

TABLE 2. Comparison of permissible and expected emissions according to regulations; waste-to-energy plants in the European Union (in relation to EC Directives) and Germany (actual figures for 2002). Source: Reimann, 2002

Country		EC			EC	EC			Germany		Germany	
Regulation		Directive 94/67/EG 16 Dec 1994 ^b			Directive 89/369/EG, 89/429/EG 1 Dec 1990	Directive 2000/76/EG 4 Dec 2000 ^b			17. Decree to BImSchG Dec 1990/Feb 1999		Yearly average, half-hourly emissions 2001	
Refuse types		Hazardous waste			Municipal waste	All kinds of waste			All kinds of waste		All kinds of waste	
Plants		New			New and existing	New and existing			New and existing		Modern & existing WTE/ municipal waste combustion	
No. Pollutant	Units ^a	100%	A=100%	B=97%		100%	A=100%	B=97%	100%	100%	Average	Max.
1 Total dust	mg/m ³	10	30	10	30	10	30	10	10	30	0.2	1.5
2 TOC	mg/m ³	10	20	10	20	10	20	10	10	20	0.02	1.7
3 HCl	mg/m ³	10	60	10	50	10	60	10	10	60	1.1	3.7
4 HF	mg/m ³	1	4	2	2	1	4	2	1	4	< 0.1	< 0.2
5 SO ₂	mg/m ³	50	200	50	300	50	200	50	50	200	1	9.7
6 NOx	mg/m ³	-	-	-	-	200	400	200	0.20 g/m ³	0.40 g/m ³	0.05	0.18
7 CO	mg/m ³	50	100	100	100	50	100	100	50	100	6	16
8 NH ₃	mg/m ³	-	-	-	-	10	20	20	-	-	0.2	4.9
9 Mercury	mg/m ³	-	-	-	-	-	-	-	0.03	0.05	< 0.0015	0.016
9a Mercury	mg/m ³	-	0.05	-	Hg and Cd: 0.2	-	0.05	-	-	-	-	-
10 Cd incl. TI	mg/m ³	-	0.05	-	Ni and As: 1.0	-	0.05	-	0.05	0.05	< 0.01	< 0.01
11 Other heavy (sum of) Sb, As, Pb, Cr, Co, Cu, Mn, Ni, V, Sn	mg/m ³	-	-	-	Pb, Cr, Cu, Mn: 5.0	-	-	-	-	-	-	-
		-	0.5	-		-	0.5	-	0.5	0.5	< 0.004	0.016
12 PCDD/PCDF	ng TE/m ³	-	0.1	-	-	-	0.1	-	0.1	0.1	< 0.001	0.013
Continuous measurement of pollutants 1-9			0.5 h		Average values over operation time		0.5 h			0.5		
Measurement 9a-11		24 h	0.5-8 h		(with adaptation)	24 h	0.5-8 h		24 h	0.5-2 h		
Duration 12			6-8 h				6-8 h			6-16 h		

^a All values for dry gases at 273 K, 101.3 kPa, 11% O₂ (9% CO₂)

^b Under this regulation, EC countries may choose between targets A or B depending on circumstances

Table 3 presents substances in domestic waste and residual emissions from domestic waste incineration plants according to the German EPA and special investigations and balances. A large-scale investigation into the dioxin TE content of waste was carried out for the Federal Office of the Environment in Berlin, 1994-6. The results indicate a dioxin TE content between 11-255 µg TE/tonne waste (as average 60 µg/tonne waste) in domestic waste, and 7-40 µg TE/tonne dry matter (average 29 µg TE/tonne DS) in sewage sludge.

The opponents of thermal energy from waste plants obtained results which attribute up to 33 µg TE/tonne. The emission of dioxin TE loads from thermal energy from waste utilization plants in Germany was in 1994 about 400 g TE/year for a waste utilization volume of about 9 million tonnes/year, equivalent to 20-25% of the total dioxin TE emission in Germany. By the dioxin TE emission limit of 0.1 ng TE/m³ since 1996 (1999/2000 in EC), the dioxin TE emission load on incinerating the recent 12 million tonnes of waste would be reduced to about 6 g TE/year (a reduction rate corresponding to a factor of about 100). In reality, the dioxin TE emission is, with highly effective flue gas cleaning systems today, at 0.008 ng/m³, equivalent to 0.5 g TE/year.

