

Relation between behavior of PCDD/F and physical properties of
carbonaceous matter in bag filter

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Introduction

The flue gas temperature and the dust composition are the major factors which affect the PCDD/F removal by bag filter (BF) ¹⁾. The PCDD/F adsorption capability of unburnt carbon is the highest among many kinds of the dust composition ²⁾. As a result, PCDD/F removal characteristics depend on the content of the fixed carbon in the dust. The amount and the physical properties of the fixed carbon released from the municipal solid waste (MSW) incinerators vary according to the type of incinerator, characteristics of the waste and the condition of combustion ³⁾. The fluctuation range of the specific surface area of the fixed carbon in the dust is as large as 200 – 1000m²/g ⁴⁾. Some of the fixed carbon has a specific surface area which is equivalent to that of activated carbon.

This experiment was focused on the fixed carbon, which is a major compound of unburnt carbon in the dust. The experiment was conducted to examine the relation between the physical property of carbonaceous matter and PCDD/F removal by using carbonaceous materials with different specific surface area.

Material and Methods

The flow diagram of the BF test plant is shown in Figure 1 and its specifications are listed in Table 1. Since the experimental object is to investigate adsorption removal of gas phase PCDD/F, the exhaust gas was branched from the BF outlet of the MSW incinerator.

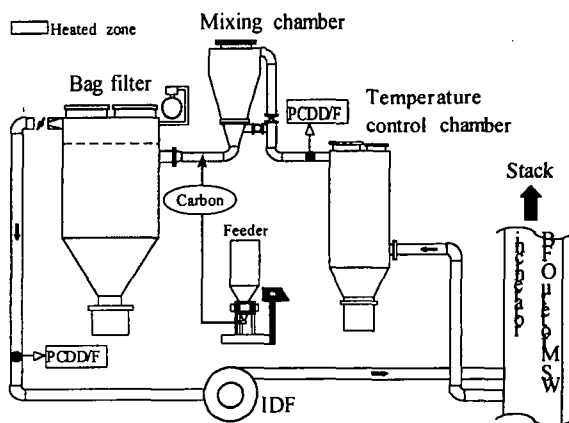


Figure 1. Flow diagram of BF test plant

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Table1. Specification of BF

filter cleaning	pulse jet by 0.25MPa compressed air
area of filter cloth	10.3 m ²
dimention of fiter cloth	D147mm?L1300mm?18pieses

Three types of carbonaceous materials with different the specific surface area were used in this experiment. Their important physical properties are listed in Table 2. The carbonaceous

materials were mixed with the powdered calcium carbonate, and then the mixture was blown into the flue gas to evenly disperse the carbonaceous materials onto the filter surface of the BF. No adsorption capability of calcium carbonate against PCDD/F was confirmed in advance.

The experimental condition is shown in Table 3. Runs 1-3 were performed to examine the effect of the specific surface area and the pore volume of the carbonaceous materials. The carbonaceous material of 50mg-C/m³_N(dry) was injected to the inlet of BF. The cleaning pulse at intervals of 90 seconds was applied to the filter cloth to minimize the adhesion amount of the filter layer⁴⁾. The adhesion amount was estimated by measuring the weight of the filter cloth and the filter cloth was replaced after each experiment.

Runs 4-6 were performed to investigate the effect of the adhesion amount of coke.

Table2. Properties of carbonaceous materials

carbonaceous materials	specific surface area	pore volume				50% median diameter
		<1nm	1-2nm	2-3nm	3-30nm	
	m ² /g	ml/g				um
coke	10	0.00	0.004		0.02	19
AC-1	555	0.2	0.08	0.033	0.15	21
AC-2	2530	0.35	0.57	0.14	0.09	37

Table3. Test conditions

Run No.	carbonaceous materials	adhesion amount of carbon [g/m ²]	carbon concentration [mg/m ³ _N]	tempreture [degC]	filtration rate [m/min]
1	AC-2	(2.5)	50	150	1.0
2	AC-1	(2.5)	50	150	1.0
3	coke	(2.5)	50	150	1.0
4	coke	10	-	150	1.0
5	coke	25	-	150	1.0
6	coke	40	-	150	1.0

Results and Discussion

The PCDD/F removal efficiencies for Runs 1-3 are shown in Figure 2. A removal efficiency of about 20% was obtained in the case of coke with specific surface area of 10m²/g. The removal efficiencies for the material AC-2 (2530m²/g) and AC-1 (555m²/g) exceeded 80%. However no remarkable difference was observed.

