

The Title of the invention is:

Process for removing halogenated organic compounds from waste gases.

THIS SHEET HAS BEEN
REPLACED

Process for removing halogenated organic compounds from waste gases



Claims

1. A process for removing halogenated organic compounds from waste gases optionally containing NO_x , characterized in that the waste gas is optionally led through a fixed bed or fluidized bed and contacted with Caro's acid H_2SO_5 or one of its salts.
2. A process according to claim 1, characterized in that the waste gas is optionally supplemented with SO_2 , optionally led through a fixed bed or fluidized bed of a solid and contacted with H_2O_2 , whereby Caro's acid is produced *in situ*.
3. A process according to claim 1, characterized in that the waste gas is led through a fixed bed or fluidized bed of a solid and at the same time a mixture of H_2O_2 and H_2SO_4 is sprayed onto the solid.
4. A process according to claims 1 or 2, characterized in that before the solid is introduced into the waste gas stream it is impregnated with H_2SO_4 and H_2O_2 is applied.
5. A process according to claims 1 or 2, characterized in that before the solid is introduced into the waste gas stream it is impregnated with H_2O_2 and H_2SO_4 is applied.

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

6. A process according to claim 1, characterized in that before the solid is introduced into the waste gas stream it is impregnated with Caro's acid or with an aqueous solution of its salt.
7. A process according to claim 1, characterized in that before the solid is introduced into the waste gas stream it is sprayed with Caro's acid or with an aqueous solution of its salt.



This Sheet Has Been Replaced



THIS SHEET HAS BEEN REPLACED

Process for removing halogenated organic compounds from waste gases

The invention relates to a process for removing halogenated organic compounds from waste gases optionally containing NO_x , especially waste gases from refuse incineration plants.

Waste gases from refuse incineration plants contain, apart from NO_x (200 ppm on average) and residual SO_2 (10-20 mg/ Nm^3 on average, = ca. 3 to 7 ppm), chlorinated dibenzodioxins and chlorinated dibenzofurans in a concentration of the order of ca. 2 to 10 ng TE/ m^3 (toxicity equivalents).

In the 17th Statutory Regulation to the Federal Law on Protection from Noxious Substances, the legislature stipulates from 1996 a limit value of 0.1 ng TE/ Nm^3 .

In public discussion, thermal treatment of waste (refuse incineration) is regarded as an emission source from which a disproportionately high environmental pollution originates, especially owing to the dioxin emissions.

The waste gases from refuse incineration are led through adsorption plants in which the environmentally harmful substances are removed from the waste gas.

The use of activated coal coke or activated carbon as adsorbent in the adsorption plants is known. In this case, the waste gas is led through a bed of solid with an incident velocity between 0.1 and 0.3 m/s (VDI Textbook 780, page 12). Another possibility, that is limited, however, to relatively

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

low flow rates, consists in using an activated carbon filter according to the cross-flow principle (VDI Textbook 972, page 2).

A disadvantage of the use of activated carbon consists in the fact that if oxygen is present in the waste gas, the activated carbon can ignite at elevated temperature, and the adsorption performance is reduced. In the extreme case this can also lead to the complete combustion of the activated carbon filter.

The problem accordingly existed of developing a process for removing halogenated organic compounds from waste gases optionally containing NO_x , especially from refuse incineration plants, that does not have these disadvantages.

The invention provides a process for removing halogenated organic compounds from waste gases optionally containing NO_x , which is characterized in that the waste gas is optionally led through a fixed bed or fluidized bed and contacted with Caro's acid or one of its salts.

In an embodiment of the invention the waste gas can optionally be supplemented with SO_2 , optionally led through a fixed bed or fluidized bed of a solid, and contacted with H_2O_2 .

The SO_2 component is added if the exit waste gas contains little or no SO_2 .

In an embodiment of the invention, apart from H_2O_2 , Caro's acid can also be applied.

The waste gas can moreover be led through a fixed bed or fluidized bed of a solid while an aqueous mixture of H_2O_2 and H_2SO_4 is sprayed onto the solid.

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

In an embodiment of the invention, before the solid is introduced into the waste gas stream, it can be impregnated with H_2SO_4 and H_2O_2 applied.

In a further embodiment of the invention, before the solid is introduced into the waste gas stream, it can be impregnated with H_2O_2 and H_2SO_4 applied.

