and ξ is the measured data set. The data set of the CSIR wind tunnel experiment consisted of two independent sets of 11 values each, on which a correlation calculation could be carried out with eq 1. The results are given in Table 2.

Conclusions from the Model Verification. The temperature prediction along the plume trajectory is accurate within 3%, with a correlation coefficient of more than 99%. This discrepancy tends toward an overprediction, which leads to a slight overestimate of the residence time within a temperature range. Additional verifications will have to be made at real stack locations to substantiate these conclusions.

APPLICATION OF THE PROPOSED PLUME MODEL

The model was applied to a high-temperature plume from the stack of a medical waste incinerator (MWI) in South Africa. This incinerator underwent intensive evaluation by the CSIR over a two-year period.[16] The meteorological conditions for the region are often relatively warm and

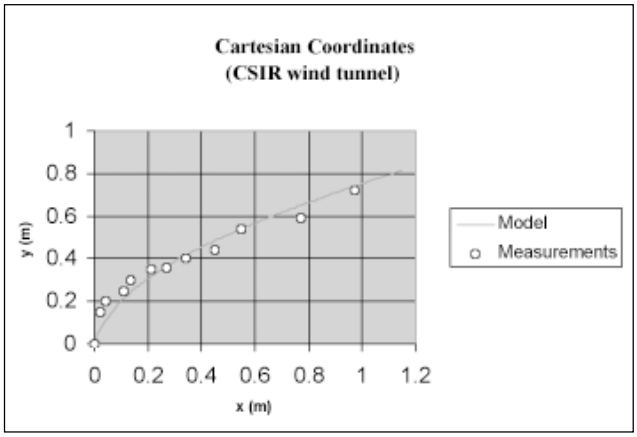

Figure 4. Plume path results of the CSIR measurement campaign.

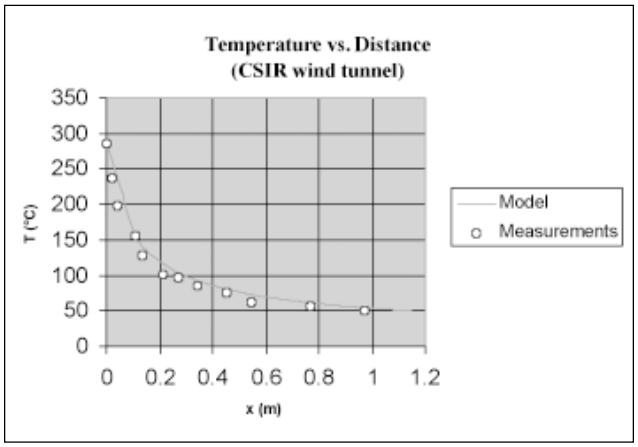

Figure 5. Temperature results of the CSIR measurement campaign.

calm. It is known that dioxin compounds are formed in the post-combustion gases of MWIs when the gases are cooled.[4] The highest amount of dioxins are formed when

- The combustion efficiency is low (<99%);
- Chlorinated plastics are present in the feed (e.g., PVC); and
- High concentrations of metallic species are present on the emission particulates (i.e., Fe and Cu).

The latter two conditions are true for the MWI in South Africa, and it is hypothesized that dioxins are formed in the plume.

Mechanisms for Dioxin Compound Formation

The dioxin group of compounds includes polychlorinated dibenzodioxins (PCDD) and polychlorinated dibenzofurans (PCDF). Four possible pathways have been proposed for the observed presence of the dioxin group of compounds in the flue gases from combustion processes,[4,27] although the contributions of different mechanisms are still under debate.[27]

- The presence of PCDD and PCDF in the waste that is burnt;
- Pyrosynthesis (i.e., high-temperature gas-phase formation);
- Formation by way of reactions between chemically related compounds (precursors), such as chlorophenols, condensed on the fly ash; and
- Formation via de novo synthesis from chemically unrelated compounds and chlorine donors on the fly ash between temperatures of 250 and 450 °C.

Table 2. Correlation coefficient for the measurement campaign at the CSIR.

