

# Chapter 7 Halogens, dioxins/furans

## 7.1 Introduction

The halogens are fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At), the latter of which need not be considered here (the total occurrence of At in earth's crust is ~ 25 grammes). Halogen compounds are found in gases from processing of fossil fuels, biomasses and human-derived waste-streams, and in off-gases from industrial activities using organo-halogen gases or solvents. The most abundant and important halogen is chlorine. In nature, fluorine is mainly found in minerals such as  $\text{CaF}_2$  and  $\text{Na}_2\text{AlF}_6$ , whilst chlorine, bromine and iodine are mainly found in seawater (Cl, Br) and seaweeds (I). These are also the sources from which the halogens are extracted. Ocean water contains 1.3 ppmw, ~1.9 %-wt, 65 ppmw and 0.05 ppmw F, Cl, Br and I, respectively; the Dead Sea contains ~ 5 kg/m<sup>3</sup> of Br.

Fluorine finds applications as HF, used in the glass industry, as  $\text{UF}_6$  used in separating <sup>235</sup>U and <sup>238</sup>U isotopes, in the gaseous electrical insulator  $\text{SF}_6$ , in the well-known polymer Teflon<sup>TM</sup>  $-(\text{CF}_2-\text{CF}_2)_n-$ , and in chlorofluorocarbons (CFCs) that are used as coolants.

Chlorine is mainly used as kitchen salt NaCl and in PVC (poly vinyl chloride),  $-(\text{CH}_2-\text{CHCl})_n-$  in which it comprises more than 50% of the weight. Other uses are in the photo-industry (silver chloride), and a very wide range of organo-halogen compounds that are used in dry cleaning (*e.g.* tetrachloroethylene), in electronics industry ( $\text{CCl}_4$ ), flame/fire retardants (chloroparaffins), as herbicides, insecticides, pesticides, or chemical weapons, (*e.g.* DDT, hexachlorohexane *i.e.* HCH), polychlorinated biphenyls (PCBs) used as lubricants, plasticisers and fire-resistant insulator liquids in capacitors and transformers, and the above-mentioned CFCs. Several important chlorine-containing organic compounds are shown in Figure 7.1. The polychlorinated dibenzo-(p) dioxins and -furans (PCDD/Fs) that are found in PCBs and may be generated during the combustion of either chlorinated organic compounds such as PVC, or in presence of chlorines such as NaCl (L section 7.6) are also shown in Figure 7.1.

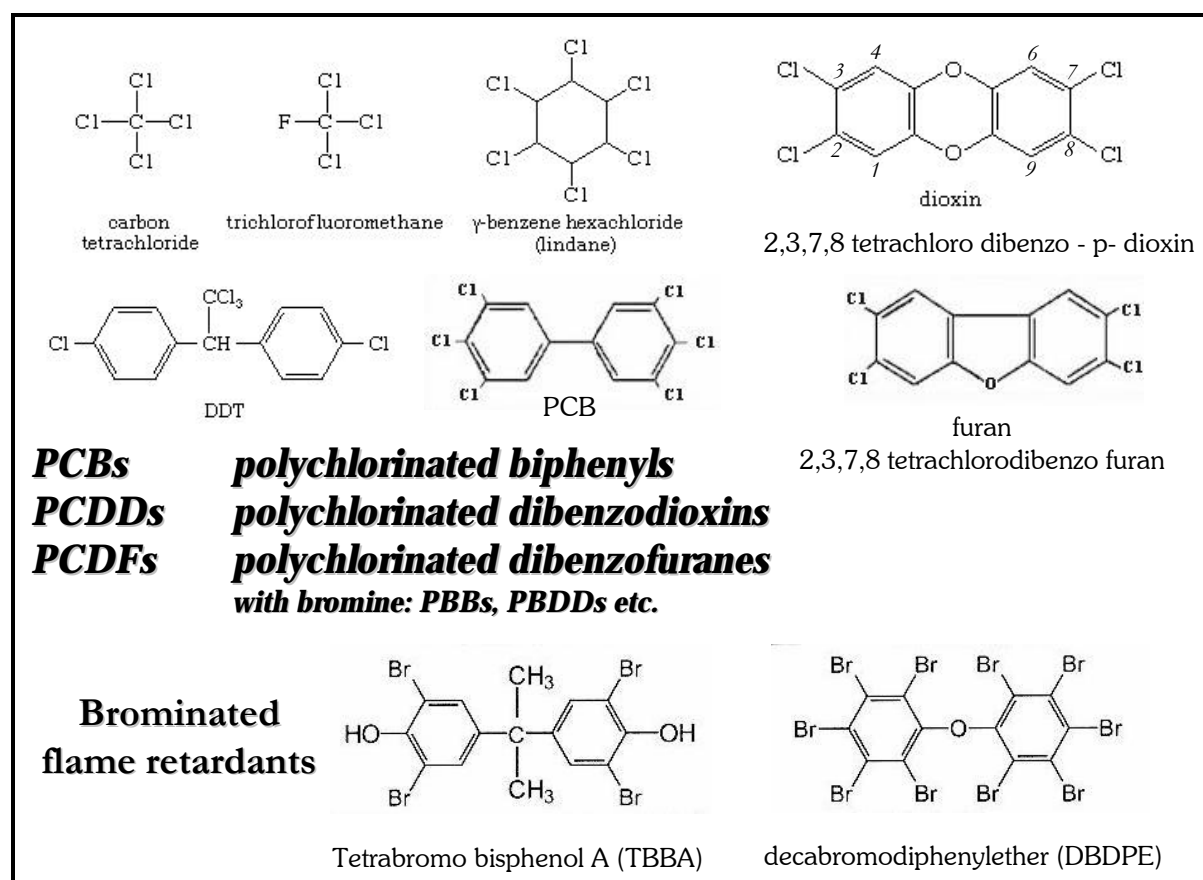


Figure 7.1      Organo-halogen compounds in flue gases, fuel gases and gaseous waste streams

Bromine is applied in medicine, in photo-industry and in some applications as HBr. An important field of application is as brominated flame (or fire - ) retardants (BFRs). Some examples of these, TBBA and DBDPE that are used in electronic circuit boards and computer monitor housings (Hedemalm *et al.*, 1995) are also shown in Figure 7.1.

Iodine, finally, finds applications in medicine, as photo-chemical and some other chemicals such as dyes. It is an essential element for the human metabolism.

