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Investigation of the Formation of Polychlorodibenzodioxins /-Furans and of other Organochlorine Compounds in Thermal Industrial Processes

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Zusammenfassung

Untersuchungen zur Bildung von Polychlordibenzodioxinen/-Furanen und anderer Organochlorverbindungen in thermischen Prozessen der Industrie

Im Rahmen des EU-Projektes MINIDIP Project Nr. ENV4-CT97-0587 "Minimization of Dioxins in Thermal and Industrial Processes: Mechanism, Monitoring, Abatement" wurden eine Reihe von Materialien aus thermischen industriellen Prozessen hinsichtlich des Potenzials der Bildung von Organochlorverbindungen, speziell von polychlorierten Dibenzodioxinen und -Furanen, untersucht. Im einzelnen handelte es sich um Proben aus der Zementindustrie, der Müllverbrennung, der Aufbereitung von Eisenerz und Zinkabfällen, sowie aus der Produktion von Edelstahl und der Elektrizitätserzeugung.

Die Proben wurden durch ausgewählte analytische Verfahren (RFA, DSC, Gesamt-organisch Chlor, GC-MS etc.) charakterisiert. Das Bildungspotenzial für Organochlorverbindungen (PCDD/F, PClBz, PClPh, PCB) wurde durch ein speziell entwickeltes Verfahren (thermische Behandlung der Feststoffe in Luft im Temperaturbereich von 250-350°C) und quantitative Bestimmung der gebildeten Organochlorverbindungen bestimmt.

Die Untersuchung der Materialien aus den verschiedenen Prozessen ergab beträchtliche Unterschiede:

Aufgrund der hohen Temperaturen im Prozess und ihrer Zusammensetzung (Kupfergehalt <<0.01 %, Cl 0.5 - 1%) zeigen Proben der Zementfabrikation nur niedrige native PCDD/F Konzentrationen und keine signifikanten Bildungsraten. Ähnlich verhalten sich Proben aus der Edelstahlproduktion und der Elektrizitätserzeugung.

Von besonderem Interesse erwies sich Material aus der Eisenerzsinterung, speziell der Flugstaub aus den elektrostatischen Abscheidern. Aufgrund des hohen Chloridgehaltes (8-32%), des Kupfergehaltes (bis 0.3%) und des Gehaltes an organischem Kohlenstoff (2.9 - 3.8%) liegen hier optimale Voraussetzungen zur Bildung von PCDD/F und anderer Organochlorverbindungen vor.

Auch in Materialien der Aufarbeitung von Zinkabfällen (Waelz-prozess) konnten teilweise beachtliche Bildungsraten von Organochlorverbindungen gemessen werden, speziell in den Flugstäuben.

Im einzelnen wurde die Abhängigkeit der Bildung von der Versuchstemperatur (250 -350°C), der Reaktionszeit (bis 240 min), der Zusammensetzung der Gasphase (Sauerstoff, Wasser) untersucht.

Neben der Bildung wurde im Detail auch die Möglichkeit der Inhibierung der Bildungsprozesse durch Zusatz von basischen organischen und anorganischen Komponenten studiert. Es zeigt sich, dass besonders durch 2-5 % Calciumhydroxid die PCDD/F-Bildung um bis zu über 90% reduziert wird; Zusätze von Natriumhydroxid (5 %) führen zu einer Erniedrigung der Bildung um mehr als 90-99%.

Insgesamt konnte gezeigt werden, dass der Bildungsmechanismus entprechend der bereits früher entwickelten Hypothese der "De-Novo-Synthese", d.h. Chlorierung und Oxidation des Restkohlenstoffs abläuft, wobei Übergangsmetall-Ionen, speziell Cu^{2+} , eine besondere Rolle spielen.

Abstract

Investigation of the Formation of Polychlorodibenzodioxins /-Furans and of other Organochlorine Compounds in Thermal Industrial Processes

Within the EU-project MINIDIP (ENV4-CT97-0587) "Minimization of Dioxins in Thermal and inustrial Processes: Mechanism, Monitoring, Abatement" a series of samples from thermal industrial processes was investigated with respect to the formation potential of organochlorine compounds, especially of polychlorinated dioxins/furans. The material was obtained from the cement industry, municipal waste incineration, iron ore processing, zinc recycling, stainless steel production and from an electricity plant.

The samples were characterized by selected analytical techniques (XRFA, DSC, Total-Organic Chlorine, GC-MS etc.). The formation potential for organochlorine compounds (PCDD/F, PClBz, PClPh, PCB) was determined by a special experimental technique (thermal treatment of the solids in air in the temperature range of 250-350°C) and by quantitative analysis of the compounds formed.

The investigation of the materials indicated considerable differences in formation:

Due to the high temperatures in the process and due to their composition (Cu <<0.01%, Cl 0.5-1%) samples from the cement fabrication showed only low native PCDD/F concentrations and no significant formation rates. Similar is the behaviour of samples from stainless steel production and from an electricity plant.

Of great interest was material from the iron ore sintering, especially of fly ash from the electrostatic precipitators. Due to the high chloride content (8-32 %), the Cu-concentration (0.3 %) and the carbon content (2.9-3.8 %) optimum conditions exist for the formation of PCDD/F and of other organochlorine compounds.

Also in material from the recycling of zinc residues (Waelz-process) considerable formation rates for organochlorine compounds could be measured, especially in fly ash.

In detail the influence of temperature (250-350°C), reaction time (up to 240 min) and the composition of the gas phase (oxygen, water) on the formation was studied.

Besides formation processes also the inhibition of the formation by adding basic organic (triethanolamine) and inorganic compounds was investigated. It could be shown, that by 2-5 % calcium hydroxide the PCDD/F formation may be reduced by more than 90%; with 5% sodium hydroxide a reduction of the formation by more than 90-99 % was achieved.

Generally it was shown that the formation mechanism corresponds to the previously developed "de-novo-synthesis", i.e. chlorination and oxidative degradation of the residual carbon, where transition metal ions, such as Cu^{2+}, play a special role.

Contents

1. Introduction

Since the discovery of polychlorinated p-dibenzodioxins (PCDD) and p-dibenzofurans (PCDF) in the flue gas of municipal waste incinerators substantial efforts have been undertaken to understand the formation mechanisms with the objective of developing technologies for the minimization of the release of these compounds in the environment. In a first approach the formation of PCDD/F was related to homogeneous gas phase reactions. Consequently experiments were performed at higher temperatures where from C_2-units a build-up of aromatic structures was observed, followed by a chlorination to yield chlorophenols and chlorobenzenes which in turn by condensation should lead to PCDD/F, as discussed by K. Ballschmitter et al. (1986,1988).

The role of gas-phase reactions of chlorophenols was summarized by Huang and Buekens (1995,1999) and Sidhu (1995). It could be shown that besides the combustion of chlorophenols to CO/CO_2 as main reaction, PCDD/F may be formed in a trimolecular side reaction. Under realistic conditions of municipal waste incineration, however, with concentrations of ca. 10-50 $\mu g/m^3$ of chlorophenols, only a formation of ca. 1-5 pg/m^3 PCDD/F is calculated. A significant contribution to realistic concentrations is therefore not to be expected by homogeneous gas phase reactions

At an early stage, however, it was concluded by Shaub and Tsang (1983) that reactions of gaseous precursor compounds on the surface of fly ash particles must be taken into consideration.

Over the last twenty years the reaction of a great variety of compounds on fly ash or on model systems was investigated with respect to their role as feasible precursor structures for PCDD/F. Extensive work has been carried out on polychlorophenols and their reaction mechanism by F. Karasek (1987), Dickson (1987) and E.R. Altwicker (1991, 1993) and M. S. Milligan (1995, 1996) resulting in a model where adsorption of precursors on active sites of the fly ash, condensation to PCDD, and desorption to the gas phase are individual steps with side reactions such as dechlorination and decomposition. In test facilities the influence of special combustion parameters on the yield was studied in detail by Gullett (1995) at EPA. In further studies with trichlorophenol as addditive to model fly ash the conversion to CO/CO_2, PCDD and PCDF was measured as a function of temperature (250-400°C) and reaction time (1-60 min) by K. Hell (1999a, 1999b). In detail investigated were also benzene, toluene (Jimenez-Leal, 1996, 1998) and dichloroacetylene (S. Sidhu, 1999) and their reaction on carrier materials. Of special interest is the role of polyaromatic hydrocarbons (PAH), as already reported by M.H. Schoenenboom (1995) and J. Wilhelm (1999, 2000). Depending on the structure dioxin analogue units such as anthracene, 9,10-dihydroanthracene, xanthene may serve as potent precursors for dioxins. On the other hand dibenzofuran related compounds such as fluorene, 9-methylfluorene, fluorenone and fluoranthene were found to be efficient models for PCDF. This finding is of special importance in connection with the fact that in municipal waste incineration under oxygen deficient conditions high concentrations of PAH are formed, which as deposits may act as sources for PCDD/F, so being responsible for the"memory effect".

A quite different way of formation - the so-called "De-Novo-Synthesis" - was proposed from our laboratory to explain the strong increase of PCDD/F on thermal treatment of fly ash in the temperature range between 300° and 450°C, as occurring in the post combustion zone of municipal waste incinerators (Vogg, 1986). In experiments with genuine fly ash as well as with model mixtures, it could be shown that particles of carbonaceous material from uncomplete combustion, present in concentrations up to 4-5%, must be considered as suitable precursor structures which by action of transition metal ions, such as copper(II), are converted to a variety of aromatic compounds from which PCDD/F are only compound classes among others (Stieglitz et al. 1989). So by similar mechanisms chlorobenzenes, -phenols, -biphenyls, -naphthalenes, -thiophenes and so forth are also formed. From the compounds studied so far the following mass balance as percentage of volatiles could be established (L. Stieglitz 1989, G. Schwarz, 1992), as given in table 1.

Table 1: Volatile compounds formed by de-novo-synthesis on fly ash of MWI plants

Compounds	Fraction (%) of measured volatiles
Chlorobenzenes, (PClBz)	84.3
PCDD	1.4
PCDF	6.5
Chlorobiphenyls (PCB)	0.15
Chlorophenols (PClPh)	0.01
Chloronaphthalenes (PClN)	2.8
Chlorobenzofurans (PClBF)	1.3
Chlorobenzonitrils (PClBN)	0.75
Chlorobenzothiophenes (PClBT)	1.0
Chlorothiophenes (PClT)	1.7

The yield of formation may be expressed by the following order:

PClBz > PCDF >PClN > PClT > PCDD > PClBF > PClBT > PClBN > PCB > PClPh

The conversion yield in mol/mol carbon at 300°C is 3.2×10^{-6} for PCDD, 8×10^{-6} for PCDF and 3×10^{-4} for polychlorobenzenes. (L. Stieglitz 1993). In addition, compounds such as chloroxanthones, -dibenzopyrones and benzophenones were identified. The formation of PCB was investigated in detail by M. Scholz (1997a, 1997b), of chloronaphthalenes by M. Schneider (1998). Further studies, especially with respect to the formation of sulfur containing compounds, were performed by R. Bechtler (1995).

In detailed investigations it was experimentally demonstrated that two different reactions are involved: a.) the formation of carbon-chlorine bonds in the carbonaceous material by a ligand transfer of chloride and b.) the successive oxidative degradation of the macromolecular structure to CO_2 as main product. The oxidation of chlorinated structures is, however, retarded resulting in the formation of chlorinated, smaller volatile units and their release to the gaseous phase (Stieglitz et al. 1989, 1990, 1993, 1994, 1996, 1998) .

In the first step, viz. the formation of organic chlorine the hydrogen in aromatic C-H structures is replaced via the action of copper(II)chloride and C-Cl bonds are formed, resulting in concentrations of organic chlorine in the range of 500 to 800 µg/g for fly ash. In this process Cu(II) is reduced to Cu(I) according to

$$\text{Ar-H} + 2\,\text{CuCl}_2 \rightarrow \text{Ar-Cl} + 2\,\text{Cu(I)Cl} + \text{HCl}$$

This mechanism was proposed by D.C.Nonhebel (1970) for liquid systems and was extended to a gas/solid phase system (K. Jay et al.1991). The reaction was applied with success to the synthesis of mixed halogenated (Cl, Br) dibenzodioxins and -furans (K. Jay et al.1996, 1997 a,1997 b).

In order to take further part in the reaction the Cu(I) must be re-oxidized to Cu(II). For this process the presence of oxygen and HCl is required. The stochiometry of the above chlorination reaction was investigated in detail by P. Weber (2000). Applying a combination of analytical techniques, among others also ESR-techniques, it could be proven that per C-Cl formed two $CuCl_2$ were reduced to CuCl , i.e. the molar ratio of C-Cl/Cu(II) is 0.5.

In the second process the macromolecular structure of the carbonaceous material is oxidized in a heterogeneous gas-solid reaction, where so-called surface oxides C(O) and C(O2) may play a role (P. L. Walker et al. 1967).

$$C(s) + O_2\,(g) \rightarrow CO_2\,(g)$$
$$2\,C + O_2 \rightarrow 2\,C(O)$$
$$C + O_2 \rightarrow C(2O)$$
$$C(O) \rightarrow CO$$
$$C(2O) \rightarrow CO_2$$

Carbonaceous material of different origin such as sugar coal (from pyrolysis of sugar), soot from a domestic oil burner and samples from the charcoal fabrication was studied and found to respond to the de-novo-synthesis reaction and to yield substantial concentrations of PCDD/F and other organochlorine compounds. (L. Stieglitz et al. 1989, 1990).

Notewothy are the following observations:

a.) As could be shown by differential scanning calorimetry, due to the presence of Cu^{2+}, especially copper chloride, the oxidation temperature of carbon is reduced from ca. 550°C to 300-350°C (L. Stieglitz, 1993). DSC-Studies of various metal compounds indicate that the decrease of oxidation temperature is primarily caused by copper chloride and bromide complexes, whereas with other copper compounds (CuO, $CuSO_4$, CuF) and transition metal chlorides the effect is much less pronounced (M. Eichberger, 1992).

b.) The kinetics of the oxidation in the temperature range of 275-400°C can be described by a combination of two exponential equations: within ca. 60 min a relatively fast degradation takes place. After that a slower process takes over, with the result that the reaction is levelling off and apparently stops at residual carbon concentrations, characteristic for each temperature. With increasing temperature the oxidizable fraction of the carbon is increased from 0.44 at 275°C to 0.73 at 400°C. This kinetic behaviour with the decrease of the oxidation rate at longer reaction times may be explained by the hypothesis that for the catalytically induced oxidation at such low temperatures partners with special structures, such as metal chlorides, are essential, which, however, during the reaction become deficient within the environment of the carbon particle and must be supplied to the reaction site by diffusion at elevated temperatures.

c.) The main product of the oxidation is CO_2, with low yields (ca. 10% relative) also of CO. The role of gaseous oxygen was studied by J. Wilhelm (1999, 2000) using a helium/ $^{18}O_2$ atmosphere. From the distribution of 18-oxygen in CO/CO_2, dibenzofurans, dibenzodioxins and phenols it must be concluded that there is an intensive interaction of the oxygen from the gas phase with the oxides/functional groups from the solid phase, followed by the oxidative degradation of the carbonaceous material.

d.) The role of the in-situ present or formed precursor structures was studied in detail by K. Hell, using mixtures of $^{13}C/^{12}C$ amorphous carbon. The distribution of ^{12}C and ^{13}C aromatic rings in PCDD and PCDF was analyzed. The results indicate that PCDD are partly synthesized by condensation of intermediate monoaromatic compounds e.g. chlorophenols, while PCDF are probably directly released after reaction from preformed dibenzofuran- or biphenyl-like structures in the carbon matrix (K. Hell 1999, 2001).

So far from the investigation of fly ash from MWI plants and of model mixtures the following conditions were found to favor the formation of PCDD/DF and other aromatic chlorocompounds:

composition of the solids : organic carbon (> 2-3%), chloride (> 4-5%), copper (II) >0.1%
composition of gas phase : oxygen >2%
temperature of solids/gas 300-400°C

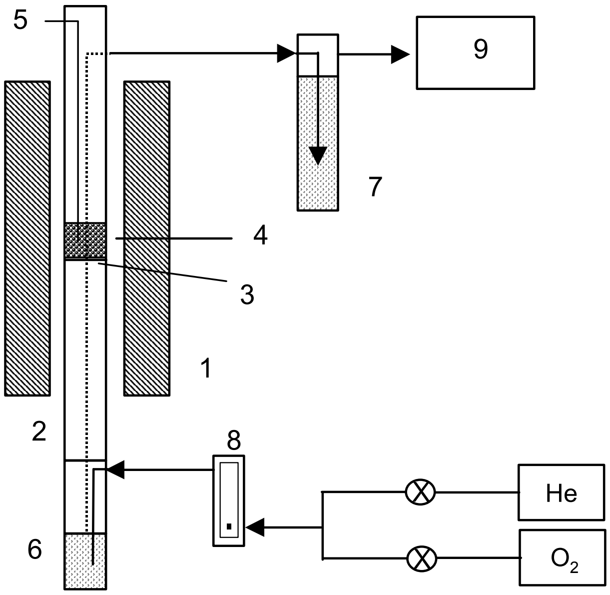
It is the objective of the following investigation to study the chemistry of materials from other industrial thermal processes, to define parameters for the formation of hazardous compounds such as PCDD/F and to find ways for an efficient inhibition of their release to the environment.

