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Assessment of off-normal emissions from hazardous waste incinerators
Part II: Assessment of off-normal emission intensity and total emission

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Abstract

This is the second paper in a series of papers which report the results of a study of off-normal emissions from operation of a liquid injection hazardous waste incinerator. Reported in this paper are the results of off-normal emission intensity and total off-normal emissions using probabilistic methods. The results show that, in general, the total off-normal emissions per year for the scenarios analyzed are roughly the same magnitude as the total normal annual emissions for principal organic hazardous constituents (POHCs) and acid gases, and are much lower for particulates. Hence, it appears that for modern liquid injection incinerators, designed and operated according to the assumptions of this study, the off-normal emissions for any emission category may not be significantly large, large enough to increase the order of the magnitude of the overall risk, unless extremely toxic or dangerous wastes are incinerated, and a destruction and removal efficiency (DRE) of 99.9999% is sought.

1. Introduction

The total quantity of off-normal emission Q_0 (kg/year) for a given category can be expressed as:

$$Q_0 = f\,D\,I\,L \tag{1}$$

where f is the frequency, times/year; D the off-normal duration, hours; I the emission intensity (or fraction) under off-normal conditions; L the pollutant load, kg/h. The rationale of the study, the off-normal emission frequency f and duration D were discussed in the first paper of the series [1]. In this paper, the off-normal emission intensity I, pollutant load L and total off-normal emission quantity Q_0 will be considered so that the significance of off-normal emissions can be seen.

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2. Off-normal emission intensity assessment

The emission intensity I for a given failure mode is assessed based on the information available in the literature. It should be noted that the information on emission intensities under off-normal emissions is very limited. Many phenomena are still not well understood. When developing the emission models, many assumptions are made.

For a given fault state, the temperature, flow rate, pressure, and oxygen level, in the combustor, which govern the emission intensity, should have certain values. Therefore, emission intensity should be also determined. In other words, emission intensity has a deterministic nature. However, many factors or parameters that influence emission intensity may not be known exactly; the emission characteristics of the members within each emission category may be different, for example, for given conditions, different principal organic hazardous components (POHCs) might have different destruction and removal efficiencies (DREs) due to the difference in chemical and physical properties. To deal with these complicated situations, the emission intensity will be treated in a probabilistic manner rather than the traditional deterministic way. Namely, emission intensities will be regarded as random variables with probability distributions. The emission intensity for each category will be assessed based on the failure modes identified in the first paper of the series [1].

The emission intensity under off-normal conditions for a given emission category depends on the type of failure mode and the degree of deviation from normal status. In order to simplify the analysis, it is assumed that the emission intensity is a constant during the off-normal emission process. This assumption may not be realistic and emission intensity can be a function of time. Because the current understanding of off-normal emission processes is very poor, it is not feasible to treat the off-normal emission intensity as a function of time for the time being. The constant intensity assumption, however, should not influence the final result significantly since the emission intensity assessed may be regarded as the average intensity during the off-normal emission process.

It is often difficult to know the degree of deviation from the normal status for a given failure mode, which is very important for assessing emission intensity. For instance, if thermocouple drifting occurs, the degree of drifting could be small (a few °F) or large (tens or hundreds of °F). In order to overcome the difficulty, the degree of deviation from the normal status is treated as a random variable with a modified exponential probability distribution. The probability distribution is combined with the emission model to obtain the emission intensity distribution for a given failure mode and scenario. The following sections consider each emission category separately.

2.1 POHC emission intensity

For the POHC category, low temperature, low excess air, high excess air, and poor atomization, four failure modes are considered in off-normal emission frequency analysis. Therefore, the emission intensity corresponding to these failure modes will be analyzed.

2.1.1 POHC emission intensity due to low temperature

Literature review shows that, at the present time, the understanding of the combustion process in the incinerator is still very limited. The only widely used model that describes the destruction kinetics of typical hazardous organic compounds is the simple pseudo-first-order kinetic model [2] and [3]. Because of this reason, this model is used to estimate the order of magnitude of the emission intensity due to low combustion temperature. According to the integrated pseudo-first-order kinetic model, if the thermal decomposition reaction occurs in an atmosphere with sufficient excess oxygen molecular relative to the concentration of waste material, the emission intensity I ($I=1-\mathrm{DRE}$) can be expressed as:

$$I=\exp(-Kt) \tag{2}$$

where t is the residence time in seconds; K is the chemical reaction rate constant, and is expressed by an Arrhenius equation:

$$K=A\exp(-E/RT) \tag{3}$$

where A is the frequency factor, 1/s.; E the activation energy, cal mol^{-1}; R the universal gas constant, 1.99 cal mol^{-1} K^{-1}; T the combustion temperature, K. The values of A and E are dependent upon the type of substance and are measured by experiment. It should be mentioned that there are big discrepancies in the values of A and E from investigator to investigator. For example, the values of A and E for 1,1,1-trichlorethane are given as 3.2×10^{12} (s^{-1}) and 4.79×10^{4} (cal mol^{-1}) respectively in [2], but they are given as 1.9×10^{8} (s^{-1}) and 3.2×10^{4} (cal mol^{-1}) in [4]. For hexachlorobenzene, the values of A and E are determined as 2.17×10^{2} (s^{-1}) and 8.8×10^{3} (cal mol^{-1}) in [5], but are 2.5×10^{8} (s^{-1}) and 4.1×10^{4} (cal mol^{-1}) in [4]. The difference in values of A and E for different materials is also very large. Although the impact of temperature on POHC destruction can be estimated using the above equations, it is found that POHC emission intensity could increase by a factor of 5 to 500 or more for every 100°F decrease in temperature, depending on the type of POHC, the values of A and E, the residence time and initial temperature level used. There is also a question about the applicability of the model used because this model is basically for a non-flame situation, but there are flame zones in the incinerator [3]. No destruction model for a flame zone is available yet since the reaction process in the flame zone is too fast to be described with good accuracy. Because the uncertainty regarding the magnitude of the emission

intensity is large, the emission intensity I is assumed to be lognormally distributed and the parameters of the distribution are determined from the assumption that every 100°F decrease in temperature below the minimum will cause the emission intensity I to increase by a mean factor of 10, 200°F by a mean factor of 100, etc., with an error factor EF of 5. Based on the above assumption, the distribution of the emission fraction I can be written as:

$$f(I)=\Lambda(\mu=\ln m-0.48,\sigma=0.98) \tag{4}$$

where $\Lambda(\mu,\sigma)$ represents a log-normal distribution with parameters, μ and σ, and m is found from:

$$m=10^{-4}\cdot 10^{\Delta T/100} \tag{5}$$

There is still a problem regarding the degree of temperature drifting ΔT. In this study, temperature drifting ΔT is treated as a random variable and assumed to be exponentially distributed with a mean of 100°F and maximum of 400°F. There are two reasons to treat temperature drifting ΔT randomly. First of all, the degree of drifting is a random phenomena and it is difficult to know how much drifting might occur before one does calibration. Secondly, for different POHCs, the minimum temperature required to achieve four nines DRE is different, and therefore the corresponding ΔT also is different. The reason to choose the exponential distribution is that the exponential distribution is a monotonically, quickly decreasing function, which is good for describing temperature drifting, since small drifting is more likely than large drifting. The mean ΔT value of 100°F is assumed since a few incinerator operators mentioned that sometimes two thermocouple readings at the same location could differ from each other by 100°F or more. Also, a few hundred degrees difference in temperature readings using different measuring devices were noticed. The reason to assume that the maximum ΔT would be 400°F is that it is very unlikely that temperature drifting more than 400°F would occur without notice. Equation (5) also requires that ΔT be less than 400°F. According to the above assumptions, the distribution of temperature drifting can be presented as:

$$f(\Delta T)=\frac{\lambda}{(1-e^{-4})}\exp(-\lambda\Delta T) \tag{6}$$

Temperature drifting can be sampled from:

$$\Delta T=-\frac{1}{\lambda}\ln\left[1-U\times(1-e^{-4})\right] \tag{7}$$

where $\lambda=\frac{1}{\overline{\Delta T}}=\frac{1}{100}=0.01$ (1/°F); U is a uniform random variable.

Using the Monte Carlo method (more details can be found in [6] and [7]),

the distribution of the emission intensity I due to low temperature can be obtained. The result is presented in Table 1. The result shows that, the 95th percentile of I is about 0.04, which corresponds to 96% of DRE due to temperature drifting.

2.1.2 POHC Emission intensity due to low/high excess air

Unfortunately, the understanding of excess air impact on destruction efficiency is also not well developed. Although the effect of excess air on destruction efficiency is known qualitatively, a quantitative description is not available. Because of lack of detailed information, the limited experimental data is used for developing the emission model due to low or high excess air.

Kramlich et al. [8] and Staley [9] did experimental studies to investigate the excess air effects on POHC destruction. The result of Kramlich et al. [8] is shown in Fig. 1. A primitive model that is completely based on Kramlich et

TABLE 1

Off-normal POHC emission intensity

Failure mode	I_5	$\bar{I}$	I_{95}
Low temperature	3.0E−5	1.5E−2	3.7E−2
Low excess air	9.5E−4	2.6E−2	1.0E−1
High excess air	2.5E−4	9.4E−3	3.6E−2
Poor atomization	9.7E−4	2.6E−2	1.0E−1