In a further embodiment of the invention, before the solid is introduced into the waste gas stream, it can be impregnated with Caro's acid or with an aqueous solution of its salt. Likewise, before the solid is introduced into the waste gas stream it can be sprayed with Caro's acid or with an aqueous solution of its salt.

As the solid, the following can be used as finely-divided, granulated or tabletted substances or as substances formed to any formed bodies, including honeycomb bodies, or applied to honeycomb-shaped supports, alone or in a mixture:

- silica gels, precipitated silicic acids, pyrogenic silicic acids, optionally in hydrophobed form;
- wide- or medium-pore natural or synthetic zeolites;
- phyllosilicates;
- aluminium oxide;
- diatomaceous earth;
- titanium dioxide;
- natural or synthetic layer silicates.

Solids that have been thoroughly checked experimentally are characterized in more detail as follows:

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

Aerosil 200 (pyrogenic amorphous silicic acid), tablets 6 x 5.5 mm (development product from the commercial product Aerosil 200 of the Degussa company, Frankfurt);

Wide-pore 12-ring zeolite, dealuminized γ -zeolite (pore width 7.4 Å, modulus 200 (Si/Al = 100)).

The solids according to the invention have the advantage that they are not combustible. They are temperature-stable up to 900 °C. They are regenerable, whereby remaining dioxins can be completely destroyed, for example by means of Fenton's reagent (H_2O_2 + Fe(II) or Fe(III) salts) or by means of another known chemical reaction or thermally. In the process according to the invention, the preponderant part of the dioxins is destroyed directly on the solid.

The amount of H_2O_2 or of Caro's acid depends on the quantity of dioxin that has to be destroyed. The destruction of dioxin achieved should be as far as possible quantitative.

The H_2O_2 is added as an aqueous solution with an H_2O_2 content of 30 to 90 wt%, preferably 50 %.

If the waste gas contains no SO_2 , SO_2 can be added to the waste gas in an amount of 0.01 to more than 10,000 ppm.

The fixed bed can be impregnated with H_2SO_4 in an amount up to the saturation of the solid.

The fixed bed can be impregnated with H_2O_2 at a concentration of 1 to 90 wt% and in an amount up to the saturation of the solid.

An aqueous solution of H_2SO_4 can be introduced into the waste gas stream in a concentration of 10 to 98 wt% and in an amount of 0.01 to 10 $\text{g/m}^3 \cdot \text{s}^{-1}$.

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

It appears to be essential according to the invention that, apart from H_2SO_4 , H_2O_2 also is present in a reaction zone. The Caro's acid formed therefrom as an intermediate appears to be the actual agent. The waste gas temperature should optionally be above the dewpoint that results from the water content of the waste gas. This is necessary in order to prevent the condensation of water on the fixed bed, which would lead to undesired dilution of the acid.

The process according to the invention has the following advantages:

For one thing, an incombustible catalyst or solid is used. For another, the dioxins or the chlorinated organic compounds are not only adsorbed on the solid but also destroyed there to the extent of almost 100 %.

Examples

In a continuous test for nitrogen oxide reduction of a waste gas from a refuse incineration plant, parallel dioxin measurements were carried out:

The object was to investigate the behaviour of the polychlorinated dibenzodioxins and -furans under the strongly oxidizing conditions (destruction or adsorption on the catalyst). To this end the experimental plant was operated continuously in 24-hour shift operation over a period of 10 days. After 7 days continuous operation the actual dioxin measurement started. To this end, gas samples were taken on three successive days, in each case before and after the catalyst over a period of 6 hours on each occasion. At the end of the test, samples of the catalyst also were taken.

SiO_2 tablets that had been formed from the pyrogenically produced silicon dioxide Aerosil 200 were used as the solid.

This Sheet Has Been Replaced

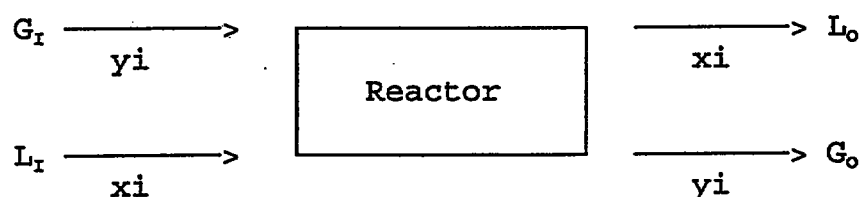


THIS SHEET HAS BEEN
REPLACED

In the course of this the following conditions were maintained:

Reactor diameter	300 mm
Bed height of the fixed bed	400 mm
Material: Aerosil 200 tablets	6 x 5 mm
Volume of the fixed bed	28-30 l
Bulk density ca.	0.5 kg/l
Temperature at the reactor inlet	69-70 °C
Temperature at the reactor outlet	69 °C
Dewpoint of the gas ca.	60 °C
Pressure drop ca.	110 mm water column
Linear velocity in the reactor	0.6-0.7 m/s
Gas throughput ca.	160 m ³ /h
	= ca. 130 Nm ³ /h moist gas
	= ca. 104 Nm ³ /h dry gas
H ₂ O ₂ (50 %) dosing rate	1 ml/min
Average SO ₂ content in crude gas	ca. 5-15 mg/Nm ³
Test duration	10 days

Mass balance



L = liquid streams

G = gas streams

I = inlet

O = outlet

x_i = concentration of component i in the liquid phase

y_i = concentration of component i in the gas phase

The sampling points can be taken from Figure 1

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

The results of the measurements are shown in Tables 1 to 9. Table 10 shows results of measurements obtained by a process according to the prior art.

The abbreviations used in the examples have the following meanings:

1. 1,2,3,6,7,8-Hexa CDF = 1,2,3,6,7,8-hexachlorodibenzofuran
2. BGA = Federal [German] Office of Public Health
3. ng = nanogram
4. TE = toxicity equivalent
5. PCDF = perchlorinated dibenzofurans
6. PCDD = perchlorinated dibenzodioxins
7. Tetra CDF = tetrachlorodibenzofuran
8. Penta CDF = pentachlorodibenzofuran
9. Hexa CDF = hexachlorodibenzofuran
10. Hepta CDF = heptachlorodibenzofuran
11. Octa CDF = octachlorodibenzofuran
12. Tetra CDD = tetrachlorodibenzodioxin
13. Penta CDD = pentachlorodibenzodioxin
14. Hexa CDD = hexachlorodibenzodioxin
15. Hepta CDD = heptachlorodibenzodioxin
16. Octa CDD = octachlorodibenzodioxin
17. Gef. Stoff. V. = Decree on Hazardous Substances
18. CC MS = Committee on Challenges of Modern Society
19. North Atlantic Treaty Organization
20. NWG = limit of detection
21. Congeners are molecules of the same basic structure of different degrees of substitution
22. SP-2331 = special column for chromatography (polar column based on siloxane)
23. 1,0134 Pa = pressure datum in Pascal
24. BGA/UBA = Federal Office of Public Health/Federal Office of the Environment

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

Conditions

Reactor charge 30 l Aerosil 200 tablets (density 0.5 kg/l) = 15 kg

The reactor is operated for 240 hours with 130 Nm³/h waste gas with a moisture content of ca. 20 % from the refuse incineration plant.

L_r = 50 % H₂O₂ + 50 % water, containing no dioxin

L_o = condensate, low volume flow rate, containing no dioxin

Calculation

1. Total quantity of gas (moist gas)
130 Nm³/h x 24 h/d x 10 d = 31,200 Nm³
2. Total quantity of gas (dry gas)
31,200 x 0.8 = ca. 25,000 Nm³
3. Dioxin content of the fresh catalyst = 0
Dioxin_{in} - Dioxin_{out} = Dioxin_{reacted} + Dioxin_{accumulated}

Exemplary calculation for 1,2,3,6,7,8-hexa CDF (TE = 0.1)

Average inlet concentration, absolute	= 3.85 ng/Nm ³
Average outlet concentration	= 0.07 ng/Nm ³
Max. concn. on the catalyst (top layer)	= 1.1870 ng/g
Average concn. on the catalyst (mixed sample)	= 0.099 ng/g
Dioxin _{in} = 3.85 x 25,000 = 96,250 ng	= 100 %
Dioxin _{out} = 0.07 x 25,000 = 1,750 ng	= 1.8 %

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

$$\begin{aligned}
 \text{Dioxin}_{\text{acc}}, (\text{max.}) &= 1.1870 \times 1000 \text{ g/kg} \times 15 &= 17,805 \text{ ng} \\
 & &= 18.5 \% \\
 \text{Dioxin}_{\text{acc}}, (\text{average}) &= 0.099 \times 1000 \times 15 &= 1,485 \text{ [ng]} \\
 & &= 1.54 \%
 \end{aligned}$$

From this there follows a reaction of 80-97 % for this component. The calculation was carried out for all components: see Table 09.