2. Experimental

2.1 Thermal Experiments

For the thermal experiments the sample, homogenized by grinding, was placed on a glass frit in the apparatus shown in fig. 1. An upward gas stream with a rate of 25-100 mL/min was passed through the fly ash. Under standard conditions the gas was synthetic air with up to 150 mg water/L. Depending on the experiment different gas compositions (oxygen, water) were also used. For kinetic measurements, where CO_2/CO was monitored by on-line mass spectrometry, a mixture of helium/oxygen was applied. The furnace was heated to the desired temperature on the upper part of the apparatus and then moved over the sample. This was recorded as start of the experiment. Volatile components were collected in a washing bottle containing toluene at ambient temperature. Reaction times varied from 15 min to 240 min. The experiments were performed either isothermally in the range from 200 to 450°C or with a ballistic temperature program. Details are given with the results of the respective samples. After the experiment the furnace was moved again on top of the apparatus, shut down and the sample cooled. The solids were removed, the apparatus washed with toluene and the washings combined with the content of the impinger.

Fig. 1: Experimental set-up for the de-novo-tests



1 oven
2 glass reactor (Ø: 1.5 cm, length: 50 cm)
3 glass frit
4 packed bed (model mixture)
5 thermocouple
6 water impinger
7 toluene impinger
8 flowmeter
9 mass spectrometer
gas flow: 50 mL/min
water addition: 150 mg/L gas

2.2 Analytical Methods

Determination of PCDD/F, chlorobenzenes, chlorophenols and PCB

The solution of the impinger and the fly ash samples were spiked with ^{13}C-labeled internal standards. The residue from the thermal treatment was extracted either in a soxhlet apparatus with toluene for 16 hrs. or with a toluene-methanol mixture in a dynamic high pressure apparatus at 150°C and 150 bar. The solution of the impinger and the extracts from the solids were cleaned-up separately. Clean-up and fractionation was performed by liquid chromatography using silica gel impregnated with concentrated sulfuric acid, (elution with n-hexane) and alumina with n-hexane, hexane-dichloromethane (98:2vol%) and hexane-dichloromethane (50:50vol%). For the determination of chlorophenols the extracts were treated with K_2CO_3-solutions, the phenolates in the aqueous phase then derivatized by acetic anhydride and the acetates re-extracted by dichloromethane, followed by a clean-up on silica gel. After concentration the fractions were measured by gas chromatography-mass spectrometry: PCDD/F were determined by HRGC/HRMS (Fisons Autospec) on a 60 m DB-Dioxin column. Polychlorobenzenes and polychlorophenols (as acetates), and PCB were analyzed with a HP 5890-MSD on a DB5 column (50m 0.25 i.d.). The quantitation was done via the ^{13}C labeled internal standards.

Determination of organic carbon in the solids (TOC)

The total organic carbon in the solids was measured in a Ströhlein C-MAT 550 PC apparatus. The sample is heated at 850°C in a stream of oxygen, the CO_2 then quantitated by infra-red spectroscopy. For the evaluation of the organic carbon the sample was treated with hydrochloride acid to remove carbonates. The detection limit is ca. 0.1%.

Determination of the total organic halogen (AOX)

The organic chlorine in fly ash is quantitated according to a modified procedure originally applied for the determination of adsorbable organic halogen from water as specified by DIN 38409: The sample (10-50 mg) is suspended in dilute HNO_3, containing $NaNO_3$ (0.16 M) and 50 mg pure charcoal for 1 hr, then filtered and washed with dilute $NaNO_3$ solution. The filter cake is introduced in an AOX-apparatus (Euroglas Delft) and oxidized at 1000°C in oxygen. The HCl is measured by microcoloumetry.

For special applications also the parameter "volatile organic halogene" VOX" was evaluated. For this purpose an aliquot of the impinger solution was injected through a special inlet into the AOX-apparatus and oxidized.

Generally by this technique chloride and bromide are measured. Since for the present investigation bromide was found not to be relevant the results obtained are interpreted as "chlorine"

Differential-Scanning Calorimetry

The measurement was performed in a DSC-apparatus (DSC-444, Fa. Netsch). The homogenized sample (50 mg) in an alumina crucible was placed at a NiCr-carrier and heated in an oxygen stream with a temperature program (4°K/min.) from room temperature to 550°C. The data (on-set temperature, peak-temperature, enthalpy) were evaluated using the software supplied

On-Line Monitoring of CO_2/CO

In some studies a mixture of helium (78,6%) and oxygen (19.4%) was used as reaction gas. With these experiments CO_2 and CO could be measured on-line with a mass spectrometer

Quadrova PGA 100 (Fa- Leybold). For the quantitation the system was calibrated before each run with a certified calibration gas (Messer-Griesheim). The concentrations of CO_2/CO/O_2 were evaluated with a program Masterquad 3.3 (Fa. Leybold) considering the measured distribution of the ion fragments.

3. Results and Discussion

During the MINIDIP-project samples from several different thermal processes from the industry were investigated and analyzed for their genuine concentration of relevant organochlorine compounds and for their formation potential of toxic components such as PCDD/F, chorobenzenes, -phenols etc. From the results a broader knowledge of the influence of composition and plant parameters on the formation of these compounds and their release to the environment was expected. A further goal was to find ways of minimizing the emission by inhibiting the formation with the application of special agents.

3.1 Cement Industry

Due to the high temperatures involved in the fabrication of cement the formation and release of PCDD/F compared with other industrial processes is minor. Nevertheless two samples from a cement kiln were investigated. The selected material was from a settling chamber and from an electrostatic precipitator. The composition is given in table 2.

Table 2: Composition (%) of dust from a cement kiln

compound	settling chamber	electrostatic precipitator
	(EU-3)	(EU-4)
CaO	52.6	13.4
SO_3	1.8	13.0
K_2O	2.5	28.2
Cl	0.58	1.11
CuO	0.006	0.01

As further analyses show the genuine material from the settling chamber (EU-3) has 5.6 % of carbonaceous material, a concentration of 12.1 µg/g organic chlorine (AOX) and low PCDD/F concentrations (0.4 ng/g PCDD, 0.98 ng/g PCDF). Within the analytical errors annealing to 300°C (2 hrs.) did not increase the total PCDD/F concentrations. Due to evaporation, however, the concentration in the residue was decreased to 0.32 ng/g PCDD and 0.7 ng/g PCDF, the rest being found in the gas phase (0.12 ng/g PCDD, 0.4 ng/g PCDF). Summing up compounds of the solid and the gas phase shows that in total no formation had occured. A reaction temperature of 450°C (2 hrs.) leads to a nearly complete destruction of all investigated compound classes.

The material (EU-4) from the electrostatic precipitator (field 3 and 4) has a slightly different behaviour: The carbon concentration is 2.6 %; the AOX 32 µg/g. The PCDD concentrations are 2.6 ng/g , PCDF 0.4 ng/g. Upon annealing to 300°C (2 hrs.) the AOX is down to 20 µg/g with the carbon concentration unchanged at 2.5%. The thermal treatment results in total PCDD (gas + solid) concentrations of 22.6 ng/g, and PCDF of 16.4 ng/g. Similarly the total concentration of polychlorobenzenes is increased from 3 ng/g to 550 ng/g. The results are

interpreted as an oxidative destruction of existing, non-volatile organochlorine compounds, with no substantial new formation of carbon-chlorine bonds.
With a reaction temperature of 450°C (2 hrs.), PCDD/F are vaporized and partly oxidized so that the total concentrations are 6.9 ng/g PCDD and 2.8 ng/g PCDF.
The differences in the thermal behaviour of the material from the settling chamber and the electrostatic precipitator can be explained by differences in the elemental composition, as shown in table 2: the material from the ESP consists of higher volatile compounds such as potassium compounds, with higher chloride and copper content, resulting in slightly higher formation of volatile organochlorine compounds. Due to the low copper content (0.01%), however, no efficient de-novo-reaction with the carbon (2.5%) can take place.

3.2 Municipal Waste Incineration

In order to be able to compare the behaviour of material from metallurgical processes also samples from municipal waste incineration plants were investigated. The material selected was from three different positions: exhaust residue (EU-37), E-filter (EU-38) and by-pass filter (EU-39). Furthermore additional material from the electrofilter from different chambers (EU-63, chamber 1; EU-64, chamber 9) was obtained and studied. The different chemical composition is among others demonstrated by the different pH-values, which are achieved by soaking the material in water: the leachate of EU-37 and EU-39 shows a pH of 13 and 12 respectively, whereas EU-38 gives a neutral solution. Analysis data for relevant components of the genuine material is given in table 3.

Table 3: Analysis of MWI-material (ng/g)

Sample	Exh. residue	E-filter	By-pass filter	E-filter, ch-1	E-filter, ch-9
	EU-37	EU-38	EU-39	EU-63	EU-64
PCDD	56.9	59.9	145	238	374
PCDF	40.5	41.1	159	100	180
PClBz	917	53	197	972	1154
PClPh	1887	32	153	47	309
PCB	44	54	53	66	60
Org. carbon ,%	3.8	<0.5	4.3	0.43	0.90
AOX, µg/g	193	362	69	n.d.	n.d.

Upon annealing at standard conditions (300°C 2 hrs.) the de-novo-synthesis proceeds to a quite different extent. The data are given in table 4.

In the sample of the exhaust residue the total organic chlorine (AOX + VOX) is increased to ca. 300 µg/g, the carbon concentration decreased to 3.02%. In this reaction the PCDD concentrations grow by a factor of 15, those of PCDF by ca. 60, whereas the chlorophenols are diminished to one half, either by oxidation or condensation reactions. With the E-filter

Table 4: Concentrations of organochloro compounds (ng/g) in annealed samples from MWI.(300°C, 2hrs.)

Sample	Exh. residue	E-filter	By-pass filter
	EU-37	EU-38	EU-39
PCDD	886	127	3340
PCDF	2340	210	2920
PClBz	15268	10888	530
PClPh	910	407	2
PCB	313	2	195
Org. carbon ,%	3.02	<0.5	4.4
VOX, µg/g	59	65	69
AOX, µg/g	240	345	135

material there is generally a slight increase of the organic chlorine compounds, that of the PClBz have a remarkable growth by a factor of 200. Material from the by-pass filter finally has the highest native PCDD/F concentration. This inventory is increased by a factor of 20. With the three samples the distribution between solid and gas phase is different: With EU-37 the PCDD/F remain adsorbed quantitatively on the solid, with EU-38 ca. 50% are evaporated, while from EU-39 more than 95% are found in the gas phase. This distinct difference in adsorption behaviour of the material can be explained by the assumption that the carbonaceous material of the exhaust residue and the by-pass filter must be completely different in origin and structure. The data are summarized by A. Buekens (1999a), by Stieglitz (1999d) and by K. Hell (1999b).

3.3 Investigation of Iron Ore Processing

3.3.1 Analysis of Different Iron Ores

As an introduction to the issue a variety of different ores was investigated. Generally the concentration of PCDD/F was found to be low: The data in ng/g are given in table 5.

Table 5: PCDD/F concentrations (ng/g) in iron ores of different origin

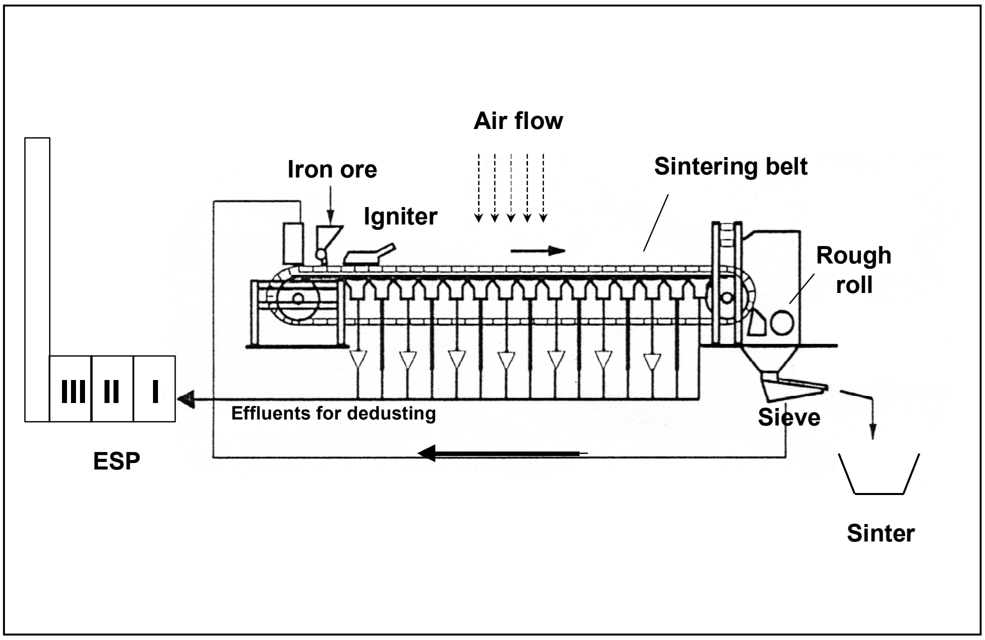
sample	PCDD	PCDF
Sesa Goa, India	0.11	0.25
Kiruna, Sweden	0.13	0.17
Carol Lake, Canada	0.13	0.18
Robe River, Australia	0.13	0.14

As can be seen the concentrations for PCDD are within 0.11 to 0.13 ng/g, those of PCDF from 0.14 to 0.25 ng/g. Due to the low values the variation is close within the analytical errors.

3.3.2 Iron Ore Processing

In an introductory study slag from an ore processing plant (IRP-I) and material from the electrostatic filter was analysed and the formation potential for organochlorine compounds investigated by thermal treatment at 300 and 450°C.
The PCDD/F concentrations in the genuine slag sample (EU-1) were low: 0.5 ng/g PCDD, 1.4 ng/g PCDF, corresponding to a TEQ (NATO) of 0.04 ng/g. PClBz, PClPh and PCB were at the detection limit, only total PAH were present in concentrations up to 670 ng/g. Thermal treatment at 300°C (2hrs.) results in slightly higher PCDD/F concentrations (total 2.9 ng/g) with ca. 25-30% being vaporized. At 450°C the oxidative degradation dominates: PCDD/F concentration is decreased to 0.8 ng/g.
The material from the E-filter contains considerably higher concentrations of organochlorine compounds: 550 ng/g PCDD, 1700 ng/g PCDF, 9600 ng/g PClBz, 1900 ng/g PClPh, 780 ng/g PCB and 2700 ng/g PAH. Upon annealing at 300°C and 450°C, respectively, only destruction (ca. 50%) could be observed.
In a more detailed investigation the formation and fate of organochlorine compounds was studied at an ore processing plant (IRP-II). The schematic of the plant is shown in fig. 2 .

Fig. 2 Scheme of an Iron Ore Sintering Plant



Investigated were the following materials: a.) material collected from underneath the sintering belt and b.) dust from the three succesive chambers of the electrostatic precipitation filter (ESP)

3.3.2.1 Material from the Sintering Assembly

Along the zones from ignition - sintering - baking - cooling siftings were gathered from the hoppers along the duct under the belt and analyzed for PCDD/F etc. Partly the material was also obtained in different particle size fractions.

The results for the zones from ignition to cooling are given in table 6.

Table 6: PCDD/F in material from different zones under the sintering belt

zone	Sample no	description	PCDD ng/g	PCDF ng/g
ignition	EU-22	#23, 0.125-1 mm	3.0	4.3
sintering	EU-26	#15, 0.063-0.175 mm	0.6	1.5
sintering	EU-27	#15, 1.0-2.0 mm	0.2	0.3
baking	EU-17	#12, 0.063-0.125 mm	1.0	3.0
baking	EU-18	#12, 0.125-1 mm	0.7	2.0
cooling	EU-8	#5, 0.0-0.075 mm	0.9	3.1
cooling	EU-9	#5, 0.075-1 mm	1.0	5.4
cooling	EU-10	#5, 0.075 -1mm	0.2	1.5

Results of the XRFA show that the main component is Fe_2O_3 with 45-52%, the concentrations of compounds relevant for the de-novo-synthesis are low: chloride is in the 0.15-0.22% range and copper mostly below detection limit (< 0.002%).