A knowledge of the highly efficient destruction of organic pollutants by thermal treatment, and communication of this information to the public, resulted in a decisive improvement in the acceptance of thermal energy from waste plants as a necessary treatment step within an integrated waste management concept. There is at present no other equally effective method for destroying organic pollutants.

Methods for minimizing dioxin TE emissions

Organic pollutants are the only substances in thermal residual waste utilization which are partly reformed, and also occur in changed forms in the flue gases after thermal decomposition at the high incineration temperatures. All other pollutants, heavy metals, salts etc. are removed from the residual waste feed; they are not destroyed but are distributed along the various streams of the thermal waste treatment (ash/flue gas) as a function of temperature, and can be balanced exactly. In dioxin TE minimization methods, a distinction should be made between the following essential possibilities:

Plant at Bamberg, Germany. Photo: Dieter Reimann



TABLE 3. MWC Bamberg – dioxin-TE balance. Source: Reimann, 2000

Residues/ emission	Dioxins/furans TE ^a concentration			TE ^a freight/tonne mixed waste		
	Unit	Range	Average	Specific amount of residue emission	TE-freight – calculated from average (µg TE/tonne)	Share (%)
Bottom ash (building material)	ng/kg DS	0.89–25.0	9.87	212 kg	2.092	6.335
Slag washing water	ng/litre	0.14–0.22	0.18	33 litres ^c	0.006	0.018
Boiler ash (300°–1100°C) together with ESP-dust (250°–300°C)	ng/kg DS	848–2180	1565	17.4 kg DS	27.231	82.463
Hydroxid sludge	ng/kg DS	409–1304	1062	3.2 kg DS	3.340	10.114
Gypsum sludge	ng/kg DS	2.9–139	70.3	4.3 kg DS	0.302	0.915
Treated wastewater from scrubber	ng/litre	< 0.1	< 0.1	108 litres	0.011	0.033
Clean gas ^b	ng/m ³ ^b	0.006–0.012	0.008	5000 m ³ ^b	0.040	0.121
Total					33.022	100

DS = Dry solid

^a Detection limits included

^b Standardized values: T = 273 K, p = 101.3 kPa, O₂ = 11 %, dry gas

^c Remaining in bottom ash

Also with reference to Table 3;

• output for 11% sewage sludge 30% DS and 89% waste – 33.0 µg TE/t mixed waste

• input announced by German EPA – 11–255 µg TE/t waste; average 60 µg TE/tonne

• input by sew. sludge 30% DS (Bamberg) – 7–40.7 µg TE/t DS sew. sludge; av. 29 µg TE/t.

- thermal destruction of dioxins and furans in feed products by controlled firing technique
- prevention of reformation of dioxin TE by chemical and mechanical methods at temperatures above 400°C with a minimum dioxin load in residues
- flue gas treatment processes for absorption by chemicals or oxidative conversion of the dioxin equivalent at temperatures below 400°C.

The individual processes are described briefly below, and appear as an overview in Tables 4a and 4b.

Thermal destruction of dioxins and furans in the furnace

The formation of dioxins and furans can be reduced primarily by omitting dioxin-containing and dioxin-producing wastes, but cannot be ruled out in this way. By optimum firing without cold

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regions (strands), as a rule coupled with regulation of firing power, it is possible to achieve virtually complete destruction of these organic pollutants at firing temperatures of over 850°C. Thorough mixing of the flue gases is essential, in conjunction with a uniform temperature distribution over the entire furnace. The above-mentioned criteria are generally met with low CO values after incineration. It has been shown that high CO values result in increased dioxin TE values. A good firing technique is the best guarantee for destruction of dioxins and furans from residual wastes and residues.

