Technologies for Dioxins and Furans Destruction

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Due to their toxicity, the release of polychlorinated pollutants poses a serious threat to public health and the environment. In particular, polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (Pcdd/Fs) have caused much environmental concern during the last two decades, so that stringent limits have been imposed on their emissions. The aim of this review is to report on established and emerging technologies for destruction and elimination of persistent organic pollutants (Pops). The specific attention is paid to technologies for destruction of dioxins and furans present in gaseous stream.

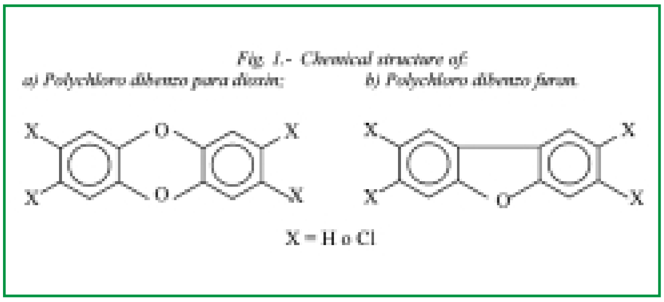

Figure 1 - Chemical structure of:
a) polychloro dibenzo para dioxin;
b) polychloro dibenzo furan

Dioxins are one of the most relevant Pops (Persistent Organic Pollutants) (Table 1). Many of the twelve Pops classes of compounds are insecticides, some are industrial products, like PCB, poly chloro biphenyls and hexa chloro benzene, while poly-chloro-di-benzo-para-dioxins and poly-chloro-di-benzo-para-furans (Figure 1), abbreviated as Pcdds and Pcdfs or Pcdd/Fs, are unintended by-products [1-3].

The only example known of commercialisation of these substances is for scientific purposes, as necessary analytical standards: the circumstances of their use are such to alleviate, if not eliminate, any environmental concern.

On the contrary great concerns are determined by their unintended production. The effort to identify systematically their sources has involved in some countries relevant and qualified resources and has produced the so called ‘sources inventories’.

Where do dioxins come from? (sources)

What is relevant in dealing technologies for prevention and reduction of Pops release is the indication of the main Pcdd/Fs sources.

Incomplete combustion, especially from the burning of hospital waste, municipal waste, and hazardous waste, was and is in many countries reported as the main source. Other combustion sources are internal combustion engines, industrial combustion for power or heat generation, process heating. Scientists realised that waste incineration is a potentially severe Pcdd/Fs source only in the late Seventies, while only in the late Nineties the so called backyard combustion was considered with more attention.

Relevant progresses have been achieved in the most developed countries in reducing Pcdd/Fs emissions from waste incineration, to the point that nowadays advanced incineration technology is claimed to be a sink rather than a source of pollutants.

In waste incineration systems Pcdd/Fs formation may happen according to several mechanisms. Since the discovery of their presence in municipal incinerators effluents in 1977 [1, 2] relevant fundamental knowledge has been acquired leading to formulations of different kinetics, as the formation chemistry is extremely complex.

Because even trace quantities are to be considered significant emissions, it is difficult to control their formation and destruction by altering feed composition and/or any single combustion parameters: simple calculation on the emission limit concentration specified by European Union for waste incineration plants (0.1 ng TEQ/Nm^3) show that in terms of chlorine content even the airborne NaCl would be a relevant source of this element. The role of chlorine in Pcdd/Fs emissions is such that no deterministic correlation may be given to predict emissions on the basis of its content in the feed. Organo-chlorine compounds, as well as organic molecules, have been addressed as Pcdd/Fs precursors: chloro-phenols, poly-chloro-biphenyls, chloro-benzene, Pvc.

Gas phase formation, as well as solid phase formation rates (enhanced by catalytic action of Cu traces, other metals, carbonaceous surfaces) have been studied. Once created, Pcdd/Fs can continue to react, adding or removing chlorine, thereby changing congener group. Even after their decomposition, formation reactions may take place (the so called de

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Table 1 - The most relevant Pops: production and use

Pop	*Date product introduced*	*Cumulative world production (tons)*	*Designed use*
Aldrin	1949	240,000	Insecticide
Chlordane	1945	70,000	Insecticide
DDT	1942	2,300,000 to 3,000,000	Insecticide
Dieldrin	1948	240,000	Insecticide
Eldrin	1951	3,119 (in 1977)	Rodenticide and insecticide
Heptachlor	1948	900	Insecticide
Hexachlorobenzene	1945	1,000,000 to 2,000,000	Fungicide, by-product, contaminant
Mirex	1959	No data	Insecticide, fire retardant
Toxaphene	1948	1,330,000	Insecticide, mixture of 670 chemicals
PCBs	1929	1,000,000 to 2,000,000	Dielectric fluid, hydraulic fluids, non-liquids
Pcdds	(^{a}1920) 1976	^{a}10 (as ITEQ with Pcdfs)	By-product of combustion
Pcdfs	(^{a}1920) 1976	^{a}10 (as ITEQ with Pcdfs)	By-product of PCBs and with Pcdds

novo synthesis is effective at temperatures between 250 °C and 450 °C).