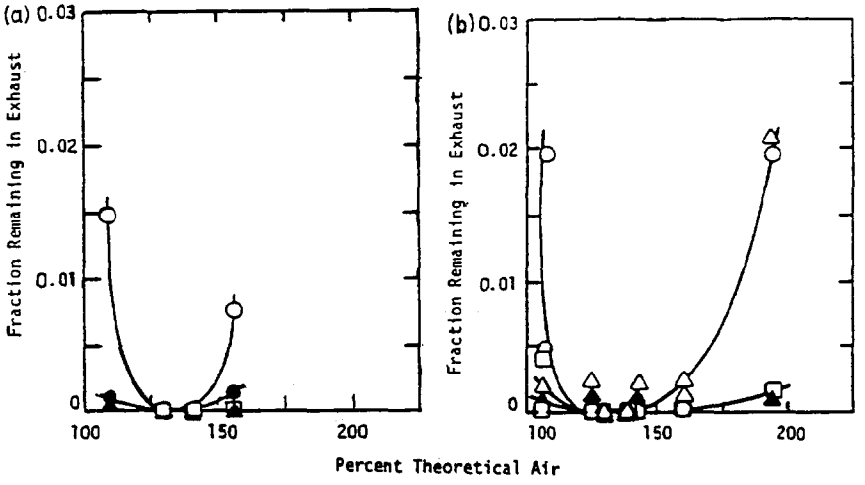

Fig. 1. Impact of excess air on POHC emission intensity (from [8]). (a) Mixture containing chloroform (○), benzene (△), acrylonitrile (▲), and chlorobenzene (□). (b) Mixture containing chloroform (○), acrylonitrile (▲), chlorobenzene (□), 1,2-dichloroethane (●).

al. experimental results is developed, since not much information is available. From the information provided by some incinerator operators and designers, usually when excess air is below 3%, low destruction efficiency could be anticipated, since perfect mixing between organic molecules and oxygen can never be achieved. Therefore, the low excess air region is considered to be in the range below 3% of excess air. It can be seen from Fig. 1 that, in the low excess air region, the emission fraction (or emission intensity) I could be approximated as a linear function of the excess air, and the analytical expression could be approximately written as:

$$\bar{I}=10^{-4}+\frac{2\times10^{-2}-10^{-3}}{3}(3-EA) \quad EA\leqslant 3 \tag{8}$$

where EA is excess air in percentage.

It should be noticed in Fig. 1 that the low excess air effect is quite different for different POHCs. Hence, using eqn. (8) to represent the relationship between the low excess air and the emission fraction of all POHCs may not be adequate. To avoid the deficiency, it is assumed that, (1) the emission intensity I is lognormally distributed; (2) the mean value of the emission intensity is determined from eqn. (8), and the error factor of the distribution is 5. Based on these assumptions, the distribution of the emission intensity I can be expressed as:

$$f(I)=\Lambda(\mu=\ln m-0.48,\sigma=0.98) \tag{9}$$

where m is determined from:

$$m=10^{-4}+(2\times10^{-2}-10^{-3})\left(1-\frac{EA}{3}\right) \tag{10}$$

Similar to the treatment of temperature drifting discussed previously, the low excess air EA is assumed to be exponentially distributed. The mean of low excess air is estimated at 1.5% because one incineration facility mentioned that it was very common for their incinerator to run at 1.5% of excess air. With these assumptions, the probability density function of the low excess air EA can be written as:

$$f(EA)=\lambda e^{-\lambda(3-EA)} \quad EA\leqslant 3 \tag{11}$$

where $\lambda=1.5$ and is determined from the mean of EA.

Since all of the information for the Monte Carlo simulation has been determined, the distribution of the POHC emission intensity for low excess air can be obtained, and the result is shown in Table 1. The 95th values of the emission intensity I is 0.1, which means that, based on the model developed, low excess air could have a very big impact on DRE. Following the same approaches, the emission intensity I corresponding to high excess air is obtained and presented in Table 1.

2.1.3 POHC Emission intensity due to poor atomization:

Kramlich et al. [10] indicated that there are two general mechanisms by which poor atomization can influence DRE. In the first one, droplets are too large to evaporate in the available time and penetrate to the reactor wall. The liquid evaporates and exits the combustor along the cold boundary layer at the wall. In the second mode, the droplets penetrate through the flame-zone without fully evaporating until well into the post-flame region, where mixing or temperature may not be sufficient to ensure complete destruction. But at the present time, it is still not possible to describe these effects quantitatively with good accuracy. There are also many factors that could influence nozzle atomization, such as low atomization pressure, nozzle worn or plugged, improper nozzle alignment, high viscosity of liquid wastes, etc. Except pressure and viscosity, others are even difficult to describe quantitatively. Different POHCs may have a different response to poor atomization. Considering these factors, the emission intensity model due to poor atomization will not be incorporated with the degree of a particular fault or the type of fault. It is assumed that the emission intensity is lognormally distributed. Based on the Kramlich et al. [10] study, it is estimated that the minimum emission intensity of an atomization failure is 10^{-3}, maximum emission intensity 10^{-1}, and these values are regarded as the 5th percentile and the 95th percentile, respectively. Then:

$$f(I) = \Lambda(\mu = -4.605, \sigma = 1.400)$$

2.2 Particulate emission intensity

Off-normal particulate emission could occur if the charging voltage of the IWS system is low, the scrubbing liquid flow rate is low, and the combustion temperature is high. The emission intensities corresponding to the above failure modes are analyzed as the following:

2.2.1 Particulate emission intensity due to low charging voltage

According to the information provided by an ionizing wet scrubber (IWS) designer [11], the voltage effect on particulate removal efficiency in an IWS system is similar to the voltage effect in an electrostatic precipitator (ESP), namely, the particulate removal efficiency of the IWS varies exponentially as a function of the operating voltage squared. The particulate removal efficiency that is expressed as a function of the charging voltage can be written as:

$$RE_V = 1 - e^{-CV^2} \tag{12}$$

where V is the charging voltage; C a constant which is independent of voltage, but depending on the flue gas flow rate, particular diameter, particle properties, etc. In principle, the effect of charging voltage on particulate removal can be calculated using the above equation. However, it is well known that, for a given voltage, the smaller the particle diameter, the lower the removal effi-

ciency. In other words, lowering voltage has a larger impact on smaller particles than larger ones. Keeping this in mind, it is easy to understand that it is necessary to have the removal efficiency expressed as a function of particle diameter under normal conditions. Fortunately, this information is provided by a company [12], as shown in Fig. 2. For the sake of convenience, it is better to have an analytical expression of the removal efficiency as a function of particle diameter. The least square curve fitting technique is used to obtain the analytical expression from Fig. 2, and the result is:

$$RE_d(d) = 0.86 + 0.412(\log_{10} d) + 0.20(\log_{10} d)^2 \quad 0.01 \leqslant d \leqslant 1$$

and

$$RE_d(d) = 1 - 0.14 e^{-4.767 \log_{10} d} \quad d \geqslant 1 \tag{13}$$

where d is the particle diameter in μm (microns).

In order to apply the above equation, the particle diameter distribution is required. At the present time, it is not possible to compute the particle size distribution accurately. Following the convention, the particle-size is assumed to be lognormally distributed. For a liquid injection incinerator, the mean particle diameter is on the order of microns according to several sources [13], [14] and [15]. Because of the uncertainty about particle size distribution, a number of mean diameters is used to see the impact of different particle size distribution.

To estimate the effect of lowering voltage, one has to know how low the

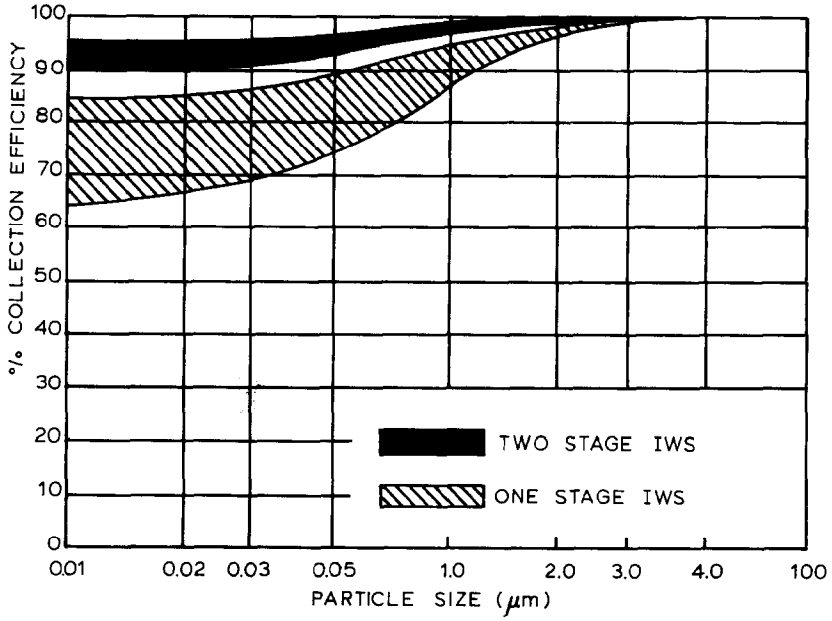

Fig. 2. IWS collection efficiency vs particle size (from [12]).

voltage goes. For the unnoticed (or drifting) scenario, the degree of voltage drifting is modeled as exponentially distributed, and the normalized voltage can be sampled from:

$$V^n = \frac{1}{\lambda}\ln[1+U(e^{\lambda}-1)] \tag{14}$$

where $V^n = V_{off}/V_n$, normalized voltage, dimensionless; $\lambda = 8$, determined from the mean value of V^n, which is assumed equal to 0.9; U random variable from the uniform distribution.

