RELATIONSHIPS BETWEEN VARIABILITY OF EMISSIONS
AND RESIDUES FROM COMBUSTION OF MUNICIPAL SOLID WASTE
AND WASTE COMPOSITION AND COMBUSTION PARAMETERS

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A serious difficulty in finding relationships between combustion parameters and emissions, especially of trace organics such as PCDD and PCDF, is the length of time required to collect samples of sufficient quantity to obtain measurements of such trace components. Tests of four to 12 hours may be needed to obtain sufficient quantities to exceed the detection limits of analytical devices. Hence, PCDD and PCDF data represent average conditions over these long periods, during which substantial variations and fluctuations have taken place. Variations in results between tests performed under supposedly identical conditions of the control variables reflect the stability of control which was maintained, as well as secondary variables.

Carbon Monoxide as a Surrogate for Good Combustion

Carbon monoxide (CO) measured in the products of combustion has been found to be a useful indicator of success in destroying organics since CO is created by the flame and is more difficult to convert to CO₂ than the other organic compounds, including methane.

The extent to which CO measurements relate to the emissions of critical toxic compounds such as PCDD and PCDF has been a matter of much debate, since the phenomena involved are complex, and related both to the combustion process and the post-combustion regions of the boiler. However, data from tests of numerous facilities show the same general linearity between CO and total PCDD+PCDF. Tests of the rotary kiln MWC in Amager, Denmark also demonstrate linearity between the Toxic Equivalent 2,3,7,8 TCDD and carbon monoxide while the furnace was operated under startup, shutdown low and high firing rates and even sludge burning.(8)(12)

Furnace Temperature and Oxygen as Control Parameters

The variations in PCDD and PCDF with combustion parameters such as temperature, oxygen and CO are remarkably similar, although the relationships are not sharply defined. Increasing temperature, reducing oxygen, and reducing CO all serve to reduce PCDD and PCDF up to a certain point.(12) Therefore controlling oxygen is an alternate method of controlling temperature, although the temperature will then vary with the moisture content of the MSW.

Figure 3 shows the PCDD plus PCDF data obtained at Pittsfield plotted versus secondary furnace temperature for 8 separate tests wherein the waste composition and operating conditions were varied. Each test condition was repeated, with all conditions maintained constant. In spite of this, a wide divergence was found between supposedly duplicate runs. If a large number of test runs had not been undertaken, it would not have been possible to establish trends in the data. Figure 3 shows carbon monoxide plotted versus temperature for comparison with Figure 4. It is apparent that CO and PCDD+PCDF have similar trends with furnace temperature, and that on logarithmic paper the data tend to follow straight lines. However, although the lines point toward zero as temperature rises, emissions increase above about 1700°F, measured after
Two phenomena require investigation in these graphs: the dispersion between pairs of duplicate test points in PCDD+PCDF data, and the increase noted with increased temperature.

Examination of data from Pittsfield in the region where CO is low (below 50 ppmv or so), shows wide scatter, as noted above. Similar increases in PCDD and PCDF were noted in PEI data at low CO. When the background data for these duplicate tests are examined in search of other variables, it is found that MSW moisture is a factor. It is noted that the higher PCDD/DF points represent tests with higher moisture and lower points have lower moisture content. Thus it appears that moisture influences either the PCDD+PCDF or the CO readings, or both.

At temperatures above the 1700°F point the Pittsfield data show that the lowest CO readings correspond to the highest PCDF emissions, indicating that another factor, probably shortage of oxygen, causes furans, rather than dioxins, to form.

Figure 3. Carbon Monoxide (CO) and Total Dioxins and Furans versus Furnace Temperature After Addition of Secondary Air.