Results

The crude gas stream has an average dioxin contamination of 4.19 ng TE (BGA)/Nm³ (3.9 - 4.61).

The average clean gas concentration is 0.014 ng TE(BGA)/Nm³ (0.010 - 0.017).

The average proportion of dioxin removed in the system is accordingly 99.67 % (see also Table 08).

On the catalyst there is on average 0.050 ng TE/g catalyst. Peak values in the top catalyst layer are about 0.635 ng TE/g catalyst.

Via the gas stream, ca. 104,750 ng TE are fed in. The amount discharged is ca. 350 ng TE. On the catalyst, ca. 750 ng TE are found. It follows from this that on average 99 % of the dioxins are destroyed on the catalyst and ca. 0.7 % accumulate over a period of 10 days.

In the period of the test as well as in the continuous operation of the plant after the test, it is observed that sulphuric acid accumulates on the catalyst. This sulphuric acid comes from the reaction of the residual SO₂ of the flue gas with hydrogen peroxide. It is present on the catalyst in highly concentrated form, since its vapour pressure is distinctly lower than that of water. It is assumed that the

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

dioxins are not oxidized by the hydrogen peroxide but by Caro's acids formed intermediately from H_2O_2 and H_2SO_4 . Mass balances are drawn up for all of the individual components. It is apparent that by oxidation the low-chlorinated dioxins and furans up to Cl_6 are destroyed preferentially. The less poisonous highly chlorinated dioxins and furans up to Cl_8 are somewhat more slowly oxidized.

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

Table 01: Description of the Solid Sampling Conditions and of the Sampling Points Concerned

Matrix or point of removal	Alloted sample number	Description
SiO ₂ (reference sample)	P 1.1	The SiO ₂ tablets are taken by the operator from a stock bin.
SiO ₂ (top layer)	P 2.1	After the end of three waste gas sampling series, the catalyst is opened at the top, and the top layer of the SiO ₂ fixed bed is removed by the operator.
SiO ₂ (mixed sample)	P 2.2	After completion of the above sampling and after removing the top layer, the whole catalyst charge is discharged into a vessel by the operator and thoroughly mixed. A sample is taken from the mixing vessel.

This Sheet Has Been Replaced

THIS SHEET HAS BEEN
REPLACED

Table 02: Description of Measuring and Sampling Points (Technical Data) for Waste Gas Sampling

Position of measuring point in flue gas path	Alloted sample number	Duct cross-section ^{a,b} (m ²)	Edge lengths (m)	Diameter (m)	Length of inflow section (m)	Length of outflow section (m)	Does the sampling point meet the requirements of VDI Guideline 2066, page 1, regarding the measuring section?
Crude gas before catalyst	P 3.1-3	0.03 (round)		0.1	0.1	0.1	the sampling was no not isokinetic; the waste gas samples were taken via a flanged glass tube.
Clean gas after catalyst	P 4.1-3	0.03 (round)		0.1	0.2	0.2	the sampling was no not isokinetic; the waste gas samples were taken via a flanged glass tube.

^a round, square or rectangular

THIS SHEET HAS BEEN
REPLACED

This Sheet Has Been Replaced

Table 03: Survey of Samples and Analyses

Matrix	Sampling date	Sampling period	Sample no.	Sample volume (m ³) ^b	O ₂ normalizing factor (x% O ₂ → 11% O ₂)	PCDF/D
SiO ₂ (reference sample)	19.09.91	a	P 1			x
SiO ₂ (top layer)	19.09.91	a	P 2.1			x
SiO ₂ (mixed sample)	19.09.91	a	P 2.2			x
Crude gas before catalyst	17.09.91	0900-1500	P 3.1	10.136	0.98	x
Clean gas after catalyst	17.09.91	0900-1500	P 4.1	10.579	0.98	x
Crude gas before catalyst	18.09.91	0830-1430	P 3.2	10.043	1.00	x
Clean gas after catalyst	18.09.91	0830-1430	P 4.2	10.804	1.00	x
Crude gas before catalyst	19.09.91	0730-1330	P 3.3	10.542	0.89	x
Clean gas after catalyst	19.09.91	0730-1330	P 4.3	10.296	0.89	x

a sampling by operator

^b referred to 0 °C, 1,013 hPa, dryTHIS SHEET HAS BEEN
REPLACEDThis Sheet Has Been Replaced


