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ABSTRACT

Results on the formation and decomposition of polychlorodibenzo-dioxins (PCDD) and -furans (PCDF) in municipal waste incinerators are summarized. Experimental data on the formation conditions of PCDD/PCDF on fly ash are reported. Essential parameters for formation are the temperature range (300°C), the reaction time, the presence of oxygen and of water vapor in the gas phase. The source for PCDD/PCDF are active carbon particulates in the fly ash which react with inorganic alkali/alkaliearth chlorides under participation of metal salts such as copper(II) chloride. The influence of carbon content and the concentration of copper-chloride on PCDD/PCDF formation is shown. Data on the decomposition of PCDD/PCDF in fly ash prove the technical feasibility of dioxin/furan degradation at low temperatures in air and in inert atmosphere as well.

Bildung und Zersetzung von Polychlorodibenzodioxinen (PCDD) und -furanen (PCDF) bei der Verbrennung von Hausmüll

ZUSAMMENFASSUNG

Ergebnisse über die Bildung und Zersetzung von Polychlordibenzodioxinen und -furanen in kommunalen Verbrennungsanlagen werden zusammengefaßt. Es werden experimentelle Daten über die Bildungsbedingungen von PCDD/PCDF berichtet. Wesentliche Parameter für die Bildung sind der Temperaturbereich (300°C), die Reaktionszeit, die Anwesenheit von Sauerstoff und Wasserdampf in der Gasphase. Die Quelle für die PCDD/PCDF sind aktive Kohlenstoffpartikel in der Flugasche, die mit anorganischen Chloriden von Alkali/Erdalkali mit Beteiligung von Metallsalzen wie Kupfer(II) chlorid reagieren. Der Einfluß des Kohlenstoffgehaltes und der Konzentration von Kupferchlorid wird aufgezeigt. Daten über die Zersetzung von PCDD/PCDF in Flugasche beweisen die technische Machbarkeit der Dioxin-/Furanzerstörung bei niederen Temperaturen in Luft wie auch in inerter Atmosphäre.

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INTRODUCTION

In 1984 at the Nuclear Research Center Karlsruhe (KfK) investigations were started on the chemistry of fly ash from municipal waste incineration facilities, in order to support research and development activities in the field of municipal waste treatment. During the following years the results obtained from laboratory experiments made a significant contribution to a better understanding of the formation conditions of polychorodibenzodioxins and -furans under incinerator conditions, the nature of organic precursor compounds and supplied conclusions for an improvement of sampling techniques. From an interpretation of the data ways for minimization of PCDD/PCDF formation and emission were suggested.

In view of the general importance of new developments and advances in the field of municipal waste treatment a fast distribution of results to the scientific community is desirable. Therefore the most important results on formation and destruction of dioxins and furans are summarized here in chronological sequence in the original language to describe the present state of the dioxin research at KfK.

The work was supported financially by the Project "Wasser, Abfall, Boden" of the State of Baden-Württemberg.

1. Thermal Behavior of PCDD/PCDF in Fly Ash from Municipal Waste Incinerators

H. Vogg, L. Stieglitz,

presented at the Fifth International Symposium on Chlorinated Dioxins and Related Compounds, Dioxin 85, Sept. 16.-19, 1985, Bayreuth,
Chemosphere 15, 1373-1378 (1986)

Fly ash from a municipal waste incinerator was heated in a crucible for two hours at temperatures of 120°, 200°, 300°, 400°, 500° and 600° C respectively. During the annealing a stream of air (40 l/h) was passed across the material and then through two washing bottles in series containing toluene. PCDD/PCDF concentrations of the fly ash after thermal treatment are shown in

Tab. 1: Thermal Behavior of PCDD in Fly Ash (Concentration ng/g Fly Ash)

	non treated	temperature (°C) 120	200	300	400	500	600
A. FLY ASH							
O8CDD	120	120	90	640	6	0.2	0.1
H7CDD	125	90	100	1000	15	0.2	0.1
H6CDD	85	65	65	1640	22	1.	0.1
P5CDD	45	35	40	570	35	1.	0.1
T4CDD	20	15	15	65	13	2.	0.1
sum (solid)	395	325	310	3915	91	4.4	0.1
B. VAPORIZED							
O8CDD	-	-	-	0.2	9	0.3	0.1
H7CDD	-	-	-	0.4	45	0.8	0.1
H6CDD	-	-	-	0.8	88	2.	0.1
P5CDD	-	-	-	0.15	100	3.	0.1
T4CDD	-	-	-	0.1	37	3.	0.1
sum (vaporized)	-	-	-	1.6	280	9.	0.1
total sum (A+B)	395	325	310	3916	370	13.5	0.1