Parameter		Correlation	
Height above stack at *x*	*y*	99.05	%
Temperature at *x*	*T*	99.19	%

It is assumed, from available evidence,[28] that medical waste contains no dioxins. The pyrosynthesis pathway is considered less important at the lower temperatures in the plume.[27] However, formation of PCDD/Fs through this mechanism[29] could take place in the high-temperature post-combustion zones before the stack tip. The reaction of condensed precursors and de novo synthesis pathways are considered as possible post-combustion formation mechanisms[27] in the plume. Metallic species, especially Fe and Cu,[30] have also been shown to catalyze these formation mechanisms.[7] A large concentration of metallic species, especially Fe, Cr, Cu, and Mn, has been measured at the MWI considered here.[16] This emphasizes the importance of these two mechanisms for the potential risk of PCDD/F formation in the plume.

Condensed Precursor Pathway of PCDD/F Formation. This heterogeneous model[7,8] for the formation of dioxins between temperatures of 150 and 450 °C follows a gas-fly ash reaction mechanism for the formation of the dioxin group of compounds. The fly ash from the incineration process is a catalyst for surface reactions. The total concentration of dioxins in the solid phase can be calculated from the actual residence time t of the gas and particulate mixture and the average particulate concentration M_p, in a temperature range T, using the equations summarized in Appendix B. The equations also calculate the desorbed dioxin. These, however, do not include all the dioxin in the gaseous phase.

De Novo Synthesis Pathway of PCDD/F Formation. The proposed empirical model[9] for de novo synthesis on incinerator fly ash between 450 and 225 °C assumes that the reaction of Cl from HCl with carbon on the fly ash results in PCDD/F formation. All reactions, therefore, take place on the surface of the fly ash, where metals act as catalyst. Empirical eq 34 in appendix C can be numerically integrated assuming a linear cooling rate and an initial dioxin concentration from the combustion process.[9] Again, the calculated concentration does not include the gaseous phase because formation in the high-temperature post-combustion stages is not considered and desorption is ignored in the model.

Case Study Incinerator Conditions

The initial conditions at the stack tip of the case study MWI are summarized in Table 3. For a conservative assessment, calm atmosphere conditions were considered, because it is not expected that the residence time of the plume within the required temperature range will be significant at higher wind speeds. The wind speed for extremely calm conditions was taken to be less than 1 m/sec. An average ambient velocity of 0.5 m/sec was chosen for the model calculations because of wind fluctuations.

Table 3. Initial conditions at the stack tip of the case study incinerator.

Parameter		Value	
Mean wind velocity	U_a	0.5	m/sec
Ambient temperature	T_a	19.7	°C
Ambient density	ρ_a	1.002	kg/m^3
Emission exit velocity	U_0	4.62	m/sec
Emission exit temperature	T_0	460	°C
Emission exit density	ρ_0	0.402	kg/m^3
Initial plume angle	φ_0	1.571	rad
Stack diameter	D	0.915	m

Plume Model Predictions

ZFE. Following the proposed plume model, the relevant parameters were calculated at the end of the ZFE. These values are summarized in Table 4. Figure 6 is a graphical representation of the calculated plume path over the whole temperature range. The transition from the ZFE to the ZEF is indicated by the arrow.

ZEF. For the ZEF, the parameters were calculated over the additional section of the plume trajectory until the target temperature was reached. The results of the calculations are plotted in Figures 6 and 7. A comparison of the two figures indicates the distance along the plume trajectory to the target cool-down temperature. The calculated values of the other plume characteristics are summarized in Table 5.

Estimation of Dioxin Formation with the Precursor Condensation Model

Using the results obtained from the plume model and specifically the residence time in the temperature range 450–150 °C, the potential for the formation of dioxin in the plume can be estimated using the precursor condensation pathway. The particle concentration at the target cool-down temperature of 150 °C is calculated from the ratios of the plume cross-sectional areas.

Table 4. Plume conditions at the end of the ZFE.