For processes based on fossil fuels the most important halogen compounds are HCl and Cl<sub>2</sub>. Thermal processing of waste streams such as electronic scrap and auto shredder residue (ASR), and conventional waste “incineration”, brings not only chlorinated but also brominated chemicals into the picture. Harmful gases generated in landfills (~ 45 %-vol CO<sub>2</sub> and ~ 50 %-vol methane, CH<sub>4</sub>) contain the chlorine compound CCl<sub>4</sub>. Fluorine is mainly found as HF in some fossil fuel-derived gases or when processing glass-containing wastes. Due to strict environmental regulations in the western world, increasing amounts of fluorine-containing wastes will have to be treated in the future, such as CFC-containing polyurethane scrap from refrigerators.

## 7.2 Halogens in fuels and waste streams

In fossil fuels halogen compounds are generally present as trace elements (< 0.1 %wt, < 1000 ppmw), in some coals as minor elements (0.1-1 %wt). Data are available for chlorine, and only scarcely for the other halogens - see Table 7.1. Natural gas and oil-derived fuels contain very small amounts of halogens. Coals and lignites contain halogens which derive from plants and seawater sediments and volcanic material. High levels of chlorine are found in coals from Japan, Australia and USA (Illinois), whilst high-bromine coals are found in Bulgaria and the Ukraine (Davidson, 1996, Vassilev *et al.*, 2000a). Typically chlorine content increases with coal rank.

**Table 7.1 Typical values for the halogen content of fossil fuels (dry mg/kg, i.e. ppmw)** Order of listing Fluorine/Chlorine/Bromine

Coal*, lignite	20 -500 / 50-2000/0.5 -90	Light fuel oil	-
Peat	~ 500	Heavy fuel oil	- / < 20
Estonian oil shale	~2000	Orimulsion™	~700
Petroleum coke, "petcoke"	~ 300	Natural gas	-

\* Iodine 0.5 - 1.5 mg/kg

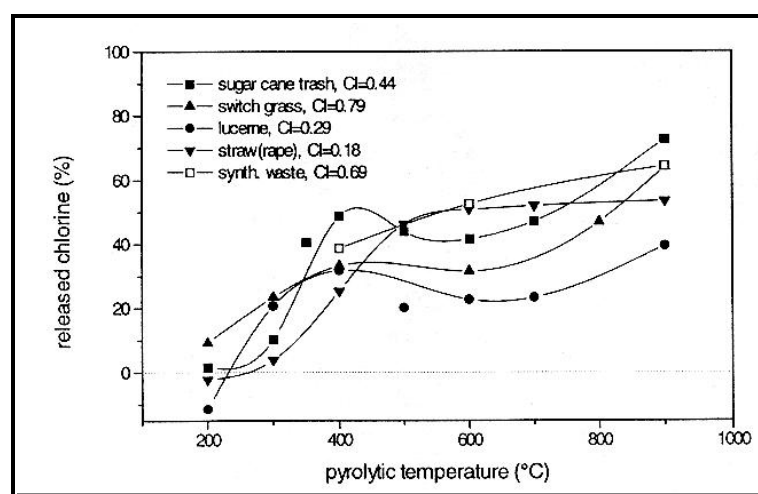
In biomasses, especially straw, the presence of halogens is largely limited to chlorine, mainly (as chloride ions) in the form of the salts NaCl and KCl, and some CaCl<sub>2</sub> (with a large dependence on location and harvesting season !) A significant amount of this can be removed by washing with water.

In wastes, waste-derived fuels and gases from waste treatment or from chemical processing the halogen compounds are most abundant and diverse. Household wastes contain mainly chlorine (as NaCl and PVC, in about equal amounts). Landfill gases contain CCl<sub>4</sub> - a value of 290 ppmw was measured at a landfill in the US (CLPSD, 1988). The Finnish waste-derived fuel fractions REF I, II and III are classified by 0.15, 0.5 and 1.5 %-wt (max) chlorine, respectively (Wilén, 1999). Medical wastes contain up to 10 %-wt PVC (mainly blood bags). Electronic and electronic equipment (E&EE) waste contains chlorine and bromine at a typical mass ratio 1 : 10 - 100 due to the presence of brominated flame retardants. Finally, off-gases from dry-cleaning and other chemical processing contain chemicals such as trichloro ethylene. Some halogen-containing VOCs were included in Table 6.2.

**Table 7.2 Typical values for the halogen content of biomasses and wastes for thermal treatment (dry %-wt)**Order of listing: Fluor / Chlorine / Bromine

Wood (firewood)	0.08 - 0.13	Municipal solid waste (MSW)	0.005 - 0.025 / 0.05 - 0.25
Bark	0.02 - 0.4	Refuse derived fuel (RDF)	0.001 - 0.07 / 0.3 - 0.8
Straw	0.1 - 1.5	Packaging derived fuel (PDF)	0.001 - 0.012 / 1 - 4
Landfill gas	~50 ppmw CCl <sub>4</sub>	Car tyre scrap	500 - 700
		Auto shredder residue (ASR)	0.5 - 2
Textile	~ 0.25		
Newsprint paper	~ 0.11	Computer circuit boards (epoxy or phenolic resins)	0.1 - 0.5 / 2 - 6
Leather waste	0.7 - 3	Computer monitor housings	~ 0.1 / ~ 2
		Electric & electronic equipment (E&E) waste plastics *	~ 3.5 / ~ 0.9
Sewage sludge	0.03 - 1		
		Mixed medical waste	1 - 4
Polyurethane foam (containing CFC11)	~ 0.7 / ~ 8 / ~ 3		
PVC	~ 50	Black liquor solids	0.05 - 0.2

\* Polymer market mix 1998



**Figure 7.2** Release of chlorine from biomass fuels (Cl content in % indicated) during pyrolysis in nitrogen (picture from Björkman and Strömberg, 1997)

The production and use of many organo-halogen chemicals mentioned above, such as DDT, PCBs and HCH has been phased out or restricted due to severe risks to the ecosystem or human health (WHO, 1996, UN, 1998). Still, these will appear in waste streams and polluted soils for years to come.

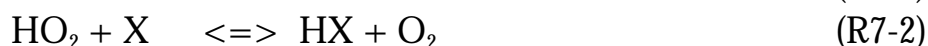
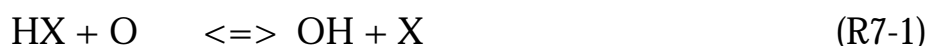
During combustion as well as gasification the F, Cl and Br

will, in general, be released mainly as HF, HCl and HBr with small amount of F<sub>2</sub>, Cl<sub>2</sub> and Br<sub>2</sub>. This applies also to the incineration of halogen-containing VOCs (Procaccini *et al.*, 2000), CFCs or processes for PCB de-hydrochlorination (Murena *et al.*, 2000). For coals it was found that ~ 96 % of the Cl and Br were released from the fuel at temperatures as low as 200EC (Shao *et al.*, 1994, Vassilev *et al.*, 2000b). Björkman and Strömberg (1997) measured the release of chlorine from biomass fuels, which appears to be completed at 400-500EC, without much effect of O<sub>2</sub>, H<sub>2</sub>O or CO<sub>2</sub> in the gas - some results are shown in Figure 7.2. Depending on other elements such as alkali and other metals the halogens will form compounds such as NaCl, KCl, PbCl<sub>4</sub>, HgCl<sub>2</sub>, NiCl<sub>2</sub> *etc.* (L chapter 8); other species that may be formed under certain conditions are chlorine or bromine-based dioxins and furans.

