ENERGY-FROM-WASTE AND DIOXIN EMISSION CONTROL: IS THERE A ROLE FOR PVC SEPARATION?

Domenico Venezia
Covanta Energy Corporation
Fairfield, New Jersey, USA

Michael Van Brunt
Covanta Energy Corporation
Fairfield, New Jersey, USA

Samuel Joshi
Covanta Energy Corporation
Fairfield, New Jersey, USA

Andrew Szurgot
Stratosphere, LLC
Paramus, New Jersey, USA

ABSTRACT

The role that chlorine and polyvinyl chloride (PVC) plays in dioxin emissions from municipal solid waste (MSW) combustion has been studied and debated for 25 years. Despite energy-from-waste (EfW) facilities’ dramatic emission reductions following implementation of USEPA’s Maximum Achievable Control Technology (MACT) Guidelines, the PVC/dioxin relationship remains a source of controversy. The issue is whether removal of PVC from waste to be combusted will result in further dioxin emission reductions, as waste separation proponents allege. This paper uses the large volume of post-MACT emission testing data to describe the relationship between MSW chlorine content and dioxin emissions at operating EfW facilities and thereby determines whether PVC separation is likely to be an effective component of a dioxin emission reduction strategy. The paper also shows chlorine and PVC contents and trends in MSW, reviews dioxin formation/destruction/collection mechanisms in EfW facilities, and presents emission data as a function of EfW facility designs. The paper concludes that dioxin emissions at existing EfW facilities are insensitive to MSW chlorine content and that pre-combustion PVC removal offers no discernable emission reduction benefit.

Keywords: Chlorine, polyvinyl chloride, dioxin, energy-from-waste, municipal waste combustion, waste separation

INTRODUCTION

Since the 1970s discovery that combustion is a source of polychlorinated dibenzo-p-dioxin (PCDD) and polychlorinated dibenzofurans (PCDF) (“dioxin”) researchers, engineers and others have published numerous papers and reports regarding dioxin formation, destruction, collection and emissions. Many of these documents deal specifically with municipal solid waste (MSW) combustion. Much has been learned about relationships among the many variables that affect dioxin emissions, including waste composition, and combustor and post-combustion air pollution control (APC) equipment design and operation. For example, it is clear that improved combustion and APC techniques are able to substantially reduce emissions. Despite these advances in understanding, uncertainties still exist.

One of the most debated issues has been the role that MSW chlorine content plays in dioxin emissions from energy-from-waste (EfW) facilities, and whether emissions can be reduced by removing polyvinyl chloride (PVC) from MSW before combustion. Published studies, government reports, and advocacy papers are divided on the matter. A report by TNO [1] commissioned by the Association of Plastics Manufacturers in Europe, assessed the effect of PVC on all aspects of EfW facility operation and environmental discharges and concluded that no significant reduction in dioxin formation is expected from a decrease in the PVC content of MSW. Costner [2] of Greenpeace reviewed various papers and studies and found that dioxin formation in waste incinerators decreases with a decrease in chlorine content. Carroll [3] issued a white paper.
on behalf of American Chemistry Council disputing the Costner paper findings.

For its part, the U.S. Environmental Protection Agency (EPA) concluded in its 2006 dioxin inventory [4] that PVC removal cannot eliminate dioxin emissions, but stopped short of saying whether removal would significantly reduce emissions. And in December 2009, EPA published its Maximum Achievable Control Technology (MACT) regulation for Hospital, Medical and Infectious, Waste Incinerators (HMIWI) [5] which contains waste separation provisions and statements supporting the notion that removal of chlorine-bearing components such as PVC could be an effective component of a dioxin emissions reduction strategy at HMIWIs. This position is important to stakeholders of EfW facilities because of the potential that waste separation programs could be required in EPA’s upcoming municipal waste combustor (MWC) MACT regulations.

Most existing data originate from laboratory or other small-scale studies which seek to identify causal relationships that may explain dioxin emissions found in full-scale facilities. These studies are normally limited to the combustion process itself dealing with dioxin formation and by their nature do not evaluate the effect of APC systems on full-scale application emissions. Identifying chlorine/dioxin relationships relevant to existing U.S. EfW facilities is especially difficult due to the predominant effect of these APC systems on emissions.