Tab. 2: Thermal Behavior of PCDF in Fly Ash (Concentration ng/g Fly Ash)

	non treated	temperature (°C) 120	200	300	400	500	600
A. FLY ASH							
O8CDF	12	11	12	218	4	0.1	0.04
H7CDF	48	42	48	1030	37	0.4	0.1
H6CDF	56	51	61	1253	80	1.4	0.1
P5CDF	129	119	129	1570	187	8.	0.2
T4CDF	113	95	122	506	140	8	0.1
sum (solid)	358	318	372	4577	448	18	0.4
B. VAPORIZED							
O8CDF	-	-	-	0.1	8	1.5	0.1
H7CDF	-	-	-	0.4	75	15	1.
H6CDF	-	-	-	1.8	180	34	2.
P5CDF	-	-	-	1.	500	93	9.
T4CDF	-	-	-	1.	390	95	15.
sum (vaporized)	358	318	372	4.	1153	238	27
total sum (A+B)	358	318	372	4581	1603	256	27

table 1 and table 2 respectively, also with the amount of PCDD/PCDF per gram fly ash vaporized at higher temperatures.

The most important results are as follows:

- In the temperature range between 250 and 350°C a tremendous increase of the concentration takes place from original 395 ppb to 3916 ppb with the dioxins (tetra to octa CDD) and from 358 ppb to 4581 ppb for the furans (tetra - to octa CDF).

- With increasing temperature the concentration maximum is shifted from the highly chlorinated dioxins to compounds with a lower chlorine content.

- At 500°C an extensive decompositon occurs, at 600°C a nearly quantitative degradation is achieved with residence times in the range of hours.

From the data the following conclusions are drawn

a) Besides the already present dioxins and furans in particulates from waste incineration, there is also a potential of additional PCDD/PCDF formation due to the presence of precursor compounds. This potential is activated by a longer thermal treatment at a temperature range around 300°C.

b) Applying the results from our laboratory experiments to the processes in waste incinerators we must consider the possibility that at least part of the PCDD/PCDF is not formed directly in the combustion chamber, but on the deposits of the inner surface of the boiler, preferably at the boiler offgas exit, where the temperature is between 300 and 400°C. Also dioxin and furan formation on the dust filters, which are often operated at temperatures around 250°C cannot be excluded, especially if the dust samples are exposed to the temperature for a prolonged time.

c) Dioxin and furan decomposition can occur on fly ash already at medium temperatures.

2. On Formation Conditions of PCDD/PCDF in Fly Ash from Municipal Waste Incinerators

L. Stieglitz, H. Vogg

presented at the 6th Symposium on Chlorinated Dioxins and Related Compounds, Sept. 16-19, 1986 at Fukuoka, Japan
Chemosphere 16 (8-9), 1917 (1987)

In continuation of the work on PCDD/PCDF formation in fly ash laboratory experiments were performed to investigate the formations conditions

- Studies with material from different municipal waste incinerators confirmed that the build-up of PCDD/PCDF by thermal reactions at 300°C is a generally observed fact for fly ash. The data are shown in table 3 for material from three plants.

Tab. 3: Formation of PCDD/PCDF on Fly Ash from Various Municipal Waste Incinerators (300°C, 2 hrs.,Carrier Gas: Air)

	CHLORINE	Concentrations in ng/g DIOXINS untreated	DIOXINS after annealing	FURANS untreated	FURANS after annealing
Plant A	Cl_8	120	640	12	218
	Cl_7	125	1000	48	1030
	Cl_6	85	1640	50	1250
	Cl_5	45	570	130	1570
	Cl_4	20	65	110	500
Plant B	Cl_8	160	280	40	70
	Cl_7	50	360	60	230
	Cl_6	24	310	30	250
	Cl_5	10	170	20	240
	Cl_4	3	50	3	180
Plant C	Cl_8	23	330	3	240
	Cl_7	18	530	11	520
	Cl_6	13	360	14	450
	Cl_5	6	180	30	500
	Cl_4	5	30	14	220

- Kinetic studies indicate that after prolonged annealing (6-8 hrs) a practically constant concentration level is approached. The concentration increase can be described by a quasi first order reaction equation.

