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THERMAL BEHAVIOR OF PAHs, HEXACHLOROBENZENE AND PCDDs/PCDFs ADSORBED ON LIGNITE COKE FROM FLUE-GAS CLEANING IN MUNICIPAL WASTE INCINERATORS

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ABSTRACT

Lignite coke is increasingly employed as an adsorbent for flue-gas cleaning, for example, in waste incinerators. The aim of the studies described here was to verify the assumed deposition reliability of moving bed adsorbers even in the case of operational malfunction. To this end, the occurrence of glow clusters in coke beds loaded with various pollutants such as polyaromatic hydrocarbons (PAHs), hexachlorobenzene (HCB), polychlorinated dibenzodioxins and dibenzofurans (PCDDs, PCDFs) was simulated and the thermal behavior of adsorbed compounds recorded by quantitative measurement of the coke pollutant and of the desorption gases. Assuming an incident that would lead to the spontaneous ignition of the adsorber, the results of our studies show that due to the desorption or decomposition reactions of PAHs, PCDDs and PCDFs, as well as HCB as a model substance for high-chlorinated compounds, only small fractions of pollutants are released.

INTRODUCTION

Coke from Rhenish lignite (HOK) is a fine-grained "carbon concentrate" produced by Rheinbraun AG. It is increasingly employed as a once-through adsorbent for environmental purposes (1). In waste air and off-gas cleaning, lignite coke as a high-quality filter material can serve to separate all emission-relevant pollutants, such as SO_2, heavy metals, HF and H_2S, chlorinated hydrocarbons like dioxins (PCDDs) and furans (PCDFs), and polyaromatic hydrocarbons (PAHs). The safety of lignite coke filters applied in waste incineration plants is of great importance under the assumed conditions of a coke fire incident, which may result in the release of adsorbed toxic organic compounds into the environment. The objective of our study was to investigate the thermal behavior of adsorbed PAHs, HCB, and PCDDs/PCDFs on HOK in the temperature range between 120 and 900°C. Laboratory experiments were conducted in two sets of apparatus varying the heating time, carrier gas composition, and temperature.

EXPERIMENTAL METHODS

Materials

Coke from Rhenish lignite (HOK) used in this study is a product from Rheinbraun AG (Cologne, FRG). HOK samples from off-gas cleaning, loaded with PCDFs/PCDDs, were obtained from different municipal waste incinerators (MWIs) in Germany. Amberlite XAD-4 resin (mesh size 20 - 60, pore size 40 Å, BET 725 m^2/g), purified by 72 h Soxhlet extraction with toluene, was obtained from Serva (Heidelberg). PAHs and hexachlorobenzene were obtained from Schmidt (Ahrensburg). 2,4,8-Trichlorodibenzofuran was synthesized in our laboratory according to Kuroki's procedure (2). 1,2,3,4-Tetrachlorodibenzodioxin, unlabeled and $^{13}C_{12}$-labeled chlorinated dibenzo-p-dioxin (PCDDs) and -dibenzofuran (PCDFs) standards were obtained from Promochem (Wesel). All chemicals were 98% pure or better. All solvents were of "distilled-in-glass" grade (Burdick & Jackson).

Apparatus and Procedures

Deposition apparatus. In order to obtain reproducible data in pyrolysis and combustion experiments, it is necessary to produce HOK samples that contain an accurately known amount of adsorbed organic model substances. Therefore, we developed a procedure to deposit organic compounds like PAHs, hexachlorobenzene, and PCDDs/PCDFs from the gas phase onto the HOK surface. Figure 1 illustrates the schematic flow diagram of the deposition apparatus. A mixture of organic compounds in n-hexane was applied to the adsorber by micropipette injection. The solvent was removed in a gentle stream of nitrogen. The reactor (30-mm ID) was then loosely packed with 30 g HOK and mounted vertically in an oven.

At a temperature of 100 or 150°C, the organics were evaporated by passing a preheated simulated municipal waste incinerator flue gas composed of 11 vol% O_2, 12 vol% CO_2, 25 vol% H_2O, and 52 vol% N_2 through the HOK bed. The process gas velocity was set to 10 cm/s; reaction time was 24 h.

Pyrolysis apparatus. The pyrolysis experiments were performed in a horizontal quartz tube reactor placed in a single-zone, electric furnace (Figure 2). The sample (7 g) was placed into the inner tube reaction zone in a quartz boat. Under a nitrogen flow of 133 mL/min, the reactor was heated to 300, 500, 700, or 900°C. The reactor tube outlet was connected to the cold trap (liquid N_2) where volatile desorption products were collected quantitatively. After a 20-min reactor run, the sample was cooled, removed from the reactor, and Soxhlet-extracted with toluene for 48 hours. The reactor and all the lines of the trapping system were rinsed with n-hexane. Following this step, the toluene extract and the n-hexane solution were concentrated and analyzed by GC/MS.

