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Technological Measures to Prevent Formation of Chloroorganics in Thermal Waste Disposal

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Abstract

The Thermoselect process is a newly developed technology for thermal treatment of municipal solid and hazardous wastes, which results in environmentally friendly end-products and low dioxin emissions. The PCDD/PCDF concentrations from a 100 t/d plant in Italy were consistently below 0.02 ng I-TEQ/m³ in the off-gases - even before flue gas cleaning technologies were applied. In addition, the small flue gas volume of 1,500 m³ (wet/t waste combusted) reduces costs for flue gas purification. Valuable goods of very low PCDD/PCDF contamination (<1 ng I-TEQ/kg) such as mineral granulates are obtained which can be directly used for other purposes without detoxification. The first full-scale facilities of this technology will go into operation soon in Germany.

Key-words: Polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans, thermal recycling, synthesis gas, dioxin formation potential

1 INTRODUCTION

Once, polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/PCDF) were detected in emissions of municipal solid waste incinerators (MSWIs) [1], PCDD/PCDF play a key-role in the discussion of sustainable waste management. As in many highly industrialized and densely populated countries, combustion of municipal waste is the ultimate technology for waste disposal, attempts were undertaken to either prevent formation of PCDD/PCDF in high temperature processes or to minimize the release of these compounds into the environment by application of highly sophisticated and expensive flue gas cleaning technology. In addition, legislation asks for reduction of PCDD/PCDF emissions from waste incinerators. As a consequence, a limit value of 0.1 ng I-TEQ/m³ was set by the authorities in Austria, the Netherlands, and Germany [2, 3]; the European Commission has released a draft to include the same value. In addition, recent efforts attempt to reduce the PCDD/PCDF concentrations not only in the stack emissions but also in the solid residues, namely slag, fly ash, and residues from the flue gas cleaning devices [4-6].

Traditionally, at least in Europe, municipal solid waste is incinerated by mass burn water wall incinerators. PCDD/PCDF emissions can be controlled by good combustion practices (Three

T's = Temperature, Time, Turbulence), control of back-end temperatures to prevent *de novo* synthesis of PCDD/PCDF, control of fine particulates, post-incineration of gases, or H₂O₂ oxidation [4]. The following technologies are frequently applied: Activated carbon reactors, carbon/coke injection, selective catalytic reduction, and lime enhanced carbon. Application of these principles and technologies were capable to meet the legal emission limit as is shown in many places. However, high investment costs are required. The Thermostelect process using high-temperature gasification of the waste in a reducing atmosphere followed by shock-cooling of the synthesis gas, is an alternative technology which, in addition, suppresses *de novo* synthesis of PCDD/PCDF [7].

2 EXPERIMENTAL - DESCRIPTION OF THE THERMOSELECT TECHNOLOGY

The Thermostelect technology can be described as a high-temperature recycling for the disposal of municipal solid and hazardous wastes, residues from chemical production and waste water treatment plants. After the thermal treatment, products such as synthesis gas can be used in generator blocks for conversion into electricity and heat and the inorganic fraction is converted into materials of "natural composition" suitable for the full range of standard applications. The metal fraction can be separated magnetically for reuse in the smelting industry.

The basics of the Thermostelect technology are that municipal, industrial or other wastes are compacted without previous treatment with an armored hydraulic press to less than one fifth of their original volume. These plugs are pushed into an indirectly heated degasification channel (wall temperature approximately 600 °C) densifying the waste, reducing the residual air content resulting in less gas volume (mainly N₂ to be heated), and sealing the channel against the press. Liquids generated during the compaction flow into cavities and bulky materials are crushed.