Apart from the release of highly acidic species such as HCl, and super-toxics such as dioxins, the major problems related to halogen compounds in thermal processes are corrosion, slagging and fouling in furnaces and boilers (see below), plus increased emissions of CO due to incomplete burnout.

It was shown by many researchers (*e.g.* Anthony *et al.* 1993, 1994, Desroches-Ducarne 1997, Desroches-Ducarne *et al.*, 1998,

Julien *et al.*, 1996, Liang *et al.*, 1991), mainly studying fluidised bed combustion, that the presence of HCl, HBr, HF and HI, say, HX, interferes with the radical pool that consists of species such as O, OH, OH<sub>2</sub> and third body species M. This results in chemical reactions such as (with X = F, Cl, Br, I):



which compete with the main CO oxidation reaction

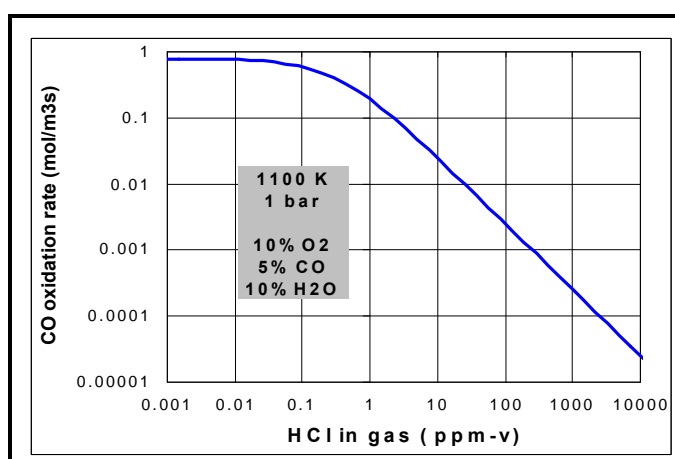


Figure 7.3 Oxidation rate of CO at FBC conditions in presence of HCl (after data from Desroches-Ducarne, 1997)

Based on a set of CFBC experiments with simulated waste-derived fuels, Desroches-Ducarne *et al.* (1997, 1998) derived the following expression for the CO oxidation rate,  $r_{CO}$ , in presence of HCl :

$$r_{CO} \text{ (mol/m}^3\text{s)} = \frac{3.25 \times 10^7 \exp(16098/T) c_{CO}^{0.5} c_{O_2}^{0.5}}{2.9 \times 10^{11} \exp(22709/T) c_{HCl} + 11.2} \quad (7-1)$$

with concentrations  $c_i$  (mol/m<sup>3</sup>). Results of this are given in Figure 7.3 for a typical FBC at 1100 K. It shows that an HCl concentration of 10 ppmv reduces the rate of CO oxidation by almost two orders of magnitude.

### 7.3 Emission standards for halogens and dioxins/furans

Emission standards for halogen compounds in flue gases from fossil fuel firing or waste incineration are given in Table 7.3 (Finland, 1994, Foster Wheeler, 1997, Werther, 1999, Wilén, 1999). Currently, HCl, HF and dioxins/furans (PCDD/Fs) are regulated. For PCDD/Fs, depending on the incinerator type the limits are 0.1 ng/m<sup>3</sup><sub>STP</sub> for municipal solid waste (burning > 3000 kg/h), 0.5 ng/m<sup>3</sup><sub>STP</sub> for medical waste (burning > 1000 kg/h) and 0.2 ng/m<sup>3</sup><sub>STP</sub> for hazardous waste (burning > 1000 kg/h) (UN, 1998).

**Table 7.3 Emission standards for HCl, HF and PCDD/Fs for various processes and locations (MSW = municipal solid waste)**

@ 11 % O <sub>2</sub> dry	Power plant Finland (1990+)	MSW incinerator Finland (1994)	MSW incinerator EU (2000)	Power plant Germany (1999)	MSW incinerator Germany (1999)	Waste incinerator USA (1995)
HCl mg/m <sup>3</sup> <sub>STP</sub>	no standard	10	10	50	10	29.1 or 99.5% red.
HF mg/m <sup>3</sup> <sub>STP</sub>	no standard	1	1	2	1	no standard
PCDD/F ng/m <sup>3</sup> <sub>STP</sub> TEQ*	no standard	1	0.1	no standard	0.1	9.63

\* Toxic equivalents - see section 7.6

## 7.4 Chlorine-related corrosion

Chlorine-related corrosion may seriously damage furnaces, boilers, exhaust pipes and other process equipment as a result of complex chemical interactions between species such as HCl and Cl<sub>2</sub>, and O<sub>2</sub>, water, metals, sulphur oxides and alkali species (Na, K).

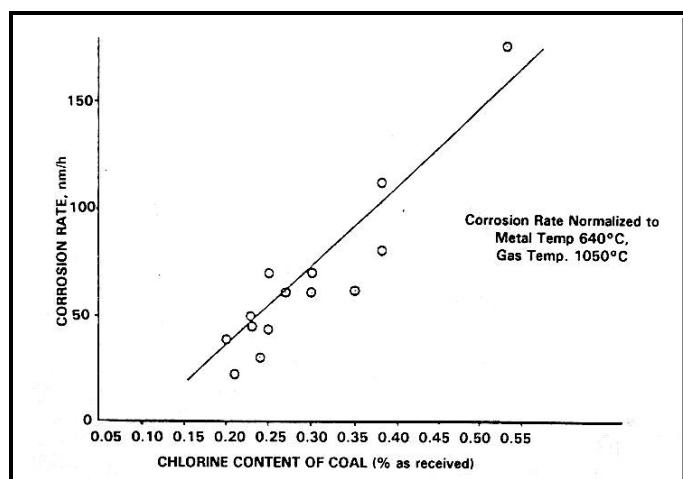


Figure 7.4 Relation between austenitic steel corrosion and chlorine in coal (picture from Bryers, 1996).