The ability of activated carbon to promote Pcdds dechlorination in post combustion conditions found in MSW (Municipal Solid Wastes) incinerators was identified only in early Nineties. These and many other studies established that dioxins and furans, once formed, can change in composition in a manner that can reflect their post-formation history as much as their formation chemistry.

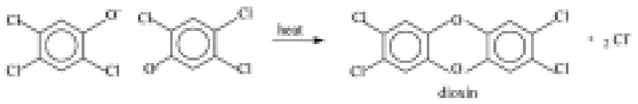
In spite of the complexity of their formation chemistry, dioxins/furans emissions from incineration processes may be attributed to the relevant source by considering their so called fingerprint, the congener typical distribution (a marked furans over dioxins prevalence is generally noted).

According to kinetic chemistry experts, the complexity is not related to any special chemistry or unknown phenomena, but is due to side reactions, which are insignificant by every day standards, but are large in the context of parts per trillion or even parts per quadrillions concentrations which can be measured using today's analytical technology.

Mechanisms of dioxins formation

Main formation routes are:

- condensation from precursors such as chloro phenols (used to produce defoliants and pesticides) in gas phase at 600 °C;



- catalytic reaction at 300 °C<T<500 °C between hydrocarbons and chlorine compound.
  Generally reaction mechanisms may be classified as [4]:
  i) chlorine transfer to a carbonaceous residue forming a C-Cl bond;
  ii) oxidative degradation of macro molecules to CO_2 and chlorinated aromatic by-products in vapour phase.

These reactions are catalysed and promoted by metallic ions such as Cu(II);

- ash gasification at 300 °C.

Main dioxins sources are incinerators, but also at a lower extent power station boilers and domestic burners may give place to their formation, under certain conditions [5]. Dioxins in incineration systems may be found in:

- flying ash;
- unburned waste (bottom ash);
- flue gases (generally for the de novo synthesis) at 200 °C<T<400 °C.

The extremely high toxicity and the related very strict emission limits (0.1 ng-TEQ/Nm^3) determined and still require proper formation prevention and emission control technologies in order to limit environmental and health impacts. Several methods are available to reduces and eliminate dioxins emissions.

Primary control measures, applied during the combustion processes, include:

- maintaining an adequate residence time (>2 sec) in the post combustion chamber at T>850 °C in order of completely destroy dioxins present in the inlet refuse/feed stream;
- controlling the oxygen component of the combustion air, the lowering of O_2 level combined with primary air preheating have already proved effectiveness;
- maintaining an high degree of turbulence, providing an homogeneous mixture of gases, turbulence helps avoid cold points or T>400 °C where dioxins formation is favoured.

In addition good combustion practice will minimise the formation of products of incomplete combustion (precursors).

Moreover, prevention of dioxins formation can be done by adding inhibitors intended to counteract their formation or by poisoning the catalysts of reformation with complexing compounds. The primary measures described above have not yet been sufficient to ensure compliance with the low limit value, so different technologies can be used as secondary measures.

Secondary dioxin decomposition/removal methods include:

- dust separation: dioxins are, to some extent, bound to dust. The fine dust fraction in particular is loaded heavily because of its high specific surface. Since the separation of the fine dust fraction is not always possible with electrostatic precipitators, fabric filters should be used for effective dioxin emission reductions;
- adsorption process (flow injection process, activated coke fixed bed process, etc.);
- catalytic oxidation;
- thermal afterburning: the afterburning of exhaust-gas components can be started thermally and, if necessary, with the help of catalysts. In a thermal reactor the exhaust gas is heated with a natural-gas burner up to a reaction temperature of at least 950 °C and is combusted completely in a vertical reactor shaft under air injection. With thermal afterburning no substances are generated which have to be disposed;
- high efficiency or fine dust absorber: dioxins are separated by fine-dust absorbers which are equipped with a large