Desorption apparatus. The experimental apparatus used in the combustion and pyrolysis (without O_2) experiments is shown in Figure 3. The system consists of the regeneration gas delivery system, the high-temperature quartz reactor, the desorption product collection, and measurement devices. The flow rates of N_2, CO_2, and O_2 are individually controlled by mass-flow controllers. The temperature of the HOK bed was measured by two thermocouples placed inside the bed (center, wall). The simulated flue gas (350 L/h) is preheated and passed through

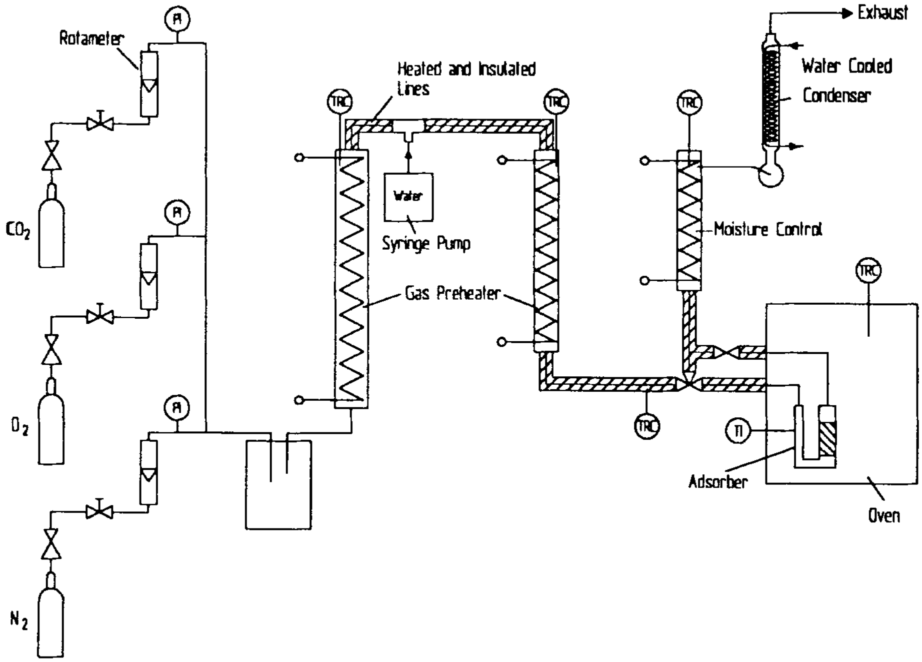


FIGURE 1. Schematic of apparatus for deposition of organic model substances on HOK.

