

Polyvinyl Chloride Plastics in Municipal Solid Waste Combustion

Impact Upon Dioxin Emissions - A Synthesis of Views

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TECHNICAL INVESTIGATION

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Prepared for the

National Renewable Energy Laboratory
Solar Energy Research Institute
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and the

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Silver Spring, Maryland

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Executive Summary

This report examines the issue of whether or not the polyvinyl chloride (PVC) plastics content of municipal solid waste (MSW) is a significant contributor to emissions of chlorinated dibenzo-p-dioxins (dioxins) that are associated with MSW combustion. Indications based on a consideration of this issue are developed through a synthesis of available information.

In summary, consideration of the representative information contained in this report, and drawn from literature that has been referenced, leads to the following indications:

- (a) Reported tests, which compare the PVC plastics wastes content of MSW that is fed to combustors with observed emissions of dioxins, do not convincingly lead to a consensus view that removal of PVC from MSW will cause less dioxins to be emitted during MSW combustion.
- (b) Evidence is available which indicates that regardless whether PVC plastics are present in MSW or not, when MSW is combusted, dioxins can be formed in amounts that presently are of regulatory concern unless control measures to limit dioxin emissions are applied.
- (c) When MSW is combusted, control measures can limit dioxin emissions to levels that are below current regulatory concern, regardless of whether or not PVC is present in MSW. The presence or absence of PVC in the MSW stream will not reduce the need to employ such control measures.

Preface

This report examines the issue of whether or not the polyvinyl chloride (PVC) plastics content of municipal solid waste (MSW) is a significant contributor to emissions of chlorinated dibenzo-p-dioxins (dioxins) that are associated with MSW combustion.

While there is convincing experimental evidence that various conditions can cause production of dioxins when PVC is thermally treated, a fundamental issue that remains to be resolved is how these findings relate to operating conditions that are characteristic of well designed, maintained and operated MSW combustion facilities, equipped with modern air pollution controls. These findings largely have been derived from laboratory or pilot scale experimentation and from limited full-scale studies that have been carried out at facilities of varying design and purpose.

This report is an examination of views of various investigators, evidenced by their published literature, as it relates to this issue.

[Note: frequently, the notations, PCDD, PCDF, or combinations of these notations, e.g., PCDD/DF or PCDD/F appear in cited literature references. These notations should be understood to refer, in the case of PCDD, to polychlorinated dibenzo-p-dioxins (referred to in this report as, dioxins); in the case of PCDF, to polychlorinated dibenzofurans (chlorinated compounds similar in many respects to dioxins, but structurally different, owing to the presence of only one oxygen atom in the central ring of furans)].

Introduction

This report examines current knowledge about the impact of the polyvinyl chloride (PVC) fraction of municipal solid waste (MSW) on waste-to-energy (WTE) facility emissions of chlorinated dibenzo-p-dioxins (dioxins).

The goal of this examination is to have, based upon an examination of currently available technical information, a comprehensive technical evaluation of what is apparent regarding the possible relationship (or not) of PVC in MSW that is fed to WTE facilities to subsequent occurrence of dioxins in emissions. In order to achieve the goal, the following issues are considered:

- What is known now;
- What should be investigated; and
- Whether present approaches to combustion of MSW that contains PVC are appropriate.

The review is of a technical nature.

Currently, there is no consensus view among all stake-holders (e.g., the public, environmental groups, public officials, facility owner-operators, etc.) concerning whether or not elevated emissions of dioxins will be produced when MSW that contains PVC is combusted in WTE facilities.

In contrast, a recent study [1] by an expert group of scientists and engineers arrived at a consensus view: that dioxin emissions from properly designed, maintained, and operated WTE facilities are not evidently produced due to the PVC waste constituent. Specifically, the expert group reported that:

"There is no correlation between plastics content of the MSW and the observed emission of polychlorinated dibenzo-p-dioxins (PCDDs) or dibenzofurans (PCDFs) from the MSW incinerator."

The experts also stated that:

"It is the opinion of the workgroup that there is no valid correlation between the amount of plastics in municipal solid waste and the concentration of PCDDs and PCDFs in air emissions from MSW incinerators when waste streams containing plastics are incinerated. While some small scale laboratory test results have shown that PCDDs and PCDFs can be produced to varying extents from

specific materials, (e.g., various chlorinated precursor molecules and certain chlorinated polymer formulations or mixtures in specialized circumstances) the carryover (demonstration of a valid relationship or significance) of these test results to full scale, well maintained and operated MSW incinerators is not supported by available evidence.