ORGANOHALOGEN COMPOUNDS

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The relation between the adhesion amount and the PCDD/F removal efficiencies for Runs 3-6, using coke, is shown in Figure 3. With the increase of the coke adhesion amount, the PCDD/F removal efficiency increased. When the coke adhesion was 25g/m^2 , the PCDD removal efficiency was 77% and the PCDF removal efficiency reached up to 92%.

Figure 4 shows the removal efficiency of each PCDD/F homologue of the coke. The higher removal efficiencies for both PCDD and PCDF were obtained for homologues with higher chlorine number. This result was coincident with the removal pattern observed in the case of the filter cloth only ⁴⁾. It indicates that the PCDD/F removal primarily depends on the vapor pressure

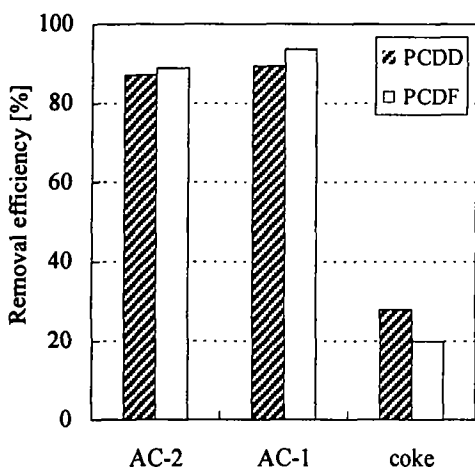


Figure 2. The carbonaceous materials and PCDD/F removal efficiencies

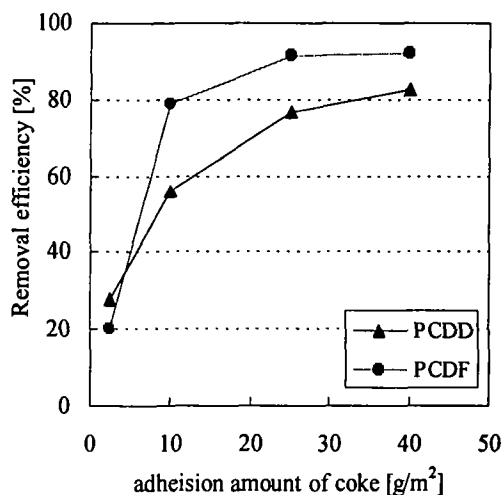


Figure 3. Relation between adhesion amount of coke and PCDD/F removal efficiency

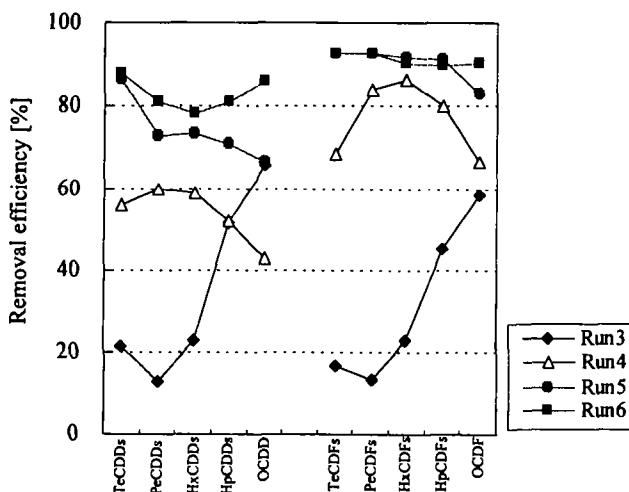


Figure 4 Removal efficiencies of PCDD/F homologues for coke experiments

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of each homologue when the adsorption capability of the carbonaceous materials is low and its amount is small.

In comparison with Run 3, a totally different removal tendency was observed for Runs 4-6 where the adhesion amount was increased. The difference in removal efficiencies among homologues is decreased and the similar removal characteristics with activated carbon were observed.

With respect to the molecule size of PCDD/F, it has been reported that for the adsorption removal of PCDD/F, the effective pore diameter of the activated carbon is approximately 2nm^{5,6)}. In our experiments, however, no correlation was observed between the pore volume of 1-3nm and the removal efficiencies. From the results, it is assumed that factors other than the specific surface area or the pore diameter affect the PCDD/F removal by carbonaceous materials.

The mass balance of PCDD/F in Runs 4-6 is shown in Figure 5. The generation of PCDD/F was apparently observed. It generally has been said that the generation of PCDD/F can be controlled by decreasing the flue gas temperature to lower than 200degC in BF. However, judging from the result of this experiment, it is clear that the existence of coke influences the generation of PCDD/F even under standard operating temperature (150degC) of bag filters.