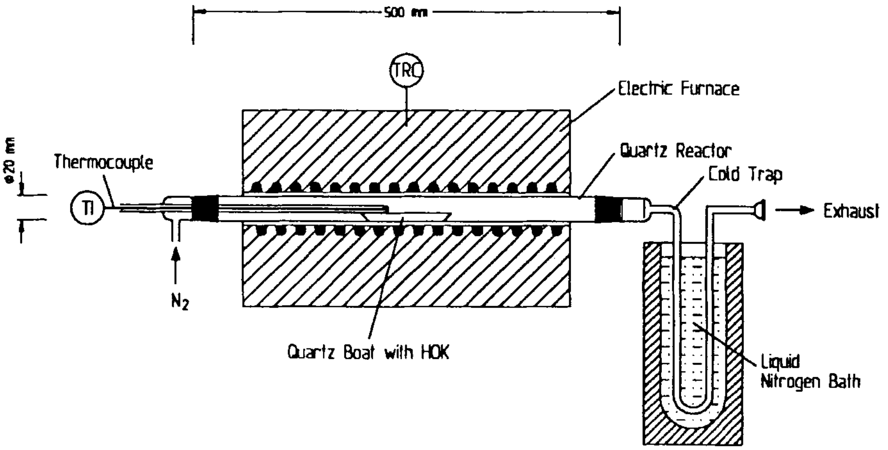


FIGURE 2. Pyrolysis apparatus

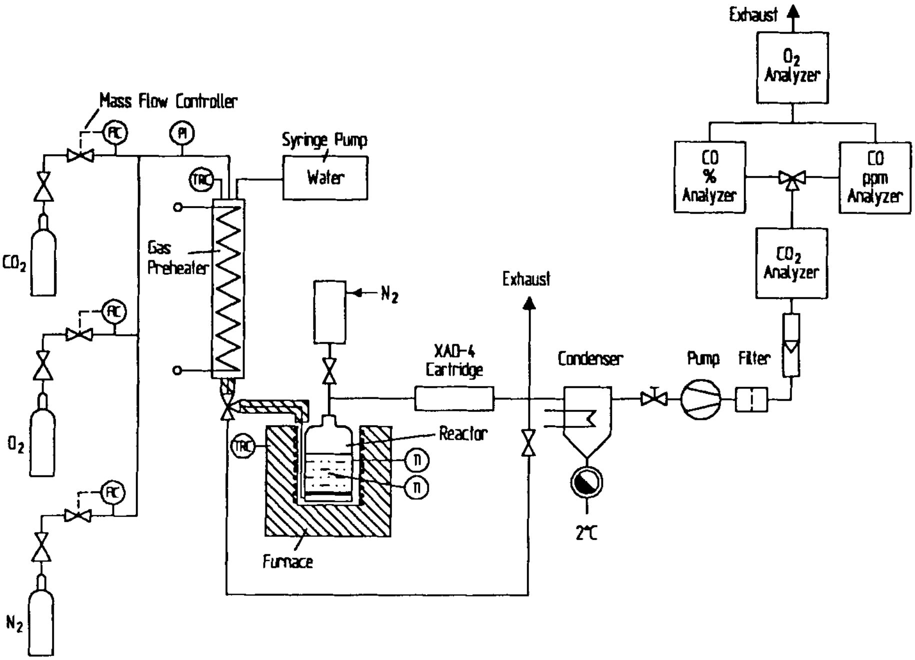


FIGURE 3. Desorption apparatus

the reactor, which is heated (13°C/min) to a temperature of 850°C. At the gas outlet of the reactor five packed beds of XAD-4 resin were installed to adsorb semivolatile compounds (PAHs, chlorinated benzenes, PCDDs, and PCDFs). Off-gas compounds - O_2, CO_2, and CO - are continuously monitored. After a reaction time of 2 h (pyrolysis) or 1 h (combustion) XAD-4 resin containing adsorbed organics and the HOK sample were individually Soxhlet-extracted, and the extracts were concentrated and analyzed by high-resolution gas chromatography/low-resolution mass spectrometry (HRGC/LRMS).

After the thermal treatment of original HOK samples from the off-gas cleaning of MWIs, the XAD-4 and the HOK were spiked with $^{13}C_{12}$-labeled internal standards (EDF 8999, Promochem) to determine the analytical recovery and then extracted for 24 h with toluene. The extracts were concentrated and cleaned by alumina column chromatography (3) and analyzed by high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS).

HRGC/LRMS. Analyses of the employed PAHs, chlorinated benzenes, 2,4,8-trichlorodibenzofuran, 1,2,3,4-tetrachlorodibenzodioxin, and lower-chlorinated PCDDs/PCDFs were carried out with a Siemens Sichromat gas chromatograph equipped with a mass spectrometer (Ion Trap Detector model 800, Finnigan MAT). A 25-m-long, 0.25-mm-ID, 0.25-µm-film-thickness XTI-5 fused silica capillary column was used. Sample aliquots of 1 µL in n-hexane (toluene) were injected on column. The temperature program for n-hexane solutions was (1) 40° for 3 minutes, (2) increasing at 5°/min to 90° and holding for 1 min, (3) rapidly increasing to 180° and holding for 1 min, (4) increasing at 4°/min to 280° and (5) increasing at 20°/min to 300° and holding for 10 min. The carrier gas pressure of He was 80 kPa, and the analyses of toluene solutions started at 90°. The transfer line temperature was set to 270°C. The mass range from m/z 70 to 320 (420) was scanned at 1 scan/s. Samples were identified and quantified on the basis of their retention times and molecular masses and/or by comparison with the mass spectra of authentic compounds or mass spectra present in the NIST library.

HRGC/HRMS. Analyses of PCDDs and PCDFs were performed with a Hewlett Packard 5890 Series II gas chromatograph interfaced directly to the ion source of a VG Autospec high resolution mass spectrometer. A 60-m-long, 0.25-mm-ID, 0.1-µm-film thickness DB 5 fused silica capillary column was used. The temperature program was 130°C (2 min) - 40°C/min - 200°C (10 min) - 10°C/min - 280°C (20 min) - 20°C/min - 300°C (8 min). The carrier gas (He) pressure was 160 kPa. The ion-source temperature was set to 270°C. PCDDs/PCDFs were detected in the electron impact selected ion monitoring (SIM) mode. Criteria used to identify PCDDs and PCDFs are:

1. simultaneous responses at characteristic ion masses,
2. isotope ratios within ±10% of theoretical value,
3. chromatographic retention times consistent with retention times of $^{13}C_{12}$-labeled internal and native standards, and
4. signal-to-noise ratios >3.