Table 04: PCDF/D Concentration in the SiO₂ (Reference Sample: P 1.3, Top Layer: P 2.1, Mixed Sample: P 2.2)

Sample number	P 1.3	P 2.1	P 2.2
PCDF/PCDD	ng/g	ng/g	ng/g
Total TetraCDF	b	3.52	0.22
Total PentaCDF	b	5.63	0.41
Total HexaCDF	b	8.16	0.64
Total HeptaCDF	0.004	6.13	0.51
OctaCDF	< 0.004	1.54	< 0.11
Total Tetra- to OctaCDF	0.004	24.98	1.78
2378-TetraCDF*	< 0.0009	0.148	0.010
12378-/12348-PentaCDF*	< 0.0014	0.483	0.035
23478-PentaCDF*	< 0.0014	0.372	0.033
123478-/123479-HexaCDF*	< 0.0015	0.880	0.069
123678-HexaCDF*	< 0.0015	1.187	0.099
123789-HexaCDF	< 0.0015	0.070	0.004
234678-HexaCDF	< 0.0015	0.816	0.084
1234678-HeptaCDF	0.0038	5.202	0.450
1234789-HeptaCDF	< 0.0009	0.123	0.010
Total TetraCDD	b	0.14	b
Total PentaCDD	b	0.49	0.03
Total HexaCDD	b	0.70	0.05
Total HeptaCDD	b	1.09	0.12
OctaCDD	0.008	1.45	0.18
Total Tetra- to OctaCDD	0.008	3.87	0.38
2378-TetraCDD*	< 0.0008	0.011	< 0.001
12378-PentaCDD*	< 0.0011	0.062	0.006
123478-HexaCDD*	< 0.0023	0.041	< 0.004
123678-HexaCDD*	< 0.0023	0.069	< 0.004
123789-HexaCDD*	< 0.0023	0.043	< 0.004
1234678-HeptaCDD	< 0.0035	0.506	0.062
Total Tetra- to OctaCDF/D	0.012	23.85	2.16
Total PCDF/D according to GefStoffv*	b	1.933	0.148
TE (BGA 1984)	< 0.0001	0.635	0.050
TE (NATO/CCMS 1988)	< 0.0001	0.639	0.053
TE (NATO/CCMS incl. NWG)	0.0036	0.639	0.056

If not specifically mentioned, undetected congeners or homologue groups are not taken into account in totals and toxicity equivalents (TE).

* Congeners not separable chromatographically on SP-2331.

b Undetectable.

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

Table 05: 2378-TetraCDD Toxicity Equivalent Factors (TEF)
According to a Proposal of the BGA, Berlin, and
NATO/CCMS

PCDF/D	BGA 1984	NATO/CCMS 1988
2378-TetraCDD	1.0	1.0
12378-PentaCDD	0.1	0.5
123478-HexaCDD	0.1	0.1
123678-HexaCDD	0.1	0.1
123789-HexaCDD	0.1	0.1
1234678-HeptaCDD	0.01	0.01
Octa-CDD	0.001	0.001
2378-TetraCDF	0.1	0.1
12378-PentaCDF	0.1	0.05
23478-PentaCDF	0.1	0.5
123478-HexaCDF	0.1	0.1
123678-HexaCDF	0.1	0.1
123789-HexaCDF	0.1	0.1
234678-HexaCDF	0.1	0.1
1234678-HeptaCDF	0.01	0.01
1234789-HeptaCDF	0.01	0.01
OctaCDF	0.001	0.001
Σ TetraCDD	0.01	0
Σ PentaCDD	0.01	0
Σ HexaCDD	0.01	0
Σ HeptaCDD	0.001	0
Σ TetraCDF	0.01	0
Σ PentaCDF	0.01	0
Σ HexaCDF	0.01	0
Σ HeptaCDF	0.001	0

The TE value of a sample is calculated by multiplying the concentration concerned by the corresponding TEF and adding the products. It should be taken into account that the calculated total values do not contain the 2378-Cl-substituted congeners of the homologue group concerned.