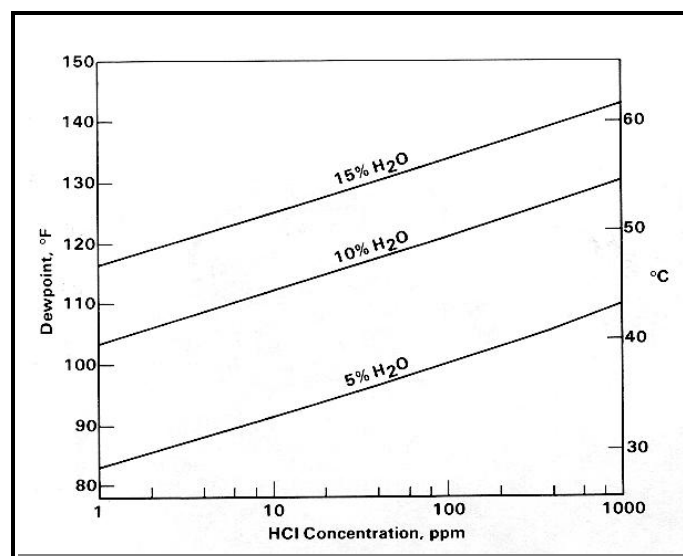
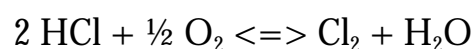


Figure 7.5 Dewpoint of hydrochloric acid as function of water and HCl vapor concentrations (picture from Bryers, 1991)

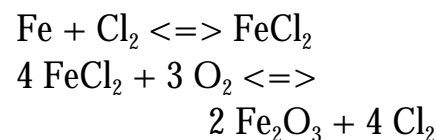
At low temperatures, *i.e.* below 100EC, hydrochloric acid is formed with water by condensation, similar to the formation of sulfuric acid from SO<sub>3</sub> and water (7 Figure 3.4). Strong liquid acids may be formed: the dewpoint of hydrochloric acid is shown in Figure 7.5.

Mainly for this reason steam temperatures in boiler tubes in waste incinerators and biomass-fired furnaces are kept below 400-450EC. A linear relation, shown in Figure 7.4, was found between corrosion and coal chlorine content under reducing conditions. Corrosion by CO is enhanced by the presence of HCl and Cl<sub>2</sub> which can be formed from each other via the Deacon reaction:



(R7-6)

Under oxidising conditions, the oxidation of iron to iron oxide (Fe<sub>2</sub>O<sub>3</sub>) is more rapid when HCl and Cl<sub>2</sub> are present, via



(R7-7,8)

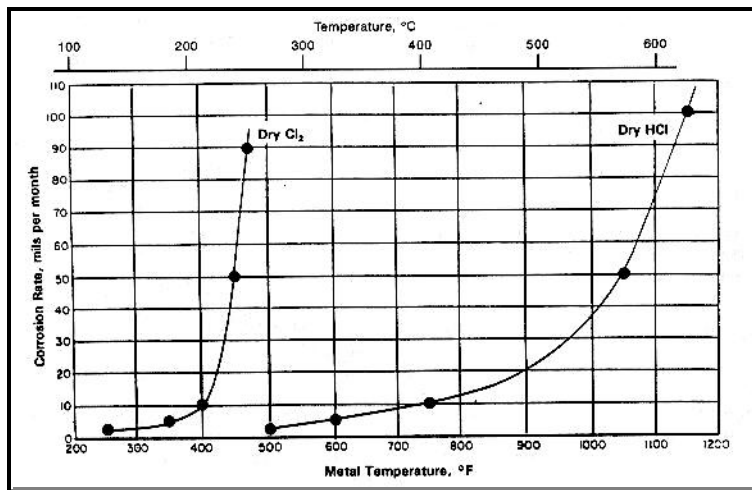


Figure 7.6 Carbon steel corrosion rates with HCl and Cl<sub>2</sub> as function of temperature (picture from Bryers, 1996).

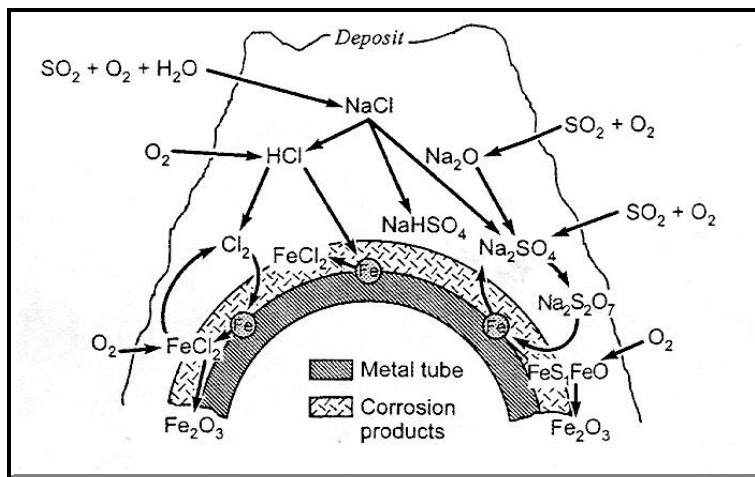


Figure 7.7 Corrosion reactions at a metal tube under typical incinerator conditions (picture from Nielsen *et al.*, 2000)

At higher temperatures, *i.e.* above  $\sim 200^{\circ}\text{C}$  for Cl<sub>2</sub> and above  $\sim 400^{\circ}\text{C}$  for HCl, metal and steel parts start suffering from chlorine attack - see Figure 7.6. It is assumed that if the presence of gas phase Cl<sub>2</sub> is not favoured by equilibrium (reaction R7-6), HCl penetrates the protective oxide scale on the metal and reacts with iron directly to form iron chloride, FeCl<sub>2</sub>, after which the reaction sequence (R7-7,8) proceeds.

In gasification the conditions are reducing and protective oxide layers are absent or weak. Sulphur and alkali both contribute to chlorine-related corrosion as shown schematically for an iron-base metal tube in Figure 7.7. Corrosion may be direct, by reaction with gaseous

components, or indirectly via deposits which undergo chemical reactions, forming corrosive species. Sulphur dioxide may react with NaCl and KCl in the gas phase to form HCl and sulphates of Na and K (Hargreaves reaction). Alternatively, deposits of NaCl/KCl may be sulphated with SO<sub>2</sub> to form Na<sub>2</sub>SO<sub>4</sub>/K<sub>2</sub>SO<sub>4</sub> and Cl<sub>2</sub>, which is considered to be an important route to metal tube corrosion in biomass-fired boilers (Nielsen *et al.*, 2000). Corrosive molten alkali trisulphates such as K<sub>2</sub>Fe(SO<sub>4</sub>)<sub>3</sub> can be formed from Fe<sub>2</sub>O<sub>3</sub>, SO<sub>2</sub> and alkali sulphates. Also chromium oxidation (Cr to Cr<sub>2</sub>O<sub>3</sub>) is accelerated by the presence of NaCl below 801°C (*i.e.* the melting point of NaCl). Nickel (Ni) reduces this problem, but Ni itself is sensitive to sulphation to NiS. More detail is found in the literature on corrosion and deposits-related problems in furnaces and boilers (*e.g.* Bryers, 1991, 1996, Nielsen *et al.*, 2000).



