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Arbetsrapport SGC A08

**REDUKTION AV DIOXIN, FURAN- OCH  
KLORFENOLER VID AVFALLSFÖRBRÄNNING**

Påverkan av utökad tid för rök-gaskylning samt  
av efterförbränning med naturgas

(På engelska)

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## INFLUENCE OF INCREASED GAS COOLING RESIDENCE TIME AND NATURAL GAS AFTERBURNING ON STACK EMISSION OF PCDD/F AND CPH IN RDF COMBUSTION

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**ABSTRACT** - The aim of this study was to measure the effect of 1) increased flue gas cooling residence time and 2) natural gas afterburning on stack emission of polychlorinated dibenzo-p-dioxins (PCDD), -furans (PCDF) and chlorophenols (CPh) in refuse derived fuel (RDF) combustion. A laboratory scale (43 kW) stoker pilot plant was used in the tests. The increased flue gas cooling residence time at temperature range 650-500°C reduced the total emission of PCDD/F. On the other hand, if the residence time was increased at temperature range 500-450°C, the total emission of PCDD/F slightly increased. Natural gas afterburning reduced the total emission of PCDD/F and CPh. The reduction was remarkable in the fly ash but the gas phase concentrations increased slightly compared to the tests without afterburning.

### Introduction

It has been shown by many researchers that levels of PCDD/F increase when flue gas is cooled after a MSW furnace at temperature range 535-220°C (Düvel et al. (1990), Wunsch et al. (1994), Benfenati et al. (1991), Fängmark et al. (1991)). Numerous experiments have also been made by annealing simulated or real MSW fly ash in different gas mixtures simulating MSW flue gas. At temperatures around 250-400°C a strong formation of PCDD/F has been observed both in the gas phase and in the condensed phase (Vogg and Stieglitz (1986), Addink et al. (1995) and many others).

Two mechanisms has been proposed to cause the formation. The first involves unburned, extractable carbon present in the fly ash matrix. This mechanism is often referred to as de novo synthesis, for the combination of unlike starting materials such as elemental carbon and sources of oxygen, chlorine and hydrogen. Milligan and Altwicker (1993) found that de novo synthesis was a source for PCDD/F, CPh and Chlorobenzenes (CB). A metal catalyst, like Cu, is proposed to promote the synthesis.

The second mechanism involves chemically similar gas phase precursors like CPh. Precursors may be formed initially as products of incomplete combustion in the furnace or in de novo synthesis. As temperature gets lower, precursors condense on the fly ash surface and react further to form highly chlorinated compounds including PCDD/F (Karasek and Dickson (1987), Milligan and Altwicker (1996)).

The carbon on the fly ash may serve as a reactant (via de novo-synthesis) but possibly also as a catalyst (Luijk et al (1994)), so increased carbon burnout in the fly ash should decrease heterogenous PCDD/F production.

Post furnace afterburning with a secondary fuel is one of the most reliable techniques for achieving low carbon content in the MSW/RDF combustion fly ash. It also promotes the break down of PCDD/F and their chemically similar precursors to simpler compounds like  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{HCl}$ .

In this work we wanted to study how the total concentration and gas phase/fly ash equilibria of flue gas PCDD/F and CPh in the stack are affected when the residence time in hot post combustion zone is increased and also when natural gas afterburner is used.

## Experimental

RDF pellets were incinerated in a laboratory scale (43 kW) stoker pilot plant. Pilot plant consisted of separate incinerator, a water cooled boiler and 0-2 insulated extension tubes between them (Figure 1).

