

## **"Relevance of PCDD/PCDF Formation for the Evaluation of POPs Destruction Technologies. – Necessity and Current Status"**

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### **Introduction**

The Stockholm Convention on Persistent Organic Pollutants (POPs)<sup>1)</sup> states in Article 6 that POPs waste should be destroyed or disposed of in a way that the POPs content is destroyed or irreversibly transformed. In this context it is critical that the destruction methods used do not create by-products that are themselves POPs<sup>1)</sup>.

Therefore one important criterion (see Table 1) for assessment of a POPs destruction technology is the potential formation of POPs and other toxic by-products, in particular if higher toxic PCDDs/PCDFs are formed and under which operation conditions their formation is relevant (for the respective POPs destruction technology).

To date, a detailed evaluation of PCDD/PCDF emissions has been performed for full-scale facilities only for incineration (the base line PCB destruction technology). Within this process the formation mechanisms of PCDD/PCDFs have been investigated thoroughly<sup>2)</sup> and strategies and technologies were developed to minimize their formation and emission<sup>3,4,5)</sup>.

The discovery of PCDD/PCDF emissions in waste incinerators resulted in difficulties of public acceptance of waste incinerators. A "safe" destruction of hazardous waste (including PCBs) demands state-of-the-art hazardous waste incinerators, which are available only in a few countries. These two challenges lead to the development of alternative non-combustion technologies<sup>6,7)</sup> for the destruction of PCB/POPs, pesticides, and other hazardous chemicals.

A detailed evaluation of non-combustion technologies with respect to PCDD/PCDF formation is, however, lacking to date.

Most information with respect to PCDD/PCDF formation in non-combustion technologies in the present stage of evaluation is provided by the companies developing or selling the facility.

In a laboratory study<sup>8)</sup> it was discovered that super critical water oxidation (SCWO), a technology listed from United Nations Environmental Programme UNEP<sup>6)</sup> as "Commercialised Technology with Considerable Experience" and from United Nations Industrial Development Organization (UNIDO)<sup>7)</sup> as "Emerging and Innovative Technologies", has the potential to form high concentrations of PCDFs (in the % range) during PCB destruction. Such elevated PCDF formations might occur even at temperatures of potential application. This highlights the necessity of a more rigorous assessment of non-combustion technologies with respect to their PCDD/PCDF formation potential and their actual applicability for PCB/POPs destruction.

The present paper provides a critical impulse in this respect, discusses the relevant formation pathways with respect to POPs destruction technologies and proposes a basic framework on how evaluations may be performed.

## **Table 1: List of criteria for evaluation of PCBs/POPs destruction technologies<sup>9)</sup>**

Applicability (target contaminants); Overall cost; Reliability and maintenance; Safety; Residuals produced (by-products: PCDD/PCDF, other POPs, other toxic compounds); Minimum achievable concentration; Public acceptability; Development status; Environmental impacts; Performance dependency on site characteristics; Clean-up time required; Decontaminated soil quality; Site data needed, etc.

## **Discussion**

### **Formation pathways and conditions of PCDD/PCDF formation (Figure 1)**

The formation mechanisms of PCDDs/PCDFs have been investigated during the last two decades in numerous laboratory studies, combustion processes and industrial facilities under various conditions and have been reviewed<sup>2-5, 10)</sup>. Two fundamental PCDD/PCDF formation pathways can be distinguished

#### **a) Formation of PCDD/PCDF from precursors**

PCDD/PCDF can be formed from various chlorinated aromatic compounds (chlorinated phenols, halogenated diphenylethers (PXDEs), PCBs etc. (Figure 1)). Depending on the precursor compound only a simple elimination step (PXDEs), an oxidation/hydroxylation (PCBs), or condensation (chlorophenols) reaction can lead to the formation of PCDDs/PCDFs.

The PCDD/PCDF formation from precursors can take place even at room temperature, e.g. photochemically by UV/sunlight irradiation<sup>10,11)</sup> or enzyme mediated<sup>10,12)</sup>. Thermally they can be formed e.g. under basic conditions at low temperatures around 150°C<sup>10)</sup>.

Unfortunately several POPs or compounds in POPs waste are themselves PCDD/PCDF precursors (PCBs, H<sub>6</sub>CBz) or can be included in large amounts in POPs waste (chlorobenzenes, chlorophenols, chlorinated or brominated diphenylethers, etc.). Further the POP destruction methods are also discussed for remediation of pesticide stockpiles which can contain potent PCDD/PCDF precursors (2,4-D, 2,4,5-T, PxCP, etc.). Therefore this formation pathway is of high relevance for POPs destruction methods (see below).

#### **b) PCDDs/PCDFs formation via *de novo* synthesis<sup>2)</sup>**

PCDDs/PCDFs can be formed during degradation of unburned carbon species (including PAHs, soot etc.) in the presence of a chlorine source (chlorine, metal chlorides). *De novo* synthesis starts at temperatures of around 250°C with a maximum rate between 300 to 400°C. Therefore this pathway is relevant for all POPs destruction technologies operating at temperatures of more than 200°C but in particular in the cooling zones of high temperature technologies.

### **A) High temperature thermal destruction processes – High temperature combustion and Non-combustion technologies (Plasma Arc, Geo Melt<sup>TM</sup>, GPCR (with afterburner), Molten Metal Pyrolysis Molten Salt Oxidation, Thermal Desorption – Pyrolysis, Others)**

The majority of destruction technologies utilize thermal degradation for POPs remediation. Three formation routes of PCDD/PCDF have to be considered for these high temperature destruction technologies:

a) Formation of PCDD/PCDFs within the high temperature zone; b) emission of PCDD/PCDF precursors from the high temperature processes and formation of PCDD/PCDFs in the cooling

zone; c) formation of PCDD/PCDFs via degradation of products of incomplete thermal destruction (soot, PAHs etc.) in the cooling zone (de novo synthesis).

State-of-the-art hazardous waste incinerators operate at temperatures above 1100°C and with a residence time of more than 2 seconds. For such facilities, only route c) has a relevant impact on total PCDD/PCDF formation (this is probably similar for other high temperature technologies which can steadily operate at appropriate high temperatures and sufficient residence time<sup>[1]</sup>, however, has not investigated or reported up to now). The state-of-art hazardous waste incinerators can reach final emission values on solids of ca. 10 µg TEQ/ton waste input and to air <0.1 µg/ton waste input. Further PCB destruction efficiencies of 99.9 to 99.99999% were reported for 16 high-temperature incinerators in a survey of the UNEP<sup>[3]</sup>. For destruction of POP waste the non-combustion technologies have to be evaluated by comparison with these emission values and destruction efficiencies (and other criterias (Table 1)).

All high temperature technologies will face the challenges of PCDD/PCDF formation during cooling and with that comes the challenge of investigating and minimising these formations. This includes also the technologies operating under pyrolysis conditions (low/no oxygen). Here it has been reported that for low temperature pyrolysis processes (450-600°C) with chlorine content of ca. 5% (lower as can be expected for POPs waste), high PCDD/PCDF concentration can be generated (up to 10000 µg TEQ/ton waste input)<sup>[4]</sup>.

## **B) Oxidative non-combustion technologies: (SCWO, Catalytic Oxidation, Mediated Electrochemical Oxidation (CerOx, AEA silver II<sup>TM</sup>), others.)**

Critical POPs for oxidative destruction are PCDD/PCDF precursors, which only require an oxygen insertion (PCBs) or a condensation step (chlorophenols) for PCDD/PCDF formation (Figure 1).

During laboratory scale PCB destruction it was shown that the SCWO technology has the potential to form high concentrations of PCDF (in the % range!) during PCB degradation even at temperatures of practical operation<sup>8)</sup>. The study showed that even for PCB destruction efficiencies of 98.7% or 99.8%, the total TEQ can (tremendously) increase considerably (by 1000% and 50% respectively) due to PCDD/PCDF formation during the PCB degradation.

On the other hand, the catalytic destruction on a TiO<sub>2</sub>-Based V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub> catalyst demonstrates that PCDD/PCDF formation during destruction of PCBs can be overcome by oxidative non-combustion technologies<sup>[5]</sup>.

Both studies demonstrate that for oxidative destruction technologies the PCDD/PCDF formation potential has to be assessed with respect to temperature/time dependence of PCDD/PCDF formation. In addition, these studies show that information on temperature and time dependence is inevitable for the evaluation of the applicability of a technology and provides the basis for the risk assessment concerning the importance of operation stability.

## **C) Reductive technologies (Base Catalysed Destruction (BCD Process), APEG, Copper Catalysed Dehalogenation, Fly Ash Catalysed Destruction (Hagenmaier Process), Sodium Reduction, Solvated Electron Technology<sup>TM</sup>, Others)**

A third approach to degrade chlorinated organics are reductive destruction processes.

***I) Base mediated destruction processes (e.g. Base Catalysed Destruction (BCD); APEG)***

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<sup>[1]</sup>For unstable operation also formation routes a) and b) have to be considered for high temperature destruction technologies.

It is known that yields of PCDDs in % range can be formed from chlorophenols under alkaline conditions at temperature as low as 150°C<sup>10</sup>. In fact, the formation of PCDDs by base mediated processes is the preferred synthesis method of PCDD<sup>10,16</sup>. In addition, high concentrations of PCDFs can be generated from PCBs under alkaline conditions at moderate temperatures (200-300°C) within minutes<sup>17</sup>. The base mediated destruction methods operate in this temperature regime. This indicates that the critical criteria with respect to the generation of high yields of PCDD/PCDFs is the destruction velocity of the PCDD/PCDF precursors (PCB, chlorophenols or chlorobenzene) in comparison to the formation rate of PCDD/PCDFs under the respective conditions (and further the degradation rate of the formed PCDD/PCDF). The long residence time e.g. of the BCD process (up to 3 hours) proposes that the destruction velocity is rather low. Therefore the risk of PCDD/PCDF formation seems high for these processes.

### ***II) Non-base mediated dechlorination processes (Copper Catalysed Dehalogenation; Fly Ash Catalysed Destruction (Hagenmaier Process); Sodium Reduction)***

The risk of formation of PCDD/PCDFs from precursors is lower for fly ash or copper catalysed dechlorination compared to base mediated processes. However, the fate of condensation reactions should also be assessed for the destruction of precursor containing waste.

Formation/evaporation of lower chlorinated PCDD/PCDF during dechlorination processes: If the initial waste material contains OCDD/OCDF (or other perchlorinated aromatics), the degradation of intermediately formed lower chlorinated, but higher toxic T<sub>4</sub>CDD/T<sub>4</sub>CDF-H<sub>6</sub>CDD/H<sub>6</sub>CDF has to be assessed for all reductive destruction technologies by monitoring for completion of dechlorination. Further, the fate of evaporation of the lower chlorinated T<sub>4</sub>CDD/T<sub>4</sub>CDF and P<sub>5</sub>CDD/P<sub>5</sub>CDF congeners has to be evaluated and included in the calculation of destruction efficiencies (e.g. it was reported for the BCD process that during soil decontamination most of the T<sub>4</sub>CDD and T<sub>4</sub>CDF were evaporated and not destroyed<sup>18</sup>).

### **D) Photolytic destruction technologies (Solar Detoxification, Photochemical Degradation, UV destruction, photocatalysis)**

Some technologies aim at the degradation of POPs by means of photolytic degradation. Certain PCDD/PCDF precursors can be transformed by photolytic processes into PCDD/PCDF. For example, during the photolytic radiation of PCBs in a water suspension, up to 0.2% of PCDF were formed; for polyhalogenated diphenylethers (PXDE) conversion rates of up to 10% were reported and for photolysis of chlorobenzenes and chlorophenols up to 1% of PCDD/PCDF were formed<sup>10,11</sup>. This indicates that for these destruction technologies the formation of PCDD/PCDF from precursors have to be considered and evaluated if the technologies are applied for destruction of POPs waste containing PCDD/PCDF precursors.

### **E) Biodegradation/Bioremediation**

The formation of PCDDs/PCDFs has even to be considered for bioremediation/biodegradation processes involving PCDD/PCDF precursors. However, since the transformation yields are in the ppm/sub-ppm range<sup>10,12</sup> the risk seems relatively low.

### **Conclusions/Recommendations**

The evaluation of PCDD/PCDF formation is an important criterion for the assessment of POPs destruction technologies. However, to date there is a lack of information/assessment for most of the proposed/listed POPs destruction technologies.

## REMEDIATION METHODS AND CONTROL TECHNIQUES

Sound evaluations are currently available only for the high temperature destruction processes of incineration. For all other high temperature technologies the fate of PCDD/PCDF formation in the cooling zone is unknown.

The detailed assessment of PCB destruction by SCWO Processes<sup>8)</sup> revealed that high concentrations of PCDD/PCDFs in the % range can be generated by a technology listed in the highest rank of non-combustion technologies from UNEP<sup>6)</sup> and UNIDO<sup>7)</sup>. This shows the necessity of a more rigorous assessment of non-combustion technologies with respect to their PCDD/PCDF formation potential and their actual applicability for POPs destruction when PCDD/PCDF precursors are in the waste feed.

Furthermore, a ballpark comparison of reaction conditions for PCDD/PCDF formation from precursor formation studies and actual applied conditions of a broad range of POPs destruction technologies indicates that the operation conditions have the potential to generate high concentrations of PCDDs/PCDFs for a number of destruction technologies if dioxin precursors are present. However, for almost all POP destruction technologies an evaluation of PCDD/PCDF formation in dependence of operation conditions is missing.

Therefore a strategy for a more profound assessment of the fate of PCDD/PCDF formation is essential for the evaluation of POP destruction technologies and for a sound risk management of POPs. This may include the following items:

Step 1: Laboratory (or pilot scale) evaluation of conditions for safe destruction and conditions associated with PCDD/PCDF formation for the respective technology. The studies of PCB destruction over TiO<sub>2</sub>-Based V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub> catalyst<sup>15)</sup> and PCB destruction in SCWO<sup>8)</sup> may serve as one example in this respect.

Step 2: Assessment of reliability/stability of long term operation conditions and the fate of irregular operation (e.g. start-up, shut down, non-stationary conditions). Up until now this has only been evaluated for high temperature incineration.

Step 3: Monitoring and supervision of pilot and full-scale operations of POPs destruction processes. The destruction efficiency has to be based on toxicity and requests the monitoring of PCDDs/PCDFs (TEQ; bio assays) including all waste streams in the monitoring (total destruction efficiency<sub>TEQ</sub>).

## References

- 1) <http://www.pops.int/>
- 2) Addink, R., Olie, K., (1995) Environ. Sci. Technol. 29, 1425.
- 3) Hagenmaier, H., (1991) Chemosphere, 23, 1429.
- 4) Kilgroe, J. D., Nelson, L. P., Schindler, P. J., Lanier, W. S. (1990) Combustion Sci. and Tech. 74, 223.
- 5) Buekens, A., Huang, H. (1998) Journal of Hazardous Materials 62, 1.
- 6) [www.basel.int/techmatters/review\\_pop\\_feb04.pdf](http://www.basel.int/techmatters/review_pop_feb04.pdf)
- 7) [www.unido.org/userfiles/galvane/ UNIDO-PUBLICATION-ICS.doc](http://www.unido.org/userfiles/galvane/UNIDO-PUBLICATION-ICS.doc)
- 8) Weber, R. "Relevance of PCDD/PCDF Formation for the Evaluation of POPs Destruction Technologies. – PCB destruction by Super Critical Water Oxidation (SCWO)" (2004) Organohalogen Compounds, this issue.
- 9) Lodolo A. Training Workshop "Initial National POPs Inventory - INPOPsI" 16 - 17 May 2002 Brno, Czech Republic.
- 10) Ballschmitter, K., Bacher, R., (1996) Dioxine, VCH Verlagsgesellschaft mbH: Weinheim, pp 92-114.
- 11) Choudry, G. G., Webster, G. R. B. (1987) Toxicol. Environ. Chem. 14, 43.
- 12) Öberg, L., Rappe, C. (1992) Chemosphere 25, 49.
- 13) [www.chem.unep.ch/pops](http://www.chem.unep.ch/pops).
- 14) Weber, R., Sakurai, T. (2001) Chemosphere 45, 1111.
- 15) Weber, R. "Relevance of PCDD/PCDF formation for the Evaluation of POPs destruction Technologies - PCB destruction over TiO<sub>2</sub>-Based V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub> catalyst" (2004) Organohalogen Compounds, this issue.
- 16) Buser, H. R. (1975) J. Chromat. 114, 95.
- 17) Weber, R., Yoshida S., Miwa K. (2001) Organohalogen Compd. 54, 189.
- 18) Kashiwagi S., Toda, H. (2001) Organohalogen compounds 54, 144.

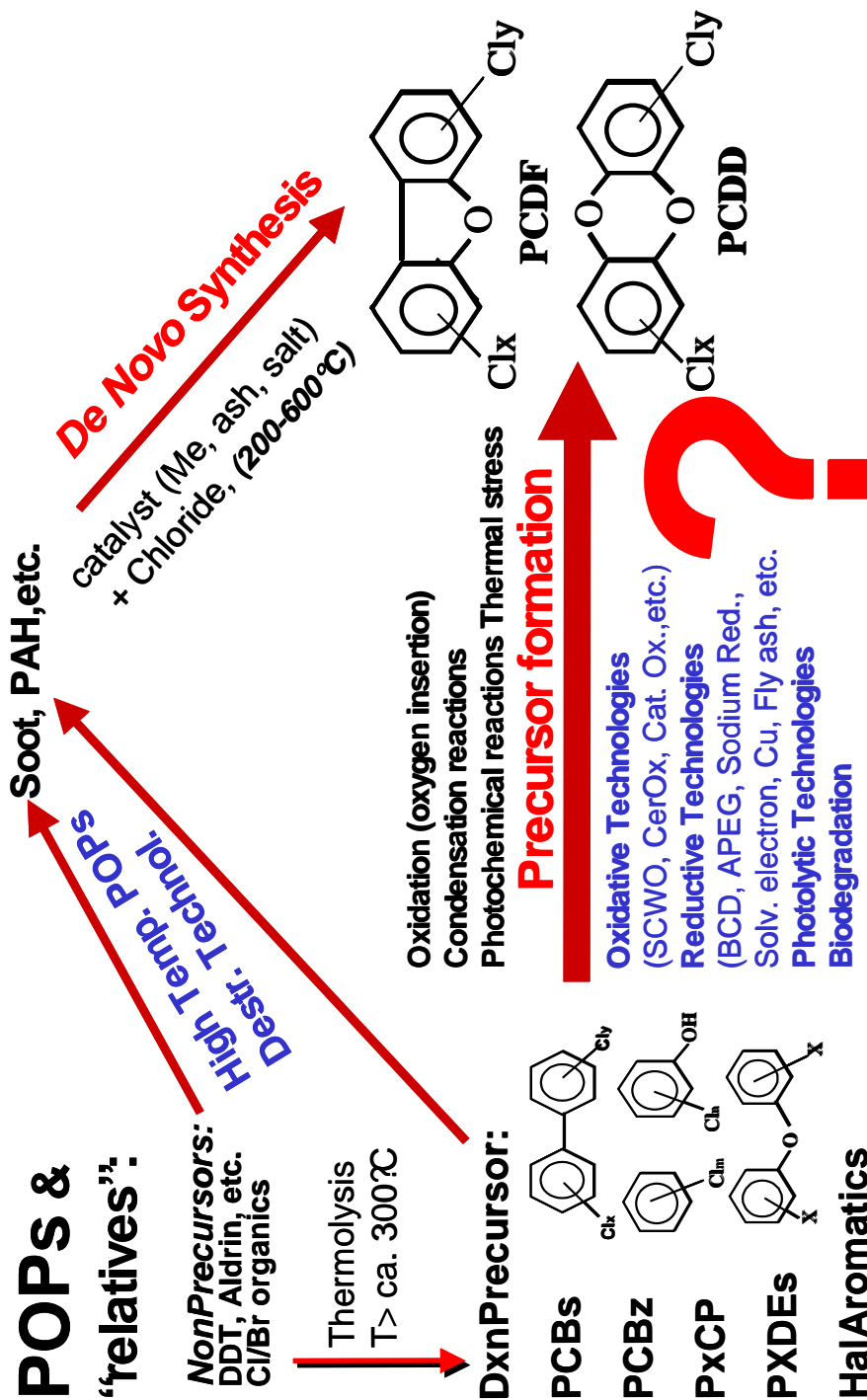


Figure 1: Potential relevance of PCDD/PCDF formation pathways for POPs destruction technologies