Further experimental details of the thermal treatment, sample preparation, and analyses are described elsewhere (4).

RESULTS AND DISCUSSION

Investigations with the Pyrolysis Apparatus

Table 1 shows the results of a series of pyrolysis experiments on HOK samples loaded with different organic model substances. The samples were isothermally pyrolyzed at 300, 500, 700, and 900°C for 20 min in nitrogen atmosphere. The flow rate was 133 mL/min, resulting in a gas velocity of 0.7 cm/s.

Penta- and tetrachlorobenzenes were formed by the dechlorination of hexachlorobenzene and naphthalene probably by the destruction of larger PAHs. Very small amounts of both input and formed substances were volatilized beginning at a temperature of 500°C. The highest recovery rate of 2.7% phenanthrene at 900°C shows that under these conditions only traces are thermally desorbed.

The results of the extraction experiments on pyrolyzed samples are presented in Table 2. The results of the "nonthermally" treated sample indicate that the extraction efficiency greatly depends on the nature of the organic compound. Only the relatively volatile compounds, such as phenanthrene, fluoranthene, pyrene, HCB, 2,4,8-triCDFs and 1,2,3,4-tetraCDD, could be extracted nearly quantitatively (>85%). PAHs with more than four rings (> pyrene) are tenaciously retained by HOK.

TABLE 1. INFLUENCE OF PYROLYSIS TEMPERATURE ON THE DESORPTION OF PAHs/HCB AND 2,4,8-TRICDF/1,2,3,4-TETRACDD FROM HOK IN NITROGEN ATMOSPHERE

Pyrolysis Temperature (°C)		300	500	700	900
Initial Compound	**I (µg)**	**C (µg)**			
Acenaphthylene	248	-	0.2	0.3	0.7
Acenaphthene	242	-	-	-	-
Fluorene	203	-	-	-	0,1
Phenanthrene	225	-	1.0	1.7	6.0
Fluoranthene	220	-	0.3	0.3	2.1
Pyrene	254	-	0.4	0.4	2.5
Benzo(e)pyrene	158	-	-	0.1	0.1
Benzo(a)anthracene	86	-	-	-	-
Indeno(1,2,3-cd)pyrene	50	-	-	-	-
Hexachlorobenzene	138	-	0.2	0.1	0.2
2,4,8-triCDF	180	-	0.2	0.2	0.2
1,2,3,4-tetraCDD	110	-	-	-	-
Formed Compound		**C (µg)**			
Pentachlorobenzene		-	-	0.1	0.1
Tetrachlorobenzene		-	-	-	0,1
Naphthalene		-	0.1	0.1	0.1

I = Initial amount per 7 g HOK.

C = Desorbed amount collected in the cold trap.

Mauldin et al. (5) report that carbonaceous particles are presumably responsible for the irreversible adsorption of PAHs on adsorbents containing significant quantities of carbon, and an increase in the molecular weight of the PAH often leads to a decrease in extraction efficiency.

The recoveries of PAHs and chlorinated compounds after isothermal treatment between 300 and 900°C decrease significantly with increasing temperature (Table 2). This extraction behavior is consistent with two different mechanisms, which explain the observations:

1. At higher temperatures, the interactions between PAHs or chlorinated compounds with HOK increase, leading to irreversible binding to the HOK surface.
2. The observed effects are due to decomposition reactions of adsorbed organics occurring on the HOK surface.

The second hypothesis is supported by the observation that small amounts of degradation products (lower-chlorinated benzenes, PCDDs, and PCDFs) formed by dechlorination/hydrogenation of HCB, 2,4,8-triCDF and 1,2,3,4-tetraCDD were observed after HOK extraction.

Since HCB (6), 2,4,8-triCDF, and 1,2,3,4-tetraCDD (7) are thermally stable in the gas phase up to 900°C, it can be assumed that HOK acts as a catalyst in this reaction. This catalytic dechlorination effect is well known with fly ash from municipal waste incinerators (8) and is due to the catalytic activity of metals (Cu, Fe).