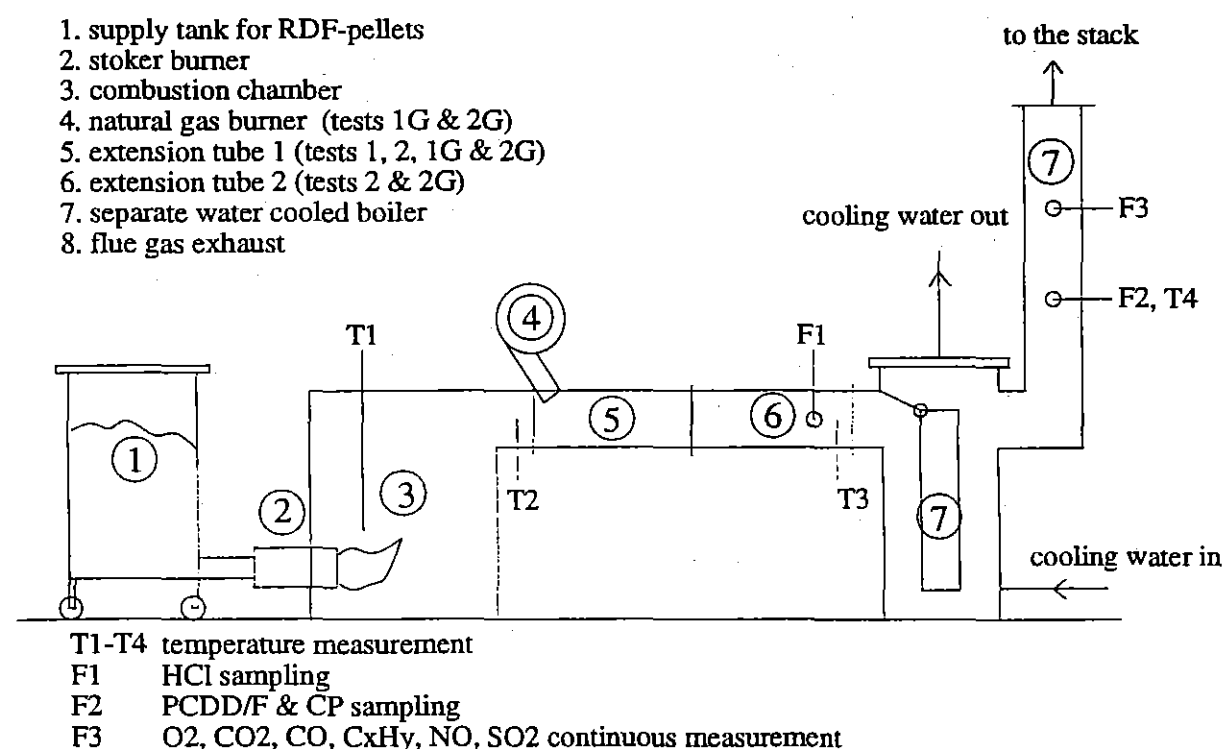


Figure 1. RDF stoker pilot plant

To study the circumstances in raw gas, no gas cleaning system was installed. Two test series were conducted. Each test was duplicated to make sure for the right conclusions. Reference tests (test no:s 0.1 & 0.2) were made for "normal" operation without the extension tubes. In the first test series increased residence time at temperature range 650.. 450°C (T2..T3) was achieved by adding 1 or 2 extension tubes between the incinerator and the boiler. The tests with 1 one extension tube are marked with no:s 1.1 & 1.2, and the tests with 2 extension tubes are no:s 2.1 and 2.2. In the second test series a 16 kW natural gas afterburner was added between the incinerator and the extension tubes. Tests were made again for 1 and 2 tubes (1G.1, 1G.2, 2G.1 & 2G.2). The flue gas temperature in the tubes was shifted to 820-590°C. In all tests PCDD/F- and CP-levels were sampled after the boiler at 160-210°C (T4).

Each tube corresponded to about 1.4 seconds residence time in the tests without afterburning and 0.9 seconds with afterburning. The fuel pellets were regular RDF-pellets made from mechanically sorted household solid waste for district heat production (Andersen, 1995). The moisture was analyzed to be 4.1 % and the lower heating value as received was 19.01 MJ/kg. The elementary composition for dry fuel is presented in table I.

**Table I** *The elementary composition for dry RDF-pellets (w-%). nd = not detected*

C	49.9
H	7.3
N	0.8
S	0.18
Cl	0.66
ash	14.2
Fe	0.153
Cu	0.0128
Ni	0.00198
Cr	0.00219
Pb	nd
Mn	0.00427
Zn	0.0258
Co	nd

Natural gas consisted of 98 % CH<sub>4</sub>, and the rest 2% of higher hydrocarbons, N<sub>2</sub> and CO<sub>2</sub>. The lower heating value was 35.6 MJ/Nm<sup>3</sup>.

The experiments were always conducted in a similar manner. After the incinerator was mechanically cleaned, the stoker burner and the natural gas burner (in the tests 1G and 2G) were injected and the operating parameters were let to stabilize for approx. 3 hours. The fuel input in the stoker burner was 2.23 g/s and in the natural gas burner 0.33 g/s.

Details of the organic chlorinated compounds sampling train are described elsewhere (Halonen et al., 1993). One sampling period lasted 1 hour, after which the train could be prepared for another test period. After a test series was over, the incinerator was cooled down and eventual modifications were made for another test series in different conditions.