Preventing dioxin TE reformation at temperatures > 400°C with residues at a minimum dioxin load

Methods of prevention of dioxin TE reformation at temperatures over 400°C, with residues at a minimum dioxin load, can be seen in Table 4a (part 1). Good boiler design and continuous optimum cleaning of the boiler pipes to prevent coating, and hence dioxin sources, are essential measures. The use of inhibitors, including those based on triethylamines and triethanolamines, at flue gas temperatures of about 400°C, is likely to reduce the dioxin TE load by up to 95%. This process technology should decisively prevent the effect of the catalysts required for dioxin and furan formation. Test results are available from pilot plants in Canada and Germany.

The catalytic effect of constituents in dusts (fly ash) plays a decisive role in dioxin formation. Dioxin formation can be inhibited by high-temperature dust removal at temperatures above 400°C. Problems may arise in the choice of material and the location of these high temperature dust removers, since the units in operation do not appear suitable for the large quantities of dust usually encountered in energy from waste plants. High-temperature dust removal units for use upstream of steam boilers at temperatures over 1000°C are available, but the danger of encrustation of possible filter elements cannot be ruled out, since higher temperatures may inevitably lead to softening or melting of the dusts. It is also necessary to clarify, on an individual basis, questions of dust extraction in the hot gas region, recycling to the furnace being one possible solution.

From the technical point of view, dust removal downstream of the steam boiler at temperatures over 400°C is significantly simpler. However, the disadvantage of this choice of location for dust removal is the considerable reduction in the energy efficiency, since the energy content of the flue gases is usually utilized not only up to 400°C but down to 200°C. Integration of a dust removal unit in a steam boiler entails technical and



Dáva district heating and power station Umeå, Sweden entered service in 2000. The fuel source includes municipal refuse. Photo: Von Roll Inova

constructional problems, and is therefore difficult to realize.

Certainly a great reduction in the formation of dioxin TE can be achieved by preliminary dust removal without the production of significant dioxin-containing residues, but it is not certain that the required dioxin limit of 0.1 ng TE/m³ can be adhered to without further primary or secondary measures.

Flue gas treatment processes for absorption by chemicals or oxidative conversion of dioxin equivalent at temperatures < 400°C

Processes for flue gas treatment using absorption by chemicals or oxidative conversion of dioxin equivalent at temperatures under 400°C are shown in Table 4b (part 2). The knowledge acquired to date shows that the preconditions for the formation of dioxins and furans - particularly hazardous organic pollutants - are favourable at temperatures of 250-350°C, in the presence of chlorides, carbon compounds, fly ash, oxygen and catalytic metal ingredients, and with a sufficiently long reaction time. These conditions normally prevail during the flue gas cooling phase, from the steam boiler to the first flue gas treatment stage.

A simple solution appears to be flue gas quenching. In this method, the hot gas at about 400°C is abruptly cooled to under

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TABLE 4a. Overview of dioxin TE minimization methods (as of 2000) – part 1

Method	Treatment point	Temperature range (°C)	Dioxins (TE ng/m ³) ^a	Advantages	Disadvantages	Comments
Preventative measures	Exclusion, during collection of waste ingredients which lead to dioxin formation	-	?	Theoretically no additional process required	None	Practically impossible to realize with residual waste since no absolute exclusion of dioxin components possible
Primary measures	Furnace and after-burning zone	> 850	< 1	Thermal destruction of organic pollutants; scarcely any dioxin-containing residues; has side effect of good insulation	Consequent flue gas cooling – resynthesis, further removal of dioxin required	Reliable method for destroying organic pollutants even in residues from flue gas treatment
Raw gas treatment > 400°C	Upstream of, inside, or downstream of the boiler with high-temperature dust removal or inhibitors	> 400	< 1	Low-dioxin residues; residue recycling to furnace for detoxification	Side effects of inhibitors have to be studied, material aspects, encrustation, costs, safety risks	Adequate only in combinations of further downstream dioxin-degrading measures
Raw gas treatment 400–200°C	Between boiler and flue gas treatment quenching process	400–200	1–0.1	Low-dioxin residues in this case	Reduced energy removal, risk of encrustations, corrosion	Uniform abrupt quenching difficult; useful