Investigations with the Desorption Apparatus

HOK samples of 30 g were heated to 850°C at a flow rate of 350 L/h. To examine the influence of the temperature, the desorption products were collected in different temperature ranges (<300, 300-500, 500-600, 600-700, >700°C) on five XAD-4 adsorption tubes in series. Under combustion conditions, only two heated (120°C) XAD-4 adsorption tubes were used.

TABLE 2. RECOVERY OF INITIAL AND FORMED COMPOUNDS FROM PYROLYZED HOK SAMPLES

Pyrolysis Temperature (°C)		NT	300	500	700	900
Initial Compound	**I (µg)**	**E (µg)**				
Acenaphthylene	248	97	11	2	-	-
Acenaphthene	242	151	4	-	-	-
Fluorene	203	29	1	-	-	-
Phenanthrene	225	198	103	31	16	2
Fluoranthene	220	187	85	27	14	2
Pyrene	254	203	92	29	15	2
Benzo(e)pyrene	158	67	22	6	4	1
Benzo(a)anthracene	86	61	22	4	4	1
Indeno(1,2,3-cd)pyrene	50	<1	-	-	-	-
Hexachlorobenzene	138	152	41	1	-	-
2,4,8-triCDF	180	158	105	34	<1	
1,2,3,4-tetraCDD	110	101	58	19	-	-
Formed Compound			**E (µg)**			
Pentachlorobenzene			15	2	-	-
Tetrachlorobenzene			3	1	-	-
Total DiCDF			<1	4	-	-
Total MonoCDF			-	<1	-	-
Dibenzofuran			-	1	-	-
Total TriCDD			3	5	-	-
Total DiCDD			<1	2	-	-
Total MonoCDD			-	<1	-	-
Dibenzodioxin			-	<1	-	-

NT = Nonthermally treated HOK sample. I = Initial amount per 7 g HOK.

E = Amount recovered after Soxhlet extraction.

Behavior of adsorbed PAHs/HCB. The data and conditions of a typical experimental run are given in Table 3. PAHs are mainly desorbed between 300 and 600°C; only negligible fractions were observed at higher temperatures. The thermal behavior of the model substances is qualitatively comparable with the findings of Table 1; desorption rates are also relatively high for phenanthrene, fluoranthene, and pyrene. The cumulative recoveries of model substances as well as decomposition products are higher, however, due to a shift of the adsorption/desorption equilibrium, resulting from significantly increased carrier gas flow rate.

This may also explain the detection of the additional decomposition products, trichlorobenzene, biphenyl, and naphthalene, which were released in amounts below the detection limit in the experiments described earlier.

In Figure 4, only the total desorption rates (recovery rates) based on initial amounts given in Table 3 are presented in order to minimize the analytical data.

To simulate a coke fire incident under real conditions, HOK samples were thermally treated up to 850°C with a carrier gas containing 25 vol% water vapor, 11 vol% oxygen, 12 vol% carbon dioxide and 52 vol% nitrogen. The effect of different adsorption temperatures (100 and 150°C) on the thermal desorption was also investigated.

Figure 4 summarizes the results obtained by applying different adsorption temperatures and desorption carrier gas compositions for the investigated model substances. The carrier gas shows little effect on the desorption. The observed effects are small and are within the experimental and analytical error ranges. An increase of the adsorption temperature results in a significant reduction of desorption rates.

This is explained by an increased bonding strength of the organic compounds, especially PAHs, to HOK at elevated temperature. The observation that even the relatively volatile PAHs (phenanthrene, fluoranthene, and pyrene) are recovered at rates of <20% between 300 and 600°C supports the assumption of a strong interaction between the PAHs or secondary products and the coke with the participation of irreversible adsorption and/or chemisorption effects.

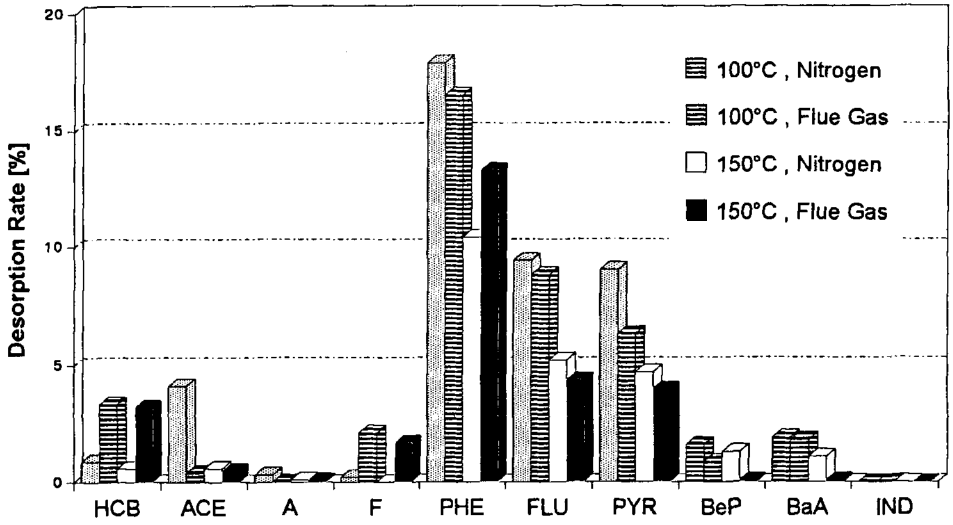
TABLE 3. DESORPTION OF INITIAL AND FORMED COMPOUNDS FROM HOK RECOVERED IN DIFFERENT TEMPERATURE RANGES