Table 2 - Comparison of some measures for dioxin removal in waste combustion plants

	Fixed-bed reactor	*Flow-injection process*	*Oxidation catalyst*
Separation efficiency	very high	high	high
Residual treatment	internal combustion	deposition	no residuals
Separation of acid gases and heavy metals	very good	good	none
Safety requirements	average	average	low
Space requirements	average	average	small
Process-relevant considerations	high efforts	small efforts	high CO concentrations entail risk of over-heating
Emission abatement	high cleaning efficiency for all types of gases	high	very high
Technical data			
Power consumption	8-12 kWh/t	7-10 kWh/t	3-5 kWh/t
Residuals	2-4 kg/t	2-3.5 kg/t	
Investment (euro per t/h)	0.2-0.4 million	0.07-0.18 million	0.07-0.11 million

t = 1 ton of municipal waste

number of pneumatic two-component jets (water and compressed air). Such high-efficiency absorbers can separate the dioxin-covered fine dust through the very fine spray-like dispersal of the absorption solution and the high speed of the water droplets. In addition, the cooling of the exhaust gases and the undercooling in the dust absorber initiate condensation and improve the adsorption of volatile compounds on the dust particles. The absorption solution is treated by waste-water processing. The addition of adsorbents may further improve the dioxin reduction. With simple absorbers for the separation of acid exhaust gases an appreciable dioxin removal is not possible.

The physical state of Pcdd/F in the flue gas determines the main removal mechanism. Investigation showed that they are present both in vapour phase and adsorbed onto fly ash particulate, but the great part of dioxins, under the special conditions in the flue gas, occurs in the phase gas. In waste combustion facilities the two fundamental technologies are the adsorption of filtration material and the catalytic oxidation with direct destruction of the pollutants in the flue gas.

Techniques for the reduction and destruction of dioxins in flue gases

Pcdd/Fs removal from flue gases is required to reduce their dispersion in environment. Their capture may be realised in cleaning systems, that are generally classified (from the technological point of view) as dry, semidry and wet. As long as it concern the capture mechanism (that is the mass transfer from the gas phase to another condensate phase, solid or liquid) only dry or wet mechanisms are generally considered.

Dry systems

The main advantage of dry systems is that they do not require liquid by product stream treatment; furthermore they operate at higher temperature than wet systems, so that clean flue gases do not have to be heated prior discharge (to avoid plume). Dry techniques include:

a) active carbon adsorption;
b) activated carbon and $Ca(OH)_2$ injection;
c) absorption on others solid absorbents;
d) catalytic technologies;
e) catalytic filtration.

Table 2 [6] summarises fundamental parameters of the principal emission reduction techniques applied in municipal waste combustion plants.

When comparing the techniques presented it has to be considered that due to the nature of adsorption techniques, other pollutants such as dust, heavy metals and acid gases can also be separated. Therefore, these techniques are suitable for a wide range of applications, a fact which offsets their investment costs which are relatively high compared to those of oxidation catalysts. Catalytic oxidation techniques reduce organic compounds in the exhaust gases and nitrogen oxides only. In general, an additional dust and heavy metal separation has to be carried out before the catalytic reactor in order to prevent the de-activation of the catalyst through catalyst poisons.

a) Active carbon adsorption - In order to enhance the separation efficiency of fabric filters, adsorbents with high dioxin and furan take-up capacities are injected into the exhaust gas stream. In general, activated carbon or hearth-type coke are used as adsorbents. In fact, as the removal system for dioxins from exhausted gas, the activated carbon adsorption tower is very effective. However, a big problem of this system is the method of treatment of used activated carbon [7, 8]. According to the method of the active carbon addition, three kinds of processes can be found: i) the entrained-flow process, ii) the moving-bed process and iii) the fixed-bed process.

In the entrained-flow process, the active carbon is injected before the bag filter and carried by the flue gas to the filter where it builds up a carbon layer which removes Pcdd/Fs from the flowing gas; the spent active carbon is cleaned off the bag together with other particulate matter at certain time intervals.

In the moving-bed process, flue gases are passed through a moving bed of active carbons, the fresh carbons are fed to the top of the bed and the spent carbons discharged from the bottom of the bed continuously or at certain time intervals.

In the fixed-bed process, flue gases are passed through a fixed bed of active carbons, and the whole bed is replaced after certain service time. In all cases, the Pcdd/Fs are removed from flue gases by adsorption on the carbon.