^a Standardized values: T = 273 K; p = 101.3 kPa; O₂ = 11%, dry gas

TABLE 4b. Overview of dioxin TE minimization methods (as of 2000) – part 2

Method	Treatment point	Temperature range (°C)	Dioxins (TE ng/m ³) ^a	Advantages	Disadvantages	Comments
Flue gas treatment > 200°C	Catalytic oxidation after the flue gas treatment	> 200	< 0.1	Downstream. dust removal; dioxin-free residues	Large space requirement, reheating of flue gas	Only in combination with SCR-NOx reduction
Flue gas treatment < 200°C	Substantial dust removal < 5 mg/m ³ flue gas scrubbing, possibly downstream active coke filter in fixed bed	< 100 > 140	< 0.1	Ideal final treatment as control filter, hardly any residues and low active coke requirement	Active coke problems, such as spontaneous ignition, costs, residues and disposal, high space requirement with fixed bed filter, unreliable process	Combination of multi-stage scrubber with additive or downstream fabric filter and activated coke flight stream process suitable for minimum total emissions
Flue gas treatment < 200°C	Flight steam process; dry/semi-dry process; flight stream and fabric filter	< 100 > 140	<< 0.1	Lowest emissions, can be used with fabric filter with little expense, lime/activated coke mixture as multifunctional flue gas cleaning, low additive consumption (3 kg/tonne waste), high safety	Special mixture between activated coke and lime, the activated coal/coke is loaded with dioxins and furans, hazardous waste	Loaded additive could be use for wastewater neutralization (wet scrubber), no extra residues beside the hydroxid sludge, dioxins not water soluble

^a Standardized values: T = 273 K; p = 101.3 kPa; O₂ = 11%, dry gas

200°C by spraying in water, steam, etc. so that the required reaction time for dioxin formation is reduced to a minimum. Since only a very low level of dioxin formation is expected at these low flue gas temperatures, good reduction in dioxin levels can be achieved by this technique. The process technology for spraying in a fine water mist or steam is state-of-the-art. As is the case for hot gas dust removal downstream of the boiler, destruction of the otherwise useful flue gas energy between

400°C and 200°C is a disadvantage. This process is used industrially on a large scale in England.

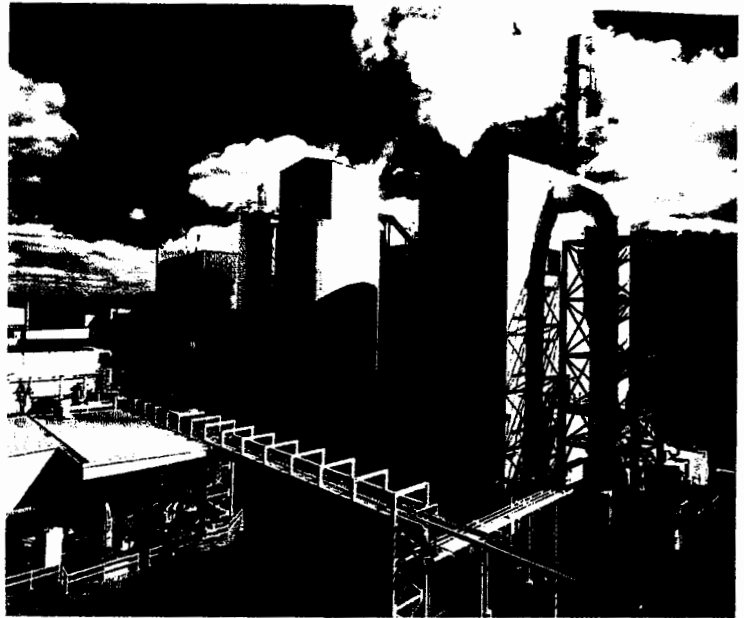
Wet flue gas scrubbing is one of the best flue gas treatments, since a greater amount of reusable residues can be produced by means of this technique. This includes not only the recovery of gypsum and possibly sulphuric acid, but in particular the production of hydrochloric acid from the washwater of the first scrubber stage when there is an

upstream quenching stage. The circulating chlorine-rich washwater from this first scrubber chlorinates the dioxins present, converting them from the lower, more toxic groups (tetra, penta), into less toxic congeners (octa). A result of this so-called further chlorination of the dioxin is that the TE dioxin value is reduced, as the higher congeners of the dioxin and furan groups have considerably lower toxicity.