As the waste plugs are pushed down the channel into an oxygen-free environment, water is evaporated and the organic substances in the refuse are either degasified or converted into a carbon-like product as the temperature increases. This flaky product and the enclosed inorganic constituents - metals, minerals - are continuously fed into a high-temperature reactor (HTR). Pure oxygen is added in controlled quantities and reacts with the material in exothermic oxidation reactions. Due to the overall under-stoichiometric conditions a combustible synthesis gas is obtained. As a result of the exothermic reaction, temperatures in the core of the HTR increase up to 2,000 °C sufficient to melt the metal and mineral components in the waste and to assure material conversion (in addition to sufficient residence times). Thus, chlorinated and other organic compounds are destroyed. Advantageous for prevention of dioxin formation is the presence of H₂S in the flue gas.

As a first step, the flue gas is shock-cooled to prevent *de novo* formation of PCDD/PCDF and other unwanted by-products and to precipitate molten particles. The gas then passes through a multi-stage cleaning process consisting of acid and basic scrubbers, and activated coke. An advantage of the Thermostelect system is the small volume of the flue gases (wet: 1,500 m³/t waste). The cleaned gases can be used as an energy carrier or as primary material for chemical processes. The inorganic material is converted and homogenized in a second chamber, the so-called homogenization reactor, directly connected to the HTR. Oxygen and combustible gases are added to reduce the residual carbon content and to maintain the temperature of the

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molten material above 1,600 °C. After water-cooling and granulation, a vitrified recycling material (mineral granulate) and ferrous alloy pellets are obtained.

Presently, there exists a Thermoselect plant in Fondotoce, Italy, processing 2.5-3 t/h (up to 100 t/d). Construction of a two-line facility in northern Bavaria (Ansbach, Germany) is permitted by the authorities, and construction of a three-line plant with 225,000 t/a in Karlsruhe (Germany) is underway. Here, we report the results obtained at the plant in Fondotoce.

A schematic drawing of the Thermoselect process (as discussed in this paper) and the sampling points are given in Figure 1. All samples date from the years between 1991 and 1994. Gas samples were taken by the RWTÜV, Essen, Cologne (Germany), according one of the German standard method for PCDD/PCDF sampling (VDI 3499 Part 1) where isokinetically, a partial flow of the gas is quickly diluted in a mixing line with dry, filtered air and - if necessary cooled with either ambient air or nitrogen to temperatures below 40 °C. The methods was recently approved in an evaluation test by the European Community. The sampling time was six hours. Clean-up, fractionation, and final detection of PCDD/PCDF was performed using standard methods and HRGC/HRMS (VG Autospec, Fisons Instruments) at a resolution of 10,000.

3 RESULTS

The results of the PCDD/PCDF measurements in synthesis gases are summarized in the following tables Table 1 and Table 2 and for the solid residues in Table 3 [8].

Most 2,3,7,8-substituted PCDD/PCDF congeners could be detected in the synthesis gas; exceptions were 2,3,7,8-Cl₄DD, 1,2,3,7,8,9-Cl₆DF, and once 2,3,4,6,7,8-Cl₆DF. The concentrations on I-TEQ basis ranged from 0.0002 (M2 at 3) to 0.016 ng I-TEQ/m³ (M1 at 2). The range for the totals ΣPCDD/PCDF (Cl₄-Cl₈) was from 0.03 to 1.38 ng/m³. 2,3,7,8-Cl₄DD could be detected in some samples at concentrations close to the limit of quantification (LOQ) of 0.003-0.0005 ng/m³.

Table 1: PCDD/PCDF in the synthesis gas (SG) at three different sampling points (For location of sampling points, see Figure 1)

Sample	M1 (ng I-TEQ/m ³)	M2 (ng I-TEQ/m ³)	M3 (ng I-TEQ/m ³)	ΣPCDD/PCDF (ng/m ³)	ΣPBDD/PBDF (ng/m ³)
SG 1	0.009			0.505	0.163
SG 2	0.009			0.607	0.191
SG 3	0.010			0.596	0.460
SG 4	0.015	0.0005	0.0010		
SG 5	0.016	0.0008	0.0010		
SG 6	0.011	0.0002	0.0025		

As can be seen from Table 2, there is almost no difference between the PCDD/PCDF concentrations in the synthesis gas before and after the gas motor. Comparing the concentrations at all sampling points, the dioxin levels were always very low; thus, indicating a low dioxin formation potential within the process. As expected, PCDD/PCDF could hardly be detected in

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the aqueous samples (Table 3), the PCDD/PCDF concentrations for the solid residues were in the low ppt-range when expressed in I-TEQ.