With this information available, the intensity of particle emissions due to voltage drifting is calculated as follows:

(1) For a given particle diameter, determine the removal efficiency under normal voltage using Equation (13). The emission intensity under normal condition is $I_n = 1 - RE_d(d)$;

(2) Determine CV^2 from Equation (12), $CV^2 = -\ln(1-RE_d(d))$;

(3) Generate V^n from eqn. (14);

(4) Off-normal emission intensity $I_{off} = e^{CV^2(1-V^{n^2})}(1-RE_d(d))$

Since two-stage IWS system is used in the facility, it is necessary to consider the two-stage effect. Although it is a two-stage system, the power supply and control systems are the same from both units. Therefore, it is reasonable to assume that if voltage drifting occurs, both units will be affected (common cause failure). Under this condition, above step 4 is modified as:

$$I_{off} = (e^{CV^2(1-V^{n^2})}(1-RE_d(d))^2 = e^{2CV^2(1-V^{n^2})}(1-RE_d(d))^2$$

The results of the particle emission intensity distribution due to low voltage are presented in Table 2. It can be seen from Table 2 that, the 95th percentile of particle emission intensity could be as high as almost 30% due to lowering charging voltage, which is large compared to the normal particle emission intensity (about 1% to 5% for IWS system). Another observation from this table is that the smaller the particle size, the higher the emission intensity, which is expected.

TABLE 2

Off-normal particulate emission intensity

Failure mode	I_5	$\bar{I}$	I_{95}
Low voltage ($d=0.2$)	9.7E−2	1.5E−1	3.0E−1
Low voltage ($d=1.0$)	4.7E−2	8.5E−2	1.9E−1
Low liquid flow	5.4E−2	1.1E−1	1.9E−1
High temp ($d=0.2$)	9.3E−2	9.4E−2	9.5E−2
High temp ($d=1.0$)	4.5E−2	4.7E−2	5.1E−2

2.2.2 Particulate emission intensity due to low scrubbing liquid rate

This should include the scenarios where, although liquid flow rate does not decrease, the flue gas flow rate increases significantly. It is the liquid–gas ratio that influences the removal efficiency. Sheppard of Ceilcote Co. (IWS manufacturer company) thinks that the effect of liquid flow rate would be insignificant or small, but admits that no data exists to support his opinion, and when scrubbing liquid is turned off completely, particle removal does degrade appreciably [11].

Since the effect of the scrubbing liquid flow rate in IWS is very similar to that of a venturi scrubber, the venturi scrubber modeling of liquid flow rate effect on particulate removal can be used. Calvert derived [16] that the removal efficiency can be expressed as:

$$RE = 1 - e^{-r B}$$

where r is the ratio of liquid flow rate and gas flow rate; B constant, independent of r.

Based on the Calvert's study [16], for normal operation of a venturi scrubber, r is in the range of 0.7 to 2.7 l/m^3. According to the above equation, when $r=0$, $RE=0$, which means no scrubbing liquid, then there is no particle removal. This is true for a venturi scrubber. However, the inertial impact is not the only mechanism that removes particulates in an IWS. As a matter of fact, the electrostatic attractive force plays a more important role for particle removal in an IWS. If it is assumed that 80% of the particles are removed by the electrostatic attractive force, 20% by the inertial impact, the removal efficiency at $r=0$ would be 80%. Considering the fact that r is in the range of 0.7 to 2.7 l/m^3 for normal operation, it is assumed that, when r is less than 1 l/m^3, there would be an appreciable impact on particle removal, and when $r=1.0$/m^3, $RE=95\%$. Using these conditions, one can get:

$$I = 1 - RE = 0.2e^{-1.386r} \quad 0 \le r \le 1 \tag{15}$$

The r is also treated as a random variable, and assumed to be exponentially distributed with a mean of 0.5, i.e.:

$$f(r) = \frac{1}{e^{\lambda} - 1} \lambda e^{\lambda r} \tag{16}$$

where $\lambda = 0.01$, determined from the mean of r.

All of the information required for determining the emission intensity is known, the the result is obtained and shown in Table 2.

2.2.3 Particulate emission intensity due to high combustion temperature

Combustion temperature is one of the most important parameters that affect heavy metal emissions. Wallace et al. [17] mentioned a case where higher metal emission was noticed due to higher temperature. Temperature has two

effects on metal emissions (in the form of particles): (i) the particle size distribution, which may affect the performance of air pollution control devices; (ii) the quantity of metal vaporized, which determines the amount of metals available for condensation to form new particles. The general trend is that, the higher the combustion temperature, the smaller the particle size and the larger the quantity of metal vaporized. For a liquid injection incinerator, the metals in the waste feed stream usually are not in solid form (dissolved in liquid), and the second effect is anticipated to be small. Therefore, the second effect is not considered for the liquid injection incinerator.