## Results and discussion

The average operating parameters and concentrations of CO, C<sub>x</sub>H<sub>y</sub>, SO<sub>2</sub>, NO and HCl in different tests are presented in table II. Peak concentrations of CO and C<sub>x</sub>H<sub>y</sub> were even 10 times higher than the average concentrations in the tests without natural gas afterburning. In the tests with afterburning, the high peak concentrations of CO and C<sub>x</sub>H<sub>y</sub> were reduced efficiently due to increased temperature and turbulence in the extension tubes.

**Table II** *Operating parameters and flue gas analyses ( $O_2$  in %, other values in  $mg/Nm^3$  dry gas corrected to 11%  $O_2$ )*

test	T1	T2	T3	$O_2$	CO	$C_2H_4$ <sup>1)</sup>	$SO_2$	NO	HCl <sup>2)</sup>	dust
0.1	888	607	-	7.8	421 <sup>3)</sup>	0	331	176	-	266
0.2	897	619	-	9.0	407 <sup>3)</sup>	2	341	198	-	293
1.1	834	655	501	6.9	716 <sup>3)</sup>	8	358	136	43	444
1.2	902	620	498	8.5	489	0	304	154	173	289
2.1	909	658	443	7.9	303 <sup>3)</sup>	0	289	209	42	345
2.2	909	671	473	8.9	164 <sup>3)</sup>	0	273	220	-	207
1G.1	870	802	681	7.6	30	0	212	172	-	82
1G.2	911	819	693	7.7	19	0	212	165	-	76
2G.1	855	823	582	8.1	3	0	168	201	-	257
2G.2	868	828	586	8.3	1	0	171	171	50	71

<sup>1)</sup> Calculated as  $CH_4$

<sup>2)</sup> Total inorganic chlorine calculated as HCl

<sup>3)</sup> unreliable value due to fault in the analyzer

Table III presents chlorophenol concentrations in different tests. The most dominant chlorophenols were low chlorinated MCP:s and DCP:s.

**Table III** *Chlorophenol concentrations ( $ng/Nm^3$  dry gas corrected to 11%  $O_2$ )*

test	0.1	0.2	1.1	1.2	2.1	2.2	1G.1	1G.2	2G.1	2G.2
2-MCP	9810	9678	14181	8073	4865	3389	2074	2977	2412	1947
3-MCP	1160	1081	970	641	663	568	170	114	197	95
4-MCP	2935	2058	2340	1379	1045	807	1270	845	1567	885
2,6-DCP	420	537	431	433	327	239	114	139	58	38
2,4+2,5-DCP	2341	2900	1788	1877	3172	3175	1549	2959	1685	165
3,5-DCP	195	224	114	123	172	170	93	81	98	60
2,3-DCP	276	378	126	116	242	192	77	81	85	48
3,4-DCP	322	344	116	181	253	210	163	86	144	94
2,4,6-TCP	383	355	183	278	471	323	258	281	190	142
2,3,6-TCP	139	173	50	73	136	128	60	54	56	31
2,4,5-TCP	425	648	136	215	559	495	228	223	235	118
2,3,4-TCP	158	205	54	85	198	172	93	94	88	48
2,3,5-TCP	192	268	55	99	278	232	128	122	135	68
3,4,5-TCP	84	118	7	31	112	77	49	32	52	26
2,3,4,6-TeCP	327	436	119	307	617	502	365	341	338	184
2,3,4,5-TeCP	202	334	55	249	471	413	223	238	388	124
Penta-CP	390	371	297	465	491	475	332	399	325	223
total	19759	20109	21023	14627	14073	11565	7244	9067	8053	4295

Figure 2 presents the distribution between gas phase and fly ash. Over 82% of the total concentrations were bound in fly ash in all tests. Afterburning reduced the fly ash concentrations considerably while the gas phase reduction was not remarkable.