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

Table 06: PCDF/D Concentration in the Crude Gas before the Catalyst (P 3.1-3)

Reference state: 0 °C, 1,013 hPa, dry, normalized to 11 % O₂

Sample number	P 3.1	P 3.2	P 3.3
PCDF/PCDD	ng/m ³	ng/m ³	ng/m ³
Total TetraCDF	58.3	42.0	50.3
Total PentaCDF	56.1	47.1	49.7
Total HexaCDF	27.5	27.0	37.0
Total HeptaCDF	15.9	16.1	17.4
OctaCDF	3.6	4.9	< 1.8
Total Tetra- to OctaCDF	161.4	137.1	154.4
2378-TetraCDF	1.61	1.55	1.78
12378-/12348-PentaCDF ^a	5.13	4.28	4.30
23478-PentaCDF	2.21	2.38	2.84
123478-/123479-HexaCDF ^a	3.21	3.22	4.45
123678-HexaCDF	3.40	3.39	4.75
123789-HexaCDF	0.23	0.29	0.30
234678-HexaCDF	1.94	3.03	3.42
1234678-HeptaCDF	12.57	12.07	14.13
1234789-HeptaCDF	0.40	0.59	0.36
Total TetraCDD	3.8	4.9	5.8
Total PentaCDD	8.8	10.6	12.1
Total HexaCDD	7.2	9.3	9.5
Total HeptaCDD	9.2	8.8	10.0
OctaCDD	10.8	11.9	10.6
Total Tetra- to OctaCDD	39.8	45.5	48.0
2378-TetraCDD	0.39	0.37	0.44
12378-PentaCDD	1.19	1.21	1.61
123478-HexaCDD	0.40	0.45	0.53
123678-HexaCDD	0.67	0.84	0.87
123789-HexaCDD	0.59	0.77	0.85
1234678-HeptaCDD	4.45	4.49	4.89
Total Tetra- to OctaCDF/D	201.2	182.6	202.4
TE (BGA 1984)	4.05	3.90	4.61
TE (NATO/CCMS 1988)	3.74	3.92	4.78
TE (NATO/CCMS incl. NWG)	3.74	3.92	4.78

If not specifically mentioned, undetected congeners or homologue groups are not taken into account in totals and toxicity equivalents (TE).

* Congeners not separable chromatographically on SP-2331.

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

Table 07: PCDF/D Concentration in the Clean Gas after the Catalyst (P 4.1-3)

Reference state: 0 °C, 1,013 hPa, dry, normalized to 11 % O₂

Sample number	P 4.1	P 4.2	P 4.3
PCDF/PCDD	ng/m ³	ng/m ³	ng/m ³
Total TetraCDF	b	0.07	0.03
Total PentaCDF	0.05	0.07	0.03
Total HexaCDF	0.15	0.17	0.10
Total HeptaCDF	0.20	0.26	0.16
OctaCDF	0.32	0.36	0.09
Total Tetra- to OctaCDF	0.72	0.93	0.41
2378-TetraCDF	< 0.004	0.004	0.003
12378-/12348-PentaCDF ^a	0.008	0.008	0.005
23478-PentaCDF	0.008	0.007	0.004
123478-/123479-HexaCDF ^a	0.028	0.021	0.014
123678-HexaCDF	0.017	0.019	0.012
123789-HexaCDF	< 0.003	< 0.007	< 0.002
234678-HexaCDF	0.037	0.042	0.027
1234678-HeptaCDF	0.146	0.184	0.114
1234789-HeptaCDF	0.007	0.016	0.009
Total TetraCDD	b	b	b
Total PentaCDD	b	b	b
Total HexaCDD	b	b	b
Total HeptaCDD	0.15	0.19	0.12
OctaCDD	0.68	0.84	0.52
Total Tetra- to OctaCDD	0.83	1.03	0.64
2378-TetraCDD	< 0.002	< 0.003	< 0.003
12378-PentaCDD	< 0.004	< 0.005	< 0.004
123478-HexaCDD	< 0.012	< 0.005	< 0.013
123678-HexaCDD	< 0.012	< 0.005	< 0.013
123789-HexaCDD	< 0.012	< 0.005	< 0.013
1234678-HeptaCDD	0.088	0.108	0.073
Total Tetra- to OctaCDF/D	1.55	1.96	1.05
TE (BGA 1984)	0.014	0.017	0.010
TE (NATO/CCMS 1988)	0.016	0.017	0.010
TE (NATO/CCMS incl. NWG)	0.024	0.024	0.020

If not specifically mentioned, undetected congeners or homologue groups are not taken into account in totals and toxicity equivalents (TE).