"Some participants of the workgroup noted that numerous tests and investigations (for example, in Canada, Denmark, France, Sweden, the United States, Germany and Italy) to find such a correlation have been attempted, and that results have been negative. Although no correlation has ever been reported between PCDD and PCDF emissions and total chlorine load in the precombusted wastes fed to an MSW incinerator that burns MSW, at least one Symposium participant noted a suggestive correlation between PCDD and PCDF emissions and the total chlorine load in precombusted wastes fed to an MSW incinerator that was burning industrial sludge wastes having significant chlorine content.

"Note: However, prior to the conduct of the Symposium, the same participant [C. Rappe] has commented that:

"The possible influence of various municipal solid waste components on dioxin formation has been the subject of research, notably in Pittsfield, USA, Hamburg and Milan. From these studies it is concluded that removal of PVC from the waste stream does not affect the quantity of dioxins produced."

"Note: Careful, peer-reviewed mathematical analyses of gas phase PCDD and PCDF formation mechanisms which have been recently carried out at the National Bureau of Standards and at the University of California (San Diego) indicate that, in the instance of combustion of industrial wastes containing high contents of chlorinated precursors, significant amounts of PCDDs and PCDFs could be formed in certain circumstances (and that such circumstances can be avoided). However, these same studies showed that: such high levels of precursor molecules are not likely to be found in municipal as opposed to industrial solid waste streams; and that since the formation rate depended on the square of the precursor concentration, significant drops of precursor concentrations down to levels characteristic of MSW incineration, should effectively prevent the occurrence of such processes.

"Note: In addition, theoretical analyses, for example those carried out at the National Bureau of Standards and at the University of California (San Diego), have shown that the determining factor which controls the process of post-combustion catalytic formation of PCDDs and PCDFs - a dominant (but controllable) process in MSW incinerators - is the availability of reactive catalysis sites on solid surfaces, e.g., fly ash residue particulate matter. In regard to catalysis, dependence on reactive sites on surfaces implies an insensitivity to plastics content (and more generally an insensitivity to total chlorine load) in the waste stream, as sources of chlorine would behave as *constant strength source terms* in mathematical representations of the combustion process; i.e., the process of formation is not expected to depend on waste feed characteristics.

"Note: In the one cited instance in which industrial waste sludges were combusted, reactive site density may not have been an issue owing to the probability of large surface areas being associated with the presence of very fine particulate matter in the sludge. Other formation processes could be possible, e.g., those occurring in, on or near the material which burns on grate beds, however, it is considered that these processes can be mitigated through good combustion control.

"Thus, in regard to incineration of MSW, given the considerations outlined in the above paragraphs, there is no correlation between PCDD/PCDF formation and total chlorine load in the MSW stream; to the contrary, the above information indicates that such a correlation is not expected in a well designed, maintained, and operated MSW incinerator facility. However, neither this report nor any other report has combined in detail evidence that can explicitly and convincingly demonstrate the validity of the expert's findings."

This report is not an analysis of dioxin formation mechanisms. Rather, the discussion which follows indicates information that, taken as a whole, provides additional background for evaluating the possible connection (or not) between PVC in the MSW stream and dioxin emissions from well designed, maintained and operated MSW combustion facilities, equipped with modern air pollution controls. The information presented is representative of current data that are available and is considered sufficiently comprehensive to enable a synthesis view of the issue.

The PVC Content of Combusted MSW

PVC plastics have been used in a number of markets, e.g., the building and construction industry, packaging, transportation, furniture, electrical and electronic markets and housewares [2]. PVC plastics applications have varied according to market use. For example, in the building and construction industry, PVC plastics have been used in flooring, lighting fixtures, panels and siding, pipe, fittings, profile extrusions, conduits, vapor barriers and wall coverings [2]. A significant amount of generated plastics wastes can be categorized as plastic packaging and plastic containers; this material has an estimated commercial use life that is less than one year in duration [3]. PVC plastics packaging applications include, e.g., use in coatings, closures, containers, lids and film. Few consensus, useful-life (i.e., time from acquisition of consumer products that contains plastics until time of discard by consumers) estimates appear to be available in regard to the generation of specific PVC plastics wastes.

The plastics industry periodically releases data through industry trade journals and magazines that indicate volumes, uses, etc. of PVC plastics that are produced. In 1990, U.S. combined production of thermoplastics and thermosets was about 25.1 million tonnes, while sales and captive use of PVC in 1990 amounted to about 4.1 million tonnes [4]. If waste generation across categories of plastics tracked production and use, PVC in the waste stream would comprise about 16 percent of generated plastics wastes, or about 1.3% of total U.S. MSW generation in 1990 [5]. However, without some understanding of the useful life of consumer products that contain PVC plastics, it is difficult to estimate what PVC plastics wastes are generated and in what amounts during a specified period of time. Moreover, data need to be adjusted to account for exports, imports and uses that do not ultimately lead to generation of some plastics wastes as components of MSW that is presently subject to combustion.