In the samples from the different positions the PCDD/F content varies, the highest concentration being found in the ignition range, with generally decreasing towards the cooling zone. The correlation is, however, not distinct. A slight correlation between PCDD/F with the surface area (decreasing particle size) is indicated. PClBz, PClPh and PCB are present in even lower concentrations.

The PCDD/F formation potential was investigated applying the standard de-novo-tests, i.e. annealing the samples in air at 300°C for 2 hrs. The PCDD/F inventory after heating is different in the respective samples: in material from the ignition zone no formation was measured, but a distinct transfer of ca. 50% to the gas phase. In samples from the sintering and baking zone an increase of PCDD/F is observed, also with high evaporation rates. The data are given in table 7.

Table 7: Total concentrations of PCDD/F (solid + gas phase) in ng/g after annealing (300°C, 2 hrs.)

Sample	PCDD	PCDF
Eu-22, ignition zone	2.2	3.3
EU-26, sintering zone	0.5	1.2
EU-27, sintering zone	0.7	1.8
EU-17, baking zone	2.0	4.1
EU-18, baking zone	1.3	3.4
EU-10, cooling zone	1.3	3.4
EU-8, cooling zone	0.9	4.0

The overall effect, however, is not remarkable. With sample EU-8 from the cooling zone also an experiment was performed, where the temperature was increased ballistically from 200°C to 600°C. In intervals of 50° C the toluene trap was changed and the content analyzed. The results are all in the range up to 100 pg/g and so close to the detection limits. Therefore no special formation potential for PCDD/DF could be found.

Differential Scanning Calorimetry

In the research for formation of PCDD/F in fly ash of MWI exothermal signals in the temperature range of 300-400°C from DCS measurements were recognized to be good indicators for the catalytically induced oxidation of carbonaceous material, which is a prerequisite for the formation and release of volatiles from fly ash. DSC measurements were carried out with the samples from the sintering belt.

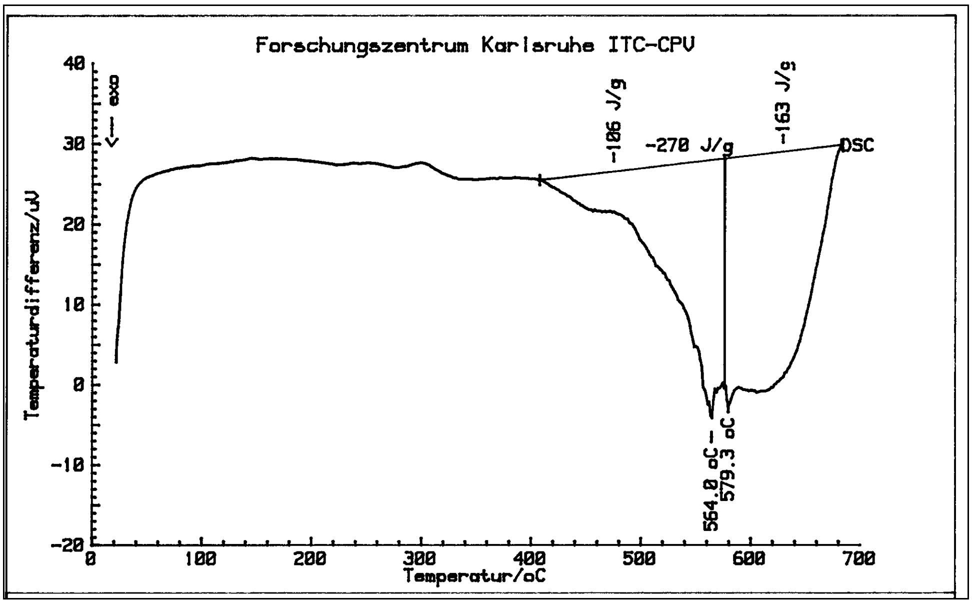
The basic data for the samples investigated are summarized in table 8.

A typical plot of material from the ignition zone is shown in fig.3. An exothermal reaction starts at ca. 460°C, with two peaks at 564 and 579°C respectively. A reaction within the temperature range of 300-350°C, characteristic for the de-novo-reaction, is not induced. This is in agreement with the low formation rates.

Table 8: Basic DSC data for samples from the sintering belt

	Peak temperature °C	Enthalpy J/g
EU-22, ignition zone	564	-186
	579	-163
EU-17, baking zone	400	5.95
	551	-147
EU-18, baking zone	376	22
	523	19
	594	25.8
EU-10, cooling zone	393.7	15.3
	610	-310
EU-9, cooling zone	397.9	35.2
	601	-226
EU-8, cooling zone	410	62.3
	569	-253

Fig. 3: DSC-plot of material from the ignition zone.



3.3.2.2 Materials from the Electrostatic Precipitator (ESP)

Overview of the Thermal Behaviour of the Different Materials

This material was obtained from the three fields of an ESP. Analysis of the samples by XRF analysis showed distinct differences in the composition. Relevant data in % are given in table 9.

Table 9: Composition (%) of the dust from the three fields of ESP

	Field 1 (EU-11)	Field 2 (EU-12)	Field 3 (EU-13)
Fe	39.7	28.3	8.5
Pb	1.1	3.5	10.6
Cl	8.8	21.2	31.6
K	4.75	13.48	19.5
Cu	0.04	0.17	0.29
Carbon	3.7	3.8	2.9

With decreasing iron content from 39.7 % to 8.5% apparently the fraction of volatile metal chlorides, notably KCl, increases, also the copper content going up from 0.04 to 0.29%. Noteworthy also is the carbon concentration in the lower percent range. The concentrations of native chlorocompounds in the genuine material (ng/g) are given in table 10.

Table 10: Initial concentrations of chlorocompounds (ng/g) in material from the ESP

	ESP 1 (EU-11)	ESP 2 (EU-12)	ESP 3 (Eu-13)
PCDD	0.4	47	29
PCDF	1.0	84.8	84
TEQ (Nato)	0.03	3.49	2.87
PClBz	612	358	1400
PClPh	97	680	3267
PCB	11	100	75
PAH	2625	17500	22650

Also determined were the concentrations of total organic chlorine (AOX) in the solids. The concentrations increase from 122 µg/g (field 1) to 747 µg/g (field 2) up to 1900 µg/g in material from field 3.

In order to investigate the formation potential for organochlorine compounds the samples were annealed in an air stream at 300°C for 2 hrs. The results for group parameters such as AOX, VOX and TOC are presented in table 11.

Table 11: Group parameters of the ESP material after annealing at 300°C (2 hrs.)

	AOX(µg/g)	VOX (µg/g)	TOX sum, (µg/g)	TOC %
ESP-1	86.9	5.9	92.8	2.8
ESP-2	500	611	1111	2.2
ESP-3	700	1725	2425	0.6

With respect to these group parameters the samples show a different behaviour upon annealing: The material from the first field EU-11 is partly oxidized, since the concentration of organic carbon decreases from 3.7 to 2.8% , in the same step the organic chlorine is diminished from 122.5 µg/g to 92.8 µg/g, only 6% being transferred to the gas phase as VOX. Sample EU-12 also undergoes oxidation, here, however, the total organic chlorine TOX (sum of AOX+VOX), is increased from 747 µg/g to 1111 µg/g, with 611 µg/g (55%) in the gas phase. The same trend is observed with sample EU-13: increase of the TOX to 2425 µg/g, with 70% in the gasphase; in the reaction the organic carbon is oxidized, the TOC going down from 2.9 to 0.6%. From these parameters it is indicated that the fundamental reactions (chlorination and oxidation) take place to a remarkable extent leading to the formation of organo chlorine compounds.

Results for PCDD/F (ng/g) are presented in table 12, as found in the annealed solid phase (SP) and in the gas phase (GP).

Table 12: PCDD/F concentrations (ng/g) in ESP-material after thermal treatment at 300°C (2hrs.), in gas (GP) and solid phase (SP).

	ESP-1 (EU11)	ESP-2 (EU-12)	ESP-3 (EU-13)
PCDD - SP	0.22	597	1700
PCDD - GP	58.6	12000	> 63000
PCDD - sum	58.8	12597	> 64700
PCDF - SP	1.7	2000	3600
PCDF - GP	99.7	45000	>110000
PCDF - sum	101,4	47000	>113600
PCDD/PCDF sum	160.2	60000	>178300
TEQ (Nato)	5.1	1632	ca. 5000

As indicated in table 12, the concentrations of PCDD/F from ESP-3 are beyond the linear range of the response of the mass spectrometer. The concentrations given therefore represent lower limits (see also table 13).

The homologue groups of PentaCDD and HexaCDD represent 60-70% of the dioxins in sample EU-11 and EU 12, whereas the PCDF consist to 70-80% of Tetra-Penta CDF. With the EU-13 Hepta- and OctaCDD dominate (80%) ; with the furans the more volatile tetra-hexa-species represent ca. 90%.

Compared with the initial concentrations the PCDD/F concentrations are increased by a factor of 117 for material from ESP-1, by 455 for ESP-2 and by more than 1500 for the dust from ESP-3.

Of special importance is the fact that in contrast to the experience with similar experiments with fly ash from municipal waste incinerators more than 95% are vaporized to the gas phase, inspite the concentration of 3-4% carbon. Apparently the matrix and structure of the carbon is quite different from that of municipal fly ash, as indicated by the low adsorptivity towards the organochloro compounds. As a consequence of this low adsorption the residence time on the solid after formation is short, thus reducing the chance for further degradation and dehalogenation. This fact is very crucial, as with the evaporation of the lower chlorinated species it leads to high TEQ values in the exhaust gas. The total concentrations (sum of solid and gas phase) of other relevant compounds (ng/g) after the thermal treatment are given in table 13.

Also in the formation of these compounds the dust from ESP-1 with lower reaction yields differs significantly from ESP-2 and ESP-3.

Table 13: Concentrations (ng/g) of relevant organochlorine compounds in ESP-material after heating (300°C, 2 hrs.)

	PClBz	PClPh	PCB	PAH
ESP-1	4430	44	57	565
ESP-2	415000	11970	13600	n.d.
ESP-3	> 575000	> 325000	31800	255000

During the thermal treatment of the sample from ESP-2 the carbon concentration decreases from 3.8 % to 2.2%, corresponding to an oxidative loss of 16 mg carbon/g. From this material a fraction of ca. 29 * 10^{-5} is converted to PCDD and a fraction of 137 * 10^{-5} to yield PCDF. Compared with the data from fly ash of MWI these values are higher by a factor of ca. 100 for PCDD and by 170 for PCDF under identical experimental conditions.
In an attempt to establish a mass balance of the volatile organic chlorine in the material from the field #2 the data from single compound analysis (table 12 and 13) may be compared with the value of the volatile organochlorine (VOX). Based on the chlorine content of the respective individual compounds, as collected in the toluene trap, the total chlorine is calculated and related to the volatilized VOX (= 611 µg/g).
The data are given in table 14.

Table 14: Mass balance of organochlorine as measured by single compound analysis in ESP-2 material

	Concentration µg/g	Fraction of VOX (%)
PCDD	6.4	1
PCDF	25.4	4
PClBz	225	37
PClPh	9.7	2
PCB	7.3	1
Sum	273.8	45

The data indicate that the compound classes investigated present only ca. 45% of the organochlorocompounds formed. For a total mass balance more compound classes such as Cl-PAH, must be considered. From previous investigations, however, it is known that from the toxicological point of view the most important compounds are quantified.

Measurements by differential scanning calorimetry (DSC)

Previous experience with fly ash had shown that the differential scanning calorimetry is a most useful technique to test the formation potential of samples for PCDD/F. One important condition for the release of volatile organocompounds is the oxidative degradation of the carbonceous matrix at relative low temperatures (300-400°C), as induced e.g. by copper chloro complexes. This process is exothermic and may be measured by DSC.

Fig. 4 presents the DSC curve for material from ESP-1. At ca. 300°C (on-set temperature) an exothermic reaction is induced, the maximum reaction rate is achieved at the peak temperature of 534° C. There is, however, due to a shoulder between 300-360°C, a substantial reaction taking place in the de-novo-region. The overall enthalpy of the reaction is -828 J/g sample. With an initial carbon concentration of 3.7 % this corresponds to -22.4 kJ/g carbon or 268 kJ/ mol carbon.

Fig. 4: DSC-plot of material from the field #1 of ESP

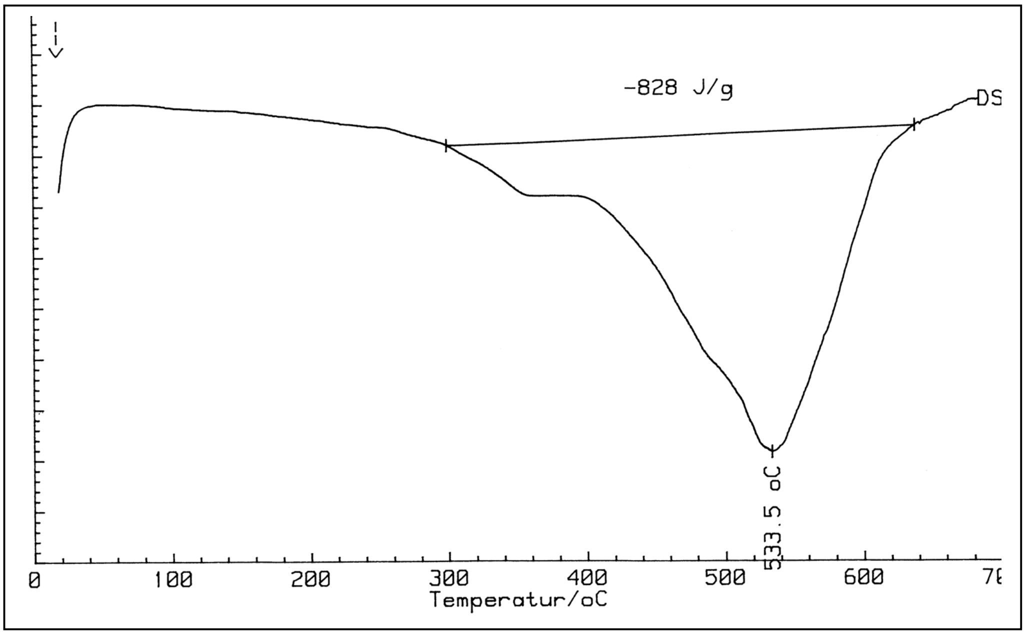
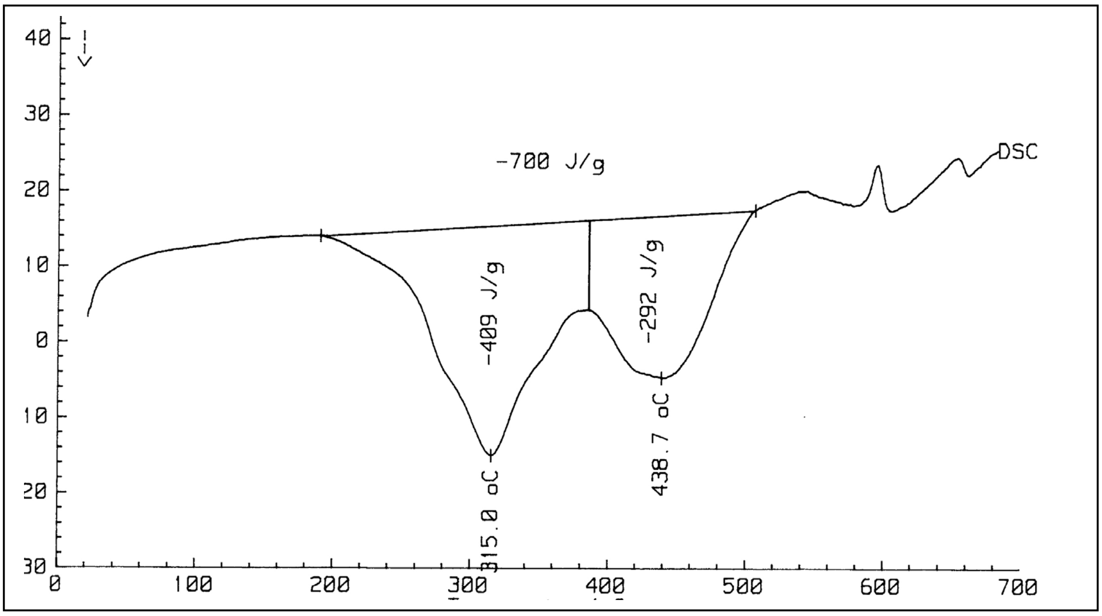