According to Friedlander [18] and Barton et al. [19], there are two mechanisms by which metal vapors can be condensed: homogeneous condensation and heterogeneous condensation. Homogeneous condensation involves the formation of new particles while heterogeneous condensation involves the formation of new surface layers on existing particles. Homogeneous condensation and heterogeneous condensation usually compete for condensing material and the dominant mechanism determines the characteristics of particle size distribution. Homogeneous condensation is responsible for the presence of the large number density of very fine particles (micron and submicron size) that are found in the effluent gases of incinerators. Particles in these ranges are particularly troublesome because they are the ones that are most likely not to be captured completely in air pollution control devices. Once they escape from the incinerator, they may travel a very long distance from the point of generation. The fine particles are also the ones most easily inhaled into the respiratory systems, and are likely to be the most toxic.

For the liquid injection incinerator, it is reasonable to assume that homogeneous condensation is dominant for particle formation since the number of the existing particles may not be very large. The size of particles formed by homogeneous condensation can be estimated based on thermodynamic considerations, as presented by Friedlander [18]:

$$d=\frac{4\sigma v_{\mathrm{m}}}{kT\ln\frac{p_{\mathrm{d}}}{P_{\mathrm{s}}}}=\frac{4\sigma v_{\mathrm{m}}}{kT\ln S} \tag{17}$$

where d is the diameter of the newly formed particle; σ the surface tension; v_{m} the molecular volume; k the Boltzmann constant; T the temperature; p_{d} the equilibrium vapor pressure; p_{s} the vapor pressure above a flat surface.

Suppose that σ, v_{m} and S are independent of temperature (this assumption may not be true and only an approximation), the temperature effect on particle size can be determined from:

$$d_{\mathrm{h}}=\frac{T_{\mathrm{n}}}{T_{\mathrm{h}}}d_{\mathrm{n}}=\frac{T_{\mathrm{n}}}{T_{\mathrm{n}}+\Delta T}d_{\mathrm{n}}=\frac{d_{\mathrm{n}}}{1+\frac{\Delta T}{T_{\mathrm{n}}}} \tag{18}$$

where d_h is the mean particle diameter at high temperature T_h; d_n the mean particle diameter at normal temperature T_n; and $\Delta T = T_h - T_n$.

The distribution of ΔT can be treated in the same way as the temperature drifting to the lower end, as discussed in the previous section. Therefore, the particle size change due to high temperature can be calculated. Using the removal function $RE_d(d)$, defined in eqn. (13), the particle emission intensity under high temperature conditions can be obtained. The results show that, for the temperature ranges modeled, the influence of temperature on the particle emission intensity is small, as shown in Table 2.

2.3 Acid gas emission intensity

2.3.1 Acid gas emission intensity due to improper pH value in the scrubbing liquid

The pH value in scrubbing liquid indirectly indicates the acid gas removal. The lower the pH value of the scrubbing liquid, the lower the acid gas removal efficiency is. This is the inference of Henry's law [20], which says that the concentration of a chemical in the gaseous phase is proportional to the concentration in the liquid phase under equilibrium conditions. On the other hand, pH value is the indication of HCl concentration in the liquid phase.

Acidity is expressed as pH, which is defined as the negative exponent of the power of ten which indicates the fraction of one mol of hydrogen ions per liter in solution, i.e. $\mathrm{pH} = -\log_{10}[H^+]$, where $[H^+]$ denotes the thermodynamic activity of hydrogen ions [21].

Based on the above definition, pH decreases by 1 unit when the activity of hydrogen ions in solution increases by a factor of 10, which implies a 10 times higher HCl concentration in the gaseous phase according to Henry's law, and thus a higher HCl emission from the incinerator stack for the current study. Although the equilibrium condition in the IWS for HCl is not likely to be reached, the equilibrium condition is assumed since the calculation of HCl concentration in gaseous phase under non-equilibrium conditions is a very complex issue and is beyond the scope of the study.

Using above arguments and assumptions, the HCl emission intensity I can be written as:

$$I = 0.01 \times (10)^{\Delta \mathrm{pH}} \quad 0 \leqslant \Delta \mathrm{pH} \leqslant 2 \tag{19}$$

In eqn. (19), it has been assumed that, under normal pH condition, the acid gas removal efficiency is 99%, which is the federal requirement. There are two reasons that ΔpH is required to be less than 2. First, an incinerator operator indicated that, from their experience, pH analyzer drifting usually was less than 2 (most of the time about 1 or less). Second, if $\Delta \mathrm{pH} > 2$ in eqn. (19), the emission intensity I would be larger than 1, which has no physical meaning.

The ΔpH is treated as exponentially distributed. The mean value is estimated as 1 according to the information given by an operator.

$$f(\Delta pH) = \frac{\lambda}{1-e^{-2\lambda}} e^{-\lambda \Delta pH} \quad 0 \leqslant \Delta pH \leqslant 2 \tag{20}$$

where $\lambda = 0.01$, determined from the mean value of ΔpH.