^a Congeners not separable chromatographically on SP-2331.

b Undetectable

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

Table 08: Proportions of PCDF/D Decomposed After the Catalyst
(P 4.1-3)

Sample number	P 4.1	P 4.2	P 4.3
Proportion removed	%	%	%
Total TetraCDF	b	99.83	99.94
Total PentaCDF	99.91	99.85	99.94
Total HexaCDF	99.46	99.37	99.73
Total HeptaCDF	98.72	98.39	99.08
OctaCDF	91.11	92.65	< 95.00
Total Tetra- to OctaCDF	99.56	99.32	99.73
2378-TetraCDF	> 99.75	99.74	99.83
12378-/12348-PentaCDF ^a	99.84	99.81	99.88
23478-PentaCDF	99.64	99.71	99.85
123478-/123479-HexaCDF ^a	99.13	99.35	99.69
123678-HexaCDF	99.50	99.44	99.75
123789-HexaCDF	> 98.70	> 97.59	> 99.33
234678-HexaCDF	98.09	98.61	99.21
1234678-HeptaCDF	98.84	98.48	99.19
1234789-HeptaCDF	98.25	97.29	97.50
Total TetraCDD	b	b	b
Total PentaCDD	b	b	b
Total HexaCDD	b	b	b
Total HeptaCDD	98.37	97.84	98.80
OctaCDD	93.70	92.94	95.09
Total Tetra- to OctaCDD	97.91	97.74	98.67
2378-TetraCDD	> 99.49	> 99.19	> 99.32
12378-PentaCDD	> 99.66	> 99.59	> 99.75
123478-HexaCDD	> 97.00	> 98.89	> 97.55
123678-HexaCDD	> 98.21	> 99.40	> 98.51
123789-HexaCDD	> 97.97	> 99.35	> 98.47
1234678-HeptaCDD	98.02	97.59	91.80
Total Tetra- to OctaCDF/D	99.23	98.93	99.48
TE according to..			
BGA/UBA 1984	99.65	99.93	99.78
NATO/CCMS 1988	99.57	99.95	99.79
TE (NATO/CCMS incl. NWG)	99.36	99.89	99.58

Undetected congeners or homologue groups are not taken into account in totals and toxicity equivalents (TE).

^a Congeners not separable chromatographically on SP-2331.

b Not calculable

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

Table 09: Percentage Contents of the Individual Components and Conversions

Components	% inlet	% outlet	Top layer % max on catalyst	In the middle average % on catalyst	% conversion average
Sum TetraCDF	100.00	0.07	4.21	0.26	99.67
Sum PentaCDF	100.00	0.10	6.63	0.48	99.42
Sum HexaCDF	100.00	0.46	16.05	1.26	98.28
Sum HeptaCDF	100.00	1.26	22.34	1.86	96.89
OctaCDF	100.00	9.06	32.61	0.00	90.94
Sum Tetra- to OctaCDF	100.00	0.45	9.93	0.71	98.84
2378-TetraCDF	100.00	0.14	5.39	0.36	99.49
12378-/12348-PentaCDF	100.00	0.15	6.34	0.46	99.39
23478-PentaCDF	100.00	0.26	9.01	0.80	98.94
123478-/123479-HexaCDF	100.00	0.58	14.56	1.14	98.28
123678-HexaCDF	100.00	1.74	18.51	1.54	96.71
123789-HexaCDF	100.00	0.00	15.37	0.88	99.12
234678-HexaCDF	100.00	1.26	17.51	1.80	96.93
1234678-HeptaCDF	100.00	1.15	24.15	2.09	96.77
1234789-HeptaCDF	100.00	2.37	16.40	1.33	96.30
Sum TetraCDD	100.00	0.00	1.74	0.00	100.00
Sum PentaCDD	100.00	0.00	2.80	0.17	99.83
Sum HexaCDD	100.00	0.00	4.85	0.35	99.65
Sum HeptaCDD	100.00	1.64	7.01	0.77	97.59
OctaCDD	100.00	6.13	7.84	0.97	92.90
Sum Tetra- to OctaCDD	100.00	1.88	5.23	0.51	97.61
2378-TetraCDD	100.00	0.00	0.15	0.00	100.00
12378-PentaCDD	100.00	0.00	2.78	0.27	99.73
123478-HexaCDD	100.00	0.00	5.35	0.00	100.00
123678-HexaCDD	100.00	0.00	5.22	0.00	100.00
123789-HexaCDD	100.00	0.00	3.50	0.00	100.00
1234678-HeptaCDD	100.00	1.95	6.59	0.81	97.25
Sum Tetra- to OctaCDF/D	100.00	0.78	8.86	0.66	98.56