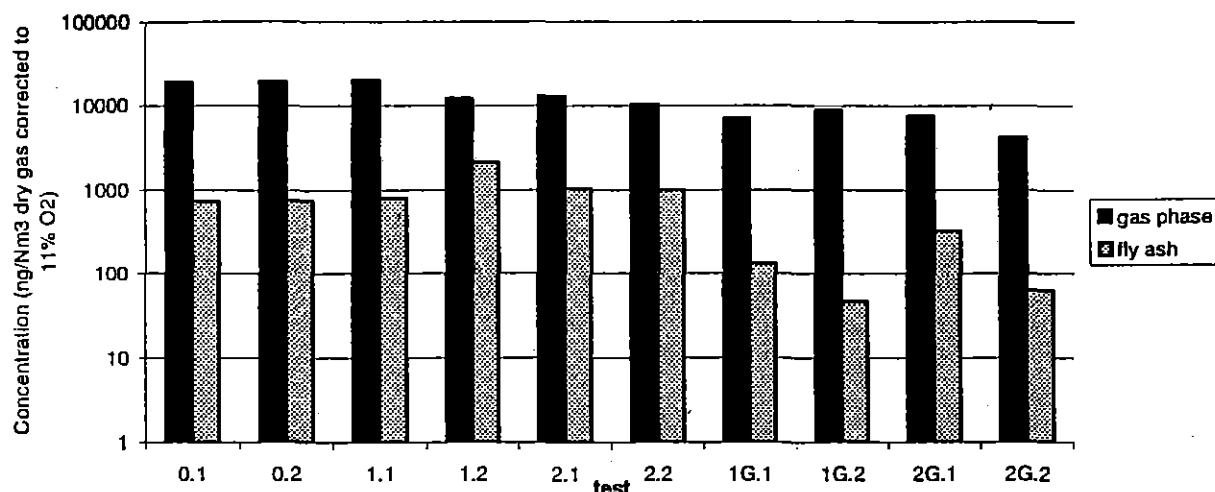


Figure 2. CPh distribution between gas phase and fly ash (logarithmic scale)

Table IV presents the concentrations of PCDD and PCDF homologues in different tests. The most abundant were penta- and heptasubstituted dioxins and -furans. Increased residence time reduced the total concentrations slightly when 1 extension tube was used, but further increase to 2 tubes (more residence time at temperatures near 450..500 °C) caused higher total concentration. Afterburning shifted the patterns slightly toward higher chlorinated compounds.

Table IV PCDD/F homologues in different tests (ng/Nm³ dry gas corrected to 11% O₂)

	0.1	0.2	1.1	1.2	2.1	2.2	1G.1	1G.2	2G.1	2G.2
T4CDD	79.64	68.73	16.44	10.17	57.45	13.53	1.83	7.10	5.36	4.11
P5CDD	307.03	214.54	63.48	24.17	152.97	42.41	23.06	16.98	18.26	5.71
H6CDD	95.79	91.48	20.40	16.42	102.81	31.02	21.48	12.26	18.76	4.70
H7CDD	30.70	17.73	4.82	6.72	49.83	15.17	26.49	14.83	14.25	6.27
OCDD	1.38	1.09	0.53	0.53	2.27	1.31	4.68	2.44	1.59	0.67
PCDD	514.5	393.6	105.7	58.0	365.3	103.5	77.5	53.6	58.2	21.5
T4CDF	430.56	583.69	229.11	194.83	453.23	229.50	14.85	51.48	50.33	1807.02
P5CDF	628.05	534.46	108.99	202.52	578.97	159.24	35.89	24.09	52.54	1696.71
H6CDF	208.61	158.45	59.10	60.00	240.66	66.74	30.95	20.84	28.72	665.48
H7CDF	80.83	52.34	19.38	33.49	146.06	41.43	36.52	24.17	25.30	378.70
OCDF	0.96	1.43	1.28	1.12	2.09	1.14	2.55	1.59	1.50	12.69
PCDF	628.0	1330.4	417.9	492.0	1421.0	498.1	120.8	122.2	158.4	4560.6

Figure 3 presents the PCDD+F concentration distribution between gas phase and fly ash. Afterburning reduced the fly ash concentrations considerably, whereas gas phase concentrations increased slightly. PCDD+F:s were considerably more bound in fly ash than CPh:s. This might suggest that adsorbed CPh:s react very fast to unknown products - including possibly PCDD/F - on particle surface.