- In the discussed reaction a number of partners play an important role. Two prerequisites are recognized as necessary: the presence of oxygen in the carrier gas. The concentration increase of PCDD/PCDF is observed only in oxygen containing atmosphere.
  The presence of ions of transition or heavy metals, which promote directly or catalytically the formation reaction. If the fly ash is treated by hydrogen sulfide prior to the annealing no additional PCDD/PCDF formation is observed. Apparently essential reaction partners are poisened and their action is blocked by the pretreatment.

- In inert oxygen-free gases such as nitrogen, carbon dioxide the build-up is replaced by a significant decrease of the concentration, especially of the higher chlorinated compounds. The degradation of PCDD in fly ash by thermal treatment in nitrogen is shown in fig. 1.

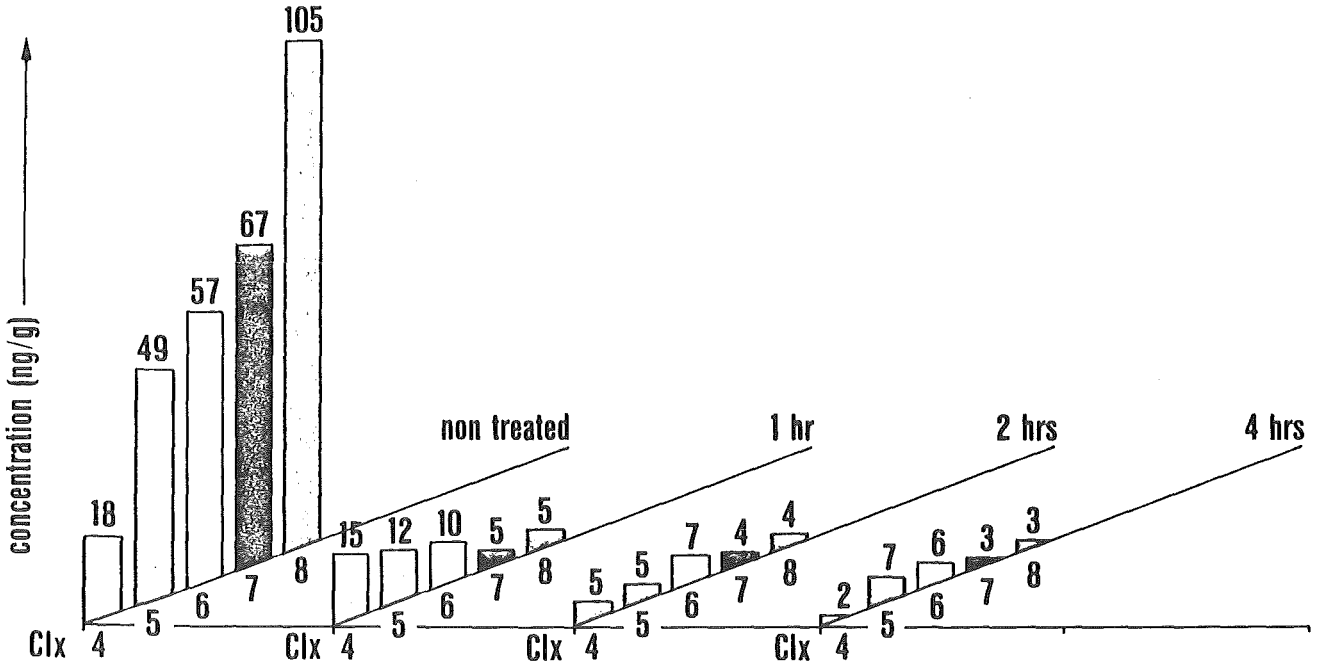

Fig. 1: Degradation of PCDD at 300°C in Nitrogen as Carrier Gas

- A detailed investigation of the formation of individual isomers indicates that isomers substituted in ortho and para positions are preferably obtained. From this fact it is concluded that a chlorination process is involved in the PCDD/PCDF production.