In a full-scale study, directed by the American Society of Mechanical Engineers (ASME), Rigo and Chandler [6] conducted detailed statistical analysis using over 1,900 dioxin measurements and found no consistent relationship between dioxin and chlorine feed rate or its surrogate, the level of hydrogen chloride (HCl) leaving the combustion chamber. They concluded that any effect that does exist is masked by combustor design and operating factors.

The ASME study database was obtained from a range of various combustor types, APC system designs, wastes, sampling locations and sampling techniques. So while the overall database was large, the number of data points which provide information on the relationship between waste chlorine content and stack dioxin emission of a specific combustion and APC technology were more limited.

In this paper we seek to describe the chlorine/dioxin relationship using the considerable amount of emission test data available since implementation of the Municipal Waste Combustor MACT Guidelines in 2000. We focus exclusively on large mass-burn U.S. EfW facilities equipped with spray dryer / fabric filter technology and EPA Reference Method test results. The sheer volume of data now available suggests that the database is representative of the range of EfW operating conditions and that simple binary analysis of dioxin/pollutant relationships would reveal significant correlations. By comparing the strength of observed trends and correlations among the emission profiles, a reasonable determination can be made whether chlorine and PVC removal from MSW is likely to be an effective dioxin emission reduction strategy.

**CHLORINE AND PVC CONTENT OF MSW**

Surprisingly little information exists on the total chlorine content of MSW; Table 1 shows reported U.S. and international values. Principal chlorine sources in MSW include PVC plastics, paper, and salt contained in organic wastes like food waste.

<table>
<thead>
<tr>
<th>Country</th>
<th>Content (% wt)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>USA</td>
<td>0.50%</td>
<td>[7]</td>
</tr>
<tr>
<td>USA</td>
<td>0.47-0.72%</td>
<td>[8]</td>
</tr>
<tr>
<td>Netherlands</td>
<td>0.59%</td>
<td>[9]</td>
</tr>
<tr>
<td>Japan</td>
<td>0.37%</td>
<td>[10]</td>
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</table>

PVC is a thermoplastic material manufactured by polymerizing vinyl chloride monomer. First produced commercially in 1933, current uses include building materials, medical applications, electrical cables and automotive applications. Of the total PVC production, 80% is used in construction for drinking water and waste water pipes, window frames, flooring and roofing foils, wall coverings, and cables. PVC is the most widely-used plastic in medical applications for containers, IV bags, gloves, and tubing. Consumer product uses include outdoor clothing, decorative leather, luggage, credit cards, furniture, and packaging materials. PVC production has increased along with those of other plastics over the last 30 years. [11]

PVC content in MSW has increased as it has become more prevalent in non-durable consumer products; however, relative to total plastics, PVC content is lower in MSW than it is in manufactured products because much of the PVC is in durables which do not readily find their way into the MSW stream. According to EPA [12], PVC currently makes up 1% of total MSW and 6% of total plastics discards.

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Pure PVC (empirical formula C₂H₃Cl) contains 57% chlorine by weight. However, PVC-based products also contain plasticizers for flexibility, and other additives which reduce the chlorine content to a range of 29-46% [1]. Overall, PVC contributes about half of the total chlorine content of MSW (Table 2).
Table 2. MSW Chlorine Content from PVC

<table>
<thead>
<tr>
<th>Country</th>
<th>Fraction from PVC (% wt)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>USA</td>
<td>50%</td>
<td>[7]</td>
</tr>
<tr>
<td>EU</td>
<td>30-70%</td>
<td>[1]</td>
</tr>
<tr>
<td>Japan</td>
<td>63%</td>
<td>[10]</td>
</tr>
</tbody>
</table>

Chlorine content can be roughly determined using uncontrolled HCl emission measurements. From Covanta Energy’s database, HCl APC inlet concentrations average about 650 ppmv @ 7% O₂ dry basis. Assuming 70% conversion of MSW chlorine to HCl, the calculated content is 0.62%, and the fraction of total chlorine due to PVC is 47%, which generally agrees with the above values.