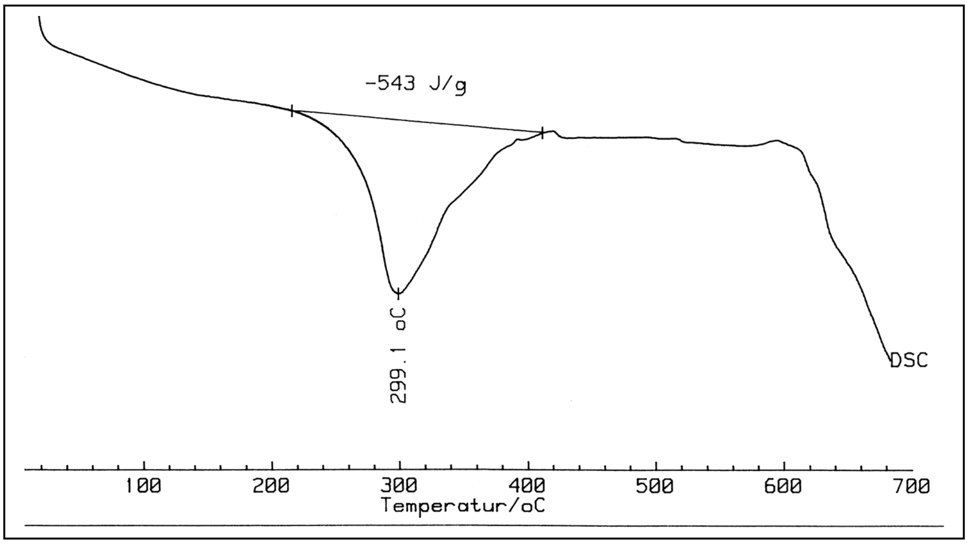
Fig. 5: DSC plot of material from field #2 of the ESP



In fig. 5 the DSC curve for the sample from the ESP, field 2, is shown. The different composition is reflected by a complete different thermal behaviour: Two major exothermic

peaks are observed: At an on-set temperature of ca. 200° C the reaction starts leading to a peak temperature of 315°C and an enthalpy of -409 J/g. A second peak is overlapping the first reaction, with a peak temperature of 439°C. In total both reactions combined have an enthalpy of -700 J/g, related to the carbon content of 3.8% , this correspondens to -18.4 kJ/g carbon or -221 kJ/ mol carbon.
In fig.6 the DSC curve of the sample from the field 3 of the ESP is shown. Also with this material the reaction starts at 200°C, and reaches a maximum rate at 299°C, characterized by an enthalpy of -543 J/g and is finished at 400°C. No second reaction is noted as with the sample from the second field. With 2.9 % initial carbon concentration the enthalpy is -18.7 kJ/g carbon or 224 kJ/mol carbon.

Fig. 6: DSC plot of material from the field #3 of the ESP



In all three samples the enthalpy of the samples measured was in the range of 220 to 260 kJ/mol carbon. This is comparable with data obtained in experiments with fly ash from municipal waste incineration. Here the values were 22.3 ± 1.3 kJ/g or 268 ±15 kJ/mol carbon. In order to investigate important reaction parameters and due to the unique reactivity of the samples a series of experiments under different reaction conditions was performed. The material from ESP-3 was so reactive that, although with repeated dilution, the concentrations of the PIC were so high that the analysis could not be performed satisfactorily. Consequently the material from ESP-2 (EU-12) was selected for further studies on experimental parameters and reaction mechanisms.

Influence of Reaction Temperature

From experiments with municipal waste incineration fly ash, the temperature range from 300°-350°C was found to be optimal. In order to study the influence of temperature, experiments were performed with material from ESP, field-2. The samples were annealed for 30 min. isothermally at 200, 250, 300, 350, and 400°C. The total concentrations in ng/g (solid+gas phase) of the selected compounds are given in table 14.

Table 14: Concentrations of organochlorine compounds (ng/g) after isothermal annealing at various temperatures for 30 min.

Temperature	PCDD	PCDF	PClBz	PClPh	PCB
200° C	54	153	439	820	100
250° C	140	250	4070	3650	370
300° C	1870	12590	175500	9200	2500
350° C	1965	17820	254000	5900	9300
400° C	210	2200	8890	2090	3340

The results confirm that also for material from sinter plants the optimal temperature range is 300-350° C.

Ballistic Experiments

In this set of experiments the sample was heated in a ballistic temperature program starting from 200°C to 450°C. The gas phase was collected in a toluene trap, which was changed during the heating in 50° C intervals, i.e from 200-250°, 250-300° etc., corresponding to a time interval of ca. 10 min. After the ballistic increase of the temperature the sample was kept at 450°C for another 70 min., so achieving a total reaction time of 120 min. The data are given in table 15 for material from the ESP-2 for PCDD/F and in table 16 for chlorobenzenes and chlorophenols.

Table 15: Formation of PCDD/F (ng/g) in ballistic experiments with material from ESP-2 (EU-12)

Temperature	200-250°C	250-300°C	300-350 °C	350-400°C	400-450°C	450°C
Cl4DD	0.9	4.9	73.0	271	20.7	21.1
CL5DD	0.2	2.6	56.9	214	17.0	12.5
Cl6DD	0.2	2.6	23.4	68.4	6.0	4.9
Cl7DD	0.3	1.3	7.6	14.5	1.5	1.8
Cl8DD	0.5	0.3	1.6	3.0	0	0.5
PCDD	**2.1**	**11.7**	**162.5**	**570.0**	**45.2**	**40.8**
Cl4DF	0.0	41.2	1180	3800	314	412
Cl5DF	0.3	15.1	345	1300	130	151
CL6DF	1.0	5.4	60.1	295	33.4	36.5
CL7DF	0.2	0.6	5.8	27.5	3.8	5.1
Cl8DF	0.7	0.0	1.2	1.4	0.6	0.7
PCDF	**2.2**	**62.2**	**1592**	**5423.9**	**481.8**	**605.3**

Compared with the yields from the isothermal experiments at 300°C the sum of the PCDD/F volatilized over a time of 120 min is lower. There is also a shift of the optimum temperature range to 350-400°C. Apparently with the ballistic program the residence time (ca. 10 min.) within the range of 300-350°C is to short for the reactions to develop sufficiently.

Table 16: Formation of chlorobenzenes and chlorophenols (ng/g) from ESP-2 material in ballistic experiments

Temperature °C	200-250	250-300	300-350	350-400	400-450	450
Cl2Bz	<1	1490	37077	95122	5980	3492
Cl3Bz	<1	2535	35893	54721	6384	4983
Cl4Bz	<1	2113	17770	25513	4528	3682
Cl5Bz	<1	399	2690	5875	1684	910
Cl6Bz	<1	0	189	515	0	152
PClBz	**<1**	**6537**	**93619**	**181746**	**18576**	**13219**
Cl2Ph	<1	286	1514	3672	66	<1
Cl3Ph	<1	456	699	727	51	<1
Cl4Ph	<1	<1	<1	<1	<1	<1
Cl5Ph	<1	<1	<1	<1	<1	<1
PClPh	**<1**	**742**	**2213**	**4399**	**117**	**<1**

Influence of Reaction Time

In order to study the formation kinetics of PCDD/F and of other chlorocompounds a series of experiments was performed isothermally at 250°C and 300°C with reaction times between 30 min and 240 min. The data are presented in tables 17 and 18 for 250°C and in tables 19 and 20 for 300°C.

Table 17: Kinetics of PCDD/F formation (ng/g) in ESP-2 material at 250°C

reaction time (min)	0	30	60	90	120	240
Cl4DD	1.9	13	38	129	191	373
Cl5DD	7.0	30	45	204	316	652
Cl6DD	13.5	43	135	202	314	536
Cl7DD	14.5	35	98	150	174	382
Cl8DD	10.3	21	58	107	57	247
PCDD	**47**	**142**	**374**	**791**	**1052**	**2189**
Cl4DF	20.3	105	261	893	1680	2877
Cl5DF	27.9	83	179	622	1114	1585
Cl6DF	23.8	49	155	374	418	1064
Cl7DF	9.7	14	37	78	89	383
Cl8DF	3.1	9	21	51	23	67
PCDF	**85**	**259**	**652**	**2018**	**3324**	**5976**

For short reaction times of 30 min. the formation of PCDD proceeds with ca. 3 ng/g*min. For longer reaction times (>60 min) an average rate of 8 ng/g*min. (± 1.5) must be considered. PCDF are formed with rates of 17 ng/g*min (± 8.7).

The total concentrations (solid & gas phase) of chlorobenzenes, chlorophenols and PCB are summarized in table 18.

Table 18: Kinetics of PCBz, PClPh and PCB formation (ng/g) in ESP-2 material at 250°C

Reaction time (min)	0	30	60	90	120	240
PClBz	358	4840	15000	50000	50000	112600
PClPh	680	3260	3200	9300	7050	14500
PCB	100	520	3100	4650	n.d.	1530

It is common to all compounds that during the first 30 min there exists a period of latency and only after that the concentrations increase.

Table 19: Kinetics of PCDD/F formation (ng/g) in ESP-2 material at 300°C

Reaction time (min)	0	30	60	90	120	240
Cl4DD	1.9	473	1200	1778	2231	2245
Cl5DD	7.0	713	2100	3307	3913	4460
Cl6DD	13.5	442	1570	2595	3415	4530
Cl7DD	14.5	188	860	1504	1661	2430
Cl8DD	10.3	53	270	407	455	840
PCDD	**47**	**1869**	**6000**	**9591**	**11675**	**12505**
Cl4DF	20.3	7515	13500	22492	26253	18800
Cl5DF	27.9	4328	12000	14781	17227	21000
Cl6DF	23.8	1553	4700	6649	6658	10700
Cl7DF	9.7	237	840	1273	1145	1850
Cl8DF	3.1	22	95	99	94	140
PCDF	**85**	**13652**	**31135**	**45294**	**51377**	**52490**
PCDD/F	**132**	**15521**	**37135**	**54885**	**63052**	**64995**

At 300°C up to 30 min. the rates are 60 ng/g*min. and then within 60-120 min. increase to 100 ng/g*min (sdt.dev. ± 10), i.e. the reaction rate is more than ten fold compared with 250°C. For the PCDF an average of 479 ng/g*min (std.dev. ± 50) is calculated. Similarly as with the experience with fly ash from MWI the formation comes to a plateau after ca. 2 hrs. After that the formation rate drops and only a slight increase of concentrations is noted with longer reaction times. The reason for this decrease of reaction rate may be the fact that during the process essential inorganic reaction partners in the environment of the copper species are exhausted and may be restored only by diffusion. Another explanation may be that in the carbon material the structures which serve as precursors are used up. In table 20 the data for PClBz, PClPh and PCB are summarized.

Table 20: Kinetics of formation of PClBz, PClPh and PCB (ng/g) in ESP-2 material at 300°C

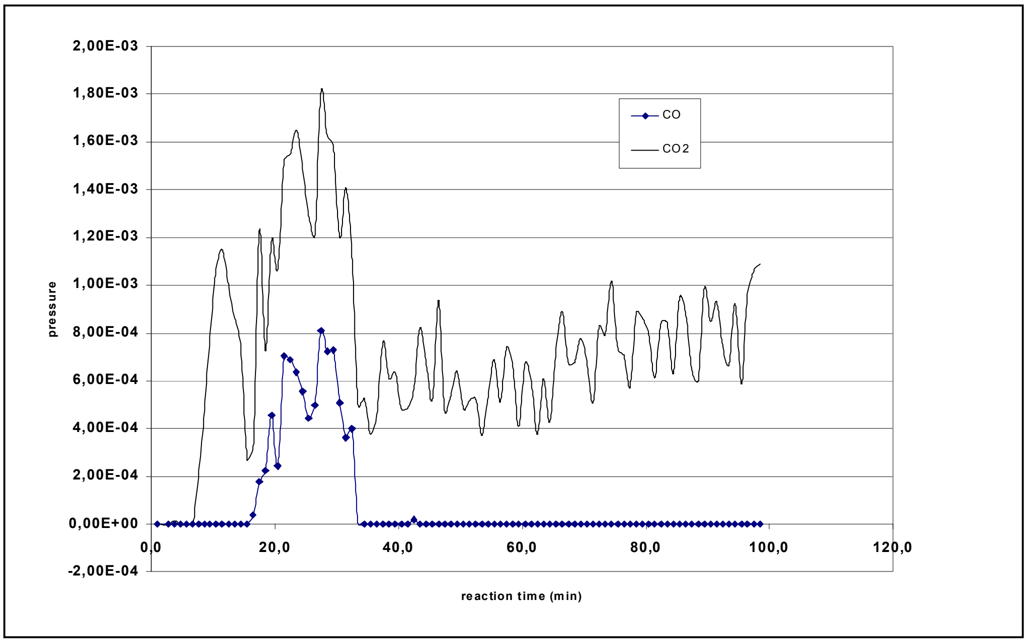
Reaction time (min)	0	30	60	90	120	240
PClBz	358	170000	335000	400000	415000	512000
PClPh	680	9200	19000	11000	12000	53700
PCB	102	2500	10000	10900	13600	25300

The concentrations of these compounds may be described by a rough linear relationship with reaction time.

On-line measurements of CO_2/CO

For the further elucidation of the processes the formation of CO_2/CO was monitored during the experiments on-line by mass spectrometry. For the experiment at 250°C the concentrations are shown in fig 7.

Fig. 7: Formation of CO_2 /CO during the thermal treatment of ESP-2 material at 250°C

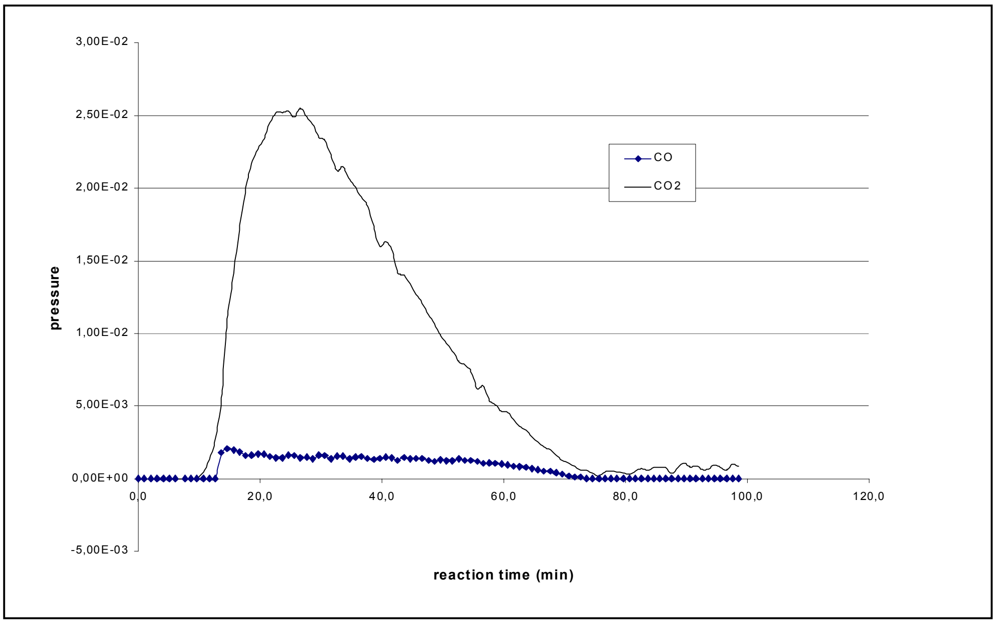


As indicated the reaction starts with the release of CO_2 and attains a maximum after ca. 30 min with a partial pressure of ca. 1.2 x 10^{-3} units. With longer reaction times the concentration drops to a plateau of ca. 7x 10^{-4} with considerable noise. The formation of CO shows a similar behaviour. The ratio of CO/CO_2 is ca. 0.7.

In fig.8 the results of CO_2/CO formation are presented for the experiment at 300°C. After a short inhibition time the CO_2 concentration rises to a maximum of ca. 2.5 x10^{-2}, which is attained after ca. 25-30 min., followed by a decrease over a period of ca. 70 min. After that only a very slight release i.e. reaction is noted. The behaviour of CO is very similar.

The data show that a.) with the thermal treatment the oxidative degradation of the material takes place resulting in the release of CO_2/CO; b.) the reaction rate is greatly reduced after longer heating times resulting in a plateau of the total amount of CO_2/CO formed. This behaviour corresponds directly to the kinetics of formation of PCDD/F, PClBz, etc., where also after ca. 90-100 min a plateau of the total concentrations is reached.