It is important to recognize that there is no one single commercial formulation [6-11] of the plastic material loosely referred to as, *polyvinyl chloride* or *PVC*. This circumstance can confound analysis of potential combustion products and emissions impacts.

The loosely used designation, PVC, refers to numerous commercial formulations, comprised of the polyvinyl chloride polymer, various copolymers, additives, e.g., plasticizers, fillers, pigments, etc. [2,6]. Additives such as: antioxidants, antistatics, blowing agents, peroxide catalysts, flame retardants, heat stabilizers, impact modifiers, UV-stabilizers, lubricants and processing aids have been added in varying amounts to commercial PVC formulations and products. These different formulations may have

significantly different chemical and physical characteristics, may be designed for a variety of applications and may behave in a variety of ways both in practical use and during plastics wastes processing [2-4,7-11].

A detailed discussion of PVC and the PVC industry is beyond the scope of this review. A thorough, general discussion of PVC technology, covering a broad range of aspects of PVC and the PVC industry has been written by Titow [10]. In all discussions contained in this report, the use of the plastics designation, *PVC*, should be recognized as a general descriptor of a broad category comprised of a large number of different commercial formulations.

The possible impact of variations in specific formulations of different PVC materials upon potential generation of dioxins has apparently not been extensively reported. Investigations which report generation of dioxins from combustion or thermal stressing of PVC materials, commonly fail to indicate the specific formulation of the particular PVC material that was investigated. This is unfortunate, as it is known with certainty that the chemical and physical characteristics of PVC formulations can have an observable, significant impact upon subsequent amounts of decomposition products that are produced [8,9] when PVC materials are thermally stressed.

There is no convincing evidence presently available that could enable a conclusion that dioxin generation from PVC is independent of the nature of the specific PVC material that is being investigated. This observation suggests that it is difficult to generalize findings regarding dioxin generation from thermal stressing of materials that contain particular PVC plastics over the entire PVC plastics category. A generalized assessment of the impact of PVC plastics wastes upon emissions of dioxins can be confounded by this lack of data.

In 1990, 14.7 million tonnes of plastic wastes were generated in the United States and of this generated amount, 14.4 million tonnes of plastic wastes were discarded without recovery [5]. In other words, very little plastics wastes were recovered from the MSW stream. Moreover, of the plastic wastes that were recovered, very little were categorized as PVC plastics wastes. The total amount of MSW processed in waste-to-energy (WTE) facilities in the United States in 1990 was reported to be 26.9 million tonnes, reported as corresponding to 15.2% of the generated waste stream [9]. These data lead to an estimate that the amount of plastics wastes that were combusted in WTE facilities in 1990 was about 2.2 million tonnes.

The amount of chlorine in MSW is known to be variable. Limited data appear to indicate that total chlorine in MSW ranges from about one-half to about one percent (mass basis) [12] of the total amount

of MSW generated. Various data are available, but intercomparison of data is difficult, as the manner in which data have been generated is not always apparent. A representative (but not definitive) estimate of a typical amount of chlorine attributable to the plastics fraction of MSW is that about half of the chlorine appears to be present in the plastics waste fraction [12]. Available data indicate that the actual amount of chlorine that is attributable to the plastics wastes fraction is variable.

It is not clear that most of the chlorine associated with the plastics wastes fraction is associated with the PVC plastics in the plastics wastes fraction of MSW. Some significant fraction could be associated with plastics additives [6]. This observation notwithstanding, it appears to be a common assumption that most, if not all chlorine in plastics wastes is associated with PVC plastics wastes.

Lower estimates of the amount of chlorine associated with PVC have been indicated by some investigators. For example, Candreva and Dams [13] report that in Great Britain, PVC is not the only source of HCl emissions and that at current mean emission levels of 274 milligrams per normal cubic meter, PVC accounted for only about 25% of the total HCl emissions. Use of this literature citation points to another problem associated with data analysis: the data cited by Candreva and Dams were generated in 1976, and there is no compelling reason to expect that such data are applicable today.

An account of amounts of other chlorinated plastics and chlorinated plastics additives found in plastics wastes not categorized as PVC plastics wastes might prove useful to resolve uncertainties. A detailed annual account of the flow of PVC plastics and other plastics and plastics additives that contain chlorine into the MSW stream, which indicates, e.g., amounts of PVC materials, type, complexity, etc., is not available. This lack of waste generation data, e.g., broken out by nature of PVC plastic material, etc., in part may be due to the externalization of generated wastes management costs in the plastics industry [14], i.e., if it is not necessary or economical to recover waste plastics, then there is no driving force that promotes record-keeping and analysis of plastics wastes materials at this specified level of information complexity.