3. Recent Findings on the Formation and Decomposition of PCDD/PCDF in Municipal Solid Waste Incineration

H. Vogg, M. Metzger, L. Stieglitz

presented at the ISWA-WHO Specialized Seminar on Emissions of Trace Organics from Municipal Solid Waste Incinerators, Jan. 20-22, 1987, Copenhagen, Waste Management & Research (1987), 5, 285-294

The hypothesis postulated in 1985, that the thermal formation of PCDD/PCDF proceeds on fly ash in the low temperature region of the boiler at 300°C was fully confirmed. In table 4 data are shown for a dust sample taken simultaneously from pass 2/3 of a boiler with temperatures between 800°C and 400°C and from pass 4 with temperatures between 220° und 400°C. Only traces of 1,1 ppb PCDD are present in the high temperature region, whilst 594 ppb PCDD are found in the low temperature region.

Tab. 4: Assay for Dioxin in Boiler Ash (ng g^{-1} of Ash)

	Pass2/3	Pass 4
8CDD	0,6	265
7CDD	0,2	124
6CDD	0,1	105
5CDD	0,1	75
4CDD	0,1	25
PCDD	1,1	594

Major parameters associated with the formation reaction are the oxygen content and the water vapor fraction in the off-gas. Data on the influence of these parameters are shown in table 5.

Observation of a color change (brightenning) of the fly ash from inside the material upon heating in an air stream at 300°C (2 hrs) led to the assumption that carbon oxidation is one of the processes occurring during the thermal treatment. This decrease of carbon content was measured quantitatively by cerimetry. Typical data are the reduction of carbon content from 4,3 % to 1,6 %, or from 1,5 % to 1,0 % and from 1,8 % to 1,0 % respectively during 2 hrs. annealing at 350°C.

Tab. 5: Influence of Oxygen on the Formation of PCDD/PCDF on Fly Ash after two Hours at 300°C (ng g^{-1} ash)

	(1) Untreated	(2) N_2	(3) $1\%O_2$	(4) $4\%O_2$	(5) $10\%O_2$	(6) $10\%O_2$ ($+H_2O$)
8CDD	146	5	187	1707	4879	292
7CDD	125	9	202	1071	2479	1898
6CDD	92	17	229	603	1150	4501
5CDD	34	26	87	125	174	2765
4CDD	16	19	33	31	26	1899
PCDD	423	76	738	3537	8708	11 355
8CDF	16	1	54	455	1065	55
7CDF	74	4	146	554	1068	706
6CDF	96	9	229	466	819	1873
5CDF	197	28	456	593	892	4992
4CDF	175	47	340	401	517	3967
PCDF	558	89	1225	2469	4361	11 593

From the fact that fly ashes leached in an acid medium (pH=3) did not show this carbon decrease it was concluded that acid soluble fly ash components play an essential role in the oxidation process. Experiments with the addition of MnO_2, $AgNO_3$, $CuCl_2$, $CuSO_4$, KCl, NaCl, $CaCl_2$, $MgCl_2$ and $FeCl_3$ either singly or in selected combination showed that only $CuCl_2$ together with KCl or other alkali and alkaline earth chlorides led to a decrease of carbon during annealing. Consequently carbon oxidation and the production of chlorine from inorganic chlorides of the fly ash by the catalytic action of $CuCl_2$ with subsequent chlorination of organic precursor material were considered important reactions occurring on the fly ash.

The quantities of dioxins and furans formed depend on a number of parameters as is shown in table 6. The treatment in air at 300°C was 2, 8 and 22 hrs. respectively. Noteworthy is the fact that upon annealing for 22 hrs. a decrease of PCDD/PCDF is observed, indicating that also at temperatures of 300°C a degradation is taking place. Also entered in table 6 are data of the composition of the fly ash. The characteristic data of fly ashes A-C prove that high carbon contents and probably also high chloride concentrations favour the formation of PCDD/PCDF. So the concentration level of elemental carbon can be used as a first measure in the evaluation of the dioxin/furan formation potential.

In summary it was concluded that the oxidation of carbon in fly ash may serve as a basis for the mechanism of PCDD/PCDF formation. Both reactions proceed by the Deacon process scheme, in which HCl is oxidzed to Cl_2 with air borne oxygen.