Fig.8: Formation of CO_2/CO during the thermal treatment of ESP-2 material at 300°C



Measurement of AOX and VOX

Besides single compound analysis also important group parameters such as Total Organic Halogen (AOX) and Volatile Organic Halogen (VOX) were measured in material from ESP-2 after experiments at 250°C and 300°C. Both parameters are given in table 21 for the kinetic experiments with material from ESP-2.

Table 21: Dependance of VOX and AOX (µg/g) from reaction time at 250° and 300°C

	Time (min)	0	30	60	90	120
250°C	AOX	747	850	1058	1310	980
	VOX	0	5.8	16.5	61.5	295
	sum	**747**	**856**	**1075**	**1372**	**1275**
	evap.(%)	0	<1	2	4	23
300°C	AOX	747	1450	966	825	830
	VOX	0	224	328	560	600
	sum	**747**	**1674**	**1294**	**1385**	**1430**
	evap. (%)	-	13	25	40	42

The ESP-2 material initially contains 3.8% of residual carbon. As already discussed above for the measured compound classes such as PCDD/F etc. the adsorption at temperatures of 300°C is reduced compared with the behaviour of MWI material. This observation is in part confirmed also for the group parameters VOX and AOX. Here the comparison of the AOX and the VOX shows that after 120 min 23% are volatilized, at 300°C even more that 40%.
The data of the VOX and the single component analyses from the 300°C experiment may be further evaluated and the fractions calculated, which are represented by the sum of the individual compound classes measured. The results are shown in table 22.

Table 22: Fraction (%) of the individual compound classes related to VOX

Reaction time (min)	30	60	90	120
PCDD	0.4	0.95	0.89	1.0
PCDF	3.0	4.8	4.1	4.4
PClBz	49	63	42	40
PClPh	0.9	3.5	0.9	1.0
PCB	1.4	1.7	0.9	1.1
sum	**54.7**	**73.95**	**48.79**	**47,5**

As outlined above also with this evaluation it is apparent that the five compound classes investigated represent only a fraction of the total organochlorine compounds released. With some outliers, the PCDD represent ca 1% of the VOX, PCDF ca. 4%, whereas the chlorobenzenes is the major fraction with 40-60%. Both chlorophenols and PCB are about 1-2 % of the VOX.
Also with the ballistic experiment the total volatile organic halogen (VOX) was measured. The results are given in table 23.

Table 23: Formation of volatile organic halogen compounds (VOX) in ballistic experiment ..

temperature	200-250°	250-300°	300-350°	350-400°	400-450°	450° (70 min)
VOX (µg/g)	47.5	24.75	132	278	39.5	55

The data confirm the fact that in the temperature range from 300-400°C a strong formation of volatile organochlorine compounds occurs.

Since more than 90% of the PCDD/F are transferred to the gas phase at 300°C a good correlation may be derived between the total PCDD/F concentration Y(ng/g) and the VOX (µg/g) with the following equation:

$$Y = 77 * VOX,$$

and may be used to have a fast estimate of the dioxin/furans released.

Influence of Water Content in the Gas Phase

In experiments with fly ash from MWI it had been demonstrated that the water content in the gas phase has a distinct influence on the formation of aromatic chlorocompounds such as PCDD/F, PCBz, chloronaphthalenes and benzothiophenes. The formation yield increased with a water content up to 250 mg/L. With higher water concentrations (400-500 mg/L) the formation decreased, probably due to lower oxygen concentration as a result of the increased water content (G. Schwarz, 1993).

De-novo-tests (300°C, 2hrs.) with dust from ESP-2 in dry atmosphere show no distinct effect due to the absence/presence of water: the formation was 9450 ng/g PCDD and 46350 ng/g PCDF, compared with 12600 ng/g PCDD, respectively 47000 ng/g PCDF with 150 mg/l water.

Influence of Oxygen Concentration in the Gas Phase

In previous experiments it had been demostrated that for the de-novo-formation of PCDD/F from fly ash the presence of oxygen is absolutely neccessary. In order to evaluate this reaction parameter for material from iron ore sintering corresponding experiments were made where the oxygen concentration varied from 0 to 50%. The reaction conditions were 300°C, 2 hrs. with a gas flow of 50 mL/min. The results for PCDD/F in ng/g are given in table 24.

Table 24 : Influence of oxygen content on PCDD/F concentrations (ng/g)
at 300°C, 2 hrs.

oxygen (%)	0	2.3	3.8	20	50
PCDD	26	178	2230	11000	14000
PCDF	45	1100	9900	47600	48000
PClBz	870	42000	172000	512000	590000
PClPh	1500	4600	18000	53700	34500
PCB	250	1900	3200	25300	20000

The correlation with the oxygen concentration is obvious: in inert atmosphere only traces of PCDD/F are released. A significant fraction (ca. 50%), see also table 10, may be due to the evaporation of adsorbed native compounds already present before annealing. Even with low oxygen content (2-4%), however, a significant increase of the concentration is noted. With 20 vol% oxygen a strong formation by a factor of ca. 800 is observed. Between 20 and 50 vol% no further increase is noted.

The results confirm that oxygen in the gas phase is an essential prerequisite for the reaction to proceed efficiently. Oxygen is necessary for the two reactions of the de-novo-synthesis: the re-oxidation of the Cu(I) and the oxidation of particulate carbon.

Influence of Gas Velocity

In an experiment with material from ESP-2 (reaction temperature 300°C) the gas flow (air) was varied from from 25 to 100 mL/min, corresponding to velocities from 0.13 to 0.53 cm/sec. The results in ng/g are presented in table 25 for the homologue groups.

The data show that with increasing velocities from 0.13 cm/sec to 0.27 cm/sec the PCDD/F formation is enhanced. It is known from the experiments with different oxygen concentrations that oxygen is necessary for the chlorination and oxidation processes in the solid. Higher oxygen supply is provided with the increased velocity. On the other hand with even higher velocity the yield drops to ca. 50% of the maximum value measured. Apparently the residence time of important precursor compounds is diminished, resulting in a final decrease of the formation.

Table 25: Effect of gasflow on PCDD/F concentrations (ng/g) at 300°C

gas flow	25 ml/min	50 ml/min	100 ml/min
velocity	0.13 cm/sec	0.27 cm/sec	0.53 cm/sec
Cl4DD	1620	2100	850
Cl5DD	3600	3700	1820
Cl6DD	2800	3140	1770
Cl7DD	2000	1610	1280
Cl8DD	450	450	314
PCDD	**10470**	**11000**	**6034**
Cl4DF	17100	23830	11854
Cl5DF	10800	15750	7440
Cl6DF	5470	6675	4800
CL7DF	985	1250	860
CL8DF	86	94	90
PCDF	**34441**	**47599**	**25044**
PCDD/F	**44911**	**58599**	**31078**

Influence of Carbon Addition on Evaporation

In order to explain the observation that more than 90% of the PCDD/F formed are transferred to the gas phase, which is in contrast to the behaviour of fly ash from MWI, active charcoal (4%) was added to a sample from ESP-2, which had been treated thermally before. The mixture was heated in the standard procedure. The data show, that ca. 86% of the PCDD and 95% of the newly formed PCDF compounds remain adsorbed on the solid phase. Therefore it must be concluded that the different adsorption behaviour of the carbon residues (coke derivatives) are responsible for the different behaviour of the ESP material.

Experiments for the Inhibition of PCDD/F Formation

In order to contribute to the minimization of the PCDD/F emission in thermal processes a series of experiments was designed and carried out. It is known from fly ashes of MWI that the formation of halogenated compounds can be inhibited to a certain extent by the addition of ammonia and other basic compounds. Due to its exceptional reactivity material from ESP-2 (EU-12) was selected for the tests. Addition of ammonia (150 mg of 0.1 N NH_4OH/ L gas, ≅ 0.255 µg NH_3/L) to the gas phase had no influence on the PCDD/F formation. The effect of other nitrogen containing additives was quite distinct, resulting in considerable inhibition. Data are presented in table 26.

Table 26: Effect of organic additives on the PCDD/F concentrations (ng/g) at 300°C with a reaction time of 2hrs.

	No additive	Urea (1%)	0.2 % TEA	0.5% TEA	1% TEA	5% TEA
Cl4CDD	2000	1340	1630	1490	1000	1380
Cl5CDD	3970	5350	2790	2245	1490	2860
Cl6CDD	3590	2280	2120	1780	1080	1360
Cl7CDD	2010	1040	1110	890	480	550
Cl8CDD	550	325	300	225	140	90
PCDD	**12120**	**10335**	**7950**	**6630**	**4190**	**6240**
Cl4DF	24530	11820	18880	17280	12690	19245
Cl5DF	16130	13730	11570	10165	7400	12010
Cl6DF	7770	5660	4535	3900	2660	4170
Cl7DF	1550	940	870	690	460	600
Cl8DF	120	75	60	50	30	40
PCDF	**50110**	**32225**	**35915**	**32085**	**23240**	**36065**
PCDD/F	**62230**	**42560**	**43865**	**38715**	**27430**	**42305**

The thermal experiments were made with EU-12 in triplicate, in order to have reliable data for comparison. The average values for initial concentrations are given in column 2. The standard deviation is for the PCDD data ± 16%, for the PCDF ±9%. With the addition of 1% urea a reduction of 15% for PCDD and of 36% for PCDF can be achieved. Even better results for inhition were obtained with triethanolamine (TEA). The effect of reduction as expressed in percent is seen in table 27.

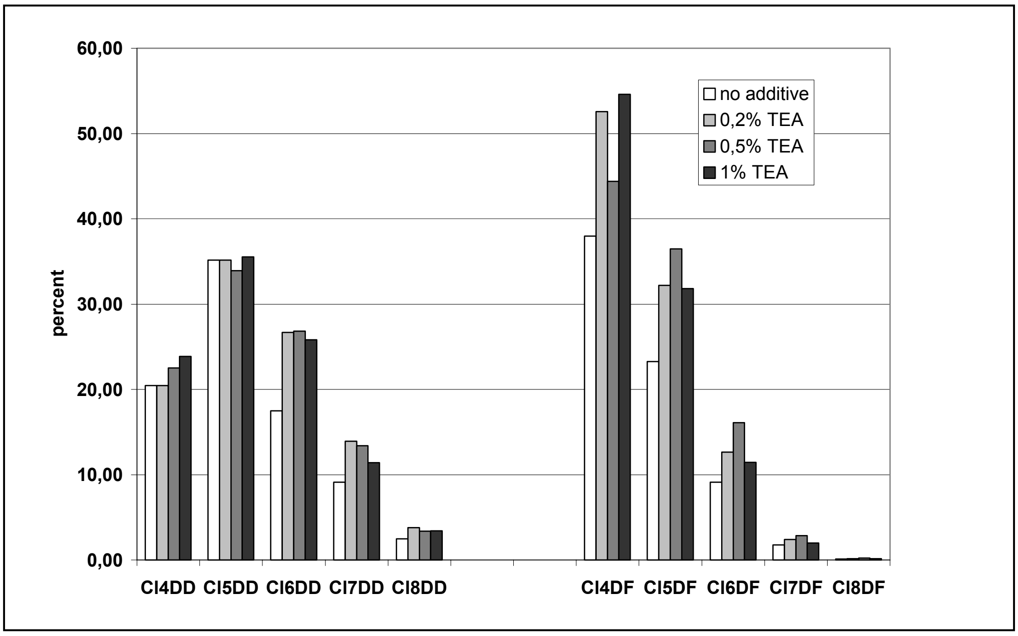
Table 27: Reduction (%) of PCDD/F formation in ESP-2 material by addition of TEA at 300°C, 2hrs.

Reduction(%)	0.2 % TEA	0.5% TEA	1.0% TEA	5% TEA
PCDD	34	45	65	49
PCDF	28	36	54	28
PCDD/F	30	38	56	32

With increasing TEA concentrations (0.2% to 0.5%) also the effect of inhibition rises from 30% to 56%. With higher concentrations (5%) a clear reversal of the effect is noted, with a total reduction of only 32%. An explanation of this counter effect is not available. Triethanolamine is of very low volatility (b.p. 277 °C at 150 mmHg), so in contrast to ammonia and urea, it can react with the active $CuCl_2$, and so interfering with the two fundamental reactions of de-novo-synthesis: chlorination and oxidation.

The percent fraction of the individual homologue groups is calculated and plotted as bar graphs in the fig 7 .

Fig 7 : Fraction (%) of the homologue groups as received through inhibition by TEA



By the addition of various amounts of TEA the formation of PCDD/F is retarded, it has, however, no significant influence on the pattern of the homologues, taking into account the standard deviation of experiment and analysis (PCDD ±16%, PCDF ±9%).

In the inhibition experiments also other compound classes were measured. The data are given in table 28.

The effect of urea addition is not significant. On the other hand with increasing TEA concentrations the formation of PClBz is reduced to ca. 50%, of PClPh to 105 and that of PCB to 15%.

Further experiments on the effect of inhibitors were performed with the addition of basic hydroxides such as $Ca(OH)_2$ and NaOH. The compounds were added in mixture with the dust. Results from tests at 300°C (2 hrs.) are shown in table 29.

The addition of 2% $Ca(OH)_2$ leads to a total reduction of formation to 63%, with 5% calcium hydroxide the reduction is 93%. Good results are also achieved with 0.5 % NaOH, where PCDD/F -formation is lower by ca. 90%. With 5% NaOH the rest concentrations are far below 1% of the initial values and close to the detection limits.

Table 28: Effect of organic additives on the formation of PClBz, PClPh and PCB (ng/g) in ESP-2 material at 300°C, reaction time 2hrs.

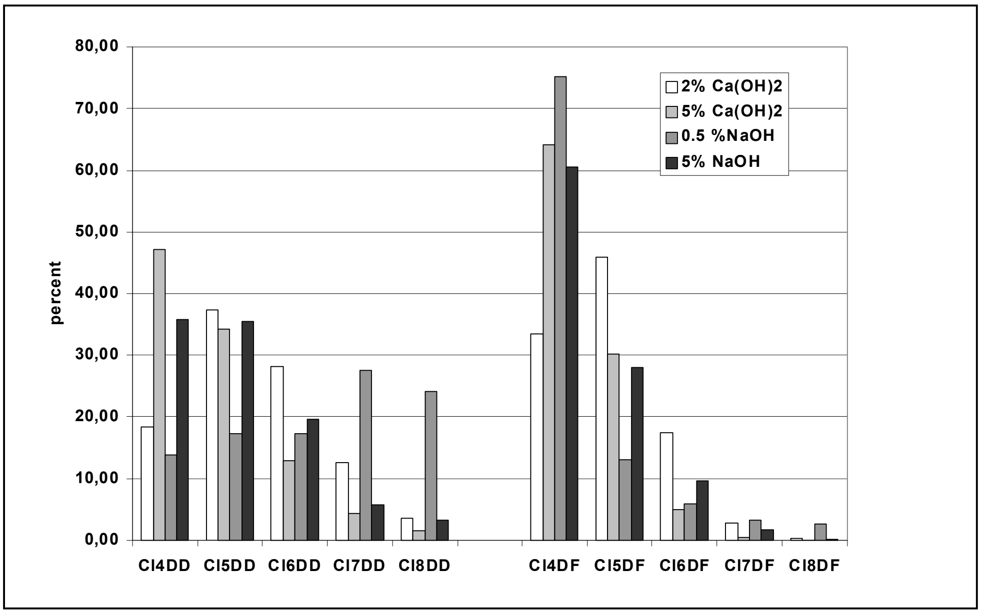
	No additive	Urea (1%)	0.2% TEA	0.5% TEA	1% TEA	5% TEA
Cl2Bz	111000	78000	10600	22000	81000	108000
Cl3Bz	166000	115000	129000	120000	103000	50000
Cl4Bz	84000	96000	93000	80000	66000	24000
Cl5Bz	20000	30000	24000	22000	17000	7000
Cl6Bz	4500	4300	3800	3400	2800	880
PClBz	**385500**	**323300**	**260400**	**247400**	**269800**	**189880**
Cl2Ph	3700	6300	1100	2800	3000	1150
Cl3Ph	4900	11400	1745	3100	2000	560
Cl4Ph	7000	8900	1400	2200	3600	140
Cl5Ph	1100	2200	630	830	430	<1
PClPh	**16700**	**28800**	**4875**	**8930**	**9030**	**1850**
PCB	**13600**	**9700**	**11500**	**11000**	**7200**	**2010**

Table 29: PCDD/F formations (ng/g) after addition of basic compounds at 300°C (reaction time 2 hrs.) to material from ESP-2

	No additive	2% $Ca(OH)_2$	5% $Ca(OH)_2$	0.5 % NaOH	5% NaOH
Cl4DD	2006	560	215	375	4
Cl5DD	3974	1140	136	373	5
Cl6DD	3586	860	58	206	5
Cl7DD	2012	390	17	60	8
Cl8DD	547	110	7	34	7
PCDD	**12125**	**3060**	**433**	**1048**	**30**
Cl4DF	24532	6640	2660	4050	115
Cl5DF	16130	9100	900	1870	20
Cl6DF	7773	3450	220	650	9
Cl7DF	1553	560	22	110	5
Cl8DF	124	60	2	9	4
PCDF	**50112**	**19810**	**3804**	**6689**	**152**
PCDD reduction		75 %	97 %	91 %	>99 %
PCDF reduction		60 %	92%	87%	>99%

The influence of the respective basic materials on the homologue pattern is presented in fig. 8.