## 7.5 Hydrogen chloride (HCl) emissions control

**Table 7.4 Halogen removal in an FGD (with forced oxidation) for coal-firing (from CIEMAT, 1998)**

Halogen	Conc. in coal combusted, mg/kg	Volatilisation, %	Conc. before FGD, $\mu\text{g}/\text{m}^3$	Conc. after FGD, $\mu\text{g}/\text{m}^3$	Removal in FGD, %
Cl	900	99	91,500	9,150	90
F	80	90	7,400	2,200	70
Br	6	60	370	20	95
I	2	90	190	40	80

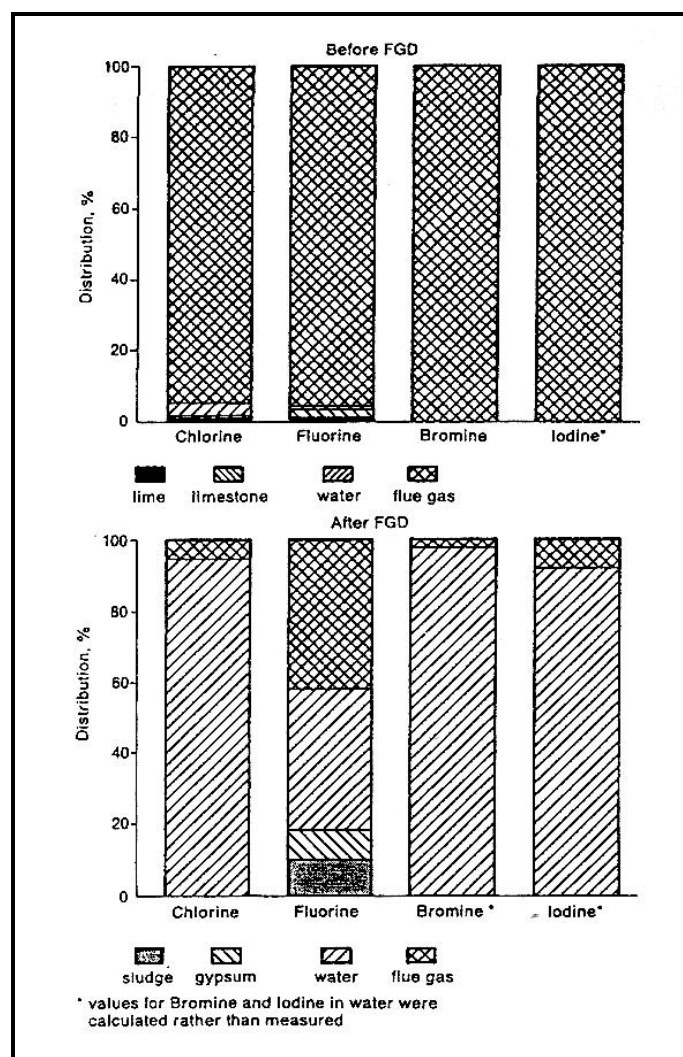


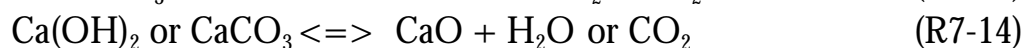
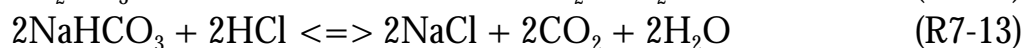
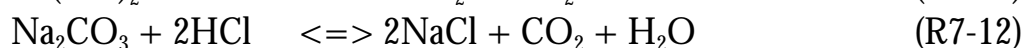
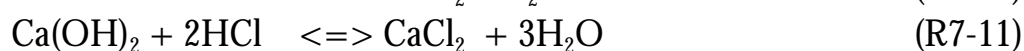
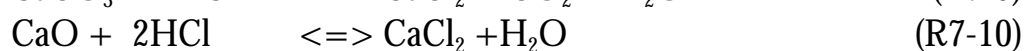
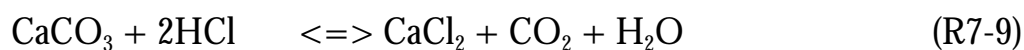
Figure 7.8 Distribution of halogens in flue gas, and FGD input and output streams (picture from CIEMAT, 1998)

For power plants firing low chlorine fuel ( $\sim 0.01$  %-wt Cl or less) the emissions of HCl and HF are usually not a problem when considering emission standards or process operation. When a flue gas desulphurisation unit (FGD) is present for  $\text{SO}_2$  emissions control this can also be used to remove small amounts ( $\sim 10 - 50$  ppmv) of HCl and HF. Measurements from a pulverised coal combustion unit with FGD (with forced oxidation of the gypsum product) in the Netherlands showed that  $\sim 90\%$  of the flue gas chlorine (mainly HCl) and  $\sim 70\%$  of the fluorine (as HF) is removed - see Table 7.4. When considering the products of the FGD most of the halogens that were captured were found in the effluent water stream. Only the fluorine was distributed over gypsum product, sludge and effluent water - see Figure 7.8.

Risks connected to this approach are reduced  $\text{SO}_2$  removal efficiency since the pH is rapidly lowered by large amounts of HCl and HF in the incoming flue gas, and problems due to the formation of  $\text{AlF}_x$  complexes (7 chapter 3.6). Also equipment upstream, at higher temperatures may suffer from corrosion or problematic

chlorine-based deposits. When chlorine concentrations or emissions need to be controlled the methods used are often based on the injection of a sorbent into the gas at low temperatures (dry, wet or semi-dry duct injection, or a separate wet scrubber) or at high temperatures (furnace injection, limestone in fluidised furnaces), very much similar to approaches to SO<sub>2</sub> emissions control (7 chapter 3) - see *e.g.* Weinell *et al.*, 1992; Gullett *et al.*, 1992; Fonseca *et al.*, 1998; Chrisholm and Rochelle, 1999.