The Pittsfield tests have provided the most comprehensive set of data on PCDD and PCDF emissions measured at the boiler outlet. Figure 3 shows both carbon monoxide (CO) and total PCDD+PCDF emissions versus the secondary furnace temperature (fully mixed after secondary air has been
added). The data are plotted as micrograms per ton rather than nanograms per cubic meter (ng/Nm$^3$), showed a somewhat more consistent correlation. The logarithm of CO emissions data falls on a straight line throughout the wide range of secondary furnace temperatures, pointing to a virtual minimum at 1700°F, indicating logarithmic decay. At higher temperatures, a leveling off, or a sharp rise is found. The highest rise is noted for tests with dry commercial waste, waste with PVC added, or tests with low oxygen. The lowest emissions were from tests with water added to the waste. (12)

These data indicate that efforts to achieve temperatures (after secondary air has been mixed in) of 1800 F or higher may be counterproductive from the standpoint of dioxin destruction. The context of these tests should be understood: the Pittsfield MWC uses flue gas recirculation as a means to adjust and maintain furnace temperatures, in addition to adjusting excess oxygen. As temperatures were increased above 1750°F, excess oxygen was reduced from 9% to as low as 6.5%, due to limitations on combustion air capacity. This caused more flue gas recirculation to be applied in order to hold down the temperature. The high moisture MSW did not call for as much recirculation, but suffered the same drop in excess oxygen with increased temperature.

Comparison of Pittsfield and Quebec Test Data

Figure 4 shows the relationship between the logarithm of total PCDD+PCDF and furnace temperature. The hollow points show the data obtained during the Pittsfield tests, and the solid points the data from the Quebec City Emission Characterization Tests. In both cases the temperatures were measured after secondary air injection. The data from both sources, one a refractory furnace, the other having a waterwall furnace, fall within the same range.

Poor operating conditions of the Quebec MWC produced total PCDD+PCDF in the 500 to 1000 ng/Nm$^3$, whereas good conditions produced emissions from 40 to 300 ng/Nm$^3$.

The range of emissions at any given temperature in both cases was generally about one order of magnitude (ten times), showing that temperature alone is not the only variable.

The Pittsfield data include points ranging from 900 down to 13 ng/Nm$^3$. The points with high moisture fuel lie at the lower boundary of the range, whereas the points representing runs with large amounts of PVC added are on the upper boundary. The data show that the high emissions at temperatures over 1800°F reflect greatly increased furans, hence may be the result of lack of oxygen at higher temperatures.

There is a remarkable correspondence between the Quebec City data and the Pittsfield data, in spite of the difference in technology. The Quebec data represent five operating conditions (15 data points), whereas the 24 separate test runs at Pittsfield represent 12 different conditions, and hence provide a more detailed continuum of data. The
evidence that best combustion occurs when undergrate air has approximately zero excess air. It must not be overlooked that this is an average over the entire grate, hence local conditions will include starved air and excess air regions. In any case, it is evident that starved air conditions are favorable in the region of rapid combustion, limiting surges in combustion, minimizing lifting of flaming material, preventing excessively high temperatures, and producing volatile gases to be burned above the grate.

Figure 5. Logarithm of total PCDD+PCDF versus Stoichiometric Ratio of Underfire Air, calculated from Quebec data.

CONTROLLING COMBUSTION

In order to control combustion and maintain optimum conditions, it is necessary to measure some parameter and use this measurement to actuate controls such as feeders and combustion air dampers. Furnace temperatures have been used, traditionally, and oxygen controls have been found to give stable control. However, furnace temperatures are difficult to measure, since the desired temperatures are destructive of the sensing devices. To avoid this problem, sensors are located at the outlet of the furnace, or beyond, so that actual flame temperatures are not measured. New temperature-measuring devices are being tried, with
Combustion fluctuations

Continuous recordings of oxygen and CO readings give important information about the relationship between these variables. When simultaneous readings are plotted against each other, a general relationship is found, as shown in Figure 6. These data, from Pittsfield tests, show a wide range of operation and specific areas representing tests where temperature was held constant within about 20°F. The variation in CO is the result primarily of excess oxygen, but the effectiveness of mixing and also of the presence of moisture can be expected to change the CO emissions even at constant temperature.