The ΔpH can be sampled from:

$$\Delta pH = -\frac{1}{\lambda} \ln[1 - U(1-e^{-2})] \tag{21}$$

Combination of eqns. (19) and (21) gives the distribution of emission intensity due to pH analyzer drifting. The result is presented in Table 3. It is interesting to note that the acid emission intensity could be as high as 79% based on the model.

2.3.2 Acid gas emission intensity due to low scrubbing liquid flow rate

Another mechanism other than chemical reaction by adding caustic solution for acid gas removal is diffusion and physical absorption. This mechanism is very much influenced by the scrubbing liquid-to-gas ratio. According to Sheppard [11], the effect of liquid flow rate on acid gas removal is very similar to that on particle removal, as discussed in Section 2.2.2. The only difference is the value of the parameters in eqn. (15). Bonner et al. [22] pointed out that, determination of the minimum liquid-to-gas ratio theoretically for acid gas removal is a very complex issue; industrial experience and test are suggested. Since the liquid-to-gas ratio r is in the range of 0.7 to 2.7 l/m^3 for the venturi scrubber as mentioned earlier, it is assumed that, when $r = 1$ l/m^3, $RE_{acid} = 99\%$, and $r = 0$, $RE_{acid} = 0$. Then:

$$I = 1 - RE = e^{-4.605r} \quad 0 \leqslant r \leqslant 1 \tag{22}$$

The distribution of r has been discussed previously and is given in eqn. (16). As shown in Table 3, based on the above acid emission intensity models, the acid emission intensity due to low scrubbing liquid flow rate is similar to that due to low pH value in the scrubbing liquid.

TABLE 3

Off-normal acid emission intensity

Failure mode	I_5	$\bar{I}$	I_{95}
Low pH value	1.2E−2	2.1E−1	7.9E−1
Low liquid flow	1.3E−2	2.1E−1	7.8E−1

3. Total off-normal emission assessment

In the previous section and the first paper of the series [1], off-normal emission frequency, duration and intensity have been discussed. In this section, the total emissions. Since frequency f, duration D, and intensity I have been solved, the remaining tasks are to determine the distributions of pollutant load L, and assemble f, I, D and L together, using the Monte Carlo simulation technique to produce the distribution of total emission Q_0. The details of the sampling procedures can be found in references [6] and [7]. In order to see the importance of off-normal emissions compared to normal emissions, the total off-normal emissions for each scenario are expressed as the ratio of normal annual emissions. For normal emissions, 99.99% of DRE, 99% of removal efficiency, and 99% of removal efficiency are assumed for POHC, particulate and acid gas, respectively. The results for POHC, particulate and acid gas are presented in the following sections.

3.1 Total POHC emissions

POHC load in feed depends on two factors: (1) POHC weight fraction fr in wastes; (2) wastes feed rate F. It should be noticed that not all of the wastes in feed is regarded as POHCs. Usually, only a small portion of the wastes in feed is POHCs and the fraction of POHCs may vary from waste to waste. The waste feed rate also could change from time to time due to different reasons. Because of these facts, both POHC fraction fr and waste feed rate F are modeled as lognormally distributed. The mean value and 95% percentile of POHC fraction fr in wastes are estimated as 0.3 and 0.8 respectively, based on the information provided by a plant. Using these assumptions, the parameters μ and σ of the distribution for fr are determined as:

$$fr = \Lambda(\mu = -1.8, \sigma = 0.78)$$

For waste feed rate, the nominal feed rate for this incinerator is designed as 1000 kg/h. Therefore, it is reasonable to assume the mean feed rate is 1000 kg/h. Although waste feed rate may change with time, it is not likely that waste feed rate varies greatly, as indicated by an incinerator operator. Hence, a small error factor of 2 is assumed for waste feed rate. The parameters are determined as:

$$F = \Lambda(\mu = 6.8, \sigma = 0.42)$$

Since the distribution of the product of two log-normal distribution variables is still a log-normal distribution, the distribution of POHC load L is also a log-normal distribution with parameters:

$$L = Fr \times F = \Lambda(\mu = 5.0, \sigma = 0.89)$$

Using the simple Monte Carlo simulation technique, FORTRAN programs are

TABLE 4

Total off-normal POHC emission

Failure mode	Q_5	$\bar{Q}$	Q_{95}
	2.3E−5	7.3E−2	1.3E−1
Low excess air	2.4E−5	2.0E−2	6.7E−2
High excess air	5.0E−4	4.7E−1	1.3E+1
Poor atomization	2.5E−5	2.2E−2	6.6E−2

TABLE 5

Total off-normal particulate emission

Failure mode	Q_5	$\bar{Q}$	Q_{95}
Low voltage (d=0.2)	6.2E−5	7.7E−3	3.1E−2
Low voltage (d=1.0)	3.2E−13	2.6E−4	1.1E−5
Low liquid flow	1.2E−4	6.8E−3	2.7E−2
High temp (d=0.2)	3.7E−5	2.0E−3	7.8E−3
High temp (d=1.0)	4.1E−5	1.9E−3	7.7E−3

written and run on the IBM 3090 machine. The results for different scenarios are presented in Table 4. As can be seen, the upper limit (95th percentile value) of POHC off-normal emissions is about 1.3 times of the normal emission.