The most suitable sorbents for HCl control are the oxides of sodium and calcium, being limestone (CaCO<sub>3</sub>), lime (CaO), hydrated lime (Ca(OH)<sub>2</sub>), nahcolite (NaHCO<sub>3</sub>), soda (Na<sub>2</sub>CO<sub>3</sub>) or trona (Na<sub>2</sub>CO<sub>3</sub>·NaHCO<sub>3</sub>). These can react with HCl via the reactions



with similar reactions with HF, HBr and HI. Potassium-based sorbents are less favourable due to the high volatility of the products KCl, KF and KBr. The solid products can be collected in the dust control system; if a fabric filter is used the uptake of halogens will continue in the filter cake. If needed the unreacted sorbent can be reactivated by water injection, similar to SO<sub>2</sub> control systems. For high temperature methods the low melting points of the salts that are produced may be a problem, as listed in Table 7.5.

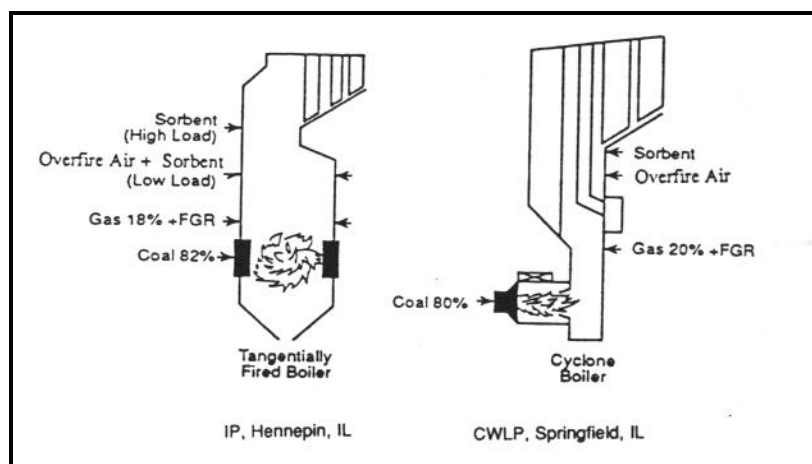


Figure 7.9 Furnace sorbent injection (hydrated lime) for HCl and HF control in conjunction with SO<sub>2</sub> control in pulverised coal combustion (picture from Hong *et al.*, 1993)

Tests with hydrated lime injection in two pulverised coal facilities in Illinois (USA) showed that HCl (uncontrolled: ~ 660 ppmw) and HF (uncontrolled: ~ 49 ppmw) can be reduced by 63-86 % and 94-99%, respectively by injection of hydrated lime at temperature ~ 1250EC.

At these temperatures the HCl and HF react with CaO after calcination of the  $\text{Ca}(\text{OH})_2$  (reaction R7-14). The coal had a sulphur content of  $\sim 3$  %-wt, the sorbent was injected for sulphur capture as well and was fed at  $\text{Ca}/\text{S} = 1.66$  (Hong *et al.*, 1993). This is illustrated by Figure 7.9.

**Table 7.5 Melting points of halogen salts of Na, K, and Ca**

NaF 988 EC	NaCl 801 EC	NaBr 755 EC
KF 1360 EC	KCl 772 EC	KBr 730 EC
$\text{CaF}_2$ 858 EC	$\text{CaCl}_2$ 770 EC	$\text{CaBr}_2$ 734 EC

For flue gas cleaning in waste incineration systems the HCl (and HF + HBr) can be removed selectively in a separate scrubber that is operated at  $\sim 70$ EC, located between the particulate control system and the equipment for the control of  $\text{SO}_2$ ,  $\text{NO}_x$  and other chemical pollutants (Chapter 10). It is operated at low pH values,  $\text{pH} \sim 1$ , which is too low for  $\text{SO}_2$  absorption. The principle of a three-stage HCl scrubber is shown in Figure 7.10 (Krupp VDM, 1999).

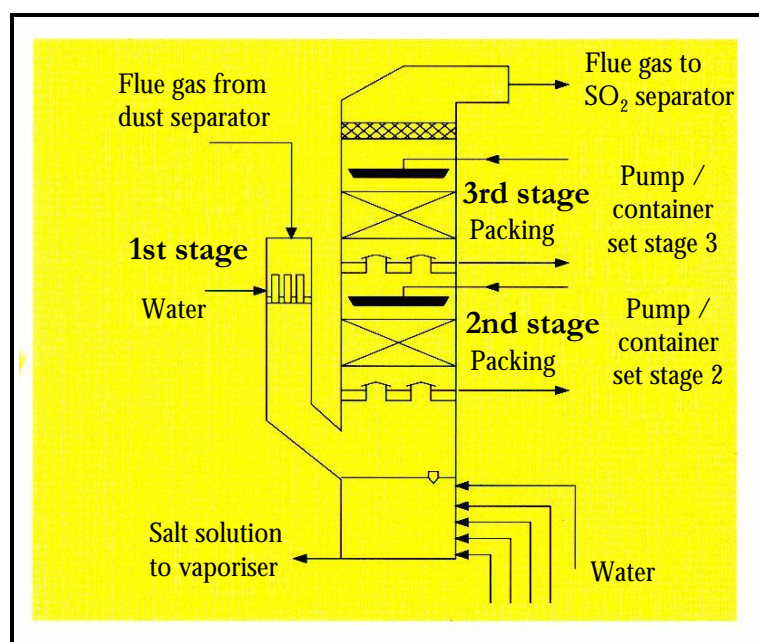
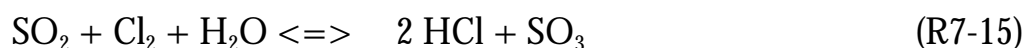


Figure 7.10 A three-stage scrubber for HCl (picture after Krupp VDM, 1999)

In the first stage, water is injected in a quencher, removing some chlorine as salts. The HCl removal as a hydrochloric acid solution is accomplished by scrubbing on two packed bed contactors. A product with 14-18 %-wt HCl in water is obtained from stage 3, where the gas is scrubbed with the product liquid from stage 2. This product is further upgraded to 30-31 %-wt HCl hydrochloric acid by evaporation.

In fluidised bed reactors HCl can be captured *in situ* by a limestone or dolomitic sorbent that is also, or primarily, used for *in situ*  $\text{SO}_2$  control (7 chapters 3.11 and 3.14). As shown in Table 7.5 the melting point of the  $\text{CaCl}_2$  is below the operational temperature of a typical FB combustor or gasifier. As a result, only 10-40 % of the HCl that is released from the fuel can be bound to  $\text{CaCl}_2$ , at high ratios of  $\text{Ca}/\text{Cl}$  or

Ca/(S+0.5 Cl) (Düsenberg *et al.*, 1997). Also Xu *et al.* (1998) report that “chlorine is not effectively captured by limestone sorbent” in an atmospheric FBC but that the efficiency for SO<sub>2</sub> uptake by the lime is improved. The formation of (molten) CaCl<sub>2</sub> as a reaction intermediate that modifies the structure of the sorbent is one explanation for this. Also the reaction



(although it was reported to be slow as a gas phase reaction) in conjunction with the Deacon reaction (R7-6) may become important - SO<sub>3</sub> is more reactive to calcium-based sorbents than SO<sub>2</sub> (Xie *et al.*, 1999, Xu *et al.*, 1998). Recently, Liu *et al.* (2000) stated that the optimum temperature for HCl capture with CaO in FBC is ~ 600EC.