![Figure 6](image)

Figure 6 Envelopes of CO and Oxygen Continuous Emission Data from Pittsfield Tests at Various Constant Furnace Temperatures.

Another factor, harder to discern, is the degree of mixing of fuel and oxygen. The importance of mixing increases as available excess oxygen decreases. It is evident from Figure 6 that below about 6% excess oxygen unstable conditions have taken place, with spikes in CO. Continuous graphs of CO during these tests show the presence of CO spikes under both the low and high temperature conditions. These can be attributed to pockets of poorly-mixed reactants, where the air/fuel ratio departs grossly from the optimum. The lower the amount of excess oxygen, on average, the greater the probability of local deficiencies, and the greater the need for high-energy mixing effort.
Control systems which attempt to maintain either furnace temperature or oxygen improve the consistency of operation, but are still subject to oscillations which create some variability in emissions. When continuously recorded data is analyzed statistically, the variation is found to have the familiar bell-shaped curve reflecting random conditions. The range of variation, which can be defined by calculating the standard deviation, conveniently reflects the 'tightness' of control. Of course the range of control can be judged directly by looking at recorder trend charts, such as Figure 7. This graph shows an upset, and reveals the amount of time the oxygen control system took to return to normal operation after an interruption in feed (about 15 minutes).

![Figure 7. Variations in Oxygen Measured at the Furnace Outlet by a Continuous Monitor Trend Recorder.](image)

Distribution of oxygen and carbon dioxide data

The control system of a MWC has the function of adjusting combustion air to suit the amount of fuel being oxidized at a given moment. Whether the control sensor measures oxygen or whether temperature is used to control combustion air, there will be fluctuations in the actual excess oxygen, and consequently in the amount of CO produced.

The histogram shown in Figure 8 represents the variations in excess oxygen readings averaged for one hour, over the course of 100 hours'
operation of a MWC. The peak is between 10.5 and 11% oxygen, dry basis, which corresponds to about 8.5 to 8% oxygen on a wet basis. The distribution is symmetrical about the mean, except for a separate population of oxygen readings close to 16% representing readings taken during a weekend shutdown when auxiliary fuel was used to keep the furnace hot.

![Histogram of Oxygen Readings](image)

Figure 8. Histogram of Oxygen Readings

The corresponding CO data in Figure 9 show a skewed histogram, with characteristic of log-normal distributions. The CO readings show less sensitivity to excess oxygen. About 3% of the data show about 93 ppm of CO, which was characteristic of firing with auxiliary fuel when MSW was not being burned.

The standard deviation and coefficients of variation of data obtained from continuous emission monitoring can be used as an indication of the quality of the combustion control system. In this case, the s.d. of the CO data, averaging 29 ppmv, was 17.5 ppm, resulting in a coefficient of variation (CV) of 60%. The corresponding oxygen data averaged 12.1%, with a s.d of 2.6 and a CV of 22%. Evidently the CO varied much more than the oxygen.
To the extent that CO varies linearly with PCDD/PCDF, it can be expected that the variation in dioxins and furans will be roughly the same as the CO variation, increasing logarithmically as temperature falls or excess oxygen increases.

Figure 9. Histogram of Carbon Monoxide Readings Averaged Over 100 Hourly Intervals, Showing Symmetry of the Logarithm of CO.

ESTIMATION OF PROBABLE EMISSIONS FROM PLANNED FACILITIES

Estimating average and maximum upset emissions

An estimation of maximum emission rates, and their relationship to the average or mean, can be made by calculating the mean plus two standard deviations, which includes 95% of the data. In this case the CO reading which is not exceeded by 95% of the data is 2.2 times the mean. None of the 100 data points exceeded 93 ppm, or 3.2 times the mean. In other words, the maximum upset CO reading in 100 hours was 3.2 times the average, and lasted for less than 1% of the time period. A maximum value of 64 ppm was exceeded for only 5 hours out of 100.
Log Probability Graphs

It has been found that the emissions reported from a series of tests of a given facility, or from tests of a number of similar facilities generally follow a log-probability distribution, that is, data plotted on these coordinates fall close to a straight line. Figure 10 shows data from 14 MWCs having lime scrubbers and baghouses as emission control devices. This graph was plotted by sorting the data in ascending order, then plotting the points equally spaced on linear coordinates. This is a simpler plot than using probability paper, but the results are almost the same, except for upper and lower tails.