Tab. 6: PCDD/PCDF Content of Fly Ash Samples (A-C) in (ng g^{-1}) after Oxidation in Air at 300°C for Various Treatment Times (h)

	A				B			C		
	0	2	8	22	0	2	8	0	2	8
8CDD	120	640	1083	507	163	280	349	23	341	81
7CDD	125	1000	2981	569	49	360	577	18	535	199
6CDD	85	1640	3516	628	24	810	647	13	377	344
5CDD	45	570	1485	214	10	170	291	6	180	236
4CDD	20	65	790	138	3	50	209	5	29	218
PCDD	395	3915	9855	2054	249	1670	2073	65	1462	1078
8CDF	12	218	346	143	43	74	91	3	240	38
7CDF	48	1030	3637	700	63	234	643	11	524	403
6CDF	56	1253	5010	915	27	248	814	14	446	734
5CDF	129	1570	6947	836	20	243	1226	29	506	1516
4CDF	113	506	3431	662	4	177	730	14	222	1096
PCDF	358	4577	19 371	3256	157	976	3504	71	1938	3787
C (%)		4.3				1.5			1.8	
Cl (%)		6.2				2.6			2.9	
H_2O (%)		2.5				1.5			1.6	
Cu ($\mu g\ g^{-1}$)		1190				1060			780	

4. Neuartige Minderungsmöglichkeiten für PCDDs/PCDFs in Müllverbrennungsanlagen

H. Vogg, J. Vehlow, L. Stieglitz

VDI-Kolloquium Dioxin, 5.-7. Mai 1987, Mannheim
veröffentlicht in: VDI-Berichte Nr. 634 (1987) S. 541 sowie
KfK-Nachrichten 19 (1987) S. 209

1. Primärmaßnahmen

Primärmaßnahmen zur Behandlung der PCDD/PCDF-Bildung in Hausmüllverbrennungsanlgen müssen verstärkt auf die Unterbindung pyrolytischer Prozesse im Brenngut auf dem Rost sowie auf die Vermeidung von Flugascheablagerungen im Niedertemperaturteil des Kessels ausgerichtet werden.

Tab.: 7 Vergleiche verschiedener Flugaschen im Hinblick auf Dioxinbildung und Zusammensetzung

	A		B		C	
PCDD (ng/g)	395[o]	3915[x]	249[o]	1670[x]	65[o]	1462[x]
C (%)	4,3		1,5		1,8	
Cl (%)	6,2		2,6		2,9	
Cu (ng/g)	1190		1060		780	

o unbehandelt
x 2 h, 300°C

Es scheint eine gute Relation der Dioxin-Werte, vor allem zu den C-Gehalten, daneben evt. auch noch zu den als Katalysator wirksamen Cu-Konzentrationen, zu bestehen (Tabelle 7, siehe auch 3).

Tab.: 8 Dioxine in Kesselasche

	Zug 2/3 Temp. 800-400°C	Zug 4 Temp. 400-220°C
O8CDD	0.6	265
H7CDD	0.2	124
H6CDD	0.1	105
P5CDD	0.1	75
T4CDD	0.1	25
PCDD	1.1	594

(Konzentration ng/g Kesselasche)

Flugstaubablagerungen im Kessel, bevorzugt in den Temperaturfeldern zwischen 400°C und 220°C sind maßgeblich für die Dioxinbildung verantwortlich (Tabelle 8, siehe auch 3).

2. Sekundärmaßnahmen

2.1 Rauchgasreinigungsverfahren

Wirksamste Sekundärmaßnahmen zur Dioxin-Emissionsminderung bestehen darin, daß eine weitestgehende Entstaubung, entweder mit Gewebefiltern oder entsprechend eingestellten Naßwäschern vorgenommen werden.

Bezogen auf die Art der Rauchgasreinigung verhalten sich die Dioxin-Emissionen in erster Näherung wie folgt (Angaben als Indexzahlen):

(E-Filter)	:	(E-Filter + 2stufige Naßwäsche)	:	(Trockenverfahren + Gewebefilter)
30	:	3	:	1

Gegenüber Altanlagen sind mit moderner Rauchgasreinigung ausgestattete neue Anlagen demnach durch einen Gewinnfaktor von mindestens 10 gekennzeichnet.

2.2 Behandlung von Reststoffen

Dioxine und Furane beginnen sich bei längeren Reaktionszeiten in Luftatmosphäre bereits bei 300°C zu zersetzen. In 4 ist die Reihenfolge der einzelnen PCDD fälschlicherweise vertauscht wiedergegeben (Tabelle 9).

Dioxine/Furane in Reststoffen der Verbrennung, vor allem in Filterstäuben, können durch thermische Behandlung bereits zwischen 400°C und 600°C quantitativ zerstört werden (Tabelle 10).