Table 2: PCDD/PCDF in the synthesis gases of the Thermostelect plant before (BGM, M3 in Figure 1) and after the gas motor (AGM, M4 in Figure 1) (concentrations in ng/m³, dry, 1,013 Pa, 273 K, 5 % O₂) i. (For location of sampling points, see Figure 1)

Sample	ΣPCDD/PCDF	I-TEQ	Sample	ΣPCDD/PCDF	I-TEQ
Synthesis gases before gas motor			Synthesis gases after gas motor		
BGM 1	0.193	0.0035	AGM 1	0.0680	0.0010
BGM 2	0.113	0.0017	AGM 2	0.0560	0.0012
BGM 3	0.099	0.0009	AGM 3	0.0602	0.0013

Table 3: PCDD/PCDF in liquid and solid residues from the Thermostelect process. (For location of sampling points, see Figure 1)

	Unit	I-TEQ		
Water from quench (WQS):				
WQS 1	pg/L		0.37	
WQS 2: Solid phase	pg/L		0.86	
Liquid phase	pg/L		1.5	
WQS 3	pg/L	0.0033	2.22	
Water from granulates: WGRAN	pg/L		0.5	
Condensate	pg/L	0.8	9.2	
Industrial water	pg/L	1.7		
Mineral granulate 1,2,3 *	ng/kg	0.338	0.11	0.19
Carbon sludge 1,2,3	ng/kg	49.3	42.8	71.9
Mineral deposit Q 1,2,3	ng/kg	0.72	3.22	
Residue after precipitation of process water Me(OH) _x 1,2,3	ng/kg	46.2	52.6	26.3
Sulfur 1,2	ng/kg	0.02	0.17	
Water before evaporation 1,2	pg/l	0.7	4.6	
Salt 1,2,3,4	ng/kg	0.15	0.16	0.05 0.44

* Corresponds to "vitrified recycling materials" in text

4 DISCUSSION

The results obtained from various emissions generated in the Thermostelect process show that the PCDD/PCDF concentrations are very low. Although, fractions or residues from the Thermostelect process cannot directly be compared with emissions from other combustion processes, following conclusions can be drawn:

ⁱ Effective O₂ concentration. According to German laws, O₂-concentrations <11% are not allowed to be "recalculated" (= diluted to 11%).

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- PCDD/PCDF - expressed as I-TEQ - are consistently low for all flue gas measurements (range in synthesis gases: 0.01-0.02 ng I-TEQ/m³) and far below the legal emission limit of 0.1 ng I-TEQ/m³ [2].
- PCDD/PCDF in water samples were between 0.4 and 2.2 pg I-TEQ/L and thus, in the range reported for dioxin concentrations in effluents from POTWs in the USA [9]. Unlike these water effluents, the water generated in the Thermoselect process is kept within the plant in closed circles and does not enter into the environment.
- PCDD/PCDF concentrations in the solid residues are in the range of uncontaminated soils or other mineral products. Generally, the dioxin levels are much lower than those reported for fly ash or bottom ashes from MSWI [4, 10].
- The smaller flue gas volume of the Thermoselect process (1,500 m³ wet/t waste compared to 8,500 m³ wet from MSWI) reduces costs for flue gas cleaning.
- Finally, the low PCDD/PCDF concentrations in samples obtained within the process and before methods are applied to destroy or remove PCDD/PCDF show that the dioxin formation potential within the Thermoselect process is low.