Temperature Range (°C)		120-300	300 - 500	500-600	600-700	700-850	120 - 850	
Initial Compound	I (µg)	C (µg)					ΣC (µg)	DR (%)
Acenaphthylene	1065	4	39	1	-	-	44	4
Acenaphthene	1035	2	1	<1	-	-	3	<1
Fluorene	870	<1	1	-	-	-	1	<1
Phenanthrene	965	2	95	75	<1	1	173	18
Fluoranthene	940	1	42	44	<1	1	88	9
Pyrene	1090	1	43	53	1	1	98	9
Benzo(e)pyrene	618	-	4	6	-	-	10	2
Benzo(a)anthracene	370	-	3	4	-	-	7	2
Indeno(1,2,3-cd)pyrene	117	-	-	-	-	-	-	-
Hexachlorobenzene	590	3	2	<1	-	-	5	1
Formed Compound		C (µg)					ΣC (µg)	
Pentachlorobenzene		1	6	1	-	-	8	
1,2,3,5-Tetrachlorobenzene		-	3	-	-	-	3	
1,2,3,4-Tetrachlorobenzene		3	8	-	-	-	11	
1,3,5-Trichlorobenzene		-	1	-	-	-	1	
Biphenyl		2	6	<1	-	-	8	
Naphthalene		6	21	3	-	-	30	

I = Initial amount per 30 g HOK.

C = Amount collected on XAD-4.

DR = Total desorption rate.



HCB = Hexachlorobenzene
ACE = Acenaphthylene
A = Acenaphthene
F = Fluorene
PHE = Phenanthrene
FLU = Fluoranthene
PYR = Pyrene
BeP = Benzo(e)pyrene
BaA = Benzo(a)anthracene
IND = Indeno(1,2,3-cd)pyrene

FIGURE 4. Effect of adsorption temperature and carrier gas on desorption of adsorbed PAHs/HCB from HOK.

Behavior of adsorbed 2,4,8-triCDF and 1,2,3,4-tetraCDD. In a separate series of experiments, the thermal behavior of 2,4,8-triCDF and 1,2,3,4-tetraCDD adsorbed on HOK was investigated under varying conditions. The influence of adsorbed amounts, carrier gas (nitrogen and simulated flue gas atmospheres), and temperature on the desorption was determined. The results show that only traces of initial compounds and lower-chlorinated PCDDs/PCDFs formed by dehalogenation were desorbed in the temperature range between 300 and 500°C. In all experiments the desorption rates were <1%.

Even the presence of oxygen in the carrier gas does not play an important role in desorption, except that decomposition efficiency was higher, because no secondary compounds could be detected (Table 4).

To evaluate the optimum temperature for the decomposition reaction, experiments were carried out at 250, 350, 450, and 550°C for 1 h in nitrogen with a flow rate of 350 L/h. The results agree with those previously described. Small fractions <1%) of initial compounds were desorbed at all temperatures, whereas secondary products were not desorbed below 450°C.

The results obtained after the extraction of pyrolyzed samples are summarized in Table 5. The decomposition of 1,2,3,4-tetraCDD to lower-chlorinated PCDDs starts around 250°C, whereas the decomposition of 2,4,8-triCDF begins at about 350°C. Therefore, we conclude that the optimum temperature for catalytic destruction is around 400°C.

A comparison of the experiments described here with the comparable ones in the pyrolysis apparatus (Table 2) shows that the destruction is not only a function of temperature but also of residence time. At a residence time of 20 min at 500°C, ~18% dioxin and furan was still found in the pyrolysed HOK (pyrolysis apparatus). Under the conditions selected in the desorption apparatus (residence time of 60 min), complete degradation can be observed at 450°C.