Daß Dioxine und Furane durch Rückführung von Reststoffen in den Verbrennungsofen quantitativ zerstört werden, ist durch Laborversuche und erste Experimente an TAMARA gesichert (Tabelle 11).

Tab.: 9 Thermisches Verhalten von PCDD in Flugasche (Zeitabhängigkeit)

	Zeit (h)			
	0	4	8	22
O8CDD	120	1022	1083	507
H7CDD	125	1962	2981	569
H6CDD	85	1654	3516	628
P5CDD	45	849	1458	214
T4CDD	20	185	790	183
PCDD	395	5672	9855	2054

(Temp. 300°C, Konzentration ng/g Flugasche)

Tab.: 10 Thermisches Verhalten von PCDD in Flugasche (Temperaturabhängigkeit)

	Temperatur (°C)				
	0	300	400	500	600
O8CDD	120	640	6	0,2	n.n
H7CDD	125	1000	15	0,2	n.n
H6CDD	85	1640	22	1,0	n.n
P5CDD	45	570	35	1,0	n.n
T4CDD	20	65	13	2,0	n.n
PCDD	395	3915	91	4,4	n.n

(Behandlungszeit 2 h in Luft) (Konzentration ng/g Flugasche)

Tab.: 11 Thermisches Verhalten von PCDD in 3-R-Rückstand (sauer extrahierte Flugasche)

(n.n. = nicht nachweisbar, Nachweisgrenze 0,03 ng/g)

	Temperatur (°C)				
	0	300	400	500	600
O8CDD	213	272	11	n.n	n.n
H7CDD	111	147	10	n.n	n.n
H6CDD	64	85	0.7	n.n	n.n
P5CDD	11	23	0.2	n.n	n.n
T4CDD	8	14	0.1	n.n	n.n
PCDD	407	542	22	n.n	n.n

(Behandlungszeit 2 h) (Konzentration ng/g 3R-Rückstand)

5. Demonstrationsanlage Oberhausen zur Rückstandsbehandlung bei der Abfallverbrennung (DORA)

K. Horch, A. Herden, J. Vehlow, H. Vogg, H. Braun
Vortrag Müllverbrennung und Umwelt, 2.-5. November 1987, Berlin
Veröffentlicht in: K.-J. Thomé-Kozmiensky (Hrs.) Müllverbrennung und Umwelt 2 EF Verlag für Energie- und Umwelttechnik, Berlin (1987)S. 756-768

An der Müllverbrennungs-Testanlage TAMARA des KfK wurden Versuche zur Zerstörbarkeit organischer Schadstoffe in Rückständen des 3-R-Verfahrens (Rauchgasreinigung mit Rückstandsbehandlung) durchgeführt. Aus 3-R-Rückständen wurden durch Zuschlag von $CaSO_4$ (Verhältnis Rückstand: $CaSO_4$ = 1:1) Pellets hergestellt, die im Ofeneintrag zusammen mit zerkleinertem Hausmüll auf den Verbrennungsrost aufgegeben wurden und nach Durchgang durch den Brennraum aus der ausgetragenen Schlacke wieder herausgelesen werden konnten.
Die mittlere Verweilzeit auf dem Rost betrug ca. 30 Minuten. Ein Pellet, das bereits nach 15 Minuten im Schlackeaustrag erschien, wurde gesondert untersucht. Die gemessenen Gehalte an PCDDs und PCDFs in diesen Pellets sind in Tabelle 12 aufgelistet.

Damit ist nachgewiesen, daß Dioxine und Furane in 3-R-Rückständen bei einer Rückführung in den Brennraum einer Müllverbrennungsanlage sicher zerstört werden können.

Tab.: 12 Zerstörung von PCDDs und PCDFs in 3-R-Rückständen in der Testanlage TAMARA (n.n. = nicht nachweisbar, Nachweisgrenze 0,03 ng/g)

Ausgangsmaterial		30 Min. VWZ	15 Min. VWZ
O8CDD	85,6	n. n.	n. n.
H7CDD	86,5	n. n.	n. n.
H6CDD	78,0	n. n.	n. n.
P5CDD	34,7	n. n.	n. n.
T4CDD	11,0	n. n.	n. n.
PCDD	295,8	n. n.	n. n.
O8CDF	< 0,1	n. n.	n. n.
H7CDF	11,5	n. n.	n. n.
H6CDF	93,0	n. n.	n. n.
P5CDF	185,0	n. n.	n. n.
T4CDF	89,0	n. n.	n. n.
PCDF	378,8	n. n.	n. n.