5 REFERENCES

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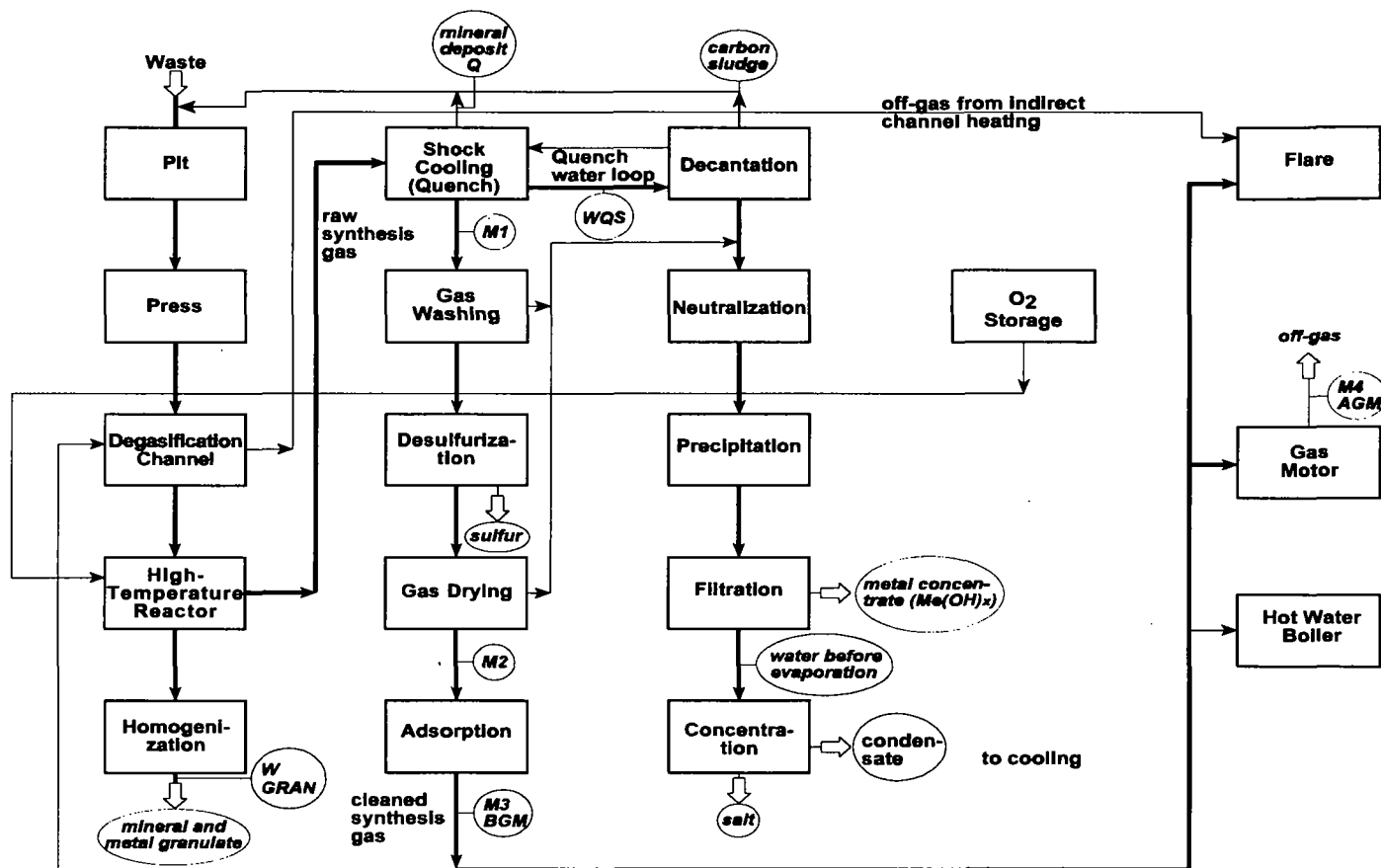


Figure 1: Schematic drawing of the Thermoselect process and sampling points (see Tables 1-3)
M1-M4: Sampling points for gas measurements

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