Parameter		Value	
Path length of the ZFE	δ	4.575	m
Plume velocity	u_1	5.1	m/sec
Characteristic plume width	b_1	0.647	m
Plume density	ρ_1	0.562	kg/m^3
Plume temperature	T_1	249.1	°C
Plume angle	φ_1	1.488	rad
Residence time	t_{01}	0.938	sec

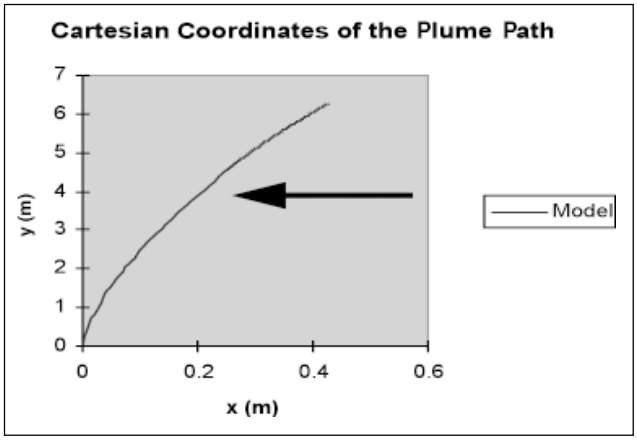

Figure 6. Plume Cartesian coordinates over the whole plume trajectory.

$$C_{\text{target}} = C_0 \cdot \frac{A_0}{A_{\text{target}}} \quad (2)$$

with[15]
$$C_0 = 0.22 \times 10^{-6}\ \text{g/cm}^3 \quad (3)$$

$$A_0 = \frac{\pi}{4} \cdot D^2 = 0.66 \quad (4)$$

$$A_{\text{target}} = \frac{\pi}{4} \cdot \left(b_{\text{target}}\right)^2 = 3.38 \quad (5)$$

The following parameters are used in the model with the assumptions and equations of Appendix B:

- An average particulate concentration of 73.2 mg/Am^3;
- A residence time of the plume of 1.3 sec between 450 and 150 °C; and
- An average temperature of 300 °C, which is also the temperature of maximum dioxin formation.[31]

Assuming that tetrachlorinated dioxins are formed with a molecular mass of 321 g/mol, the total solid-phase dioxins are calculated to be 6.97 ng/Nm^3. The desorbed concentration is insignificantly small. The results are shown in Table 6.

Sensitivity of the Condensed Precursor Model. A change in the particulate concentration has a very small influence on the PCDD/F solid-phase formation calculation with the precursor condensation model. The calculation is linear with residence time (i.e., a fluctuation of 10% in the total residence time results in a similar change in PCDD/F concentration prediction). The average plume temperature, however, has a significant influence on the overall concentration, with a 10% higher temperature resulting in a factor 2 increase in concentration. This is shown in Figure 8.

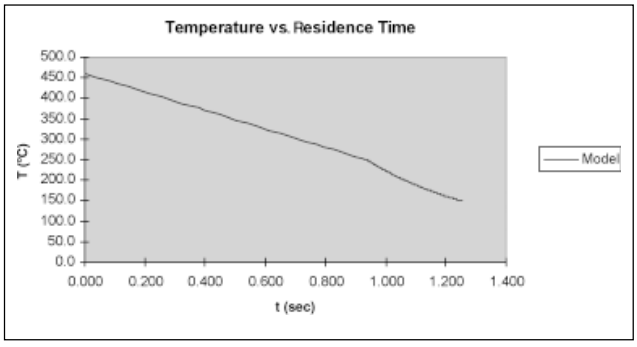

Figure 7. Cool-down rate over the trajectory of the case study plume.

Table 5. Parameter values at the target temperature after cool-down of the plume.

Parameter		Value	
Target temperature	T_{target}	150	°C
Reference density	ρ_{target}	0.694	kg/m^3
Density difference	ρ^*_{target}	–0.308	kg/m^3
Plume width	b_{target}	2.075	m
Height above the stack	y_{target}	6.277	m
Distance from the stack	x_{target}	0.428	m
Distance along trajectory	s_{target}	6.325	m
Plume velocity	$u^*(s_{\text{target}})$	5.7	m/sec
Residence time in ZEF	t_{target}	1.252	sec

Estimation of Dioxin Formation with the De Novo Synthesis Model

Similar to the precursor formation model, the average particulate concentration required for the de novo synthesis model can then be calculated using eq 3. The following parameters are used together with the equations of Appendix C:

- An average particulate concentration of 78.8 mg/Am^3;
- A residence time of the plume of 0.98 sec between 450 and 225 °C; and
- An average temperature of 337.5 °C.