When combusted, MSW chlorine coverts predominately to HCl. The fate of chlorine in EfW facilities is independent of its chlorine form or origin in the waste [1]. Very little chlorine is needed to generate the small amounts of dioxin formed in EfW facilities, there being a million times more chlorine than is necessary [3]. In that respect, it is impossible to remove all MSW chlorine and thereby eliminate the formation of chlorinated products of incomplete combustion like dioxin.

DIOXIN FORMATION, DESTRUCTION, AND COLLECTION MECHANISMS IN EFW FACILITIES

Dioxin is generally formed through two pathways (Figure 1): precursor formation, and re-synthesis or de novo synthesis. Dioxins contained in the MSW feed can pass though the combustion process intact for ultimate release, but this is not a significant portion of the total dioxin from the stack [13]. Any combination of carbon (C), hydrogen (H), and chlorine (Cl) from a process can form dioxins depending upon combustion conditions.

The precursor formation of dioxin involves the thermal breakdown and molecular rearrangement of aromatic precursors either originating in the feed or forming as a product of incomplete combustion [14]. Chlorinated aromatic precursors such as polychlorinated phenols, benzenes and biphenyls act as precursors for dioxin formation downstream of the combustion chamber.

Reference: [14]

Re-synthesis or de novo synthesis involves the heterogeneous solid-phase formation of dioxin in the post-combustion environment on the surface of fly ash. Such heterogeneous chemistry occurs from the oxidation of carbon within the fly ash and subsequent reactions with organic and inorganic chlorine, and the oxidative breakdown of macromolecular carbon structures and oxychlorination reactions of aromatic precursors on fly ash surfaces, leading to dioxin formation. De novo synthesis is likely to be several orders of magnitude faster than precursor formation in actual combustion systems.

Post-combustion dioxin formation may be due to reactions occurring on particles entrained in the flue gas during the brief time they pass through the temperature zone of 400 deg. C to 200 deg. C (752 deg. F to 392 deg. F). It is estimated that due to short residence time for the flue gases in this temperature zone, desorption of dioxin molecules from the particle surface is not probable; rather a high rate of dioxin formation on deposited particles may be the significant contributor to the observed stack gas dioxins concentrations.
**Dioxins Destruction and Minimization**

A well designed municipal waste combustor has defined combustion characteristics with temperature zones (Figure 2), defined flue gas residence times, adequate oxygen/excess air, and strong turbulence in the combustion chamber. Dioxins present in the waste are volatized and combusted into innocuous substances at temperatures above 870 deg. C (1562 deg. F) with adequate residence time [15], the prevailing conditions in modern EfW facilities. Unfortunately, due to presence of unburned carbon, hydrogen, and chlorine in the presence of oxidizing agents the formation of dioxins is possible downstream.

Figure 2. Typical Mass Burn Boiler Temperature Profiles

Dioxin formation downstream of the combustion chamber can be reduced by limiting the residence time within the critical temperature range. This is achieved by installing heat exchangers with high flue gas capacities, maximizing combustion efficiency to reduce unburned carbon, and limiting fly ash deposits in the critical temperature range via soot blowers.

Municipal waste combustors in the U.S. utilize advanced combustor design to maximize dioxins destruction and minimize the formation. Further reduction of dioxins is achieved by post combustion APC equipment that controls stack dioxin and other pollutants [4].

**Spray Dry Absorbers**

The primary purpose of spray dry absorbers (SDA) is the removal of acid gases and particulate matter through the addition of a lime slurry. By itself, the spray dry absorber is not a significant reducer of dioxin but cools the flue gas enough to minimize formation.

**Dry-sorbent Injection**

The dry-sorbent injection is utilized for removal of organic pollutants like dioxin and for heavy metals like mercury. Gaseous and solid phase dioxin are adsorbed on activated carbon, which is subsequently removed in the fabric filter (baghouse). The dry sorbent material is injected at a temperature of about 140 deg. C (285 deg. F) and collected on the fabric filter. Both gaseous and solid phase dioxin can be removed from the flue gas.