Field tests reported in literature show that: 1) the Pcdd/Fs removal efficiencies are typically >95% and the Pcdd/Fs concentrations in the treated gases are below the 0.1 ng-TEQ/Nm^3 emission limit; 2) active carbon consumption is relatively low in moving or fixed bed systems; 3) the operating temperature of bag filters is a very important factor affecting the Pcdd collection efficiency and should be below 200 °C [6].

b) Activated carbon and Ca(OH)$_2$ injection - As indicated, powdered activated carbon (Pac) injection is one of the most convenient and cost effective technology for Pcdd/Fs removal in flue gas from municipal solid waste and industrial incinerators [9]. As serious retrofitting is expensive, many incinerators in the world applied this technology. The essential characteristics of Pac for gaseous Pcdd/Fs removal are considered to be large pore size, suitable particle size distribution, and safety [10]. However, it is not well-known that Pac has catalytic activity for Pcdd/Fs formation. Durkee and Eddinger [11] reported that coal based Pac produced Pcdd/Fs in dust collector and increased Pcdd/Fs concentration in fly ash greatly. Excess formation of Pcdd/Fs like is undesirable from the viewpoint of total emission control. Therefore, the development of special Pac which has both high absorption ability and very low catalytic activity seems to be necessary. The Pcdd/Fs formation activity of Pac could be suppressed markedly by so called inhibitors such alkaline compounds. Furthermore very often the use of alkaline compound is anyway required to neutralise acidic components in the flue gases (mainly HCl).

c) Adsorption by solid sorbents - As activated carbon is generally combustible due to its high carbon content, the demands to be observed with respect to safety engineering are accordingly high, namely, preventive measures for fire and explosion protection must be taken. This entails additional investment operational costs.

Therefore, dioxins may be selectively absorbed on other non-combustible adsorbents that also exhibit a highly selective separation behaviour [12]. It was reported that dioxins may be selectively absorbed on micro pores of a zeolite [13] or a ceramic monolithic medium (Figure 2). Main advantages of this technique are:

- simple operation and installation;
- low operating cost;
- absence of particles in the treated gas;
- low pressure drop;
- absence of solid residues such as carbon;
- high adsorbent efficiency.

In Figure 3 the pore structure of (left) the selective adsorbent, and (right) activated carbon powder are reported. Space limitations often hinder the effectiveness of activated carbon. Despite activated carbon's large surface area, the material's smallest pores typically remain inaccessible.

Generally, the modified zeolites is used as sorbent for its hydrophobic properties, its resistance to high temperature and its stability to acids.

Recently, a plastic based, thermally renewable, dioxins removal system, has been demonstrated in pilot scale [14, 15]. This system is based on the properties of polypropilene (PP) of adsorbing dioxins at low temperature (about 80 °C), and releasing the adsorbed dioxins, in air, at about 130 °C when installed in a fixed bed reactor.

d) Catalytic technologies - Catalytic oxidation with direct destruction of Pcdd/Fs in the flue gas is a proven technology to reduce Pcdd/Fs stack gas concentrations to below the regulatory limit. It has been shown that the TiO$_2$-based V$_2$O$_5$/WO$_3$

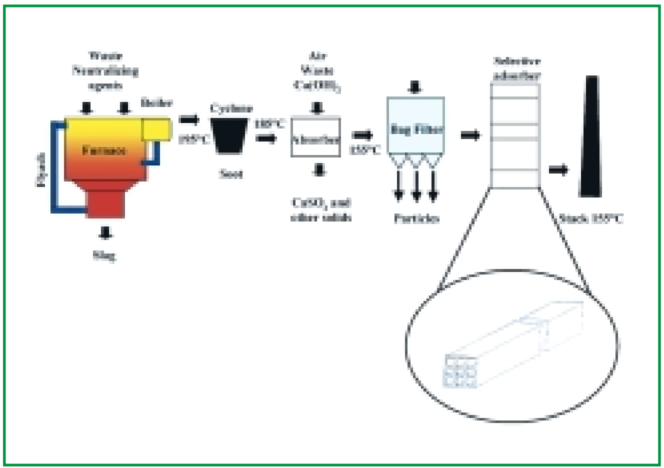


Figure 2 - Plant schematic with selective adsorber

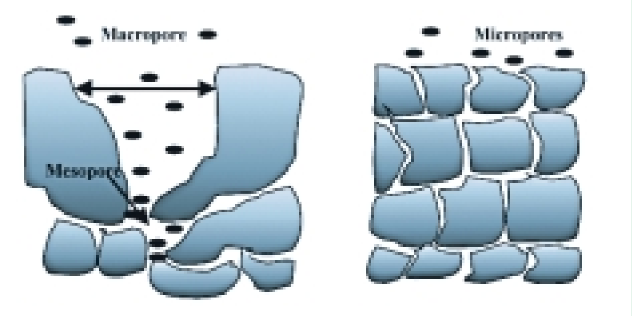


Figure 3 - The pore structure of (left) the selective adsorbent and (right) activated carbon powder