Fig 8: Homologue pattern as obtained by the addition of basic compounds



The influence of 2% $Ca(OH)_2$ on the pattern is not remarkable. With 5% calcium hydroxide the fraction of the tetrachloro-dioxins is increased from 26% to 50%, possibly as a result of the hydrolysis of hexa-/octachloro compounds. The fraction of the latter compounds decreases to 13%, 4% and 2% respectively. Similarly distinct is the result of the hydrolysis of the dibenzofurans: The percent fraction of Cl_4DF rises from 49% to 70% whereas the hexa-to octachloro species represent in total only ca. 6% of the PCDF.

Table 30: Formation of chlorocompounds (ng/g) after addition of basic compounds at 300°C (reaction time 2 hrs.) to material from ESP-2

	No additive	2% Ca(OH)2	5% Ca(OH)2	0.5 % NaOH	5% NaOH
PClBz	**385500**	**222700**	**116420**	**153590**	**5990**
PClPh	**16700**	**10010**	**6565**	**6505**	**406**
PCB	**20297**	**4167**	**2773**	**3770**	**163**

The inhibition experiments were also performed with the highly active material from the ESP-3. 5% $Ca(OH)_2$ was added to the dust prior to the experiment and heated isothermally at 300°C for 2 hrs. The results are summarized in table 31.

Table 31: Effect of addition of 5% $Ca(OH)_2$ on the formation of chlorocompounds in material of ESP-3 at 300°C (2 hrs. reaction time)

	No additive	5 % $Ca(OH)_2$	
	ng/g	ng/g	reduction
PCDD	> 65000	1290	>98%
PCDF	>110000	5700	>95%
PClBz	575000	99000	83%
PClPh	325000	13800	96%
PCB	31800	2400	93%

As can be seen the inhibition process is also efficient with the highly active material from ESP-3. The reduction of the formation, especially with PCDD/F, is > 95%.

Generally the effect of the studied additives may be explained by the destruction of the catalytic sites of copper/iron-chloride. The result of the interaction of the basic inhibitors with the catalytically active metal-chloro compexes is the formation of basic chlorides or even oxides, which are not active in the conversion of C-H to C-Cl-strucures and therefore do not favor the formation of organic chlorine. The alkaline compounds, however, could also interact with the oxidation process, since, as could be seen from DSC measurements CuO has a peak temperature of 507°C for the oxidation of carbon, compared with ca. 300°C for the copper chloride system.

In order to be able to explain the influence of the additives on the individual reactions DSC measurements were carried out with the systems containing the inhibitors. A typical plot is presented in fig.9 for the system ESP-2/ 2% $Ca(OH)_2$. As can be seen the oxidation starts already at temperatures as low as 220°C, and besides a shoulder at 276°C shows two distinct peaks at 351° C and 449°C. An increase of the Ca(OH)2 concentration to 5% has no significant influence on onset temperature and peak temperature. The appearance of the plots is similar to the system without additive (see fig. 5), which also shows the splitting of the exothermal peaks. The onset temperature in the system without inhibitor is 200°C, with two exothermal peaks at 315°C and 439°C.

In fig 10. the DSC curve of the system ESP-2/5% NaOH is shown. The reaction is represented by a single exothermic peak at 345°C with an on-set temperature of ca. 210-230°C. With this system apparently the oxidation also takes place within the temperature range of the de-novo-synthesis.

Generally from the DSC measurements it may be concluded that the presence of the inhibiting additves Ca(OH)2 and NaOH does not significantly interfere with the oxidation of the residual carbon.

Fig. 9: DSC-plot of the system 2% $Ca(OH)_2$/ESP-2 material

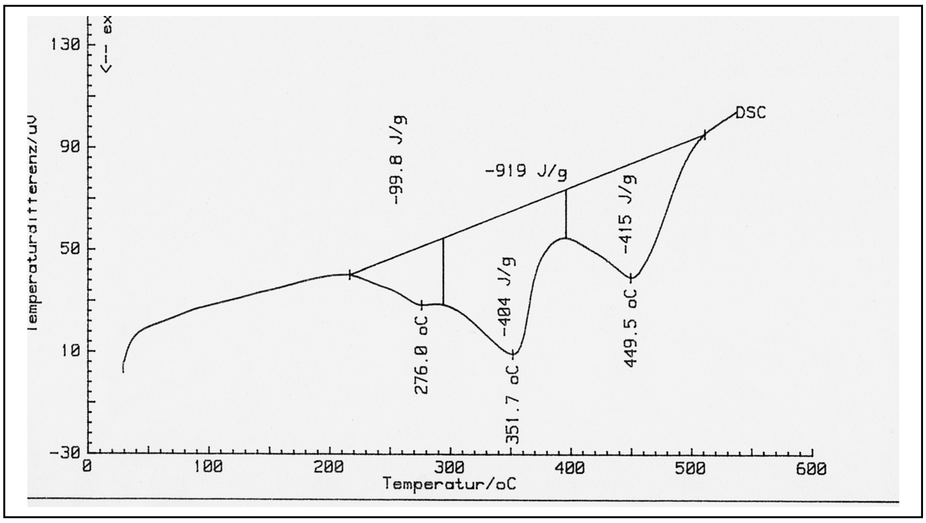
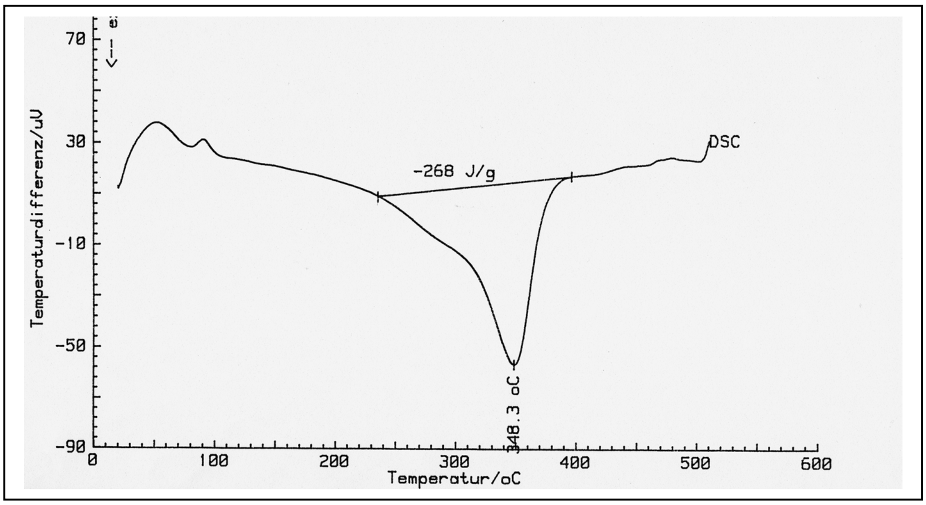


Fig. 10: DSC-plot of the system 5% NaOH/ESP-2 material

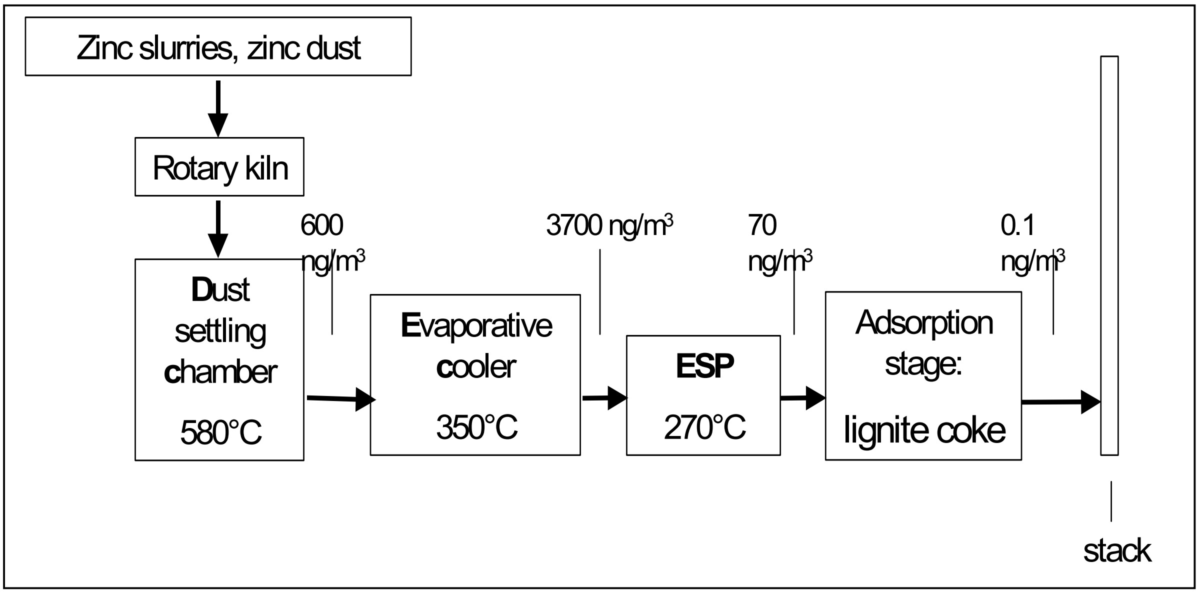


The results of this study were summarized in a series of contributions (A. Buekens 1999 b, 1999c, 1999d; L. Stieglitz 1999a, 1999b 1999c; R. Weber 1999a) .

3.4 Investigation of the Zinc Recycling Process

Scrap dust from the iron and steel industry, composed mainly of iron oxide, contains valuable concentrations of zinc, lead and to some extent also copper. This material is reprocessed in the so-called Waelz process to a crude zinc oxide. The scheme is presented in fig. 11.

Fig. 11: Scheme of the Waelz -Process



In this process crushed coke is added to the raw material and introduced at ca. 950°C in a high temperature rotary kiln. The material is moving from the feed side to the slag discharge side. In a counter currrent stream hot gases provide additional heat for the reduction. In the mixture with the carbon a reducing atmosphere is created and zinc and lead reduced to metal vapors which enter the gas phase.

So in the load the following processes take place:

$$CO_2 + C \rightarrow 2\,CO$$
$$ZnO + CO \rightarrow Zn + CO_2$$

Above the solid charge the gas phase conditions are oxidizing, so that the volatilized zinc fumes are again oxidized to zinc oxide. The gas phase is freed from the coarse particulates in a settling chamber and the coarse dust recycled to the rotary kiln. The finely divided Waelz oxide is carried along by the gas and collected in a bag house filter. Samples were obtained from two plants which differ in the slagging mode (acidic or basic slag).

3.4.1 Material from Plant A, Acidic Slagging Mode

In this plant zinc slurrries and ores are recycled. The result of this process among others is an acidic slag. The dust samples are collected in three different chambers: dust chamber (EU-79), evaporative cooler chamber (EU-80) and electrostatic filter (EU-81). The concentrations (%) of relevant components are shown in table 32.

Table 32: Concentrations of relevant components (%) in the respective materials from the Waelz process with acidic slagging

	dust settling chamber (EU-79)	evaporative cooler (EU-80)	ESP (EU-81)
Fe	10.5	3.1	1.8
Pb	3.1	3.4	6.5
Cu	0.1	0.1	0.1
Zn	52.2	63.4	64.5
Cl	1.4	1.5	3.2
Carbon	2.5	4.0	1.5

The samples consist mainly of zinc oxide, with 2 - 4% organic carbon, 1.5 - 3% chloride and 0.1% of copper. From experience with material from other metallurgical processes the composition indicates a favorable formation potential for PCDD/F and other aromatic chlorocompounds.

The initial concentrations of organochlorine compounds in the samples are given in the table 33.

The data indicate that on the passage of the dust from the settling chamber to the ESP generally the concentrations of the organochlorine compounds decrease to a certain extent, except that of chlorophenols.

Table 33: Initial concentrations (ng/g) of relevant organochlorine compounds in material from the Waelz-process with acidic slagging

	dust settling chamber (EU-79)	evaporative cooler (EU-80)	ESP (EU-81)
PCDD	16	23	5
PCDF	37	8	8
TEQ (Nato)	1.04	0.46	0.21
PClBz	240	60	30
PClPh	400	450	400
PCB	130	90	80

In order to study the thermal behaviour of the samples DSC measurements were carried out in oxygen from room temperature to 550°C with a rate of 4 °C/min .

The DSC curve the sample from the dust settling chamber (EU-79) is presented in fig.12

With the dust from the dust settling chamber the on-set temperature is 350°C, the peak temperature 448°C, with an enthalpy of - 315 J/g. Based on the initial carbon concentration of 2.5%, this corresponds to 151 kJ/mol carbon, lower than the values obtained from ESP material from the iron ore sintering. The material from the evaporative cooler (fig.13) exhibits an on-set temperature of ca. 300°C, and a peak temperature of 369°C, with an enthalpy of - 824 J/g, i.e. 247 kJ/mol carbon.

Fig. 12: DSC plot of dust from the settling chamber

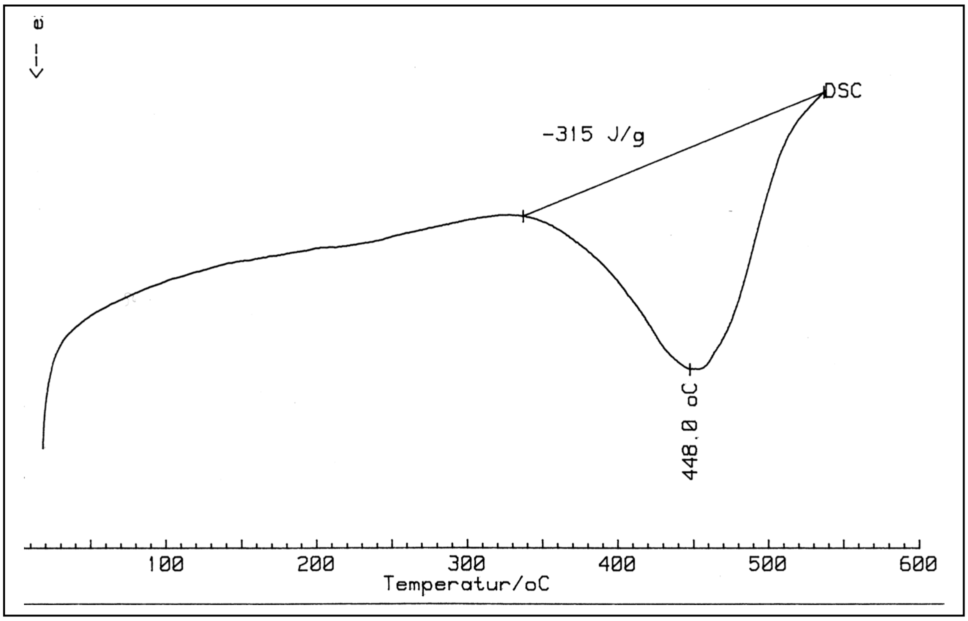
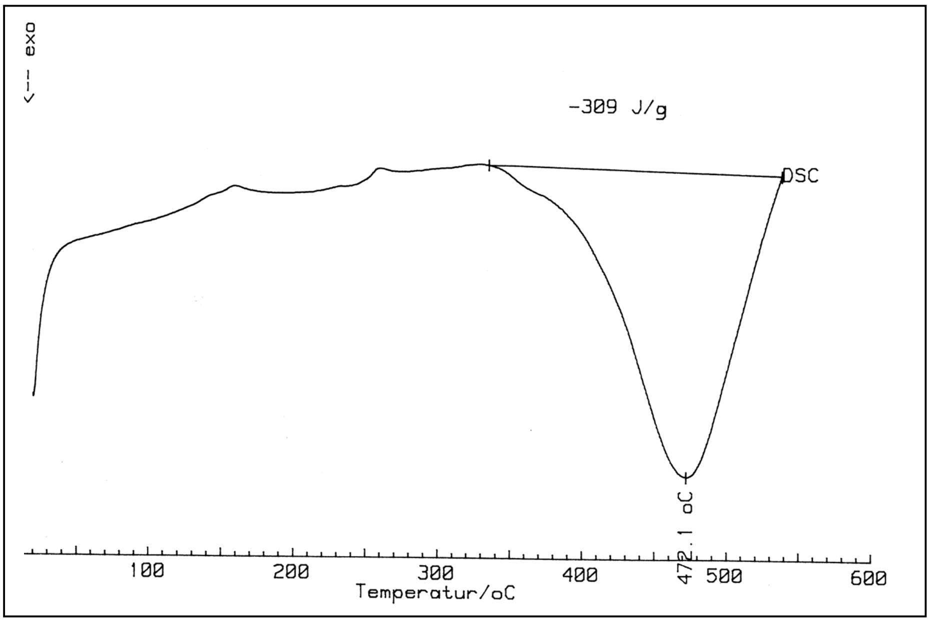
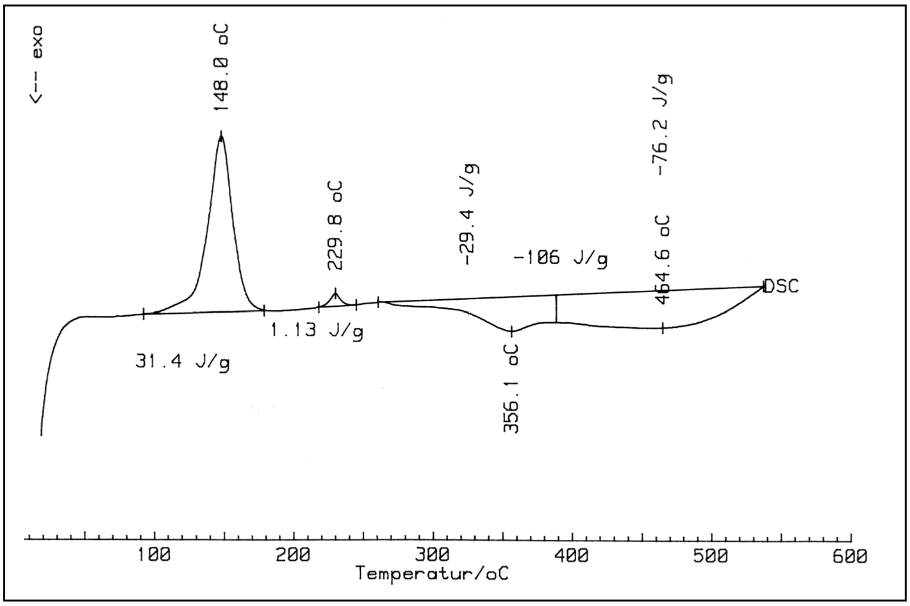