The range of variation in Figure 10 is largely due to the different scrubbing temperatures, since these temperatures control the amount of trace organics which are condensed on collected particulate. These data show that the 2,3,7,8 TCDD Toxic Equivalents (EPA) did not exceed 0.3 ng/nM³, and averaged about 0.12 ng/nM³. The maximum value was less than 3 times the mean. The Swedish goal for T.E.(Eadon) is 0.1 ng/nM³; this is equivalent to a T.E.(EPA) of about 0.05 ng/nM³, which was met or exceeded by three of the plants.

It should not be overlooked that post-combustion emission controls employing temperature reduction to the vicinity of 300°F with suitable particulate controls will capture essentially all organic emissions, regardless of the input quantities. The use of these controls reduces the requirement for achieving minimum emissions from the combustion process. However, the organics will then reside in the collected particulate matter, increasing concern that it be disposed of properly.

Figure 10. Toxic Equivalent Dioxin Emissions from Municipal Waste Combustors Equipped With Acid Gas Scrubbers.
THE IMPORTANCE OF MIXING IN ASH RESIDUE MANAGEMENT

The management of flyash and bottom ash residues from combustion of MSW requires attention to basic principles in the same manner needed in management of its combustion. The composition and leaching properties of flyash, scrubber residues and bottom ash residues from combustion of MSW are highly variable, and dependent not only on the composition of the MSW, but also on the conditions to which the waste and its products have been subjected. Statistical analysis shows that these residues normally exhibit consistent and random properties, but that higher variability can result from poor wetting and mixing of these different types of residues. The variations in ash properties obtained from a series of tests may be a direct and useful indication of the mixing effectiveness of materials handling operations.(1)

Failure to mix residues properly has led to highly variable test data, resulting in public concern about the toxicity of ash residues. Flyash generally contains higher concentrations of soluble heavy metals than bottom ash, since metals such as lead and cadmium condense on flyash surfaces in the soluble oxide form or become soluble chlorides. The solubility of certain forms of these metals is highly dependent on the pH of leaching water. If flyash is not well mixed with bottom ash, samples may contain abnormally large fractions of flyash and consequently exhibit high concentrations of lead and cadmium when subjected to leaching tests.(1)(12)

When lime scrubbers are used, the lime will tend to cause the lead and cadmium to be converted into insoluble compounds or complex cementicious formations in the presence of sufficient moisture. However, if mixing and moisture addition are not uniform, a larger fraction of these metals may remain in water-soluble forms, and may thus fail leaching tests. The unique physical and chemical properties of flyash, scrubber products and bottom ash offer potentials for reuse to avoid landfilling, and in any case require careful handling so that they do not harm the environment.

CONCLUSIONS

As a result of extensive research on the relationship between refuse composition and combustion conditions on the quantity and nature of emissions, it has been found that, while refuse composition varies widely, emissions from combustion are consistent in their variability, and range within rather narrow limits when modern combustion control devices are applied.

In addition to providing sufficient furnace volume to complete combustion, it is necessary to find and maintain the range of excess oxygen (or corresponding furnace temperatures) which achieve optimum combustion, the optimum balance between underfire and overfire air, the best injection points, and the optimum configuration of high-intensity mixing of the fuel and air.
In order to encourage environmentally sound disposal and reuse of ash residues, attention to proper management is required, much as fuel and combustion air must be properly controlled to minimize emissions.

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REFERENCES