While the carbonaceous materials works as an adsorption material of PCDD/F, depending on its physical properties it can also influences the generation of PCDD/F. Therefore, not only removal but generation of PCDD/F by carbonaceous materials have to be evaluated at the same time to understand the behavior of PCDD/F in BF.

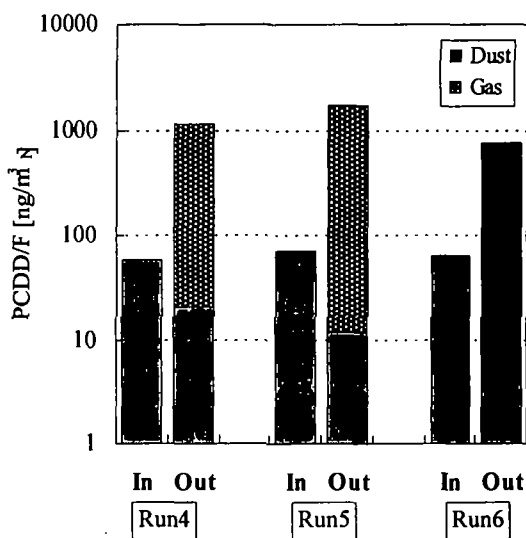


Figure 5. Mass balance of PCDD/F

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KOMBISORBON™ PROCESS, A COMBINED ACTIVATED CARBON BASED ADSORBENT FOR REMOVAL OF ECO-TOXIC COMPONENTS LIKE DIOXINS FROM FLUE GAS

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Introduction

Ever increasing demands are made on plant operators and plant engineers with respect to the conceptual design of the off gas cleaning section in order to comply with the emission limits imposed by the legislation for the off gas content of dioxins/furans and heavy metals as toxic components. Other halogenated contaminants like PCB's or polybrominated hydrocarbons and also residual organic compounds like polychlorinated types are coming into discussion. The process presented is a fixed bed process which constitutes a method for safe compliance with the emission limits and for retaining all the above mentioned toxic components which relies on non-inflammable mixtures of carbon-containing adsorbents and inorganic inert material.

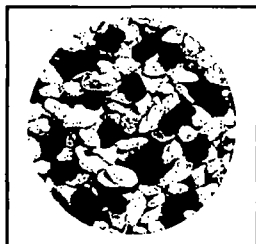
Capabilities of Activated Carbon

Fixed-bed adsorbers working with AC are built in a large variety of types and are employed with highly successful results in cleaning the most varied waste air, waste gas and product gas streams. A vast fund of experience has been acquired in such areas as solvent recovery, removal of mercury as well as aromatic and aliphatic hydrocarbons from natural gas, and removal of heavy metals, hydrocarbons, carbon disulphide, sulphur oxides, ketones, alcohol's, etc..

Adsorbent KOMBISORB

Since the mid-eighties, after coming into force of the German Clean Air Act (TA-Luft 1986), the use of AC has also been playing an important part for flue gas cleaning. But flue gases from waste incineration plants that have undergone preliminary cleaning usually contain residual amounts of SO₂ which is converted to sulphuric acid on the carbonaceous based adsorbent. Typical flue gas operating temperatures are 140 -195 °F (60 to 90 °C) after wet systems or 250 - 300 °F (120 to 150 °C) after dry cleaning systems.

The problems encountered in connection with the use of carbon adsorbents, fouling and corrosion as well as the hot spot hazard, have prompted the development of the KOMBISORB™ process,



which has since been advanced to commercial maturity.

The new adsorbent was to be based on the tried-and-tested extruded AC which provides very high adsorption efficiencies and gas purity levels. The basic idea was to obtain a non-clustering AC in order to prevent hot spots from progressing once they are formed. This effect was achieved by admixing an inert material to the AC. Admixing of an inert material results in additional, beneficial effects. AC fouling is appreciably retarded, sticking is avoided and flowability is also ensured at high

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sulphuric acid loading. Moreover, the heat of adsorption liberated is taken up by the inert material and dissipated. Gases can flow unhampered through the bed and uniform flow conditions as well as optimum adsorption conditions are maintained.

The inert material itself has to exhibit certain properties. It must be hydrophobic, i.e. takes up virtually no water and SO_2 . Its particle size and bulk density ranges are similar to those of the shaped AC so that segregation during process operation or the required handling operations is ruled out. Moreover, the grain should be chemically inert in order to prevent reactions with flue gas components like SO_2 , HCl , etc. and it should also be distinctively less expensive than formed AC.