The results are shown in Table 7. The total PCDD/F calculation is higher than the calculation estimate of the precursor condensation model by a factor of 16.

Sensitivity of the De Novo Synthesis Model. The PCDD/F solid-phase formation calculation is linear with particulate concentration (i.e., a fluctuation of 10% in the average

Table 6. Solid-phase PCDD/F calculations using the precursor condensation model.

Parameter	Precursor Condensation Model	
Applicable temperature range	450–150	°C
Residence time in range	1.252	sec
Total predicted dioxins and furans	7.0	ng/Nm^3
TEQ estimated as 1/15th of the total concentration	0.46	ng/Nm^3

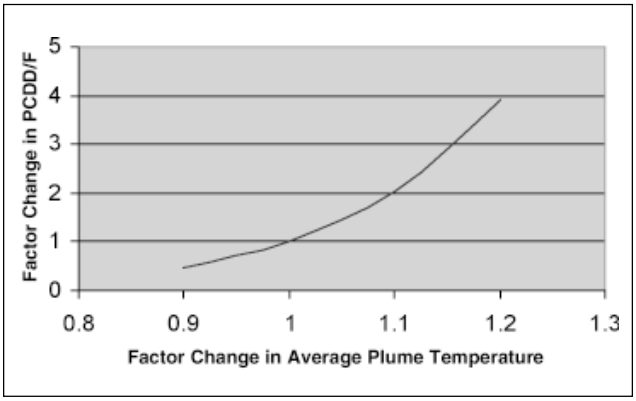

Figure 8. Sensitivity analysis of the precursor condensation model with temperature.

particulate concentration results in a similar change in PCDD/F concentration prediction). The residence time and average plume temperature do not have a significant influence on the de novo synthesis model.

Discussion on the Dioxin Formation in an Incinerator Plume

Dioxin formation in plumes from MWIs can be reduced by a rapid decrease in the stack temperature and the precursor and metallic emission concentrations from the stack.

Exit Temperature. A rapid quench in the stack with a consequent exit temperature of 250 ºC would reduce the amount of dioxins formed through both formation mechanisms. The PlumeDIOX model predicts a reduction in the residence time by up to 16% at an average temperature of 200 ºC (precursor mechanism) and up to 66% at an average temperature of 237.5 ºC (de novo mechanism). A total absorbed dioxin concentration of 0.28 ng/Nm^3 is calculated through the precursor condensation mechanism (i.e., a factor of 25 lower than 7 ng/Nm^3), while the PCDD/F formation through the de novo synthesis mechanism is insignificant.

Precursor Concentrations. The PlumeDIOX model predicts that reducing the precursor concentration of polychlorinated phenol to 150 µg/m^3 by increasing the combustion efficiency of the incinerator would lower the total amount of dioxins formed by a factor of 2 (i.e., to 3.45 ng/Nm^3). If the toxic equivalent quotient (TEQ) of dioxin is further estimated at one-fifteenth of the total concentration,[15] the emission of dioxins is 0.23 ng/Nm^3 TEQ, which is approximately equal to the South African and United States regulations.

Table 7. Solid-phase PCDD/F calculations using the de novo synthesis model.

Parameter	De Novo Synthesis Model	
Applicable temperature range	450–225	ºC
Residence time in range	0.977	sec
Total predicted dioxins and furans	110.1	ng/Nm^3
TEQ estimated as 1/15th of the total concentration	7.34	ng/Nm^3

Metal Emissions. A reduction in the concentration of metallic species, especially Cu and Fe, in the stack emissions would reduce the catalysis of the formation reactions. As an example,[6] lowering the Fe concentration by a factor of 2 could reduce the concentration of absorbed dioxins on incineration ash by a factor of 2.4.