Also for pressurised systems such as PFBC and IGCC processes based on gasification HCl (and HF) control is needed. For the combustion of a gasification product gas in a gas turbine a typical limit of 1 ppmw HCl+HF is given by the gas turbine manufacturers - see Table 5.16. For typical entrained bed coal gasification of coal the (theoretical) concentrations of HF and HBr are given in Table 7.6. Since gas streams are 4-5 times smaller in volume than combustor flue gases, the concentrations higher.

**Table 7.6** Typical HCl and HF concentrations in entrained bed gasification of coal (fuel 0.2 % Cl, 0.04 % F) (data from Alderliesten *et al.*, 1990)

Shell entrained bed gasifier	~ 600 ppmw HCl	~ 224 ppmw HF
Texaco entrained bed gasifier	~ 500 ppmw HCl	~ 188 ppmw HF

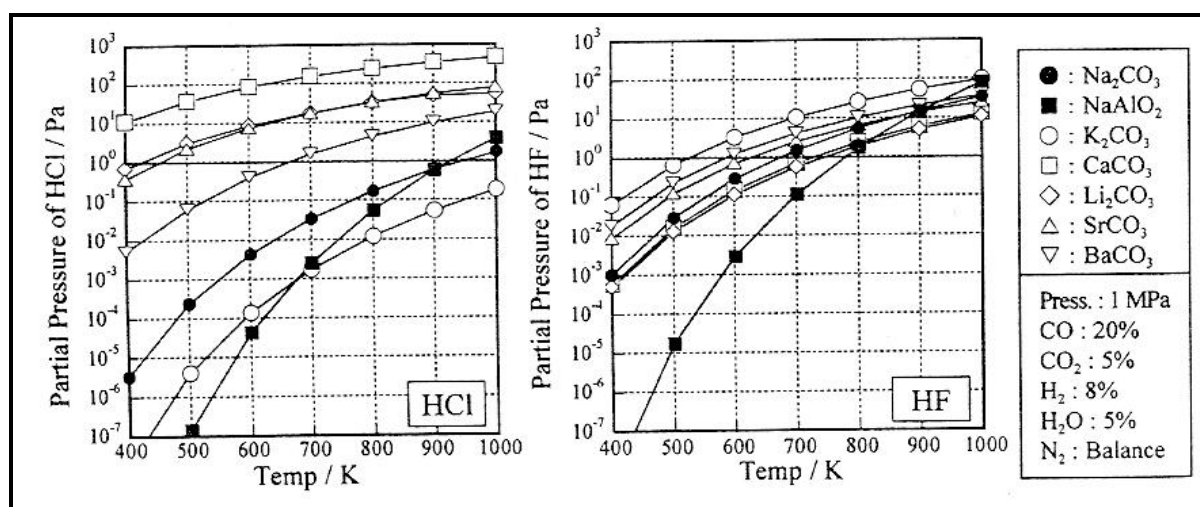
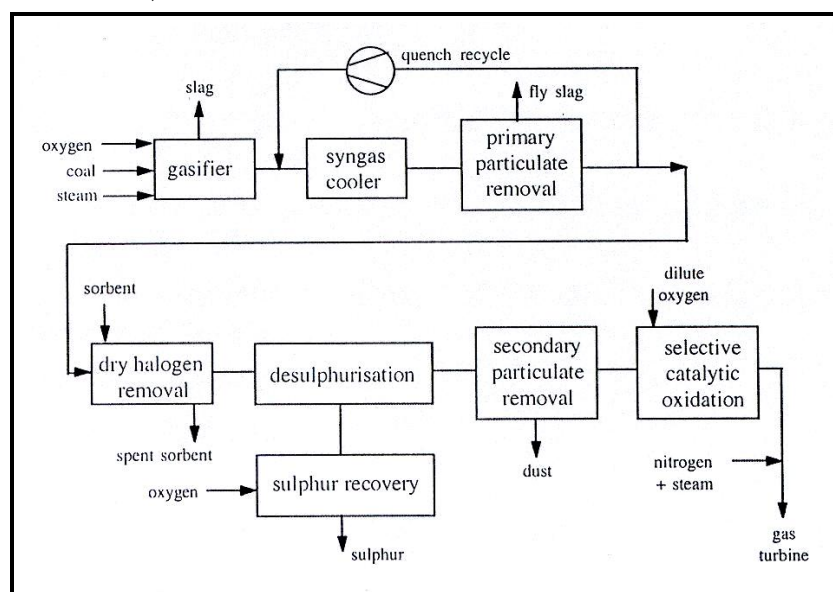


Figure 7.11 Equilibrium partial pressures of HCl and HF during reaction with carbonate sorbents at 10 bar under reducing conditions (picture from Nunokawa *et al.*, 1999)

Based on thermodynamic calculations such as shown in Figure 7.11 and the melting points of potential sorbents, the sodium-based sorbents  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$  are considered to be the most suitable for HF and HCl from gasifier product gases, at temperatures in the range 250 - 600 EC. At the same time, the HCl and HF uptake by sodium-based sorbents is hardly influenced by  $\text{H}_2\text{S}$ , allowing them to be used upstream of the desulphurisation unit (Alderliesten *et al.* 1990, Kiel 1997, Nunokawa *et al.* 1999).



**Figure 7.12** Dry halogen removal with soda/trona for IGCC gasifier product gas at 400-500EC (picture from Kiel, 1997)

A process suggested for the Buggenum IGCC process, shown in Figure 7.12, is based on a soda/trona sorbent for use at 400-500EC. Based on laboratory tests this sorbent was found to be preferable over nahcolite for reasons of pore plugging and sorbent capacity (Kiel 1997, Duo *et al.* 1996).

A study by Nieminen *et al.* (1997) concentrated on the use of calcium-based sorbents for halogen control in pressurised fluidised bed gasifier product gas containing 200-1000 ppmw HCl, at 350-500EC, 3-10 bar. Sorbent injection / filter scrubbing gave HCl removal efficiencies of 10-60 %. Problems were encountered due to recarbonation of the sorbent ( $\text{CaO}$  to  $\text{CaCO}_3$ ) at temperatures above 450EC as a result of high  $\text{CO}_2$  partial pressures.