Therefore, safety precautions normally required when applying activated carbon or coke, like temperature control system of the adsorber, a delta-CO-measurement and others are unnecessary which makes the entire plant concept and scope of required plant equipment very simple.

By varying the proportion of the mix components activated carbon/inert material (typically in the range of 30:70 to 70:30) and the bed depth of the charge (typically 40 to 80 cm) as well as by additional impregnation of the AC, a wide spectrum of application is given for the KOMBISORBON™ process and provides simultaneous capture of most organic and inorganic contaminants. Selecting the proper AC type, the following components can be removed by physical adsorption:

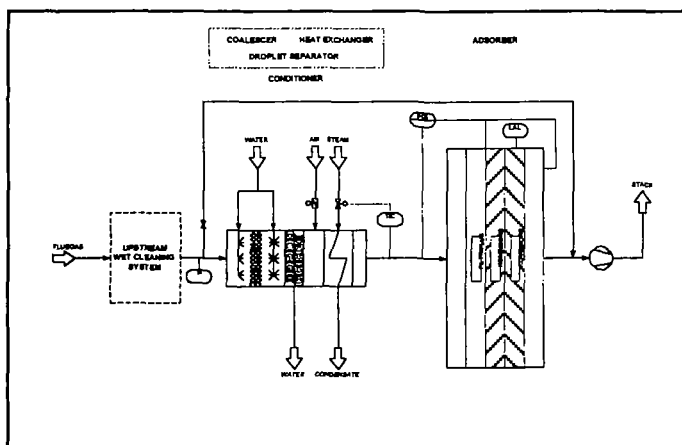
- polychlorinated di-benzo dioxins and -furans (Dioxins)
- co-planar polychlorinated biphenyls (PCB's)
- chlorinated or bromated hydrocarbons like hexachlorbenzene
- polychlorinated paraffins or naphthalens
- polyaromatic hydrocarbons (PAH)
- ionogenic mercury like HgCl_2

Using a special sulphur impregnated AC, chemical adsorption can be achieved of:

- metallic mercury ($\text{Hg} + \text{S} \rightarrow \text{HgS}$) or cadmium ($\text{Cd} + \text{S} \rightarrow \text{CdS}$).

The disposal of the spent mix can be effected in the usual way for activated carbon or coke by incineration in the upstream unit or in a suitable external disposal plant.

Plant and Process Description



The KOMBISORBON™ system, comprising a gas conditioning unit and the fixed-bed adsorber, is usually integrated before the stack as the last step of the waste gas cleaning system.

Depending on the type of adsorber apparatus design, vertical or horizontal arranged adsorption material layers are foreseen, as well as one layer filled with purely inert material for dust protection.

The vertical layer type

adsorber is containing one or more beds of a predetermined thickness through which the gases flow successively in horizontal sense. The horizontal bed type contains only one layer for

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adsorption, which is flexible in layer thickness. On top of this layer, a dust protection layer can also be foreseen. As the function of various plant parameters like dioxin and/or mercury content of the feed gas, accompanying residual pollutant contents, dust load, etc., the charge of the individual beds is to be exchanged for a fresh charge at intervals of one to two years typically.

Whilst the extremely fine dust essentially moves through the bed, a small amount of it will deposit in the first centimetres of the bed and after some time lead to a gradual pressure drop increase which may require an exchange of the charge. This can be prevented by arranging upstream the already mentioned dust protection bed.

The raw gas entering the adsorption step needs to have certain conditions depending on the removal task, either to be cooled down or heated up with or without droplet separation included. After scrubbing systems the flue gas is typically water saturated at 140 – 160 °F (60 – 70 °C). Such gas also contains water droplets which may cause fouling problems in a fixed bed, depending on amount of droplets and particulate matters. In order to prevent the formation of water condensate in the fixed bed adsorbent, it is essential to safeguard a raw gas temperature level which has a sufficient gradient with respect to the water dew point

Process Application and Design Parameters

Gas temperature for Hg ^o removal for Dioxin / PCBs removal	40 – 85 / 100 – 185 40 – 130 / 100 – 265	°C / °F
Operating temp. above dew point	min. 15	K
Operating range of flue gas throughput	40 to 110	%
Dust concentration at inlet	10, better 5 or less	mg/m ³
SO ₂ concentration at inlet	max. 500	mg/m ³
HCl conc. (only for Dioxin; not Hg)	max. 200	mg/m ³
Typical inlet concentrations		
Dioxins	1 – 30	ngTE/m ³ N
Hg ^o	0.5 – 10	mg/m ³ N
PCBs	0.1 – 0.4	ngTE/m ³ N

The main process design parameters: type of AC, shape and grain size of AC, mixing ratio AC/inert material, thickness of layer, number of layers and gas velocity provides a high flexibility for retrofitting of existing plants or for installation in new plants.