CONCLUSIONS

A plume model (PlumeDIOX) has been developed to describe the cool-down of a hot plume to ambient temperature. A verification of the model against temperature measurements along the plume trajectory reveals the model to agree within an experimental accuracy of ±3%. The model was incorporated into a computer program that can be used to determine the residence time, together with other characteristics, of a hot plume within a certain temperature range in a calm atmosphere.

The model was used to estimate the formation of the dioxin group of compounds by previously published mechanisms of condensed precursor reactions and de novo synthesis. The calculated values are summarized in Tables 6 and 7. The current regulation of South Africa[1] for dioxin emissions from hazardous waste incinerators, similar to that of the U.S. Environmental Protection Agency[32] in 1996, is 0.2 ng/Nm^3 TEQ. Using the proposed PCDD/F formation mechanisms, and assuming a TEQ fraction of one-fifteenth of the total dioxins,[15] this model calculates the PCDD/F formed in the plume to be above the current regulations for calm weather conditions by a factor of 2–40.

The compiled plume model (PlumeDIOX) can, therefore, be used to indicate possible PCDD/F formation in the plume from high-temperature processes. This does not include the gaseous formation of these compounds at high-temperature post-combustion zones through possible pyrosynthesis mechanisms. The inaccuracies of PlumeDIOX in terms of overall PCDD/F concentrations in the plume need to be verified further. However, PlumeDIOX does indicate that atmospheric quenching of incinerator plumes may not be adequate to prevent the formation of dioxins.

NOMENCLATURE FOR THE HOT PLUME MODEL

b(s)	Local characteristic width of the plume, or radial length scale	(m)
C_d	Drag coefficient	

D	Stack diameter	(m)
F_D	Densimetric Froude number	
g	Gravitational acceleration	(m/sec^2)
ℓ	Characteristic length	(m)
P	Pressure of the ambient atmosphere	(kg/m.sec^2)
r	Radial distance of a point inside the plume to the plume axis	(m)
R	Radius of the plume	(m)
s	Distance along the plume axis from the origin of the zone of established flow	(m)
t	Residence time for cool down	(sec)
T	Temperature of the plume	(ºC)
T_a	Ambient temperature	(ºC)
T_{target}	Target temperature for the cool-down evaluation of the plume	(ºC)
$u(s,r,\varphi)$	Plume velocity at a point in the plume along the direction of the tangent to the plume axis	(m/sec)
$w(s,r,\varphi)$	Plume velocity, perpendicular to the plume axis	(m/sec)
$u^*(s)$	The maximum plume velocity at a certain point on the plume axis, relative to the surrounding atmosphere, in the direction of the tangent to the plume axis	(m/sec)
u'	Entrainment velocity caused by atmospheric turbulence	(m/sec)
U_0	Exit velocity from the stack	(m/sec)
U_a	Mean wind velocity	(m/sec)
x	Cartesian coordinate	(m)
y	Cartesian coordinate	(m)
z	Cartesian coordinate	(m)
α_1	Entrainment coefficient of a free jet	
α_2	Entrainment coefficient of a line thermal	
α_3	Entrainment coefficient caused by atmospheric turbulence	
λ^2	Turbulent Schmidt number	
$\rho(s,r,\varphi)$	Plume density at a point inside the plume	(kg/m^3)
ρ_a	Density of the atmosphere	(kg/m^3)
ρ_{a0}	Density of the ambient at the stack exit	(kg/m^3)
$\rho^*(s)$	Density difference between the plume axis and the ambient	(kg/m^3)
ρ^*_0	Density difference between the plume and the ambient at the stack exit	(kg/m^3)
φ	Angle between the plume axis and the horizontal	
β	Temperature coefficient	(K^{-1})
δ	Length of the zone of flow establishment	(m)
ε	Eddy energy dissipation	(m^2/m^3)

If not stated otherwise, the subscripts

- "0" refer to conditions at the stack exit,
- "1" refer to the conditions where the flow changes from one zone to the other, and
- "target" or "2" refer to the target temperature and density to which the plume gases must cool down.