**Fabric Filer / Baghouse**

A high percentage of the dioxins once formed are fixed to particulate matter. Therefore the fabric filter, as a particulate matter control device, removes dioxins associated with particulates and any vapor phase dioxins that adsorb onto the particulates.

**EFW DIOXIN EMISSIONS AND TRENDS**

Emissions of dioxins from EfW facilities have significantly improved over time. These improvements are mainly due to use of improved post-combustion APC equipment, increasingly strict government emission regulations, and improved combustion practices.

EPA’s initial dioxin inventory prepared in 1987 reported that municipal waste combustors (MWCs) accounted for 63% of the nationwide emissions. A large fraction of that amount was emitted from a relatively few, older facilities which did not have modern combustion and APC systems. By 2002, MWCs’ contribution had fallen to 1% largely due to the closure and upgrading of those facilities (Figure 3).

Figure 3. Change in Dioxin Sources in the U.S., 1987-2002

Reference: [16]

Similarly, EPA’s Office of Air Quality Planning and Standards compiled dioxin emission estimates for both large and small MWCs for the period 1990 to 2005. These estimates also show dramatic reductions. From 1990 to 1999, reductions were due largely to shutdown or retrofit of older EfW facilities and incinerators. Reductions since 1999 are attributable to
further controls needed to meet EPA’s MACT standards. MACT dioxin emission limits for large MWCs, those units with capacities exceeding 250 tons per day, became effective in 2000. Small MWC MACT limits became effective in 2005. As shown in Figure 4, emissions have been reduced by 99.7% since 1990, to a total of 14 grams toxic equivalents (TEQ) per year in 2005.

Figure 4. Dioxin Emissions from Municipal Waste Combustors, TEQ Basis

References: [17][18]

To further demonstrate the significant reductions in dioxin emissions achieved in the US, EPA provided data to the British Columbia Clean Air Forum in March 2009 demonstrating the impact of federal regulatory action on dioxin emissions (Table 3).

Table 3. Mass Emissions per Year and Reductions Achieved From 1990 to 2005

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>1990</th>
<th>2005</th>
<th>Reduction</th>
<th>Percent Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dioxins, total, kg</td>
<td>226</td>
<td>0.706</td>
<td>226</td>
<td>99.7%</td>
</tr>
<tr>
<td>Dioxins TEQ, kg</td>
<td>4.42</td>
<td>0.0138</td>
<td>4.4</td>
<td>99.7%</td>
</tr>
<tr>
<td>Hg, tons</td>
<td>56.7</td>
<td>3.72</td>
<td>53</td>
<td>93.4%</td>
</tr>
<tr>
<td>PM, tons</td>
<td>18,630</td>
<td>1,066</td>
<td>17,564</td>
<td>94.3%</td>
</tr>
<tr>
<td>SO2, tons</td>
<td>38,270</td>
<td>6,118</td>
<td>32,152</td>
<td>84.0%</td>
</tr>
<tr>
<td>NOx, tons</td>
<td>64,900</td>
<td>49,500</td>
<td>15,400</td>
<td>23.7%</td>
</tr>
<tr>
<td>Cd, tons</td>
<td>9.61</td>
<td>0.55</td>
<td>9.1</td>
<td>94.3%</td>
</tr>
<tr>
<td>Pb, tons</td>
<td>172</td>
<td>8.7</td>
<td>163</td>
<td>94.9%</td>
</tr>
<tr>
<td>HCl, tons</td>
<td>57,400</td>
<td>2,538</td>
<td>54,862</td>
<td>95.6%</td>
</tr>
</tbody>
</table>

Reference: [19]

FACILITY OPERATING DATA

The efficacy of PVC separation on EfW dioxin air emissions is contingent on lower total chlorine contents in waste leading to measureable decreases in effluent dioxin concentrations. To evaluate the relationship between total MSW chlorine content and dioxin air emissions, a comprehensive evaluation of facility test data was completed.