All PVC formulations are characterized as containing substantial mass percentages of chlorine. For example, one commercial PVC plastic pipe formulation is reported to contain approximately 40% (mass basis) polyvinyl chloride polymer and 60% (mass basis) fillers, etc. [15]. The PVC component of the pipe itself was reported to contain 56.8% (mass basis) chlorine, so that the PVC pipe contained a total of 22.7% chlorine (mass basis). A considerable amount of generated PVC plastics wastes are film plastics or container plastics, which contain considerably higher amounts (mass basis) of chlorine [7-11].

If the chlorine content of combusted MSW is comparable to the amount of chlorine in MSW generally, then based on information presented above in this report, the 26.9 million tonnes of MSW combusted in W-E facilities in the United States in 1990, could (based on a chlorine content range of 0.25 - 0.5% by weight) potentially contain a chlorine content in the range of 67 - 134 thousand tonnes.

If about half of this amount is associated with PVC in the MSW stream, and if the chlorine content of PVC plastics wastes is in the range 25 - 50 percent by weight of PVC, then the amount of PVC plastics wastes combusted annually in the United States could amount to between 67 and 268 thousand tonnes of PVC plastics. Based upon a previous estimate that 2.2 million tonnes of plastics wastes were combusted in WTE facilities in the United States in 1990, it therefore can be crudely estimated that PVC plastics wastes comprise between 3 and 12% of all plastics wastes in MSW that are combusted. [Note: These estimates of amounts of PVC combusted are to be compared to the prior estimate that PVC comprises about 16 percent of all plastics used in producing consumer products - uncorrected for export/import practices and management of some plastics wastes in non-MSW streams.] The broad range indicated in this example calculation suggests that data used in a general manner do not enable refined calculations to be carried out without additional direct MSW plastics wastes content characterizations in specific instances. In other words, if actual sample data from a test run are not available, great care is warranted when attempting to draw conclusions based upon previous generalizations about input feedstream characteristics.

Representative Data Which Indicate That PVC Decomposition Can Lead To Formation of Dioxins and Dioxin Precursors

In-lab flow tube experiments, in which various forms of PVC (described as: hard-PVC, soft-PVC and PVC-fibers) were heated under controlled, oxidative conditions at temperatures up to 600 degrees Centigrade, have been carried out by Theisen and co-workers [16]. Dioxins were observed to be formed in amounts ranging from a few hundred to thousands of nanograms of dioxins per gram of PVC material decomposed.

Christman and co-workers [17] have reported formation of dioxins from various forms of PVC (described as: high molecular-PVC, low molecular-PVC, PVC-cable and PVC-coated wire) under both pyrolytic and oxidative conditions at temperatures that ranged from about 350 degrees Centigrade to 950 degrees Centigrade. Hundreds of nanograms of emissions of PCDDs/PCDFs were observed per gram of PVC material that was decomposed.

Rappe and other investigators [18] have similarly reported formation of dioxins from oxidative decomposition of PVC under controlled conditions in a quartz-flow tube apparatus heated up to 800 degrees Centigrade. Approximately one microgram of PCDDs/PCDFs were formed per gram of PVC that was decomposed.

Care must be exercised in deciding how to view the opinions of various investigators. For example, it is not unusual, in view of the rapidly increasing base of data, that investigators modify their point of view, based upon new information. For example, Rappe indicated in 1989 [1] that:

"The possible influence of various municipal solid waste components on dioxin formation has been the subject of research, notably in Pittsfield, USA, Hamburg and Milan. From these studies it is concluded that removal of PVC from the waste stream does not affect the quantity of dioxins produced."

This statement stands in contrast to his observation made in 1985 that [18]:

"The laboratory pyrolysis of PVC and Saran clearly shows that PVC and other organochlorine polymers can be precursors to the PCDDs and PCDFs found in various incinerators."

These two statements are not necessarily contradictory. The latter remark is an indication that, as noted, dioxins can be a decomposition product of PVC, while the former remark is an opinion that such dioxins (or dioxin precursors) as may be produced do not account for measurements of dioxins in full-scale MSW combustors. The two statements are reconciled if, for example, it is demonstrated that any dioxins (or dioxin precursor compounds) that may be produced from PVC decomposition in a MSW combustor are: (a) subsequently destroyed; or (b) are present in insignificant amounts compared to production of these compounds due to other processes that may take place in a MSW combustor, regardless whether or not PVC is present; or (c) the processes observed to lead to production of these compounds in laboratory or pilot-scale experiments occur to a minimal extent under MSW combustor operating conditions.

In addition to the above mentioned investigations which call to focus production of dioxins, it is known [8,9,19-25] that most PVC materials typically rapidly release about 95% of the chlorine content of these materials as an emission of hydrogen chloride at moderately low temperatures, i.e., lower than or comparable to those temperatures that are likely to occur on and within thermally degrading MSW placed on the grate beds of MSW combustors. While the main chlorine-containing decomposition product is hydrogen chloride, numerous other chlorinated and non-chlorinated organic products of decomposition have been reported, as cited in the references indicated in this paragraph.

Chlorinated phenols are produced, as are chlorinated benzene compounds [8,9,19-25]. The former are believed to be precursors of dioxin formation, while the latter are believed to play a more secondary role, i.e., it is suggested that conversion of chloro-benzenes to chlorophenols is a prerequisite to dioxin formation [26].

The main point to stress, is that these reported results support a suggestion that thermal degradation of PVC materials probably takes place in or on the mass of MSW material that is introduced onto the grate bed of a MSW combustor facility. This assumption is probably valid, unless there is extensive buoyant entrainment of film-like PVC wastes in the gas stream - a circumstance that has not been reported. When PVC film is combusted in RDF facilities which utilize in-stream, over-grate injection of refuse derived fuel, this possibility may not necessarily be discounted out of hand, however, there does not appear to be any persuasive evidence that this has been a major concern.

Dioxin Production From the Combustion of MSW That Contains PVC: An Examination of Findings

This section provides an examination of and comments concerning current representative literature that report investigations of dioxin production from the combustion of MSW that contains PVC or from the combustion of other types of waste streams that contain PVC. Unless indicated, it should be assumed that the exact composition of the PVC materials that were studied, was not specified.

PVC and a mixture of PVC and polyethylene materials were combusted in an EPA laboratory-scale rotary kiln combustor, under conditions which correspond to transient overcharging that can occur when waste-filled drums or containers are batch fed into rotary kiln combustors [27]. The waste feed composition and in-lab kiln operating characteristics were examined in relation to production of products of incomplete combustion. The investigators found that combustion of mixtures of PVC and polyethylene could produce parts-per-trillion (volume basis) amounts of dioxins in the effluent stream from the kiln under transient puff conditions, but did not observe any dioxin emissions when only PVC was combusted in the laboratory-scale rotary kiln. These findings appear to indicate the following:

- (a) Dioxins can be produced under certain transient-puff conditions in a laboratory-scale rotary kiln combustor when a mixture of PVC and polyethylene are combusted. The waste stream composition, combustion conditions established during the reported investigations, and the utilized apparatus were not comparable to the operating conditions and design of MSW combustors used to process MSW in the United States [28-30].
- (b) When a mixture of PVC and polyethylene is combusted under stated conditions, the combustion of the PVC and polyethylene do not take place in an independent, parallel manner. Rather, there appears to be an interaction between the combustion of the two materials. Under stated conditions, combustion of PVC alone did not produce observable dioxin emissions.
- (c) The amounts of dioxins observed from combustion of the mixture of PVC and polyethylene under stated conditions were small, a few parts-per-trillion (volume basis) compared to amounts (a range of thousands to tens of thousands of nanograms of dioxins per dry standard cubic meter) observed to be emitted from MSW combustors under poor design or operating conditions [28]. This observation appears to suggest that if MSW combustors were poorly designed and operated, the resulting dioxin emissions could not be accounted for on the basis

of the results reported concerning the in-laboratory investigation, particularly since the amount of PVC present in MSW is much less than the amount of PVC contained in the PVC/polyethylene mixtures combusted in the in-laboratory rotary kiln combustor.

The test results obtained at the EPA test facility were, in the context of a report concerning MSW combustion, apparently interpreted by Clarke and co-workers [31] to indicate support for a view that PVC removal from MSW is warranted prior to combustion of MSW in order to reduce emissions of dioxins. These investigators reported that:

"Tests conducted by the Environmental Protection Agency indicated that mixtures of PVC and polyethylene (another common consumer plastic, used in such materials as soft drink bottles and shrink wrap), under test conditions generally considered optimal for combustion, produced a large number of chlorinated organic compounds, including dioxins, furans, and dioxin/furan precursors. While other factors (such as temperature and the presence of chlorinated compounds in other materials) also affect the production of dioxins and furans, reducing the amount of these plastics being burned, as well as designing incinerators to assure more efficient combustion, should help reduce emissions of these pollutants under real, as well as test, conditions."

Lenoir and co-workers [32] investigated various combinations of refuse derived fuel (RDF) with PVC and polyethylene (PE) in a pilot scale fluidized bed combustor (FBC) that consumed 40 kilograms of fuel per hour. [Note: For comparison, a 500 tonnes per day MSW combustor that is operated 24 hours per day consumes more than 20 thousand kilograms of MSW per hour.] Operating conditions were varied and statistical analyses of collected data were examined to establish whether any relationships that may be indicative of a potential role of PVC in production of dioxin emissions could be observed. The investigators reported that:

"PCDD/F emissions did not depend on the HCl [hydrogen chloride] concentration in the flue gas.

"The investigated fuel types varied in their chlorine content which, in some experiments, was increased by adding NaCl or polyvinyl chloride (PVC). Only the addition of 3% PVC to polyethylene resulted in an increase in PCDD/F concentrations. Apart from this single experiment, no effect of fuel type on PCDD/F emissions was observed.

"...PCDD/F did not depend on the chlorine concentration of fly ash, as could [previously] be found by Vogg et al.

"...The lack of relationship between PCDD/F and HCl levels described above indicates that the chlorine of the fuel, from which HCl is formed, had no influence on PCDD/F emissions. Indeed, burning RDF with 0.09 g chlorine/g, wood chips with 0.002 g Cl/g, and PE with .0004 g Cl/g led to about the same PCDD/F emissions. Emission from combustion of cellulose fiber with the same chlorine content as the wood chips was lower than the mean values, but within the standard deviation of values for the other fuels. Adding NaCl to PE and to cellulose fiber, and adding 0.5% PVC to cellulose fiber did not increase PCDD/F concentrations. However, addition of 3% PVC to PE increased PCDD/F levels by a factor of 3 compared to the mean value for pure PE combustion. This statement lacks statistical significance, since the treatment was not repeated, but it is one of the few experiments where an influence of larger amounts of PVC on PCDD/F emissions was observed in waste incinerators. Conversely, it has frequently been published that the addition of PVC to municipal waste and waste paper did not increase PCDD/F emissions. Nevertheless, in laboratory experiments PCDD/F were formed during burning of PVC and PVC-cable coatings. PVC is also suspected to be responsible for PCDD/F emissions from metal reclamation plants."

As the above investigators have noted, various experiment characteristics limit the use of the data that have been generated. It is unfortunate, for example, that these investigators did not examine further the inter-relationship of the PVC/PE/RDF waste matrix and emissions of dioxins. Additional experimentation possibly could have established stronger indications of the relationship (or not) of dioxin emissions to this waste fuel mixture. On the other hand, if one were to arbitrarily accept as true the reported finding, that dioxin emissions were increased when the PVC/PE/RDF matrix was combusted in the pilot-scale FBC unit, it would still be difficult, at present, to establish any consensus relationship between the results of this test and the behavior of PVC in MSW that is combusted in well designed, maintained and operated MSW combustor facilities, equipped with modern air pollution controls. This is because the amount of PE and PVC incorporated in the test of the PVC/PE/RDF matrix was far in excess of the amounts of PE and PVC that are ordinarily found, or expected to be found in the foreseeable future, in MSW [5]. Moreover, the importance of design and operating differences between the pilot-scale FBC unit and full-scale MSW combustors commonly in use in the United States has not been established.

Other investigators have, for various reasons (often not explicitly stated), arrived at a conclusion that the presence of PVC in the MSW stream does not bear a significant relationship to subsequent emission of dioxins from these facilities. Reiman [20] reports that:

"Reduction of chlorinated compounds fed to the incinerator is not likely to make any significant difference [re dioxin emissions]...

"...even if PVC is excluded, at least 50% of the chlorine content remains in the waste. This is still sufficient for dioxin formation."

Moreover, a detailed theoretical analysis of the extent to which chlorine in the waste stream may influence subsequent dioxin formation has been carried out [26]. This investigation reported that if dioxin formation in well designed, maintained and operated MSW combustion facilities, equipped with modern air pollution controls is dominated by catalysis at low temperatures, which in turn is controlled by rate-limiting site clearance reaction steps, then far greater removals of chlorine than that which could be accomplished by only removing PVC from MSW would have to be realized in order to limit dioxin formation by attempts at control of chlorine levels in MSW. The projected level of control of chlorine in MSW necessary to affect the extent of dioxin formation was suggested to be impractical to achieve.

Investigations of full-scale MSW WTE facilities operated in a stable combustion mode, have provided data which indicate that dioxin emissions from these units are largely associated with low-temperature, post-combustion formation processes [35,37-40]. These observations lead to a conclusion that if PVC plays a role in promoting dioxin formation, it is probably an indirect role, e.g., the data cited below suggest that any dioxins formed in or on the grate bed or in the combustion chamber of a MSW combustor operated under optimal conditions, even if associated with PVC, are either produced in insignificant amounts or are destroyed prior to transport to cooler regions, e.g., the air pollution control equipment environment, of a MSW WTE facility. Under these circumstances, if PVC plays a role in promoting dioxin formation, it is an indirect role, i.e., PVC decomposition leads to production of direct or indirect precursor compounds that at latter stages of the total MSW combustion process, subsequently play a role in promoting dioxin formation (or in suppressing dioxin destruction).