This process technology will become more important where these wet processes for flue gas treatment with the production of hydrochloric acid are already in existence, or where conversions or new plants are planned. This process is already carried out in two waste incineration plants in Germany.

The further stage of condensation of the flue gases below the saturation temperature of 60°-65°C in the flue gas results in a reduction of dioxin TE emissions. The effect of subsequent dust removal during condensation or in the wet electrostatic precipitator appears to be of particular importance. The introduction of dioxin-scavenging additives in the low temperature range is particularly successful at a Swedish waste incineration plant. Another multifunctional flue gas treatment method involves the use of catalysts, which have already proved their worth on a large scale in power stations for reducing levels of NO_x. These catalysts are generally used at temperatures of 250°-350°C in residual waste utilization plants for NO_x reduction in the low dust range. Measurements have shown that these catalysts function by catalytic oxidation of organic substances, including PCDD/PCDF, and hence reduce the emissions of organic pollutants without producing residues. Results exist from different waste incineration plants; the space required for additional catalyst areas should be taken into account.

As in the catalytic process, the fixed bed processes using open-hearth furnace coke or active coke/carbon require substantial upstream treatment of the flue gases, so that only residual emissions and residual organic pollutants are present in the clean gases to be treated. This applies in particular to the fixed bed process, which can be used only after treatment of the total flue gas. In the fixed bed process, which is operated by the counter-current method or by simple or multiple crossflow,



Von Roll flue gas scrubbers. Photo: Von Roll Inova

the organic pollutants, including dioxins and furans, are absorbed onto the active coke/carbon and at the same time residual emissions, such as dust, SO₂, HCl and in particular mercury, are removed.

This fixed bed filter installed upstream of the chimney thus acts as a control filter, so that extremely low residual emissions result. The disadvantages of this process technology, which is used on a large scale industrially, are the disposal of residues from the contaminated active coke, the very high space requirement of the fixed bed process (flow rate about 0.1-0.2 m/s) and the possibility of spontaneous ignition of the active coke bed in the event of insufficient ventilation. The choice of open-hearth furnace coke (procurement costs between DM 250-400/tonne [€130-200]) or active coke (at up to DM 7000/tonne [€3600]) may also result in not-inconsiderable operating costs. With the addition of NH₃, the nitrogen level can also be minimized by several active coke filters connected in series.

The flight stream process can be used as an alternative to the fixed bed process in dry and semi-dry processes equipped with fabric filters. In this process, an active coke-lime-limestone mixture is blown into the flue gas in order to obtain an active coke content of about 3-10% in the precoat layer on the fabric filter. This carbon considerably reduces the level of organic pollutants, and hence also the dioxin TE value, and at the same time removes a fair amount of mercury. In this, combining the main dust removal stage with the addition of active carbon or coke, a mixed product consisting of active coke/dust/salt and lime is obtained, and generally has to be disposed of as a special or hazardous waste. Because of the low active coke content, the danger of spontaneous ignition is extremely low if the plant is operated properly and faults in the system are prevented.

If an additional fabric filter is installed downstream of the flue gas treatment plant, which may also be a useful solution in wet processes, a higher active carbon or coke content (up to 20%) may be present on the fabric filter without any danger. By means of these active coke fabric filters downstream of the flue gas treatment stage, it is possible to achieve a residual dust

The flue gas cleaning system can only be seen in its entirety during construction, as at this plant in Halmstad, Sweden. Photo: Rambøll



emission of 1-2 mg/m³ and to minimize the level of organic pollutants and residual emissions of HF, HCl and SO₂. Because of the simultaneously high dust removal rate and the removal of organic pollutants and other residual emissions, this process technology appears to point the way ahead, since many functions of flue gas treatment can be achieved in a single step by means of known reactions. The space requirement is considerably less than that of a fixed bed active coke filter.

The reaction temperatures are about 100°-140°C and can be maintained without significant reheating of the flue gases - even after the scrubbing stage.

The use of liquid or filter-like solid sodium for binding the chlorides from dioxins and furans was also under discussion, although the considerations are at present only of a theoretical nature.