HCl concentration at the inlet to the APC equipment, used as a surrogate for total chlorine concentration in the MSW, was measured using EPA Reference Method 26. The fraction of total MSW chlorine that ends up as HCl at the APC inlet is expected to be independent of the total chlorine content of the MSW, i.e. the partitioning of chlorine is not expected to be dependant on total chlorine content of MSW.

Total dioxin concentration at the APC outlet was measured using EPA Method 23. The actual point of sample collection may vary by facility, but is in all cases downstream of the APC equipment and is consistent with the location for air permit monitoring. All concentration results (HCl and dioxin) were corrected to 7% O2, dry basis. Consistent with EPA methods, each dioxin and HCl test result is generally an arithmetic mean of three individual test runs.

Inlet HCl and outlet dioxin concentrations were collected from 30 different large MWC facilities, each equipped with a spray dryer and fabric filter as primary APC equipment. Several of the facilities use activated carbon dry sorbent injection upstream of the fabric filter to assist with dioxin, Hg, and trace organics removal.

Data were collected during annual compliance stack tests performed at the facilities from 2000 to 2008, all after large MWC MACT dioxin emission limits became effective. HCl and dioxin test results were paired by stack test event, resulting in an overall dataset of 447 samples. Although the measurement of HCl and dioxin may be separated by up to five days, this is not expected to significantly impact the results, given the size of the data sample evaluated. To evaluate potential relationships, regression analyses were performed using Microsoft Excel® on the data following common log (log base 10) transformations. The raw data was not normally distributed and attempts at linear regression of the raw data yielded non-normal residual distributions. The log transformations resulted in both more normally distributed data and regression residuals.

RESULTS

The evaluation of HCl and dioxin results showed virtually no correlation between inlet HCl concentration and total stack...
dioxin air emissions over an inlet HCl range of 300 to 1,400 ppmv (Figure 5). Descriptive statistics pertaining to the dataset used for the evaluation are provided in Table 3. No statistically significant linear correlation between log transformed inlet HCl concentration as the independent variable and log transformed dioxin concentration as the dependant variable was observed at a confidence level of 90% (P-value of 0.64). The analysis resulted in an R-squared value of 0.05%, indicating that an extremely minor portion of the variation in dioxin concentrations could be explained by variation in the inlet HCl concentration.

Figure 5. Dioxin Stack Concentration as a Function of Inlet HCl

Table 3. Descriptive Statistics

<table>
<thead>
<tr>
<th></th>
<th>HCl (ppmv)</th>
<th>PCDD / PCDF (ng / dscm)</th>
</tr>
</thead>
<tbody>
<tr>
<td># of Results</td>
<td>447</td>
<td>447</td>
</tr>
<tr>
<td>Average</td>
<td>650</td>
<td>3.68</td>
</tr>
<tr>
<td>Median</td>
<td>646</td>
<td>1.74</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>154</td>
<td>4.73</td>
</tr>
<tr>
<td>Minimum</td>
<td>304</td>
<td>0.066</td>
</tr>
<tr>
<td>Maximum</td>
<td>1,277</td>
<td>27.6</td>
</tr>
</tbody>
</table>

Regression analysis of log transformed data was also performed for dioxin outlet concentrations using inlet CO, HCl, and SO2 concentrations as independent variables. Statistically significant relationships (at a 90% confidence level) were observed for inlet CO and inlet SO2 (P-values of 0.09 and 0.04 respectively); however, in combination with inlet HCl, were able to explain only 3.4% of the variation in dioxin stack concentration. Inlet CO exhibited a positive relationship, and inlet SO2 exhibited a negative relationship, meaning increases in inlet SO2 were correlated with lower dioxin concentrations.

DISCUSSION

Inlet HCl concentrations are a reliable indicator of MSW total chlorine content. Results collected from 30 large MWC facilities over nine years of stack dioxin emissions showed no correlation with inlet HCl concentrations over the range evaluated. Consequently, changes in MSW chlorine content, achieved by separation programs targeting chlorine containing items such as PVC are unlikely to have an impact on dioxin air emissions from EfW facilities.