It has been established that at a crude gas concentration of ca. 4.2 ng TE/m³ ca. 99.67 % of the PCDD/F's are removed from the gas. Ca. 0.7 % accumulates on the catalyst. On average, 98.95 % is destroyed oxidatively. The individual component analyses gave the result that the lower-chlorinated (and with that, more poisonous) compounds up to Cl₄ are oxidized preferentially. The so-called Seveso dioxin (2,3,7,8-TCDD) is completely destroyed. It is assumed that the residual SO₂ content of the flue gas plays a decisive role for the oxidation reaction. In the course of this, SO₂ is very probably converted with H₂O₂ via the H₂SO₄ stage to H₂SO₃.

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

(Caro's acid). It has further been established that sulphuric acid concentrates on the catalyst. This sulphuric acid can form Caro's acid with the hydrogen peroxide. The oxidizing action of Caro's acid is considerably greater than that of hydrogen peroxide alone, and is supposed to be sufficient to destroy dioxins.

The following methods were used in making the measurements:

SO₂ UV Adsorption, Rosemount company, Binos series

NO_x Chemiluminescence, Rosemount company, Type 950 or 951

Dioxins For the analysis of the PCDF and PCDD before the reactor, the HRGC/LRMS system (MSD) was used; and for the analysis after the reactor the HRGC/HRMS system. The sample was taken with the XAD-z cartridges with C-1234 TetraCDD standard.

This Sheet Has Been Replaced



Table 10 PCDD/PCDF Waste Gas Cleaning in Refuse Incineration Plants

Incineration Plant	PCDD/PCDF Waste Gas Cleaning	PCDD/PCDF Concentration in ng TE/m ³		Waste Gas Amount, m ³ /h
		Crude Gas	Clean Gas	
Pilot Plants				
MVA Düsseldorf	Activated coke adsorber	2.4-2.7 ⁽¹⁾	0.022-0.025	2,000
MVA Stapelfeld	Activated coke adsorber	1.6-5.8 ⁽¹⁾	0.026-0.079	100
MVA Flözersteig	Activated coke adsorber	0.6-1.0 ⁽¹⁾	0.03-0.05	200
SMVA Simmering	Activated coke adsorber	1.0-9.3 ⁽¹⁾	0.05	200
Operating Plants				
SMVA Schöneiche	Dry additive process with addition of activated coke	0.34-1.74 ⁽²⁾	0.011-0.022	17,000
MVA Neufahrn	Dry additive process ⁽³⁾	not measured	0.09	18,000
MVA Düsseldorf	Hearth-type furnace coke/activated coke adsorber	1-5 ⁽⁵⁾	< 0.1 ⁽⁴⁾	3 x 160,000
RZR Herten	Hearth-type furnace coke/activated coke adsorber	1-5 ⁽⁵⁾	< 0.1 ⁽⁴⁾	70,000

⁽¹⁾ measured after the removal stages for dust, halogens and sulphur dioxide

⁽²⁾ after steam generator

⁽³⁾ without special steps for cleaning PCDD/PCDF from waste gas

⁽⁴⁾ design value

⁽⁵⁾ after electrofilter

MVA = refuse incineration plant

SMVA = special waste incineration plant

Source: Statutory regulations and measures for limiting dioxin and furan pollution,
Prof. Dr. Ing. Michael Lange, VBA Berlin
Lecture at VDA Meeting, 17-18/09/1991, Munich

THIS SHEET HAS BEEN REPLACED

THIS SHEET HAS BEEN REPLACED

The process according to the invention is illustrated in Figure 1. In detail, the figures have the following meanings:

- 1 Induced draught of the refuse incineration plant at Heusenstamm after the flue gas wash
- 2 Condenser for reducing the water vapour content
- 3 Condensate discharge
- 4 Condensate discharge
- 5 Condensate discharge
- 6 Electric heater
- 7 Fixed bed reactor of glass
- 8 Condensate discharge
- 9 Condensate discharge
- 10 Condensate discharge
- 11 Washer overflow (HNO_3)
- 12 Packed washer
- 13 Pump for washer circulation
- Ⓟ Pressure measurement

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED