

**FORMATION OF DIOXINS AND DIBENZOFURANS DURING
INCINERATION AND PYROLYSIS OF PVC.
A CONTROVERSIAL ISSUE**

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ABSTRACT

The paper will review the controversial issue of formation of PCDDs and PCDFs during incineration of PVC-contaminated MSW. The best way to minimize the emissions is by optimizing the burning and flue-gas cleaning.

INTRODUCTION

The occurrence of PCDDs and PCDFs in emissions from MSW incinerators is now non-controversial. The same is true for all incinerators burning halogenated compounds such as hazardous waste incinerators and metal reclamation plants. However, at present the reactions or reaction sequences leading to PCDDs and PCDFs are not well understood. In addition to PCDDs and PCDFs other polyhalogenated compounds such as chlorophenols, chlorobenzenes and PCB are also reported to be found in the emissions from incinerators. A series of controlled laboratory experiments in the 1970s showed that these chloro-aromatic compounds can also be converted into PCDDs and PCDFs under pyrolytic conditions, but it is still unclear whether, in a real incineration situation, the two groups of compounds are formed in competitive or consecutive reactions or whether we have a situation with a series of equilibria including all types of organo-chlorine compounds; aromatic as well as aliphatic.

It is clear that chlorine compounds in the feedstock are a prerequisite for the formation of PCDDs and PCDFs in all types of incineration, but a key issue is the efficiency of the conversion of various compounds into PCDDs and PCDFs. The role of PVC is very much discussed and is also quite controversial, especially in MSW incineration.

PVC AND EMISSIONS OF PCDDs AND PCDFs

Marklund *et al.* studied the pyrolysis of PVC in the laboratory (1). They found the same typical pattern of pentaCDFs in these experiments as in samples from an MSW incinerator. Christmann *et al.* report that during laboratory combustion or pyrolysis of pure PVC, PCDDs and PCDFs are formed in significant amounts, up to the ppm range (2). In general PCDFs were formed as dominating compounds, especially hepta- and octaCDFs in the pyrolysis experiments, whereas lower chlorinated PCDFs were produced by combustion.

In other experiments it has also been found that burning PVC-coated cable sheathing or wire reclamation leads to the emission of large quantities of PCDDs and PCDFs (1, 3, 4). However, it is unclear to what extent these laboratory experiments are relevant to real fires or to MSW incineration. Marklund *et al.* have reported on a fire in the early part of 1987 in a plastic carpet company in northern Sweden. A wooden warehouse containing 200 tonnes of pure PVC plastic and 500 tonnes of plastic carpets was completely burned out (5). A series of snow samples was collected and analyzed. During the fire the ambient temperature was very low, -30°C , and thus resulted in the formation of an inversion layer. It was estimated that the total deposition of PCDDs and PCDFs outside the plant, within a radius of 1500 meters, was less than 3 mg, calculated as dioxin equivalents. It is interesting to note that the quantities found after this fire, involving some 400-500 tonnes of PVC in various PVC products, were no more than *one thousandth* of the quantity generated per year in any municipal incinerator using early 1980's technology having a similar quantity of PVC present in the waste stream.

Other snow-samples were collected and analyzed after a fire in 1989 in a municipal landfill, also in northern Sweden, containing an unknown amount of PVC. The results indicate emissions in the μg range (6).

A series of studies can be found in the literature where an additional amount of PVC has been burned together with the normal MSW at existing MSW incinerators. The emission levels of PCDDs and PCDFs from these incinerators have been measured, and the results are contradictory and controversial. Some of the studies indicating a correlation could have been biased by carry-over of minute amounts of PCDDs and PCDFs on soot particles from earlier activities. It is practically impossible to clean a full scale MSW incinerator completely between the different test burns. In addition these studies have other major drawbacks. They are often poorly designed especially from a statistical point of view, the sampling and trace analysis of PCDDs and PCDFs are performed using non-validated methods, the emission levels for the incinerators are usually quite high, and on some cases conclusions are drawn after substantial data reduction.

A recent study in Denmark has been reported to show a correlation between the amount of PVC and the emission levels of PCDDs and PCDFs. It is stated that doubling the amount of PVC increased the emissions of PCDDs and PCDFs by 32% (7). However this conclusion is based on very few data points (including only two experiments with a high addition of PVC) and data reduction due to low recovery of the clean-up surrogate.

In the same study it is also reported that the emission of PCDDs and PCDFs is increased by NaCl, a doubling of the amount results in a 17% increase. However, the four highest levels of PCDDs and PCDFs were found in experiments with no addition of PVC or NaCl or after only minor additions. These experiments were performed immediately after a cleaning of the boiler and they were included in the

statistical analyses with a correction factor of 1300% or 200%. In our opinion it is difficult to support the conclusions in the Danish study.

Studies performed at Hamburg, FRG, Milan, Italy and Pittsfield, MA, USA do not show any correlation between emission of PCDDs and PCDFs and additional amounts of PVC (9-10). However, the study in Hamburg was poorly designed. All emission levels were unusually high both in the experiments with and without additional PVC. In only one experiment additional PVC was added to the fuel, but in this case the basic fuel was paper and not MSW, not allowing any direct comparison (8).

In the Italian study, normal MSW was burnt together with up to 10% of PVC by weight. All the results for PCDDs and PCDFs were below the detection level. However the analytical technique is not further discussed (9).

In the Pittsfield study, performed in 1985-86, in total 8 experiments were performed with four different types of waste (10).

Normal MSW
Normal MSW + PVC
PVC-Free MSW
PVC-Free MSW + PVC

In all experiments the emission levels were higher than in modern incinerators today. In other experiments at the same incinerator it has been found that there is a direct correlation between incineration temperature and emission levels. In the experiments with and without PVC the temperature was found to vary between 940°C and 1030°C. The specific incineration experiments, which should be compared, were not performed at the same temperature, consequently a direct comparison or correlation is difficult to perform. It is reported that additional PVC did not significantly affect the emission levels of PCDDs and PCDFs.

However, only four pairs of duplicate runs were made and "eye ball statistics" of Figure 4 in the report indicate somewhat higher levels for the experiments with additional PVC.

RECOMMENDATIONS

The best way to control and minimize the emissions of PCDDs and PCDFs from incineration of MSW - whatever its composition - is to perform the incineration under well controlled conditions including sufficiently high temperature, appropriate residence time, excess of oxygen, and good turbulence. In addition modern pollution control equipment should be used. Good results have been obtained with dry or dry/wet scrubbing using fabric filters. This has been recognized in recent national and international (EEC) legislation.

The experience up to now clearly shows the difficulties to evaluate the role of PVC in full scale operations. The fluctuation in temperature and other burning parameters (like CO) make it more or less impossible to perform experiments that could directly be compared. The full scale operations are quite expensive and the carry-over problems can never be fully controlled or eliminated.

It is our opinion that the role of PVC in the formation of PCDDs and PCDFs should be investigated in carefully controlled experiments. In order to avoid artifacts due to carry-over problems, we suggest the use of a laboratory scale fluidized bed incinerator, which we have used for some time for incineration of a well defined "synthetic waste". The burning of this "synthetic waste" in this incinerator yields normal level and normal composition of the PCDDs and PCDFs (11). This incinerator can be cleaned between the test-burns, and incineration experiments can be performed at conditions (temperature, residence time) similar or identical to a full scale incinerator. Known amounts of PVC of different qualities could be used as fuel together with our well studied synthetic waste (11). This incinerator is quite cheap to operate and burning experiments could be performed in replicate runs allowing accepted statistical methods to be used to evaluate the results.

In addition a laboratory scale incinerator allows the use of PVC labelled with the stable ^{37}Cl isotope. The mass spectrometric analytical technique allows a quantitative determination of the role of PVC in the formation of PCDDs and PCDFs.

REFERENCES

1. Marklund S *et al.* In Chlorinated Dioxins and Dibenzofurans in Perspective. Eds. Rappe C, Choudhary G and Keith L (1986) 79. Lewis Publishers, Chelsea, MI, USA.
2. Christmann W, Kasiske D, Klöppel K D, Partscht H and Rotard W, Chemosphere **19** (1989) 387.
3. Tysklind M, Söderström G, Rappe C, Hågerstedt L-E and Burström E, Chemosphere **19** (1989) 705.
4. Kuykendal W B, Lamason W H, Miles A J and Keating M H, Chemosphere **18** (1989) 1227.
5. Marklund S, Andersson R, Tysklind M and Rappe C, Chemosphere **18** (1989) 1031.
6. Marklund S. Thesis. University of Umeå, Sweden (1990).
7. Miljøstyrelsen, Klorokilders betydning for dioxindannelse ved forbrænding. Miljøprojekt nr 118 (1989). Copenhagen, Denmark
8. Martin J J E and Zahltén M, Abfallwirtschaftsjournal **1** (1989) 41.
9. Gigliano M, Cernuschi S and Ghezzi U, Chemosphere **19** (1989) 407.
10. Gottesman R T, Carro Jr. W F and Fishbein L, Energy Process **8** (1988) 148.
11. Marklund S, Fängmark I, Rappe C, Berge N and Strömberg B, Chemosphere. In press.