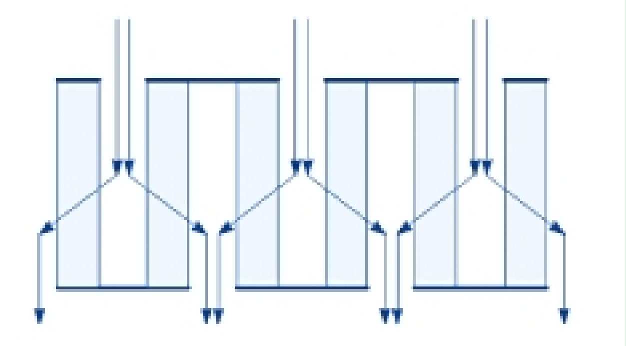


Figure 4 - The lateral flow reactor (LFR)

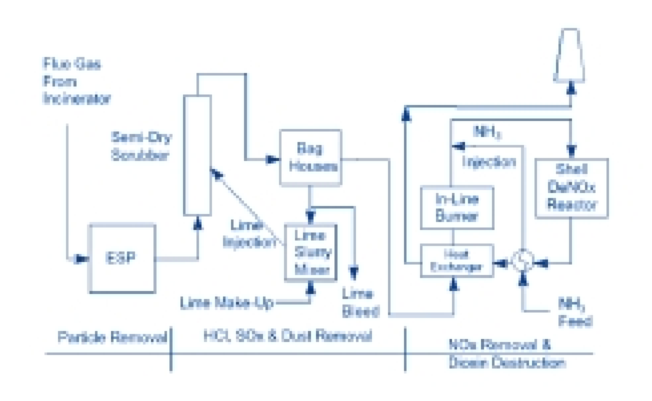


Figure 5 - Schematic drawing of off-gas cleaning system at Watco Mwi

Table 3 - Commercial catalytic technologies for elimination of dioxins and furans

Company	*Characteristics*	*Results*
Allied-Signal (1993)	Laboratory-scale Catalyst: Pt/Al_2O_3 - cordierite monolith With 36 cells/in^2 (cpsi); test treated 30 ppm of o-DCB (ortho-dichlorobenzene) with 12.0% O_2 and 2.5% H_2O	>90% $x_{o\text{-}DCB}$ Mean life: >150 h Operating Temperature (T_0): 350 °C
Basf (1993)	Industrial NOx - dioxins (NH_3) Installed in four chemical waste -incineration plants, three of them in 1995 Catalyst: V_2O_5-WO_3/TiO_2 monolith Total flow: Ranges widely Dioxins exit conc.: ranges widely Position: After electrostatic precipitator	99% x_{dioxin} Mean life: 24,000h or 3 years T_0: 250-350 °C
Siemens AG (1993)	Industrial NOx - Dioxins (NH_3) Catalyst: TiO_2 monolith Position: after electrostatic precipitator Dioxin exit conc.: 5 mg TEQ/m^3	97-99.5% x_{dioxin} treatment capacity: >0.1 ng TEQ/m^3 Mean life: 5,000 h T_0: 320 °C
Shell (CRI) (1996)	Industrial NOx - Dioxins (NH_3) Catalyst: TiO_2 monolith Dioxin exit conc.: ranges widely	Treatment capacity: 0.1 ng TEQ/m^3 Mean life: 3 years T_0: 160-240 °C
Haldor Topsøe (1992)	Industrial NOx - Dioxins (NH_3) Catalyst: Pt monolith Total flow: 125,000 Nm^3/h Dioxin exit conc. <5 mg TEQ/m^3	Treatment capacity: 0.1 ng TEQ/m^3 T_0: 280-350 °C

x indicates the percentage of material destroyed - in this case ortho-dichlorobenzene or dioxin

catalysts, originally designed for the removal of nitrogen oxides by the Selective Catalytic Reduction (Scr), are very effective in the oxidation of these compounds at the same temperature utilized for the DeNOx reaction. In fact, in the oxygen rich flue gases they also act as oxidation catalysts.