Based upon observations of concentrations of chemical species in full-scale MSW WTE facilities, Hagenmaier and co-workers [35] reported that:

"PCDD/PCDF concentration in the flue gas leaving the combustion chamber can be reduced to below the detection level. The fact that, despite these combustion conditions, high dioxin and furan concentrations can again be measured in the raw gas at the end of the boiler is attributable to two formation mechanisms during the cooling down of the flue gas:

- formation from chlorinated precursor compounds in the gaseous phase
- formation by de novo synthesis on the particulate matter."

Similarly, Takeshita and co-workers [40] have demonstrated in experiments performed at full-scale MSW WTE facilities that while dioxin concentrations in flue gases that exit the combustion chamber can be dramatically suppressed by careful control of the combustion process, large increases in dioxin concentrations occur when the flue gas passes through control equipment (the facility studied was equipped with an electrostatic precipitator (EP)). A ten-fold to hundred-fold increase in dioxin concentrations was reported when the facility studied was operated under well-maintained conditions, while much higher levels of post-combustion dioxin concentrations were observed under poor combustion conditions - characterized by poor control of temperature and levels of carbon monoxide in the combustion chamber. [Note: In the latter (poor combustion) condition, most of the formation is shown to have occurred prior to entrance to the air pollution control devices.] The investigators suggest a relationship to factors such as particulate loading in the control device, amount of HCl in the post-combustion gas flow stream and the rate at which the temperature of the flue gas is cooled. Their observations are stated as follows:

"...there were no great differences in the PCDDs/Fs concentration levels in the gas among three concentration levels [Note: *low, medium, and high*, levels of HCl are stated to refer to concentration respectively, below 100 ppm, about 150 ppm and 200-300 ppm.] of HCl at any gas temperature. This indicates that HCl did not contribute to PCDDs/Fs formation during the process of the flow of gas from the furnace to the EP inlet."

However, the investigators reported a different opinion regarding PCDDs/Fs in EP ash:

"At any of similar gas temperature, the amounts of PCDDs/Fs formed at the high HCl level were higher than those formed at the middle HCl level..."

"...each amount of PCDDs/Fs in the EP closely correlates with the amount of the corresponding dust in the EP inlet."

[Note: It appears that these investigators use the word, correlate, in a subjective sense, i.e., to express an opinion, rather than in the sense of a mathematical evaluation of parametric relationships. It is not clear if the HCl dependence is statistically significant, based upon information that has been presented.]

In summary, these investigators find that:

"...When an EP is used to remove fly ash, it is necessary to reduce the flue gas temperature to below at least 250 degrees Centigrade, and decrease the HCl level in the EP to control PCDDs/Fs formation in the EP."

Taken as a whole, these observations suggest that attempts to look for relationships between dioxins and HCl concentrations may need to take into account confounding influences of dust loadings in the flue gas stream, etc. An implication is that some prior attempts to correlate HCl with dioxin emissions by other investigators may require re-examination.

U.S. Environmental Protection Agency (EPA) investigators [39] have also reported that dioxin concentrations were observed to increase, typically one hundred-fold, as flue gas passed from the inlet to the outlet of an electrostatic precipitator. These tests were performed at a full-scale MSW WTE facility. In concurrence with the findings reported by Takeshita and co-workers, the EPA investigators observed that increases of EP inlet temperature from 150 degrees Centigrade to 300 degrees Centigrade led to increased production of dioxins.

As to influences of HCl (a major by-product of PVC decomposition) upon formation of dioxins, numerous investigators have produced reports of findings or of theoretical analyses. Some of these observations are noted and remarked upon in the discussions which appear above in this report. In contrast to the investigation of Takeshita and co-workers [40], De Fre and co-workers [36] reported that:

"The graphical representation of PCDD and PCDF concentrations in emissions vs. HCl or PVC contents showed that there was no relationship present for a sample of 14 data for the two [MSW] incinerators combined."

[Note: HCl was an assumed surrogate of PVC content in the MSW stream studied.] It does not appear that De Fre and co-workers attempted to account for the possible influence of differences in fly ash loading levels, etc. in the post-combustion zones upon the outcome of the attempt to look for relationships among dioxin production and HCl levels or PVC fuel content.

Nottrodt and Ballschmitter [37] investigated combinations of MSW, PVC-reduced content MSW, and a mixture of paper, scrap metal and PVC in relation to production of dioxins in MSW combustors. As reported:

"...the PCDD/PCDF concentrations were in the same range for all used fuels."

Neulicht and co-workers [37] investigated the possible relationship of dioxin emissions to PVC content of MSW through tests carried out at a modular combustor in which the fuel feed included various levels of PVC in MSW. No statistically significant relationship was reported between PVC content of the waste feed and observed levels of dioxins produced at the facility.