In an overall consideration of all the results presented in this section, it becomes apparent that the slight release of relevant pollutants is the result of the following processes proceeding parallel to each other:

1. The pollutants employed are largely catalytically destroyed so that only a very small fraction can be released in an undecomposed form.
2. The decomposition products formed are similarly only detectable to a very slight extent; in addition, low-molecular-weight pollutants may possibly be formed and desorbed, which, however, cannot be identified by the analytical methods available here.

TABLE 4. DESORPTION OF 2,4,8-TRICDF AND 1,2,3,4-TETRACDD FROM HOK WITH FLUE GAS

Temperature Range (°C)		120 - 600	600 -900	120 - 900	
Compound	**I (μg)**	**C (μg)**		**ΣC (μg)**	**DR (%)**
2,4,8-triCDF	773.4	2.59	0.26	2.85	0.37
1,2,3,4-tetraCDD	472.0	0.26	<0.10	0.26	0.06

I = Initial amount per 30 g HOK.
C = Amount collected on XAD-4.
DR = Total desorption rate.

TABLE 5. RECOVERY OF INITIAL AND FORMED COMPOUNDS FROM PYROLYZED HOK-SAMPLES

Pyrolysis Temperature (°C)		250	350	450	550
Initial Compound	**I (μg)**	**E (μg)**			
2,4,8-triCDF	773.4	594.8	129.8	4.5	1.5
1,2,3,4-tetraCDD	472.0	290.0	11.0	0.1	0.2
Formed Compound		**E (μg)**			
Total DiCDF		-	47.0	0.5	-
Total MonoCDF		-	3.9	0.1	-
Dibenzofuran		<0.1	1.0	-	-
Total TriCDD		19.4	13.4	0.5	-
Total DiCDD		0.9	8.7	<0.1	-
Total MonoCDD		-	2.0	-	-
Dibenzodioxin		-	0.4	-	-

I = Initial amount per 30 g HOK.
E = Amount recovered after Soxhlet extraction.

Behavior of HOK samples from different MWIs. HOK samples from three different plants (A - C) were heated (15°C/min) up to 700°C (1 h) in a nitrogen stream. Desorption products were collected on one XAD-4 tube. After pyrolysis the HOK samples were extracted with toluene.

The results of the studies are compiled in Table 6. Apart from the concentrations of the toxically relevant 2,3,7,8-substituted single isomers, the total concentrations are also given for the single-isomer groups. However, the sum totals are not suitable for a toxicological evaluation of the samples analyzed. To this end, the toxicity equivalents (TEs) are given in the bottom line of the table and are calculated according to an international evaluation scheme (NATO-CCMS). The samples (HOK_{A-C}) originating from various waste incinerators have different PCDD/PCDF contents, between 9.3 and 154.6 ng/g HOK, relative to the summation values of the tetra-OCDD/F. If one considers the overall summation values and the TE measured data, then the essential findings are as follows:

- Irrespective of the initial concentration, >95% of the dioxins and furans was destroyed; this can be seen from a comparison of pyrolyzed and nonpyrolyzed HOK samples.
- However, the essential aspect is, that during thermal treatment under the given conditions, no, or only traces of PCDDs/PCDFs are released.

Thus, these findings confirm the results of the extensive thermal studies on 2,4,8-triCDF- and 1,2,3,4-tetraCDD-doped HOK samples.

CONCLUSIONS

The thermal behavior of various hazardous organic compounds, such as PAHs, hexachlorobenzene (HCB), dioxins (PCDDs), and furans (PCDFs), deposited from the gas phase on lignite coke (HOK) was investigated in the temperature