Fig. 13: DSC plot from dust of the evaporative cooler



The DSC of the sample from the ESP, as presented in fig. 14, is very complex: At 148°C there is a distinct endothermic peak with an enthalpy of 31.4 J/g. At increasing temperature a slight exothermic peak shows at 356°C and a second one at 464°C, with a total enthalpy of -106 kJ/g. From these measurements a different behaviour of the samples with respect to the PCDD/DF formation should be expected.

Fig. 14: DSC plot of dust from the ESP



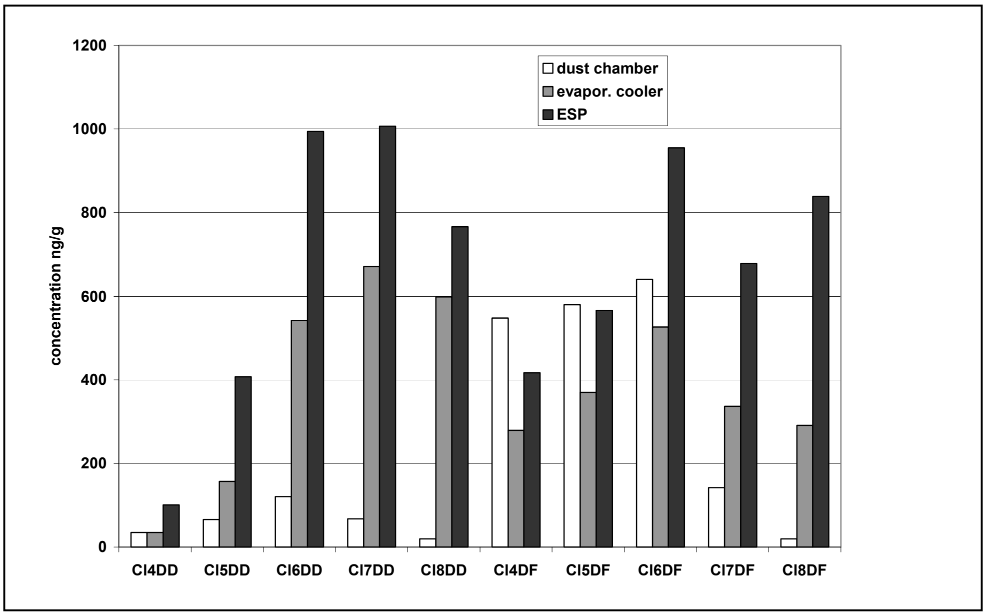
Since the temperature of the evaporative cooler is at 350°C and the DSC measurements indicate oxidation processes also at 350°C the de-novo-tests were performed at 350°C. The data for PCDD/F are given in table 34.

Table 34: Total concentrations (solid + gas phase) of PCDD/F (ng/g) after annealing at 350°C (2 hrs.)

	dust.settl.chamb (EU-79)	evaporative cooler (EU-80)	ESP (EU-81)
Cl4DD	35	35	101
Cl5DD	66	157	407
Cl6DD	121	542	994
Cl7DD	67	671	1007
Cl8DD	19	598	766
PCDD	**308**	**2003**	**3275**
Cl4DF	548	279	417
Cl5DF	580	370	566
Cl6DF	640	526	955
Cl7DF	142	337	678
Cl8DF	19	291	839
PCDF	**1930**	**1803**	**3454**
PCDD/F	**2237**	**3806**	**6729**

With the experiments the distribution between solid- and gasphase is similar to the material from iron ore sintering: more than 95% of the dioxins/furans are transferred to the gas phase. The results for the three samples are summarized in the bar graph for the PCDD/F in fig.16.

Fig. 16: Concentrations (ng/g) of of PCDD/F after annealing at 350°C in material from the Waelz process (acidic slagging)



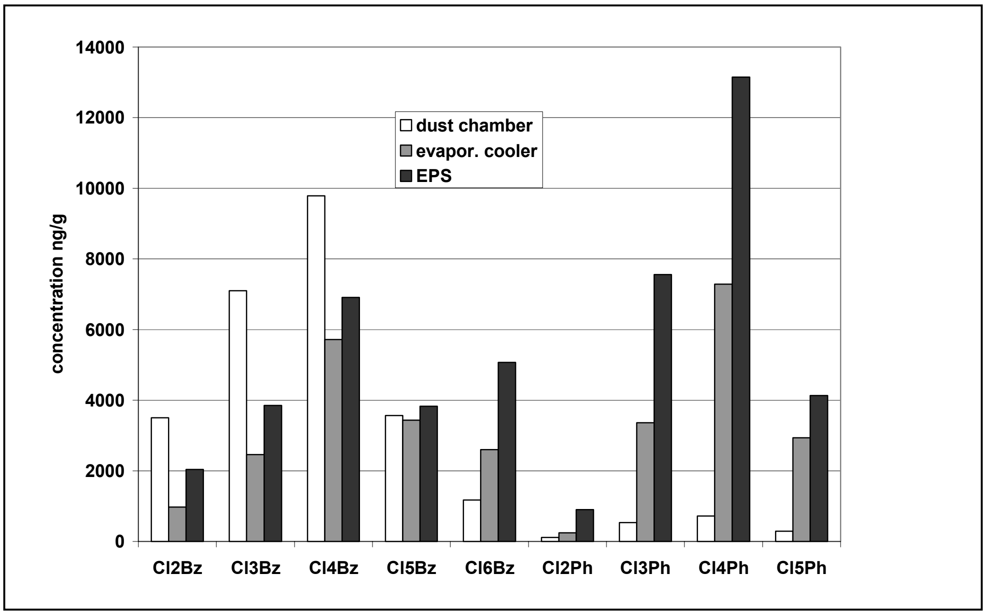
Generally on the passage from the dust chamber to the ESP the formation potential increases for the dioxins and the furans. On this way the chlorination degree is shifting from lower to higher chlorinated species
Besides PCDD/F also PClBz, PClPh and PCB were analyzed. The data are given in table 35.

Table 35: Concentrations (ng/g) of PClBz, PClPh and PCP in annealed samples (350°C) of the Waelz process with acidic slagging

	dust settling chamber (EU-79)	evaporative cooler (EU-80)	ESP (EU-81)
PClBz	25100	15170	21700
PClPh	1660	13830	15700
PCB	240	180	440

The corresponding data for the chlorobenzenes and chlorophenols are shown as bar graphs in fig. 17.

Fig. 17: Concentrations (ng/g) of PClBz and PClPh in the different samples after annealing at 350°C (acidic slagging)



Comparing the initial concentrations and those obtained on annealing an increase factor may be evaluated as ratio of the concentrations after and prior to the heating. The data are presented in table 36.

Table 36: Increase factor for the thermal treatment (350°C, 2hrs.) for organochlorine compounds

	Dust settling chamber	Evaporative cooler	ESP
PCDD/F	42	120	500
PClBz	100	250	720
PClPh	4	30	40
PCB	2	2	5

The formation potential of the material clearly increases on the way from the dust settling chamber to the electrostatic precipitator.

Besides single compound analyses also the group parameters AOX and VOX were measured. Due to the thermal treatment there is an increase of the organic chlorine (µg/g) in the annealed material: in the sample from the dust settling the total organochlorine concentration is increased by a factor of 6, in the material from the evaporative cooler by 8. During the experiment 80% to 90% of the total organochlorine from material of the dust settling chamber and of the evaporative cooler are transferred to the gas phase. The sample taken from the ESP shows a different behaviour: Here the increase of the total organochlorine (TOX=

AOX+VOX) is only from 83 to 132 µg/g, corresponding to a factor of 1.6, from the TOX only 47% enter the gas phase.
The data are presented in table 37.

Table 37: Concentration of organic chlorine (µg/g) before and after annealing at 350°C

	before annealing	after annealing (350°C)		
	AOX	AOX	VOX	TOX (sum)
dust settling chamber	94.6	118	468	586
evaporative cooler	80	56	573	629
ESP	83	70	62	132

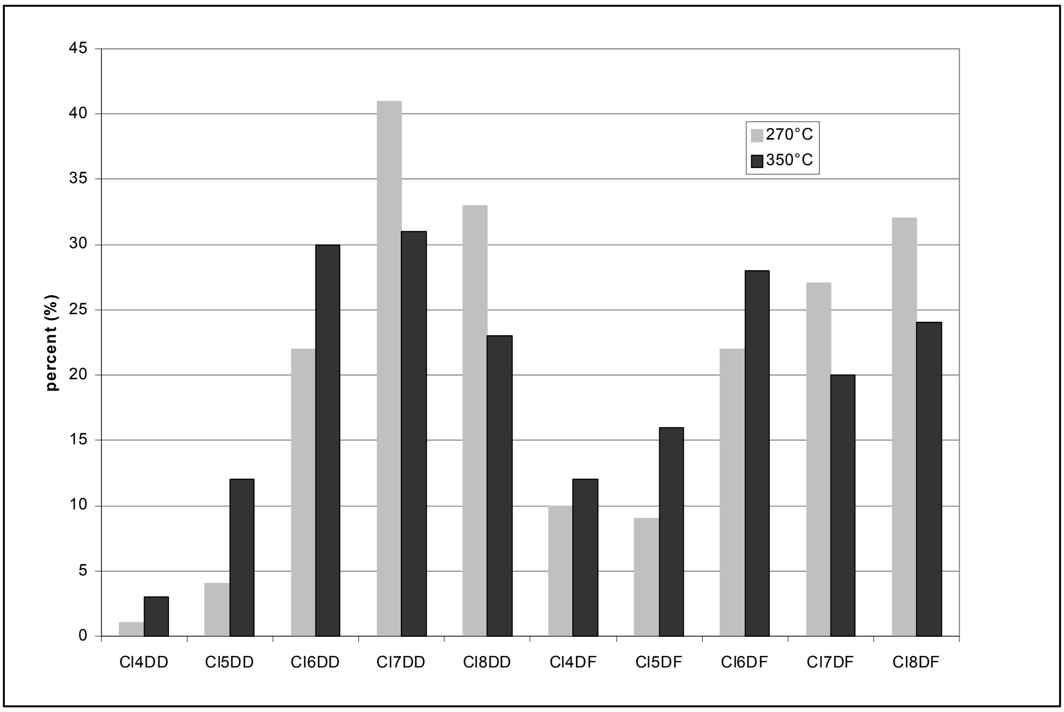
In the plant the ESP filter is operated at 270°C. For this reason and for comparison with the 350°C data experiments were also made with ESP material at 270°C (2hrs.). Generally the formation rates are lower: the total PCDD concentrations achieved are 1853 ng/g, PCDF 1081 ng/g, i.e a reduction to 57% for the dioxins and to 231% for the furans. In the experiment the PCB and chlorophenols decrease to ca. 45%, the PCB to 29%. The data are summarized in table 38.

Table 38: Concentrations (ng/g) in ESP material after annealing at 270°C

	Concentration (ng/g)		
	Solid residue	Gas phase	Sum (SP+GP)
Cl4DD	<1	9	9
Cl5DD	<1	72	72
Cl6DD	4	374	378
Cl7DD	16	700	716
Cl8DD	18	660	678
PCDD	**38**	**1815**	**1853**
Cl4DF	2	96	98
Cl5DF	2	96	98
Cl6DF	2	214	216
Cl7DF	9	290	299
Cl8DF	14	357	371
PCDF	**28**	**1053**	**1081**
PCDD/F	**66**	**2868**	**2934**

Also at 270°C there is a nearly complete transition of the volatiles to the gas phase, inspite the presence of carbon, which should act as an adsorptive site.
The pattern of the homologue groups of dioxins and furans, as received with 270°C and 350°C , is slightly different, depending on the temperature. The fraction of the respective chlorinated species (in %) relative to the total concentration of tetra-octaDD and tetra- to octaDF is calculated and presented in fig. 18.

Fig .18: Fraction (%) of the individual homologues as formed at 270°C and 350°C



There is a slight difference in the pattern : at 270°C the hepta- and octachloro dioxins and furans are formed primarily, whereas with a higher temperature at 350°C a dechlorination occurs with a relative increase of the lower chlorinated species such as tetra to hexachlorodioxins and -furans.

Inhibition Experiments with Material from the Evaporative Cooler

Since with material from the iron ore sintering the de-novo-formation could be suppressed successfully by adding calcium hydroxide similar experiments were made with material from the evaporative cooler (EU-80). 2%, respectively 5% of Ca(OH)2 were added to the sample and then heated in air to 350°C over a period of 2 hrs. The results are summarized in table 39.

Table 39: Inhibition of de-novo-synthesis in the material of the evaporative cooler by addition of calcium hydroxide

	Without additive	2% $Ca(OH)_2$		5% $Ca(OH)_2$	
		ng/g	reduction	ng/g	reduction
PCDD	2003	48.6	98%	23	99%
PCDF	1803	394	78%	183	90
PClBz	15173	7725	49%	2017	87
PClPh	13828	150	99%	37	>99%
PCB	181	n.d.	n.d.	69	62%

Similarly as with the material from iron ore sintering a substantial inhibition is obtained by the addition of calcium hydroxide: Even with 2% inhibitor a drastic reduction of the formation of the PCDD of 98% and that of the PCDF of 78% is observed. With 5% additive the effect is between 90% and 99%.

3.4.2 Material from Plant B, Basic Slagging Mode

The experiments with material from a Waelz process were extended to include material from a process with basic slagging mode. Samples were obtained from the dust settling chamber #1, (EU-91) and #9 (EU-92), from the cooler and from the product filter. The samples were characterized by analyses for native organochlorine compounds. The results are given in table 40.

Table 40: Initial concentrations of organochlorine compounds (ng/g) with basic slagging

	dust settling chamber EU-91	dust settling chamber EU-92	cooler EU-93	product filter EU-94
PCDD	1.1	0.6	3.3	7.7
PCDF	10	4.75	4.06	21.1
TEQ (Nato)	0.27	0.11	0.10	0.4
PClBz	380	160	10	4
PClPh	7	2	6	25
PCB	11	20	10	14

The concentrations are low. A tendency is indicated for an increase of the concentration on the way from the dust settling chamber to the product filter.
The de-novo-formation potential was investigated by performing the standard tests at 300°C (2hrs.) in air. The results are summarized in table 41.