Main advantages of this catalytic systems are:

- no toxic by product from the destruction of dioxins/furans (converted in CO_2 and undetectable HCl);
- no chemicals/adsorbents are required;
- low pressure drop;
- easy operation;
- low maintenance requirement, when properly operated;
- combination with NO_x removal;
- only spent catalyst as residue, which can be taken back by the catalyst manufacturer;
- optimal solution for final polishing step and for retrofitting existing plant.

Removal efficiency may be from 75% up, according to catalyst bed volume [16].

Commercial process for elimination of dioxins and furans are summarized in Table 3, active species are mixture of various oxides of Ti, V, W o Pt-Al_2O_3.

The Shell DeNOx System (SDS) is a system for destruction of dioxins developed from the NO_x Scr technology. The catalyst is a commercially manufactured extrudate consisting of a proprietary mix of titanium/vanadium/components. The reactor system is based on Lateral Flow Reactor (Lfr) modules, as shown in Figure 4.

An example of the SDS was installed as the part of the off-gas cleaning system at the full scale Watco Mwi (200 Mt/day) in Roosendaal, the Netherlands in 1996. The Watco Mwi contains, in addition to SDS, an electrostatic precipitator (ESP) and a lime/activated carbon injection system (Figure 5). The SDS typically operates at low temperature (225-230 °C), following re-heating of the flue gas from bag-houses via a heat exchanger and an in-line burner, with a dioxin removing efficiency higher than 99.5% [17]. In a complementary laboratory study [18], the removal efficiency not only for dioxins, but also for dioxin precursor and related compounds has been determined. This study indicated that dioxins are removed and destroyed at efficiencies >98% and that:

- PCPs (poly chloro phenols) and PAHs (poly-cyclic hydrocarbons) are removed and destroyed almost as effectively as dioxins;
- PCBzs (poly chloro benzenes) are partially removed but all removal is destruction;
- PCBs are removed (>87%) and destroyed (>69%) fairly successfully.

The benefits of utilising low temperature DeNOx catalyst are particularly interesting where carbon injection system are employed, in fact, in addition to dioxin reformation, there is always a risk of carbon carryover releasing adsorbed dioxins in-

Table 4 - The Basf DeNOx and dioxin catalysts

Basf catalyst	*Active metal(s)*	*Primary form(s)*	*Application*
O 4-80, O 4-81	V_2O_5	Extrudates, 4 mm	SCR catalysts for DeNOx applications on low-sulfur offgases, by selective catalytic reduction with NH_3. Developed primarily for use on nitric acid plant stacks, and offered with Basf's licensed nitric acid process technology
O 4-82	V_2O_5	Honeycomb monolits in modules	SCR catalysts for DeNOx applications on low-sulfur offgases, by selective catalytic reduction with NH_3. Developed primarily for use on nitric acid plant stacks, and offered with Basf's licensed nitric acid process technology
O 4-85	V_2O_5	Honeycomb monolits in modules	Includes a wide range of honeycomb SCR catalysts, for removal of NOx by selective catalytic reduction. For DeNOx applications on flue gases from utility boilers, gas turbines, process boilers, fired heaters, etc.
O 4-86	V_2O_5	Honeycomb monoliths in modules	Destruction of dioxins and furans in the flue gases from chemical- or municipal-waste incinerators. Typically used in conjunction with O 4-85 for removal of both NOx and dioxins in the same unit
R 0-25/15, R 0-25/30, R0-25/50	Pd	Extrudates, 6 mm	VOC Catalysts, designed for catalytic incineration of VOC's in vents and offgases

to the atmosphere, particularly during incinerator start-up.

In the Basf dioxin catalyst the catalyst was developed taking as a basis the DeNOx catalyst characteristics. Table 4 reports a summary of the Basf commercials catalysts for DeNOx and Dioxins decomposition.

The Basf dioxin catalyst is typically utilized in the so called "joint reactor", in combination with the DeNOx catalyst, for simultaneous removal of dioxins and nitric oxide (figure 6). As with the conventional SCR method, the NOx is reduced in the upper section of the reactor by ammonia, while in the lower section the dioxins are converted in CO_2 and water. HCl is produced in negligibly small quantities as a by-product. The influence of ammonia is seen only with elevated NH_3 loads. Basf designs the combined removal process for a service life of 24,000 hours or three years for both the DeNOx and the dioxin catalyst.

e) Catalytic filtration - The catalytic filter system consists of a Gore-Tex membrane laminated to a catalytically active felt. The felt is composed of a chemically active fibres containing a variety of specially produced catalysts. As gases pass through the felt, a catalytic reaction is induced and dioxins/furans are decomposed into harmless gaseous components. During the last 5 years, it has been demonstrated that catalytic filter can destroy Pcdd/Fs below the regulatory limit.