6. New Aspects of PCDD/PCDF Formation in Incineration Processes

L. Stieglitz, H. Vogg

Proceedings of the International Workshop on Municipal Waste Incineration, Oct. 1.-2., 1987, Montreal, Quebec

In order to evaluate the role of particulate organic carbon in the formation of PCDD/PCDF, laboratory experiments were carried out with mixtures of carbon-free fly ash or magnesium-aluminium silicate as inorganic matrix containing the following additives: carbon of different origin (1% - 8 %), 1 % KCl and Cu^{2+} (0,08% - 0,4 %) as copper chloride. The mixtures were annealed in air at 300°C for 2 hrs. The results show that in incineration of municipal waste -apart from possible gas phase reactions- PCDD/PCDF are formed under moderate temperatures in air from particulate organic carbon in fly ash by gas-solid reactions with oxygen and halides, influenced and activated by copper(II). The following facts are observed and conclusions drawn:

a) The formation potential of PCDD/PCDF as evaluated by a thermal treatment of the mixtures in air at 300°C for 2 hrs is proportional to the content of particulate carbon. The data are shown in table 13.

Tab.: 13 Formation of PCDD/PCDF as a Function of Carbon Content (Activated Carbon, Purified by Exhaustive Extraction)

System: Mg-Al-Silicate, 1 % KCl, 0,4 % Cu, Annealed at 300°C (2 hrs.) in Air (150 mg H_2O/l).

	PCDD/PCDF concentration (ng/g) Percent charcoal			
CONGENER	1%	2%	4%	8%
T4CDD	15	22	40	74
P5CDD	60	104	210	277
H6CDD	210	360	800	820
H7CDD	280	520	1160	1160
OCDD	200	510	1210	980
Sum PCDD	765	1510	3420	3310
T4CDF	205	440	850	1300
P5CDF	530	1160	2560	3320
H6CDF	890	1850	4300	5070
H7CDF	650	1200	3200	3410
OCDF	150	340	1260	1150
Sum PCDF	2425	4990	12170	13240

b) The optimum temperature for formation is 300°C
c) Carbon of different origin (activated charcoal, sugar coal, soot) may serve as source for the dioxin and furan synthesis, except graphite which shows no reaction.
d) The isomer pattern of the congener groups is similar to that of fly ash samples
e) A number of other aromatic halide compounds such as chlorobenzenes, chloronaphthalenes und -biphenyls are also produced.
f) The formation of PCDD/PCDF is promoted only by addition of copper(II) chloride, not by halides of metals such as alkali, alkali earth, Fe, Zn, Mn, Hg, Cd, Ni, Sn, Pb.

The production of PCDD/PCDF by annealing the synthetic mixtures depends sensitively on the concentration of copper(II). The data are shown in table 14.

CONGENER	PCDD/PCDF concentrations (ng/g) Percent Cu^{2+} added			
	0	0.08	0.24	0.4
T4CDD	1.3	8	20	13
P5CDD	1.0	20	80	65
H6CDD	0.9	37	240	400
H7CDD	0.3	24	230	860
OCDD	1.0	12	200	110
PCDD	4.50	101	770	1448
T4CDF	7	100	310	260
P5CDF	11	310	1290	1550
H6CDF	3	230	1150	3100
H7CDF	1.6	100	690	2730
OCDF	0.07	20	200	840
PCDF	22.6	760	3640	8480

Tab.: 14 Influence of Copper(II) Concentration on the Formation of PCDD/PCDF

System: Mg-Al-Silicate, 1 % charcoal, 1 % KCl, Annealed at 300°C (2 hrs.) in Air (150 mg H_2O/l)

From the correlations between the content of particulate organic carbon, the concentration of copper in the fly ash on one side and the formation of PCDD/PCDF on the other side it is concluded that minimization of dioxin/furans may be achieved in incineration plants by

- high burn-out of the fly ash, with low residual organic carbon
- low residence times for fly ash and particulates in the low temperature zone (300°C)
- removal/recycling of metallic incombustable material, especially copper, prior to incineration.