TABLE 6. PCDD/PCDF DESORPTION FROM ORIGINAL HOK SAMPLES FROM DIFFERENT MUNICIPAL WASTE INCINERATORS

Sample	HOK$_A$			HOK$_B$			HOK$_C$		
PCDD/PCDF	**B**	**A**	**X**	**B**	**A**	**X**	**B**	**A**	**X**
Total T4CDD	1.06	<0.01	<0.01	9.62	0.02	<0.01	0.48	n.d.	<0.01
Total P5CDD	0.80	0.04	<0.01	6.80	0.02	<0.01	0.35	0.01	<0.01
Total H6CDD	0.47	0.12	<0.01	4.76	0.07	0.01	1.11	0.01	<0.01
Total H7CDD	0.29	0.11	<0.01	2.25	0.06	0.01	0.61	0.01	<0.01
OCDD	0.25	0.10	<0.01	2.43	0.07	0.01	0.44	0.01	<0.01
Total T4-OCDD	2.86	0.37	<0.02	25.86	0.24	0.04	2.98	0.04	<0.01
2,3,7,8-T4CDD	0.12	<0.01	<0.01	2.13	<0.01	<0.01	0.03	n.d.	<0.01
1,2,3,7,8-P5CDD	0.10	<0.01	<0.01	0.50	0.01	<0.01	0.07	<0.01	n.d.
1,2,3,4,7,8-H6CDD	0.04	<0.01	n.d.	0.22	0.02	<0.01	0.03	<0.01	n.d.
1,2,3,6,7,8-H6CDD	0.04	<0.01	n.d.	0.37	0.02	<0.01	0.13	<0.01	n.d.
1,2,3,7,8,9-H6CDD	0.06	0.03	n.d.	0.54	0.02	<0.01	0.26	<0.01	<0.01
1,2,3,4,6,7,8-H7CDD	0.15	0.08	n.d.	1.11	0.02	<0.01	0.43	<0.01	<0.01
Total T4CDF	12.98	0.03	<0.01	62.93	<0.01	n.d.	1.50	0.05	<0.01
Total P5CDF	8.57	0.07	<0.01	54.13	0.05	<0.01	1.55	0.06	<0.01
Total H6CDF	1.83	0.25	0.03	10.99	0.08	<0.01	1.82	0.02	<0.01
Total H7CDF	0.51	0.10	0.02	26.73	0.04	n.d.	1.27	0.01	<0.01
OCDF	0.06	0.03	<0.01	1.02	0.04	<0.01	0.16	0.01	<0.01
Total T4-OCDF	23.95	0.48	0.05	128.8	0.22	<0.01	6.30	0.15	<0.01
2,3,7,8-T4CDF	1.24	<0.01	<0.01	10.73	<0.01	n.d.	0.30	0.01	<0.01
1,2,3,7,8-P5CDF	0.92	0.01	<0.01	3.13	<0.01	<0.01	0.33	<0.01	<0.01
2,3,4,7,8-P5CDF	0.62	0.02	<0.01	4.45	0.04	n.d.	0.04	0.01	<0.01
1,2,3,4,7,8-H6CDF	0.43	0.03	<0.01	4.97	0.02	<0.01	0.25	<0.01	<0.01
1,2,3,6,7,8-H6CDF	0.31	0.11	<0.01	1.36	0.02	n.d.	0.84	<0.01	<0.01
1,2,3,7,8,9-H6CDF	0.14	0.06	<0.01	1.08	0.02	<0.01	0.36	<0.01	<0.01
2,3,4,6,7,8-H6CDF	n.d.	0.01	n.d.	n.d.	0.02	n.d.	0.37	n.d.	n.d.
1,2,3,4,6,7,8-H7CDF	0.40	0.04	<0.01	1.95	0.02	n.d.	0.46	0.01	<0.01
1,2,3,4,7,8,9-H7CDF	0.05	0.02	n.d.	0.15	0.01	n.d.	0.31	<0.01	<0.01
Total T4-OCDD/F	26.81	0.86	0.08	154.7	0.47	0.05	9.28	0.18	0.03
TE NATO/CCMS	0.72	0.04	<0.01	6.26	0.04	<0.01	0.34	<0.01	<0.01

B = Amount before desorption.
A = Amount after desorption.
X = Amount collected on XAD-4.
n.d. = not detectable.

range from 120 to 900°C. Desorbed products were collected and analyzed by GC/MS. The following results may be regarded as the essential points:

- The organic compounds studied here are almost completely and irreversibly bound to the lignite coke matrix with increasing temperature.
- PAHs are recovered at rates of <20% between 300 and 600°C, showing a strong interaction, including possibly irreversible adsorption and/or chemisorptive effects, between the PAHs or secondary products and the coke. Pyrolysis products of PAHs are naphthalene and biphenyl.
- Adsorbed organic pollutants (e.g. PCDD/F, HCB) are catalytically decomposed during the thermal treatment of lignite coke.
- HCB decomposes forming bi- to penta-chlorinated benzenes.
- Small amounts of low-chlorinated dioxins and furans were formed in the pyrolysis of adsorbed 2,4,8-trichlorodibenzofuran and 1,2,3,4-tetrachloro-dibenzodioxin on HOK.
- Pyrolysis of HOK samples from the off-gas cleaning of different municipal waste incinerators yielded >95% destruction of original PCDFs/PCDDs.
- Only traces of pollutants are locally released in the bed but a release into the atmosphere in the case of glow"fires" can be ruled out.

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