3.2 Total particulate emissions

Particle load in the flue gas depends on three factors: waste ash content (expressed as the percentage of the waste weight), waste feed rate, and the fraction of the bottom ash. For liquid injection incinerators, it is reasonable to assume that the amount of bottom ash is negligible, and all of the ash becomes fly-ash. In this case, particle load in flue gas only depends on the waste ash content and waste feed rate. Since waste ash content may vary from waste to waste and from time to time, it is assumed to be log-normally distributed. The distribution of waste feed rate has been discussed in the previous section and will not be repeated here. For liquid waste, the ash content AC is seldom larger than 3%. Therefore, it is assumed 95th percentile of ash content is 3%, 5th percentile 0.1%. Using these values, the parameters of ash content distribution are determined as:

$$AC = \Lambda(\mu = -5.207, \sigma = 1.034)$$

Particle load function L is:

$$L = F \times AC = \Lambda(\mu = 1.6, \sigma = 1.1)$$

The results for off-normal particulate emissions are presented in Table 5.

TABLE 6

Total off-normal acid emission

Failure mode	Q_5	$-Q$	Q_{95}
Low pH value	3.9E−3	4.2E−1	1.8E+1
Low liquid flow	3.8E−4	6.1E−2	2.5E−1

Compared to normal annual particulate emissions, the off-normal particulate emissions are not significant (maximum about 3% of normal annual emission).

3.3 Total acid gas emission

It is assumed that HCl is the major acid gas that is of concern. The HCl load in flue gas depends on: (1) the weight fraction of Cl_2 fr in wastes; (2) waste feed rate F. Namely, the HCl load function L can be written as:

$$L=fr\times F\times 1.03$$

Since one kilogram of Cl_2 can convert into $36.54/35.54=1.03$ kilogram of HCl, a correction factor 1.03 appears in above equation. The fraction of Cl_2 in wastes varies greatly, and is assumed to be log-normally distributed. According to the information provided by an incineration plant, the mean fraction of Cl_2 (by mass) in their wastes was about 5%, and sometimes it could reach 15% or higher. Although the concentration of Cl_2 in wastes is plant specific, those values provided by the operator are quite typical and used to determine the parameters of the fraction distribution, i.e., the mean of 5th and 95th percentile of 15% are assumed. Based on these values the distribution of Cl_2 fraction in wastes can be determined as:

$$fr=\Lambda(\mu=-3.430,\sigma=0.9317)$$

Therefore, the HCl load distribution is:

$$L=1.03\times fr\times F=\Lambda(\mu=3.419,\sigma=1.023)$$

The results in Table 6 show that off-normal acid gas emission could be as high as 1.8 times of the annual normal acid emissions.

4. Conclusions and recommendations

From the current study, the following conclusions can be drawn:

(1) The off-normal POHC emissions for the scenarios considered should not increase significantly the overall risks arising from incinerator operation. This conclusion is based on the fact that, for the worst case (95th percentile value), the total off-normal POHC emissions are roughly equal to the annual normal POHC emissions (four nines of DRE for normal POHC emissions).

Based on the current dose-response information, for most of the chemicals, an increase in source term by a factor of two is not a significant increase, and should not affect the order of magnitude of the overall risks that arise from incineration. However, for very toxic materials, such as chemical weapons, etc., usually six nines of DRE are required for normal operation, which means the normal POHC emission Q_n is 10^2 times lower than that of four nine DRE case. Consequently, for the same quantity of off-normal emission Q_0, the ratio Q_0/Q_n would be 10^2 times higher than that for four nines of DRE case. This large increase implies that off-normal POHC emission could be significant when extremely toxic wastes are incinerated.

(2) The results show that, the off-normal particulate emission is not significant compared to the annual normal particulate emission for all of the failure modes and scenarios considered (the maximum 95th percentile is about 3% of the normal annual particle emission).

(3) For acid gas emissions, the mean off-normal emission is about 40% of the normal annual acid gas emission, and the 95th percentile about 180%. Since the toxicity of acid gases to human is not very high, the direct impact of off-normal acid emission on human health may not be significant. However, it might be important for the natural environment.

In general, the conclusion is that, based on the current study of a modern incinerator design, the off-normal emissions for any emission category may not be significantly large, i.e. large enough to increase the order of the magnitude of the overall risk, unless extremely toxic or dangerous wastes are incinerated, and a DRE of 99.9999% is sought.

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