Other investigators have re-analyzed the data that were generated. For example, Hershkowitz and Clarke [42] have, by selectively choosing data elements, suggested that there is an apparent relationship between chlorine in MSW and dioxin/furan emissions at the boiler outlet. However, no mathematical basis for the data manipulation that was undertaken was indicated, nor is a basis evident.

Synthesis of Views

This synthesis is derived from consideration of the representative information contained in this report and from literature that has been referenced in this report. The following observations are indicated by the information that has been examined:

The variability of the chlorine and PVC content of MSW necessitates that investigations of relationships between dioxin emissions and PVC content of MSW fuel must be characterized by direct measurement if tests of full-scale MSW combustors are to be used as a basis of investigation, e.g., reference to a generalized data base of MSW stream compositional characteristics may not be reasonably representative of test conditions. An alternative approach that has been carried out has been to investigate the thermal behavior of various PVC formulations under in-lab or pilot scale conditions. It has been difficult to relate the outcome of these experiments to investigations of full-scale MSW combustors.

PVC found in MSW cannot be characterized as a single, unique compound. Rather, there are various commercial formulations of PVC. These formulations can undergo different decompositions when thermally stressed, leading to different types and amounts of decomposition products. Most investigations of PVC have not included explicit indications of the nature of the PVC plastics wastes compositions. This may confound interpretations of observed phenomena and collected data.

The decomposition of PVC can occur at temperatures that are achieved on or in grate beds of MSW combustors, with most of the chlorine content of the PVC released as hydrogen chloride. While it is known from various experiments that decomposition of PVC can produce dioxins as decomposition by-products, observation of dioxin production from decomposition of PVC in or on the grate bed of a MSW combustor apparently has not been directly observed. The possibility that dioxins are formed in or on the grate bed of a MSW combustor cannot be ruled out. However, any dioxins formed can then be expected to be exposed to the environment of the combustion zone of the MSW combustor. Any chlorinated organic decomposition products or generated chlorinated organics which may result during subsequent complex interactions, in principal can be thermally decomposed in the combustion zone of the MSW WTE facility.

The flue gas emissions from the combustion zone of a MSW combustor are not reported to be completely free of dioxins or of dioxin precursors. However, it can be demonstrated that in well designed, maintained and operated WTE facilities, the concentrations of dioxins in flue gases that exit the combustion zone of

MSW combustors are much lower than the amount of dioxins that can be subsequently formed in cooler regions, e.g., by catalysis in the air pollution control equipment. It is less clear whether reduction of dioxin precursors such as chlorophenols in the effluent from the combustion zone can be accomplished under conditions sufficient to mitigate ultimate emissions of dioxins without considering the consequences of subsequent low-temperature formation processes. Hydrogen chloride produced from decomposition of PVC and other chlorine containing materials in MSW is present in flue gases emitted from the combustion zone.

If most dioxins produced in well designed, maintained and operated MSW combustor facilities are formed at low temperatures as can occur in air pollution control equipment, the formation processes are probably produced by catalysis reactions involving precursors. It is not entirely clear what precursors or catalytic formation mechanisms are involved in dioxin formation, but it does not appear that in this cooler region of the combustor, that PVC is a direct precursor to dioxin formation.

Therefore, any influence of PVC upon dioxin emissions is expected to be indirect, i.e., PVC leads to precursor formation, which in turn leads to dioxin formation through some complex series of reaction steps involving catalysis. However, because catalysis is involved and is apparently sensitive to temperature and morphological characteristics of reactive surfaces, the presence of precursor compounds may not be a limiting influence upon dioxin formation, i.e., reactive site clearance rates may control the progress of dioxin formation. Under these circumstances, the influence of PVC upon precursor formation may not necessarily be significant. While these issues have not been clearly resolved, it appears reasonable to conclude that the total mechanism which describes dioxin formation is likely to be so complex that, measurement limitations notwithstanding, a clear mathematical relationship between dioxin emissions and PVC content may be difficult to establish.

At present, direct comparison of PVC plastics wastes content of MSW that in various tests has been fed to MSW combustors, with observed emissions of dioxins, does not convincingly lead to a consensus view that removal of PVC from MSW will cause less dioxins to be emitted. Taken as a whole, no significant reduction in dioxin emissions as a result of limiting the amount of PVC in combusted MSW has been demonstrated. Stakeholders have not agreed to a consensus view.

Evidence is available which indicates that when MSW is combusted, regardless whether PVC plastics are present in MSW or not, dioxins can be formed in amounts that presently are of regulatory concern unless control measures to limit dioxin emissions are applied.

When MSW is combusted, control measures can limit dioxin emissions to levels that are below regulatory concern, regardless of whether or not PVC is present in MSW. The presence or absence of PVC in the MSW stream will not reduce the need to employ such control measures.

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