Summary

To adhere to the dioxin limit of 0.1 ng TE/m³, improved and also expanded process technologies are required, extending from the primary side - incineration - to the control filter at the end of the flue gas treatment upstream of the chimney. As a rule, optimization in the firing region can be achieved by minor conversion measures and by controlled firing, so that only very low dioxin TE contents are detectable in the hot raw gas.

In the area of the steam boiler, high-temperature dust removal is possible but cannot as yet be considered state-of-the-art, in the case of thermal residual waste utilization with a high dust content. Improved cleaning of the boiler regions can be achieved without significant conversion measures, in order to prevent the 'resynthesis' of the dioxin. The possibility of passing through the critical, dioxin-forming temperature range of about 350°C to 200°C in a minimum time depends on the boiler design and layout, and on suitable units which permit abrupt cooling of the flue gases from about 400°C to under 200°C by spraying in, for example, water. The latter processes involve passing through the temperature zone of 'resynthesis', so there is a chance that dioxin/furan formation might take place under certain conditions.

The flue gas treatment method required in all cases for adhering to the allowable residual emissions can be realized in various ways, preferred processes being those in which individual steps perform multiple functions, for example, simultaneous dust removal, salt removal and separation of heavy metals, as occurs in scrubbers.

Process technologies employing active coke/carbon, both in the fixed bed and in the flight stream process, appear to be particularly promising because, on the basis of the 17th BImSchV, the NO_x value is stipulated as 0.2 g/m³ and SNCR processes would be sufficient for reducing NO_x levels. The use of expensive catalysts for NO_x removal, coupled with oxidative dioxin conversion, would then be questionable.

In the future, multi-stage wet processes will increasingly be used for adhering to the dioxin TE limit of 0.1 ng TE/m³ and also the other emission limits, for example, 0.05 mg/m³ for mercury. These processes permit substantial reduction of the flue gas temperature (with simultaneous condensation of the vaporized salts and heavy metals) and also the production of reusable residues. The various combination processes for this wet flue gas treatment do not rule out, where required, the use of a downstream active coke filter in the form of fixed bed or of an additional fabric filter in the flight stream process for

ISWA Publication Award

Each year ISWA honours an outstanding publication with the ISWA Publication Award. This year the Award was given to Dr Dieter Reimann for the articles 'Dioxin Removal and Destruction' and 'Problems about Sewage Sludge Incineration' at the ISWA General Assembly 7 July 2002 in Istanbul, Turkey.

Jeff Cooper writes in his reason for recommending Dr Reimann for the Award:

Both (papers) provided clear evidence of his skill and expertise in the analysis of dioxin issues in a wide range of thermal treatment facilities.

His contribution to the study of dioxin formation and removal has been world class. His analysis of interactions between input of waste, thermal processing technologies and controls and the pollution abatement options has enabled incinerator operators to build plant and fine-tune their operations to minimise the emission of dioxins.

A nomination for the ISWA Publication award requires a submission to the ISWA General Secretariat of the following:

- a copy of the paper/article/book that qualifies the nominee; the material submitted must be in English either as published or carefully translated
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- a short statement by the nominator as to particular qualities of the publication and the nominee.

A panel evaluates the submitted material, and forwards its recommendations to the Chair of the Publication Committee and the ESPC (the board of ISWA).

The ISWA Publication Award was introduced in 1998 and a cash prize of DKK 20,000 (~ €2700) is given to the recipient.

Dr Reimann's article on problems of sewage sludge incineration will be published in a future issue of *Waste Management World*.

minimizing dioxin levels. The reheating of the clean gases to 100°-140°C, which is necessary for this purpose, can be achieved with little expense. Flue gas treatment processes with fabric filters upstream of the chimney are today the state-of-the-art flue gas treatment technology, and ensure adherence dioxin emissions for below the dioxin equivalent of 0.1 ng TE/m³.

In choosing the dioxin reduction process, it is necessary to bear in mind not only the degree of reduction of emissions and costs but in particular the type of residues produced and their utilization or treatment and disposal, as well as the achievable safety in the process.

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