NOMENCLATURE FOR CONDENSATION REACTION CALCULATIONS

g_o	Gas-phase precursor number density	(molec/cm^3)
k_1	Rate constant for dioxin formation	(sec^{-1})
k_2	Rate constant for dioxin desorption	(sec^{-1})
N_p	Fly ash number density	(particles/cm^3)
M_p	Fly ash concentration	(g/cm^3)
P	Equation variable	
Q	Equation variable	
r_p	Radius of a fly ash particle	(cm)
R	Universal gas constant	(J/mol/K)
t	Residence time for cool down to the reference temperature	(sec)
T	Absolute temperature of the plume	(K)
ρ_p	Density of the fly ash	(g/cm^3)
σ_g	Effective precursor radius	(cm)
σ_p	Effective fly ash radius	(cm)
θ_g	Fractional coverage of fly ash by precursor molecules	

NOMENCLATURE FOR DE NOVO SYNTHESIS CALCULATIONS

A_s	Surface area available for reaction	(m^2/g)
d	Surface mean diameter	(m)
M	Molecular mass of HCl	(g/mol)
m_p	Concentration of PCDD/F	(g/g)
R	Universal gas constant	(J/mol/K)
r_{ads}	Rate of adsorption	(mol/m^2/sec)
r_{dest}	Rate of thermal destruction	(sec^{-1})
T	Absolute temperature of the plume	(K)
t	Residence time for cool down	(sec)
X_p	Moles of PCDD/F	(mol)
α	Fraction of gaseous molecules partaking in the reaction	
β	Rate of cooling	(K/sec)
ρ	Density of the fly ash	(kg/m^3)

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APPENDIX A: MATHEMATICAL EQUATIONS OF THE HOT PLUME MODEL

ZFE

A deflected jet approximates the first part of the trajectory path. However, in the case of a plume with a high temperature, buoyancy will play an important role in the rise of the plume. As has been shown,[19] the ratio of velocity to the initial exit velocity will have its maximum at the end of this zone

$$\frac{u_1}{U_0} = f_w(F_{D0}) \tag{6}$$

where

$$f_w(F_{D0}) = \begin{cases} 1.66 & F_{D0}^2 < 8 \\ 1.99 - 0.24 \times \ln(F_{D0}^2/2), \text{ for } & 8 < F_{D0}^2 < 128 \\ 1.00 & F_{D0}^2 > 128 \end{cases} \tag{7}$$

and

$$F_{D0}^2 = \frac{U_0^2}{R_0 \times (\rho_a - \rho)_0} \tag{8}$$

with

$$R_0 = \frac{D}{2} \tag{9}$$

R_0 represents the radius of the stack as shown in eq 10, and replaces the Gaussian radial length of the plume at the source. The local Gaussian characteristic radial width of the plume at the origin of the ZEF is defined as

$$b_1 = \sqrt{2} \times R_0 \tag{10}$$

The radial width is defined[12,19] as the "*e* folding distance" [i.e., the point along radial plume cross-section where the velocity is that of u_{max} (center of plume) divided by the transient number *e*]

The density can be determined from

$$(\rho_a - \rho)_1 = \frac{1 + \lambda^2}{2 \times \lambda^2 \times f_w(F_{D0})} \times (\rho_a - \rho)_0 \tag{11}$$

with

$$\lambda = 1.257 - 1.606 / F_D^2 \tag{12}$$

and

$$F_D^2 = \infty \tag{13}$$

Equation 14 is taken for a jet region[19] as assumed by this model. The temperature can subsequently be calculated from $P = \rho_1 R_g T_1$. The length is defined from published studies of turbulent defected jets in a cross flow,[9] where the maximum turbulence intensity has been noted (i.e., the uniform core of the jet has been totally eroded)

$$\delta \approx 5 \times D \tag{14}$$

The length of this zone will be overestimated slightly because of the buoyancy characteristics in the first part of the plume. This length is only true for exit-velocity to

wind-velocity ratios (U_0/U_a) of more than 4. Because of the volumetric difference of stack plumes as opposed to experimental jets, the path of the jet is not taken to be vertical in the ZEF, as expressed in eq 15. Instead, the path is taken to follow a slight modification of the Briggs equation for bent-over buoyant plumes[11]

$$y = 3.2 \times \left(g \cdot U_0 \cdot \left(\frac{D}{2}\right)^2 \cdot \frac{T_s - T_a}{T_s} \right)^{\frac{1}{3}} \times x^{\frac{2}{3}} \times U_a{}^{-1} \quad (15)$$

The angle (φ) and the path length of the plume at the end of this zone is determined by differentiating eq 17 at small increment steps of x over the path trajectory until the length δ is reached.