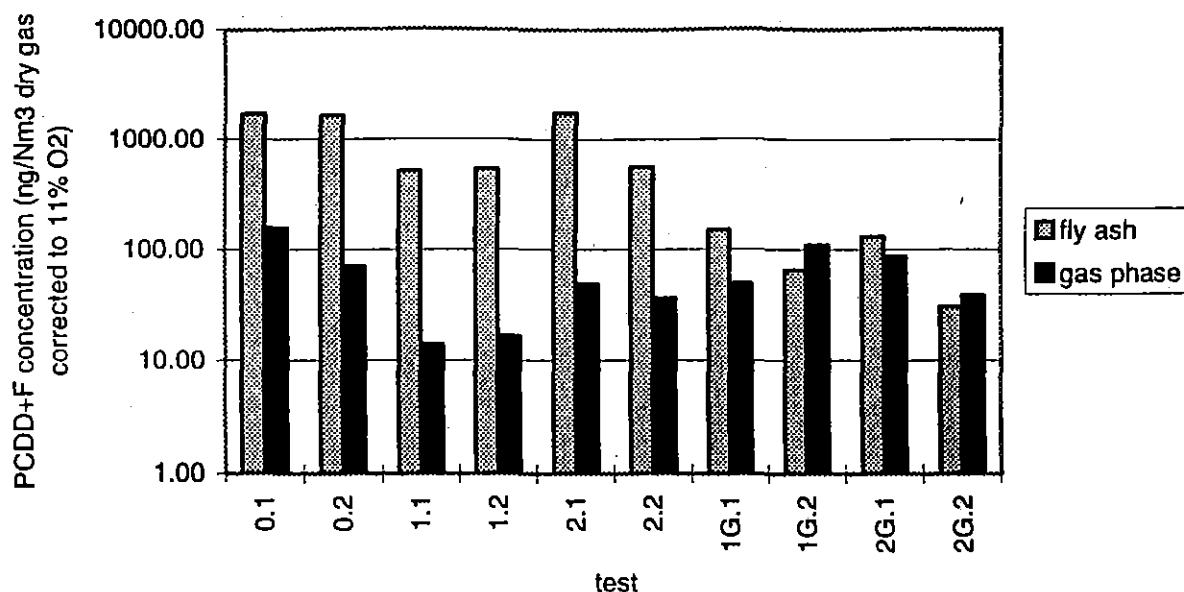


Figure 3. Distribution of total PCDD+F between gas phase and fly ash presented in logarithmic scale

Table V presents PCDD/F toxicity in I-TEQ concentrations in different tests.

Table V Toxicity of PCDD/F in different tests (I-TEQ ng/Nm<sup>3</sup> dry gas corrected to 11% O<sub>2</sub>)

test	0.1	0.2	1.1	1.2	2.1	2.2	1G.1	1G.2	2G.1	2G.2
PCDD/F	87.96	68.93	16.89	18.16	74.50	21.38	8.31	6.44	8.90	2.49

Toxicity decreased as residence time was increased with 1 extension tube. Second extension tube caused higher toxicity. With afterburning the toxicity was much lower, but there was no evident difference between the tests with 1 and 2 tubes.

## Conclusions

In the reference tests the total PCDD/F-concentrations were very high. Increased residence time at temperature range 650-500°C with 1 extension tube reduced the total concentration of PCDD/F approx. 70 % compared with the reference tests. The reduction was more clear in the gas phase than in the fly ash. In the 2 extension tube tests, the average PCDD/F-concentrations were higher than in the 1 tube tests although there was a great variation in the results.

In the second test series (natural gas afterburning) the total PCDD/F-concentrations were further decreased. The big reduction rate was achieved especially due to low fly ash concentrations of PCDD/F. On the other hand, the gas phase PCDD/F-concentrations were higher than in the corresponding tests in the first test series. Chlorophenol concentrations were lower than in the first test series both in the gas phase and in the fly ash.

Very low concentration of fly ash CPh supports the theory of fast precursor conversion reactions to PCDD/F and unknown products on fly ash surface.

Table VI is a quick summary of the results in our tests.

**Table VI** *Quick summary of the results.  $t_r$  = residence time*

test run	1	2	1G	2G
reference test	0	0	1	2
operation	increased $t_r$ between 650..500°C	increased $t_r$ between 650..450°C	ng afterburning	ng afterburning
PCDD/F toxicity (TEQ)	-	=	-	-
PCDD/F concentration in particles	-	=	-	-
PCDD/F concentration in gas	-	-	+	+
PCDD/F chlorination	=	=	+	=
CPh concentration in particles	+	+	-	-
CPh concentration in gas	=	-	-	-
+ higher toxicity/concentration/chlorination than in the reference test				
- lower toxicity/concentration/chlorination than in the reference test				
= equal or contradictory results				

In the table VI, (+) and (-) conclusions were only made when all test results showed the same tendency. Chlorination tendency is decided by observing eventual change in the most abundant homologue.

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