Several reliability measurements have been conducted on the Ivro municipal waste incinerator located in Roeselare, Belgium [19]. As shown in Figure 7, the plant consists of a Stoker-Boiler-ESP-dry lime injection-fabric filter bag-house. The bag-house operating temperature varies between 200 °C and 230 °C. The Gore-Tex membrane provides particulate collection, while the catalytic substrate destroys highly toxic gaseous pollutants.

The temperature range in order for the catalytic reaction to occur varies from as low as 140 °C to 260 °C. A minimum temperature of 180 °C is preferred. The expected life of the filter is in excess of five years, confirming the findings of many catalyst companies, which indicates that catalytic honeycomb systems exceed three-year lifetimes, if not exposed to incinerator dust. Moreover, the total Pcdd/Fs emissions of the plant including gaseous stack emissions and solid phase by product, were reduced by more than 93% (Table 5). This reduction was mainly due to a minimization of the amount of Pac utilized.

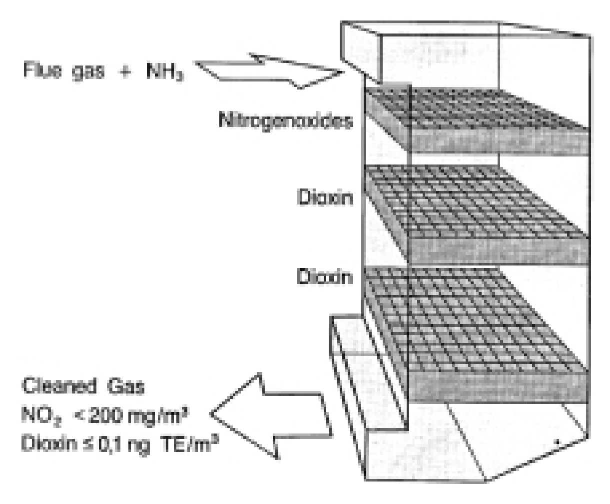


Figure 6 - Combined reactor for DeNOx and dioxin destruction in flue gases

Recently [20], the destruction efficiencies for Pcdd/Fs of catalytic filter were tested in the laboratory and compared with data from field operation. The comparison shows very similar values; the laboratory test showed that the catalyst in the filter destroys Pcdd/Fs by more that 99%; moreover, the lab comparison confirmed that this activity did not decrease after 2

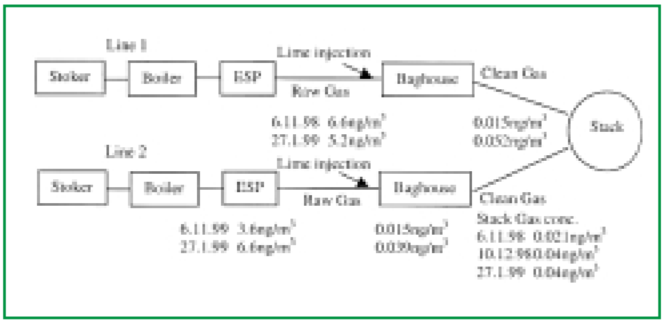


Figure 7 - Ivro Plant schematic with current dioxin concentrations in raw gas (before the bag-house), clean gas (after bag-house) and stack using catalyst filters. All dioxin/furan emissions in Iteq at 11% O_2

Table 5 - Comparison of the total release of Pcdd/Fs from the baghouse into the environment per ton of municipal waste burned

Technologies	Using Pac	Using catalytic filter
Emission	69 mg/ton	4.7 mg/ton

Figure 8 - Rotary atomiser

years of operation. Due to the retention time in the filter, the catalytic decomposition of these compounds strongly depends on their volatility and oxidative behaviour, both related to the degree of chlorination.

Semi-dry systems

A spray drier characterises semidry systems; generally a $Ca(OH)_2$ and activated carbon suspension is atomised and injected into the flue gases.

For example, the rotary atomiser (Figure 8) consists of an atomising disk rotating, which literally cuts the slurry into a fine mist of droplets.

The high rotational speed guarantee that no segregation or solid deposit takes place on the disc, a homogenous distribution of flue gases throughout the reactor and a intense mixing of the flue gases with fine atomised liquid.