ZEF

For the ZEF, changes of the plume properties with time have been modeled through the conservation of mass, momentum, and energy. Through these conservation fundamentals, the entrainment properties of a plume,[12,14,20] and the Gaussian similarity profile assumed in the ZEF,[12,19,21] the conservation equations can be expressed as

The Equation of Conservation of Mass

$$\frac{d}{ds}\left(\int_0^{b\sqrt{2}} \rho u 2\pi r.dr \right) = 2\pi b \rho_a \left\{ \alpha_1 \left| u^*(s) \right| + \alpha_2 U_a \left| \sin\varphi \right| \cos\varphi \right\} \quad (16)$$

The Equation of Conservation of Momentum in the x *Direction*

$$\frac{d}{ds}\left(\int_0^{b\sqrt{2}} \rho u^2 2\pi r \cos\varphi.dr \right) = 2\pi b \rho_a U_a \left\{ \alpha_1 \left| u^*(s) \right| + \alpha_2 U_a \left| \sin\varphi \right| \cos\varphi \right\} + C_d \pi b \rho_a U_a{}^2 \left| \sin^3 \varphi \right| \quad (17)$$

The Equation of Conservation of Momentum in the y *Direction*

$$\frac{d}{ds}\left(\int_0^{b\sqrt{2}} \rho u^2 2\pi r \sin\varphi.dr \right) = \int_0^{b\sqrt{2}} g(\rho_a - \rho) 2\pi r.dr \pm C_d \pi b \rho_a U_a{}^2 \sin^2 \varphi \cos\varphi \quad (18)$$

with plus sign for $-\pi/2 \le \varphi < 0$
minus sign for $0 \le \varphi \le \pi/2$

The Equation of Conservation of Energy

$$\frac{d}{ds}\left\{ \int_0^{b\sqrt{2}} \rho u \left(\frac{1}{\rho} - \frac{1}{\rho_a} \right) 2\pi r.dr \right\} = 0 \quad (19)$$

Equation 20 implies that the layer of atmosphere through which the plume rises is neutrally stratified

$$\rho_a = \rho_{a0} \quad (20)$$

APPENDIX B: MATHEMATICAL EQUATIONS FOR THE CONDENSATION REACTION MECHANISM FOR PCDD/F FORMATION

The reaction mechanism of the precursor condensation formation of dioxins can be summarized as follows:[7,8]

$$\begin{aligned} g + s &\xrightarrow{k_a} g_s \\ g + g_s &\xrightarrow{k_1} d_s \\ d_s &\xrightarrow{k_2} d \end{aligned} \quad (21)$$

where g is the gaseous precursors (e.g., polychlorinated phenol), s is the solid fly ash particles, g_s is the absorbed precursors, d_s is the absorbed dioxin, and d is the desorbed gaseous dioxin.

The assumptions for the model are[8]

- The post-combustion zone (after the secondary combustion chamber) of the incineration process is characterized by an average temperature of 700 ºC;
- Gas-phase polychlorinated phenols are present at concentrations of ~300 μg/m³;
- The average diameter of the fly ash particles is 10 μm, and the particles have the same composition;
- The particles are spherical solids;
- Fly ash has the same density as silica (i.e., 2.5 g/cm³);
- The number of adsorption sites on the fly ash is 3×10^{14} sites/cm² of surface area;
- The molar ratio of polychlorinated phenols to other molecules capable of undergoing adsorption is 10^{-2}:1; and
- Molecular species that compete with polychlorinated phenols for adsorption sites on the fly ash have adsorption and desorption rates approximately the same as those of polychlorinated phenols.