7) On the Novo Synthesis of PCDD/PCDF on Fly Ash of Municipal Waste Incinerators

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submitted for publication in Chemosphere

Experiments with model mixtures of carbon free fly ash or of Mg-Al-silicate with particulate organic carbon (charcoal, sugar, coal, soot), potassium chloride and copper(II) chloride show that at 300°C in an airstream considerable amounts of PCDD/PCDF are produced. The yield depends

- on reaction time: After 2 hrs. the reaction is complete. The data for the tetra- to octa congeners are shown in fig. 2.

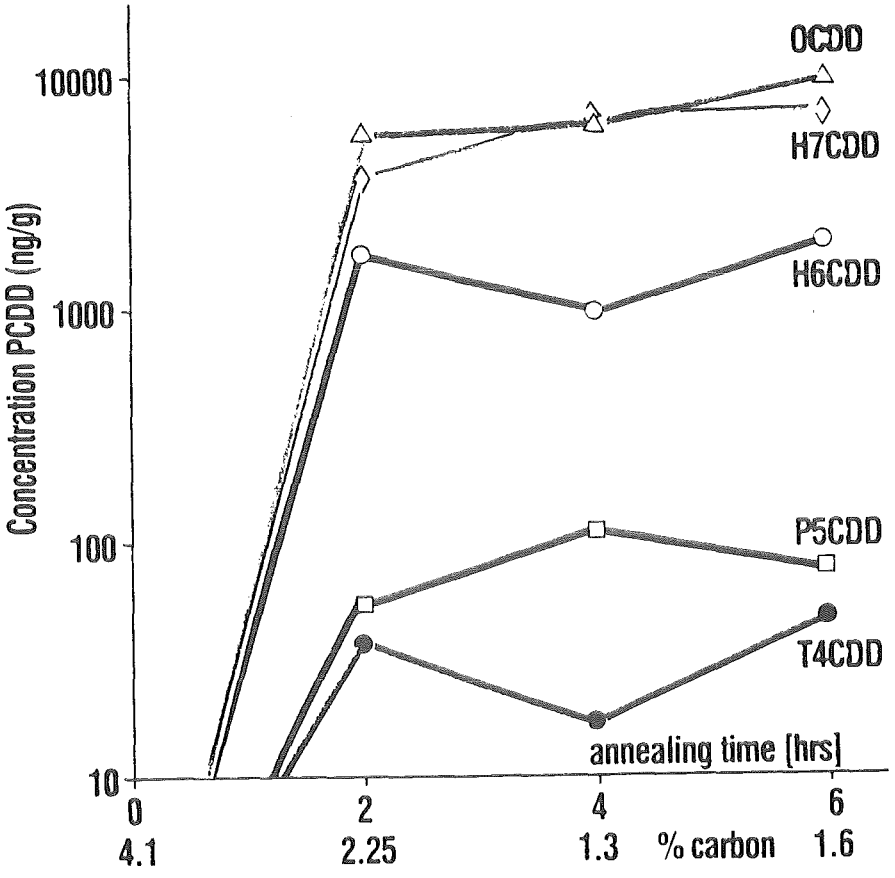

Fig.: 2 Formation of PCDD in Synthetic Mixtures as Function of Annealing Time.

The formation of PCDD/PCDF is accompanied by a decrease of the carbon content from originally 4 % to 2,25 % after 2 hrs. and to 1,3 % / 1,6 % after 4 and 6 hrs. annealing. Additionally the formation of total extractable organic bound chlorine was determined as 81 ug/g and the total organic chlorine as 778 ug/g.

- on the concentration of carbon and of copper(II) chloride (see also 6)
- on the nature and origin of carbon added
- on the presence of water vapor in the gas phase

Besides PCDD/PCDF other chlorocompounds formed are: 2 isomers of pentachloro- and hexachloronaphthalenes, and 2 isomers of heptachloro- and octachlorobiphenyls. Chlorobenzenes are formed in concentrations as follows: 50 ng/g 1,3,5-trichlorobenzene, 450 ng/g 1,2,4-trichlorobenzene, 610 ng/g 1,2,3-trichlorobenzene, 1030 ng/g 1,2,3,5-tetrachlorobenzene, 650 ng/g 1,2,4,5-tetrachlorobenzene, 2700 ng/g 1,2,3,4-tetrachlorobenzene, 11650 ng/g pentachlorobenzene and 8800 ng/g hexachlorobenzene.

From the results it is concluded that in municipal waste incineration particulate organic carbon is the primary source for PCDD/PCDF formation, as well as for other organochlorocompounds.