The amount of lime milk entering the reactor can be constantly adjusted to obtain a desirable lime consumption for the actual fluctuating pollutant levels and the required emission standard.

As the semi-wet acid removal is usually followed by filtration of the flue gases by means of a bag filter, the 'cake' of unreacted $Ca(OH)_2$ on the filter bags generally functions as an important secondary reaction zone, capable of assimilating the typical fluctuations in pollutant concentrations that unavoidably occur during the incineration of municipal waste.

Wet systems

Wet scrubbing may be considered an effective option for Pcdd/Fs abatements, as long as proper scrubber design and sorbent addition are applied. Tested removal efficiency exceeded 98% with outlet loading largely below 0.05 ngTEQ/Nm^3. Dioxins removal by wet scrubbing does not reduce performances in heavy metals and acid gas abatement. On the contrary advantages may be observed in Hg capture. Condensation/diffusion mechanisms both played a relevant role in the observed phenomena, but careful attention must be paid to the case specific conditions, in fact standard wet scrubbing for acid gas and volatile metals removal are not very effective in Pcdd/Fs abatement. Simultaneous Pcdd/Fs, acidic gases, heavy metal capture may be therefore realised in the same unit optimising the design criteria and the additive utilized.

A direct comparison, on the flue gas of the municipal solid waste incinerator of Bolzano [21], cleaned by the installed catalytic units, composed by a SCR system, plus an organic compound degradation system (CatOx), and by a wet scrubber bench scale apparatus, showed that both systems can be very effective.

A commercial example of high efficiency scrubber system is the Airfine process [22].

The heart of this process is a fine scrubber system (Figure 9) where specially developed dual flow nozzles eject water and compressed air as high-pressurised fine droplet spray into the cooled and water saturated waste gas stream. This allows for the removal of the finest dust particles and undesired gas components to a degree of efficiency which is unattainable by employing conventional systems.

The process consists of three steps:

- quenching to realise a primary separation, cooling the flue gases and their saturation with water;
- scrubbing for a further separation and gas cleaning;
- water treatment, to separate by products.

Optimal choice for Pcdd/Fs removal is related to their concentration and specific chemical nature and structure.

Alternative technologies for Pops destruction

Alternative technologies for Pops destruction are:

- base catalysed decomposition: Pops in the presence of NaOH and a catalyst are destroyed at 300 °C [6];
- hydrodechloruration: of Pops, hydrodehalogenation with hy-

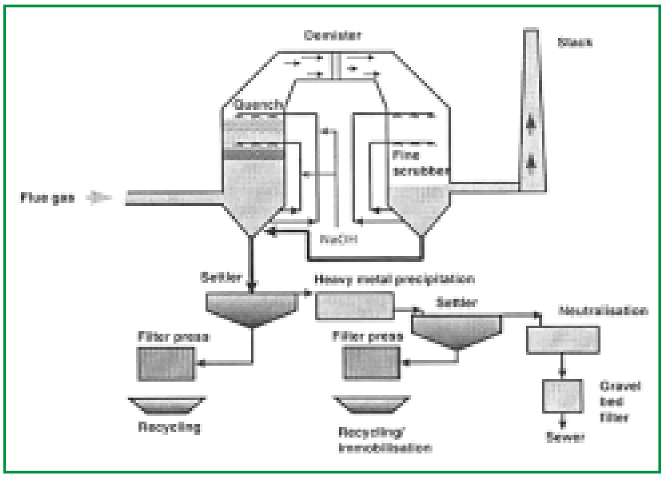


Figure 9 - Airfine system scheme

drogen in liquid phase with Ni-Pd/C catalyst at 50 °C [23, 24];
- incineration in dedicated plants or in existing incineration facilities (temperature>1,100 °C; contact time>2 sec; concentration O_2>6%) [25].

Conclusions

Industrial combustion plants can achieve relatively low Pcdd/Fs emission levels by optimising combustion through high combustion temperatures, prolonged residence times, and high turbulence of exhaust gases. In general, the limit values of 0.1 ng TEQ/Nm^3 cannot be achieved with primary measures alone; therefore, various secondary technologies have to be adopted to comply with emission concentration limits in flue gases. Optimal choice may be related to several aspects, such as:
- other pollutants presence and concentration (they may interfere with dioxins removal, or may be simultaneously removed);
- availability of water treatment systems or the feasibility of spent activated carbon incineration /disposal;
- need to retrofit existing plant or new plant or cleaning train erection;
- operability of the technology;
- dioxins and dioxin like substances concentration, chemical nature and structure as well as polluted medium characteristics.

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