The following mathematical relations have been derived[7,8] for the condensation reaction mechanism of eq 2:

$$d_s = \left(\frac{Q}{P}\right) \times \left[1 - e^{(-Pt)} \right] \quad \text{(molec/cm}^2\text{)} \quad (22)$$

$$d = \left(\frac{k_2 Qt}{P}\right) - \left(\frac{k_2 Q}{P^2}\right) \times \left[1 - e^{(-Pt)} \right] \quad \text{(molec/cm}^3\text{)} \quad (23)$$

with

$$Q = k_1 g_0 \theta_g \quad \text{(molec/cm}^3\text{/sec)} \quad (24)$$

$$P = \left[\frac{k_1 g_0}{2 \cdot N_p} \cdot \left(\frac{\sigma_g}{\sigma_p} \right)^2 \right] + k_2 \quad (\text{sec}^{-1}) \quad (25)$$

and

$$\theta_g = 0.01 \quad (\text{molec/cm}^3) \quad (26)$$

$$\sigma_p = 5 \times 10^{-4} \quad (\text{cm}) \quad (27)$$

$$\sigma_g = 3 \times 10^{-8} \quad (\text{cm}) \quad (28)$$

$$k_1 = 275 \sqrt{\frac{T}{973}} \cdot e^{\left(\frac{-14{,}850}{R \cdot T} \right)} \quad (\text{sec}^{-1}) \quad (29)$$

$$k_2 = 10^{13} \cdot e^{\left(\frac{-45{,}740}{R \cdot T} \right)} \quad (\text{sec}^{-1}) \quad (30)$$

$$N_p = \frac{M_p}{\left(\frac{4}{3} \right) \cdot \pi \cdot r_p^{\,3} \cdot \rho_p} \quad (\text{particles/cm}^3) \quad (31)$$

APPENDIX C: MATHEMATICAL EQUATIONS FOR THE DE NOVO SYNTHESIS MECHANISM FOR PCDD/F FORMATION

The model assumes the halogenation of the carbon-containing surface of fly ash, either directly from gaseous HCl or from metallic chlorides already absorbed on the surface

$$(C)H + CuCl_2 \longrightarrow (C)HCl^* + CuCl \quad (32)$$

$$(C)HCl^* + CuCl_2 \longrightarrow (C)Cl + CuCl + HCl \quad (33)$$

where (C) denotes a carbon atom in the edge of graphitic layers or in aromatic compounds. Because the carbon is comparatively prevalent, the Cl supply for the reaction mechanism is taken as limiting. The average Cl atoms per molecule of PCDD/F is taken as six, and the rate of PCDD/F formation is, therefore, one-sixth of the Cl absorption rate. The change in concentration of PCDD/F is then calculated from the difference in formation ($r_{ads}/6$) and thermal destruction rates (r_{dest})[9]

$$\frac{dm_p}{dt} = 380 \cdot \frac{A_s}{\beta} \left[\frac{r_{ads}}{6} - r_{dest} \cdot X_p \right] \quad (\text{PCDD/F g/g/sec}) \quad (34)$$

with

$$r_{ads} = \frac{\alpha P}{\sqrt{2\pi MRT}} \quad (\text{mol of HCl/m}^2\text{/sec}) \quad (35)$$

$$r_{dest} = 6.3 \times 10^{12} \exp\left(-\frac{167{,}000}{RT} \right) \quad (\text{sec}^{-1}) \quad (36)$$

and

$$A_s = \frac{6}{1000 \cdot \rho \cdot d} \quad (\text{m}^2\text{/g}) \quad (37)$$

About the Authors

Alan Brent (corresponding author; e-mail: abrent@eng.up.ac.za) has been involved with emissions and process measurements for five years. Further expertise has been directed toward the optimization of large incinerators and the design of small-scale incinerators for rural applications. This work is the result of a master's degree thesis partially conducted at Chalmers University of Technology, Sweden, and the CSIR, South Africa. Alan Brent now fills the Chair in Life Cycle Engineering at the University of Pretoria, whose aims are to develop a competency in life cycle engineering in South Africa. Dave Rogers has been involved in environmental, materials, and process-related measurements for more than 20 years, and incineration for five years. He is currently working on health care waste management projects for developing countries and has been appointed as a temporary advisor to the World Health Organization (WHO) in this field.