Even complete removal of PVC from the waste stream, a near impossibility given its ubiquity in manufactured goods, is unlikely to achieve meaningful results. For example, at the average dataset HCl concentration of 650 ppmv, removal of all of the PVC, which could potentially halve the total chlorine in the waste, could be expected to generate an inlet HCl concentration of 325 ppmv. As demonstrated in the analysis above, there is no statistically significant relationship between inlet HCl and dioxin stack emissions over this range.

Notwithstanding the fact that no statistically significant relationships between inlet HCl concentration and dioxin stack concentration were observed, the “least squares” method employed by the regression analysis can still be used to estimate a linear relationship in the log transformed data. However, the estimated relationships explained little of the variation in dioxin stack emissions. HCl inlet concentrations alone could only explain less than 0.1% of the variation in stack dioxin emissions. Inlet HCl, SO2, and CO together could only explain 3.4% of the variation in stack dioxin emissions.

The results of this study are supported anecdotally by looking at historic PVC production, disposal, and EfW dioxin emissions. Despite increases in PVC production and an increase in PVC disposal, albeit smaller than the increase in production, dioxin air emissions have actually dropped over a similar time period, due generally to improvements in air pollution control.

Considering dioxin formation mechanisms and because of the stoichiometric excess of HCl present in EfW flue gases, the amount of HCl is not a likely limiting factor in dioxin formation. If all chlorine could be eliminated, dioxin formation would be impeded; however, this elimination is virtually impossible.

Removal of PVC from the waste stream can result in other benefits. With their high heating value, PVC wastes consume about twice times as much of the plants’ thermal capacity as average MSW whose higher heating value is near 5,000 BTU per pound. The HCl produced from PVC combustion is a contributor to boiler tube corrosion [9], consumes lime in the spray dry absorbers, and adds weight to fly ash that must be disposed. All in all operators would prefer to have no PVC in
MSW. That stated, EfW facilities are designed to handle the inevitable PVC components in the range of levels normally found in MSW, both in terms of combustor and air pollution control equipment that must meet stringent HCl emission limits.

FINDINGS AND CONCLUSIONS

PVC and other MSW components including food wastes and paper serve as chlorine donors for dioxin formation. However, to the extent that all chlorine cannot be removed from combusted MSW, removal of PVC will not eliminate dioxin formation.

Analysis of actual operating data from large EfW facilities in the United States shows no correlation between inlet HCl concentration, a surrogate for MSW chlorine concentration, and dioxin air emissions either alone or in combination with inlet concentrations of CO or SO2. The lack of a statistically significant correlation and the extremely minor percentage of variation in dioxin emissions explained by inlet HCl concentration over a wide range of concentrations casts significant doubt on the ability of PVC removal programs to reduce dioxin emissions from modern EfW facilities. These findings confirm those from the ASME study reported by Rigo and Chandler, specifically for the combustor and APC system designs predominately employed at EfW facilities.

Clearly, other variables have significantly more impact on dioxin stack emissions. The implementation and operation of advanced APC equipment is likely a major driver in the improved performance and, together with closure of older facilities, was likely responsible for the precipitous drop in dioxin emissions from large MWCs observed since 1990. Better control over boiler operations and improved boiler design to limit the residence time of stack gases in the temperate range favoring dioxin formation are also likely significant factors.

Future test programs focused on additional variables can have significant value in understanding how to further decrease dioxin air emissions from EfW facilities. Such test programs could look at concentrations of potential catalysts, including copper, temperature profiles, and concentrations of unburned carbon together with inlet HCl, SO2, and CO to determine if any significant relationships can be observed in operating large MWCs.

Removal of PVC by existing recycling programs could still have other beneficial outcomes. Efforts to recover recyclable plastics from the waste stream, such as PVC, help reduce GHG emissions and energy consumption associated with manufacture of these good from raw materials. Lower PVC content in waste would reduce EfW fossil CO2 emissions, and would likely reduce concentrations of HCl, a corrosive gas that increases facility maintenance costs and necessitates additional lime use for air pollution control. However, based on results from actual EfW facilities, removal of PVC from the waste stream is unlikely to result in reductions in dioxin emissions.

ACKNOWLEDGEMENTS

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and S in various components of municipal solid waste”, Waste Management, 24, pp. 623-632.