Compared to all other processes, an adsorbent bed with a defined layer is the safest technology to overcome any fluctuations in plant operation, like unforeseen heavy peak loads of contaminants. It is a safe air pollution control for components which are not measured online continuously and may fluctuate.

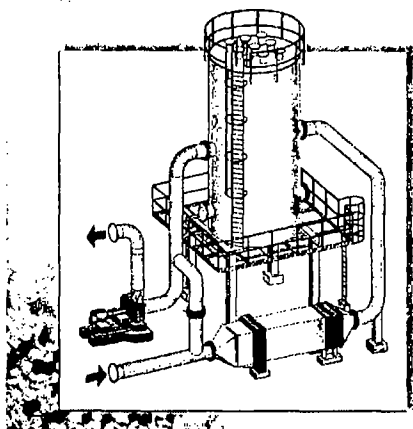
For certain retrofitting cases, especially elder MSW incinerators, despite of an existing dry reduction step for SO₂ and HCl, stack concentrations of 100 to 500 mg/m³ of SO₂ and/or 50 to 200 mg/m³ of HCl are quite normal. These high concentrations are not a limiting factor to install a KOMBISORBON™ unit for removal of the dioxins, for example.

Fixed-bed Adsorber

The individual layers are filled through filling nozzles by means of a simple mobile hopper and a crane for big bag handling. The emptying nozzles are furnished with flat gates being connected with a mobile barrel or big bag filling device for emptying which is typically made available by an external service provider. In one unit, up to 60,000 acfm may be handled. The respective construction height is about 23 meters for this case. The standard dimensions are 3 meters or 4

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meters in diameter. The adsorber can be constructed from either carbon steel, stainless steel or preferably FRP.



The pressure drop across the adsorber is about 20 mbar in the standard design for dioxin and mercury removal based on raw gas loads of 1 ng TE/m³ and/or 500 µg Hg/m³ with three beds including a dust protection layer

Operating Experience

The first commercial-scale KOMBISORBON™ process was installed in 1994 at a sewage sludge incineration plant in the Netherlands. The plant was designed to comply with the strict demands imposed by the Dutch "Verbanding 1989" which means maximum levels of 50 µg/m³ Hg, 0.1 ng TE/m³ D/F and 50 µg/m³ cadmium. This first filling was in operation, without interruption,

for nearly four years, before it was exchanged for fresh material. The dioxin concentrations determined by the official emission measurements averaged between 0.008 and 0.03 ng TE/m³, 0.01 ng TE/m³.

Other plants are in operation in the U.K., in Germany, in Sweden and recently the first one in the U.S.A.. Because of the easy and safe operation, several crematorium operators in Germany have selected the KOMBISORBON™ process for retrofitting their existing as well as their new incineration plants to meet the new regulations regarding dioxin emission. Such plants have relatively low flue gas rates of 2000 to 2500 acfm per line.

In the following table dioxin and PCBs measurements are shown taken during a pilot plant test in an MSW incinerator in Japan. The upstream flue gas cleaning comprises a quench and an ESP only. Operating temperature was between 120 and 140°C.

Contaminant	Gas inlet [ngTE/m ³]	Gas outlet [ngTE/m ³]
Dioxin (after 1 months)	10	< 0.0001
Dioxin (after 2 months)	9.4	< 0.0001
PCB's (after 2 months)	0.37	0.00074

Conclusions

With the KOMBISORBON™ fixed bed process, a technology is available which can be used for both, retrofitting of existing plants and in new plants. The KOMBISORBON™ process uses an activated carbon/inert material mix which is compatible with safety aspects and can be employed for a wide range of separation tasks such as, for example, heavy metals, dioxins/furans, other chlorinated aromatic hydrocarbons, etc. Depending on the type of pollutant, the respective AC types are available. Plant operators obtain a universal process which solves not only actual but also future regulation changes. The process has been in commercial-scale operation for several years now with excellent success and has proven to be a most economical with minimum operating costs.