Table 41: Concentrations of organochlorine compounds (ng/g) after annealing 300°C, 2 hrs. (sum of solid and gasphase)

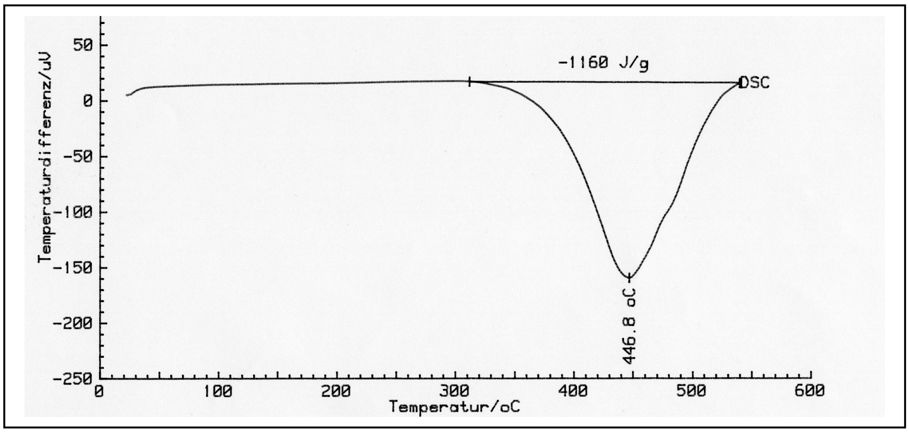
	dust settling chamber EU-91	dust settling chamber EU-92	cooler EU-93	product filter EU-94
PCDD	8.5	5.0	48	50
PCDF	260	44	65	85
TEQ (Nato)	4.0	1.0	2.8	2.6
PClBz	32700	5450	3700	6200
PClPh	80	17	43	30
PCB	560	250	210	240

From all the organochlorine compounds more than 90% are in the gas phase.

The DSC measurements show that the samples exhibit quite different behaviour: over the temperature range from room temperature to 550°C in the material from the dust settling chambers a distinct exothermal reaction is noted. The sample from the chamber #1 (fig.19) has an onset-temperature of ca. 340°C, a peak temperature of 446°C and an enthalpy of -1160

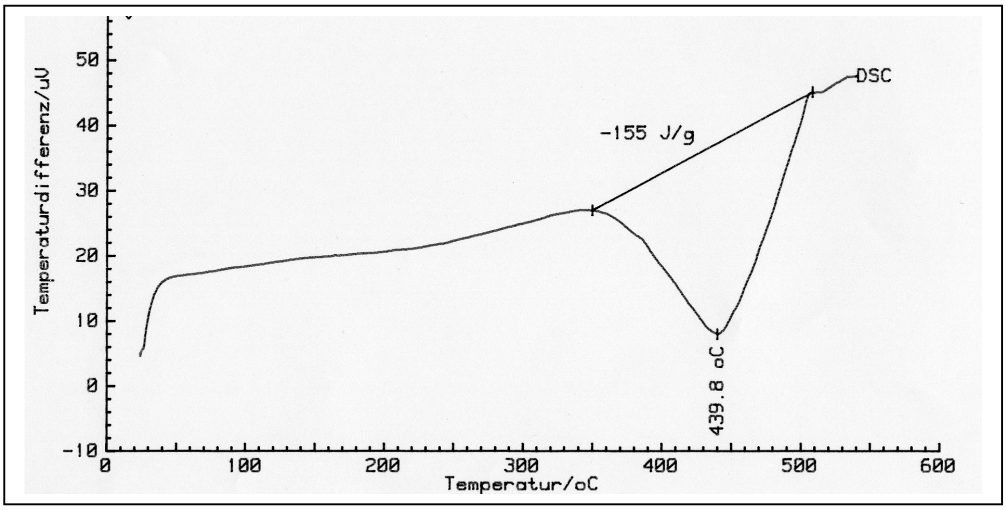
J/g. The dust from chamber #9 with an on-set temperature of 350°C, peak temperature of 439°C reacts with an enthalpy of - 155 J/g (fig 20).

Fig. 19: DSC-plot of material from the dust settling chamber #1



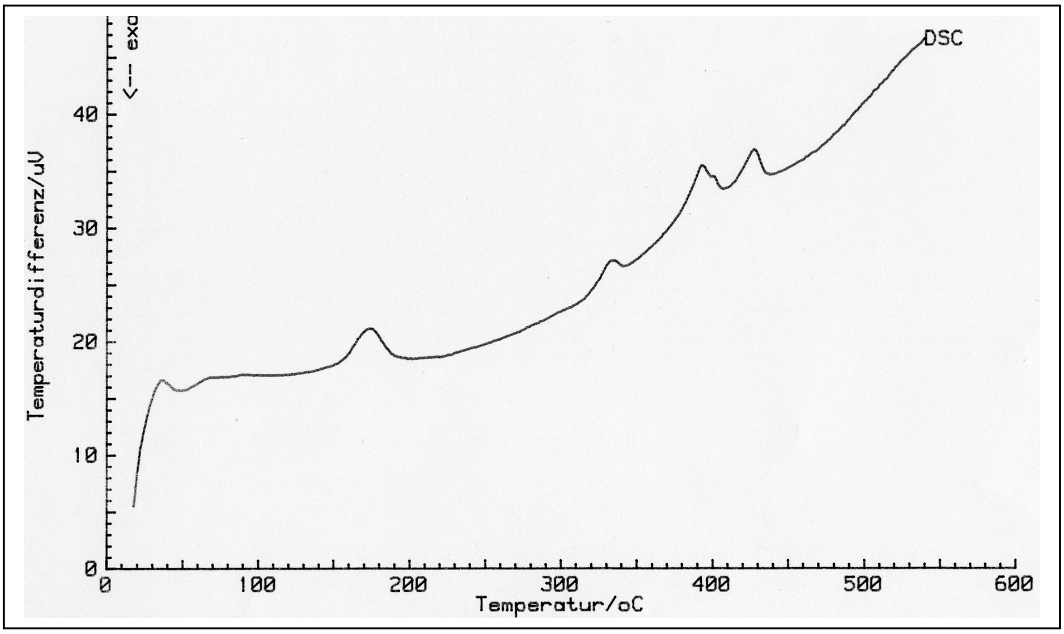
Although both samples exhibit an on-set temperature in the critical range for the de-novo reaction the enthalpies are different by a factor of ca. 8: This fact is reflected in the lower formation in sample from chamber #9.

Fig. 20: DSC plot of material from dust settling chamber#9



On the other side the material from the cooler and the product filter show no distinct exothermic reaction over the whole temperature range. As example is shown the DSC plot of material from the cooler (fig. 21)

Fig. 21: DSC plot of material from the cooler



From the comparison of the material from acidic and basic slagging the following conclusions may be drawn:

Generally the initial concentrations of the organochlorine compounds in the material of the acidic slagging process are higher by a factor of 10-15.

The thermal treatment results also in higher concentrations of the organochlorine compounds in the material with acidic slagging. By this fact the observation is confirmed that the presence of caustic compounds results in the inhibition of the de-novo-process.

The results were summarized at Dioxin 2001 by A. Buekens (Buekens A. 2001).

3.5 Analysis of Dust Samples from a Stainless Steel Production Plant

The samples were collected in the silo (EU-65), in the pre-separator (EU-66) and in the sparkling catcher (EU-67), a device to reduce the electrostatic energy.
Analysis by XRFA shows that besides iron oxide the samples contain silica (5-7%), chloride (1-2%), CaO (14-18%) and also traces of CuO (0.4-0.5%), but no carbon. As a result of this composition no exothermic reaction could be found by DSC measurements.
The routine analyses were performed for the organochlorine compounds. The data are presented in table 42.

Since no organic carbon was present in the samples the de-novo-synthesis could not proceed due to the lack of efficient precursor structures.

Table 42: Initial concentrations (ng/g) of organochlorine compounds in material from stainless steel production

	Silo	pre-separator	sparkling chamber
	(EU-65)	(EU-66)	EU-67)
PCDD	6.9	0.8	5.9
PCDF	23.9	0.8	6.3
TEQ (Nato)	0.76	0.03	0.30
PClBz	24	13	60
PClPh	78	4	22
PCB	820	45	95

3.6 Investigation of Dust Samples from an Electricity Production Plant

In order to extent the field of investigations also samples from an electricity production plant were included. This plant is interesting, as different combustible material, e.g. coal, oil and gas are applied. The samples were collected at different zones (DES zone 1-3 , Kanal zone 1-3). The main components are alumina (35-38%) and silica (50-52%), minor constituents are phosphate (0.8-1.3%), magnesium oxide (0.3-0.5%) and sulfate (0.2-0.3%). Copper oxide was present at trace level (ca 0.005%), no chloride could be detected.

From the DSC measurements the following conclusions can be drawn: the samples EU-45 and EU-48 show no signal within the temperature range up to 550°C. With sample EU-51 an exothermal peak at 543° with an enthalpy of -152 J/g is noted, which may correspond to ca. 4% carbon. Also the samples in the Kanal zone show exothermal reactions, however, all with peak temperatures of ca. 550°C. These reaction may be ascribed to the oxidation of traces of residual carbon, which, due to the lack of copper and chloride, must proceed without catalytic action requiring higher temperatures. Under these conditions no de-novo-synthesis is to be expected

In agreement with the DSC measurements the concentrations of the samples of organochlorine compounds were found to be rather low. Data are given in the table 43.

Table 43: Concentrations of organochlorine compounds (ng/g) in dust from an electricity plant

	DES zone			Kanal zone		
	#1 EU-45	#2 Eu-48	#3 EU-51	#1 EU-54	#2 EU-57	#3 EU-60
PCDD	0.1	0.15	0.11	0.60	0.04	0.37
PCDF	0.13	0.16	0.47	0.72	6.7	2.8
TEQ (Nato)	0.02	0.015	0.02	0.05	0.07	0.04
PClBz	4	5	3	1	7	4
PClPh	5	8	9	<<1	14	8
PCB	47	98	78	31	49	50

The low concentrations of organochlorine compounds confirm the fact that in plants for electricity production the conditions for PCDD/F formation are unfavorable.

4. Summary and Conclusions

In the present study a variety of samples from different industrial thermal processes, such as cement production, municipal waste incineration, iron ore sintering, scrap metal reprocessing, and stainless steel production was investigated with regard to the formation potential of hazardous compounds such as PCDD/ F.

From experiments, applying the standard de-novo-test procedure (annealing at 300°C , 2 hrs. in air) the folllowing conclusions may be drawn for the various materials with regard to their formation potential for volatile organochlorine compounds:

Cement Industry: Dust collected in the settling chamber and in the electrostatice precipitator, showed on heating no distinct formation of PCDD/F, due to the lack of Cu^{2+} (<0.02%).

Municipal Waste Incineration: material from exhaust residue shows a behaviour known from previous investigations: growth of the PCDD by a factor of 15, that of PCDF by ca. 60, a decrease of the carbon concentration from 3.8% to 3.0%, with the compounds remaining adsorbed nearly quantitatively on the solid.

Iron Ore Processing: Investigated were the following materials

a.) siftings from underneath the sintering belt, characterized by low concentrations of native PCDD/F (2-7 ng/g) and other chlorocompounds, somewhat depending on surface area and zone of sampling. Upon heating only a slight increase of the PCDD/F is noted, with ca. 50% reporting to the gas phase.

b.) Dust from successsive fields of the electrostatice precipitator: The material, main component iron oxide, contains substantial concentrations of chloride (5-20%) and copper (ca. 0.3%) and also carbon (3%). Starting from low concentrations of native compounds a remarkable reaction takes place at 300°C leading to a drastic increase of PCDD/F, PClBz, PClPh and PCB, especially in the material from the second and third field of the ESP. The difference in the yield may be clearly ascribed to the difference in the composition. The influence of reaction parameters, such as temperature, time, oxygen concentration of the gas phase was studied in detail. Noteworthy is the finding that the de-novo-reaction may be inhibited markedly by the addition of triethanolamine, calcium hydroxide and sodium hydroxide, with reduction of yields by 95-99%.

Zinc Recycling Process (WAELZ-process):

In this process scrap residues are treated to give a crude zinc oxide particles, which are removed from the gas phase in a dust settling chamber, followed by an evaporative cooler and an electrostatic precipitator. Material from these stages, with zinc oxide (>60%) contains chloride (1-3%) , carbon (1.5-4.0%) and 0.1% copper. The formation potential at 350°C for organochlorine compounds shows a strong increase going from the dust settling chamber to the ESP. By the de-novo reaction PCDD/F concentrations of 2200 ng/g (dust settling chamber) up to 6700 ng/g (ESP) are produced. The multiplying factor increases from the dust settling chamber to the ESP, rising for PCDD/F from a factor of 47 (dust settling chamber) to 500 (ESP), for PClBz from 100 to 700, and for PClPh from 4 to 40, not significant is the new production of PCB with a factor of 2-5. The formation of these compounds may be successfully inhibited by the addition of 2-5% calcium hydroxide, achieving reductions between 90% (PClBz) and 99% (PCDD).

Further material from stainless steel production and from an electricity producing plant, due to its composition, did not response to the de-novo tests.

Regarding the influence of the composition on the de-novo-synthesis and of other reaction parameters some conclusions had been arrived at in previous work with fly ash from municipal waste incineration. With some modifications the previously derived conditions were confirmed and may be defined as follows:

Composition: So far in the material from the different processes three ingredients are essential for a de-novo-synthesis:

Carbonaceous material (>2%) stemming from pyrolysis or incomplete combustion of organics or added as reactant for the process (e.g. coke derivatives). In these macromolecular structures, containing >C-H bonds, the hydrogen is replaced by chlorine in direct chlorination with elemental chlorine or more probably by a ligand transfer reaction, especially promoted by $CuCl_2$. So concentrations of 800-1200 µg/g organochlorine may be achieved.

Copper chloride (> 0.1), with some inclusion of other tranition metal chlorides ($FeCl_3$). So far especially $CuCl_2$ was found to act in a two fold way: a.) as chlorination agent for C-H.units and b.) as a very efficient promotor for the oxidative degradation of the macromolecular structure, where chlorinated aromatic substrucures survive and are re-organized to volatile chlorocompounds. In the presence of $CuCl_2$ the oxidation temperature for carbon is reduced from 550°C to 300° C. Other copper species such as CuO, $CuSO_4$ are much less efficient in this role.

Inorganic chloride (>4%), necessary in order to guarantee the existence of chlorocomplexes such as $CuCl_4{}^{2-}$ .The yield of PCDD/F increases with chloride concentrations up to ca 6-8%, then a constant value is obtained.

Reaction parameters:

Gas atmosphere: Under oxygen deficient conditions the reaction is not favored. At 2 vol% of oxygen already a measurable formation of chlorocompounds is noted, reaching an optimum level at ca. 20 vol% oxygen.

Temperature: As a consequence of the composition (carbon, copper, chloride) the oxidative degradation takes place already at ca. 300-350°C, leading to a conversion of the macromolecular structure of the carbon to CO_2/CO as main product and of a great variety of volatile organochlorine compounds as by products in trace concentrations.

From the various techniques applied the **differential scanning calorimetry (DSC)** was found to be a fast, simple and inexpensive method for screening various samples of different origin: A de-novo-activity with high formation rates is alway indicated by strong exothermic reactions with peak temperatures in the range from 300-400° C.

Distribution between Solid/Gas Phase: Depending on the structure of the residual carbon these chloroaromatics are either evaporated at 250-300° C or remain adsorbed on the solids where they may undergo further reactions such as oxidation and halogenation/dehalogenation. With the fly dusts from iron ore sintering and scrap zinc processing more than 90-95 % of all compounds are transferred to the gas phase, in contrast to the behaviour of fly ash systems from municipal waste incineration.

Inhibition of the formation: The de-novo-synthesis in the material of the processes investigated may be very succesfully retarded or even inhibited by the addition of basic compounds. The efficiency of the measure, with inhibitor concentrations in the low percentage range, increases in the order triethanolamine < $Ca(OH)_2$ < NaOH. With calcium hydoxide and sodium hydroxide a reduction of the concentrations formed by more than 90-99% is achieved.

Generally by the investigations the knowledge of the mechanisms leading to the formation and release of chlorinated aromatic compounds could be extended to include other thermal processes such as metal processing. Formerly formulated path ways could be confirmed. The so called "de-novo" synthesis proves to be a general reaction taking place in solids of thermal processes, if the requirements regarding the composition are met. Destroying the essential reaction partners, e.g. copper chloro complexes, by the addition of inhibiting reagents leads to a nearly complete reduction of the formation and emission.

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