A comparison between  $\text{Ca}(\text{OH})_2$  and  $\text{Na}_2\text{CO}_3$  as sorbents for HCl in fluidised bed gasifier product gases at 400EC, as well as the effect of fines from Ca-based sorbent that is used in the fluidised bed for sulphur capture, is given in Figure 7.13. At 500-600EC the HCl removal efficiencies of  $\text{Ca}(\text{OH})_2$  and  $\text{Na}_2\text{CO}_3$  were similar (ETSU, 1998). Several other studies came to the same conclusion that nahcolite or soda/trona sorbents are capable of removing HCl from gasification products gases, or PBFC flue gas to below 1 ppmw at temperatures between 400 and 650EC (Harrison, 1995, Krishnan *et al.*, 1996a,b, Rutkowski *et al.*, 1996).

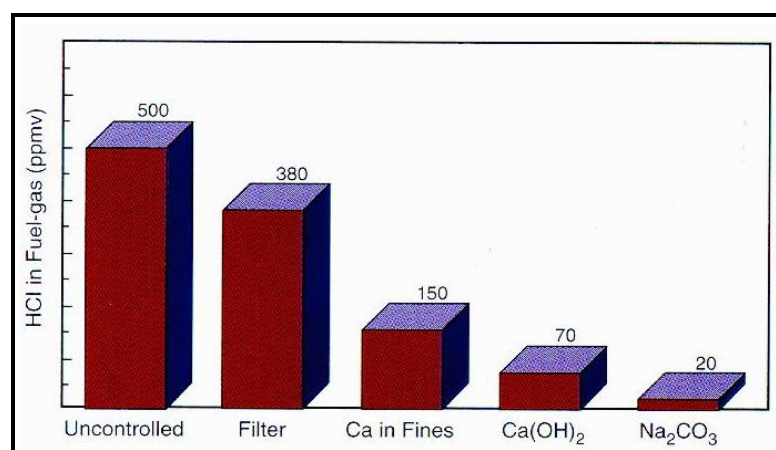


Figure 7.13 Removal efficiencies for HCl from fuel gas by various sorbents (picture from ETSU, 1998)

Gupta and O'Brien (2000) analysed the effect of HCl in gasifier product gas on the removal of H<sub>2</sub>S with a zinc titanate regenerative sorbent (7 chapter 3.12). It was found that HCl catalyses the uptake of H<sub>2</sub>S by the zinc titanate: some ZnCl<sub>2</sub> is formed which very rapidly reacts with H<sub>2</sub>S to form ZnS and HCl. During

high temperature or low steam operation some sorbent deterioration may result from HCl attack on the sodium-based binder.

## 7.6 Formation of dioxins/furans (PCDD/Fs)

Poly chlorinated dibenzo - (p) dioxines and - furanes (PCDD/Fs)(7 Figure 7.1), are extremely toxic compounds present as trace contaminants in chemicals such as chlorinated phenols, phenoxy herbicides, PCBs and so on. During the late 1970s they were also detected in exhaust gases from waste incineration. The latter forms a threat to environment and human health, which resulted in a very tight emissions standard of 0.1 - 1 ng/m<sup>3</sup><sub>STP</sub> TEQ @ 11 %-vol O<sub>2</sub> (dry), depending on the type of waste incinerator (see section 7.3). Recently it was reported that also heavy-duty diesel vehicles emit PCDD/Fs, at ~ 0.03 - 0.1 ng TEQ/km, being ~ 65% as PCDFs (Ryan and Gullett, 2000). Apparently the trace amounts of chlorine in diesel fuel or fuel additives are sufficient for these emissions.

The presence of (a small amount of) chlorine is a first prerequisite for PCDD/F formation. Chlorine is present in waste fractions mainly as kitchen salt (NaCl) and the polymer PVC. Numerous factors determine whether PCDD/Fs emissions will be a point of concern when chlorine-containing chemicals or wastes are thermally processed or incinerated. A simple relation between NaCl or PVC and PCDD/F emissions has not been found, although many reports or studies (from not always unprejudiced organisations) seem to give evidence for a direct relation between PCDD/Fs and PVC, or the absolute absence of such a relation (Greenpeace 1997, ASME, 1995, Chlorophiles, 1996). NaCl is largely excluded from these discussions.

The most important stationary sources for PCDD/Fs are 1) waste incineration and co-incineration facilities, 2) thermal metallurgical processes 3), combustion plants for heat and power generation, 4) small scale residential combustion and 5) certain chemical processes (UN, 1998). PCDD/Fs can be considered as chlorinated PAHs.

Depending on the number of chlorine atoms 75 different PCDDs and 135 different PCDFs can be distinguished which do not all form an environmental or health hazard. The most toxic, often referred to as “the” dioxin is 2,3,5,7 tetra chlorodibenzo (-p-) dioxin, *i.e.* 2,3,7,8 TCDD. See Figure 7.1 for the numbering of chlorine positions in PCDD/Fs. Based on a toxicity factor TEF = 1 (toxicity equivalence factor) for 2,3,7,8 TCDD, the relative toxicity of other PCDD/Fs has been defined by several international TEF standards which are almost identical. The most important international TEF standard, referred to as I-TEF (NATO, 1988) is given in Table 7.7. Note that I-TEF values are zero for PCDD/Fs without chlorine at the 2,3,7 and 8 positions.

**Table 7.7 International Toxic Equivalence Factors (I-TEF) for dioxin/furan toxicity**

Dioxin	I- TEF	Furan	I - TEF
2,3,7,8-TCDD	1	2,3,7,8-TCDF	0.1
1,2,3,7,8-PCDD	0.5	1,2,3,7,8-PCDF	0.05
1,2,3,4,7,8-HxCDD	0.1	2,3,4,7,8-PCDF	0.5
1,2,3,6,7,8-HxCDD	0.1	1,2,3,4,7,8-HxCDF	0.1
1,2,3,7,8,9-HxCDD	0.1	1,2,3,6,7,8-HxCDF	0.1
1,2,3,4,7,8,9-HpCDD	0.01	2,3,4,6,7,8-HxCDF	0.1
1,2,3,4,6,7,8,9-OCDD	0.001	1,2,3,7,8,9-HxCDF	0.1
		1,2,3,4,6,7,8-HpCDF	0.01
		1,2,3,4,7,8,9-HpCDF	0.01
		1,2,3,4,6,7,8,9-OCDF	0.001

Similarly, a Nordic standard table was defined which is identical to the I-TEF table except for the lower value TEF=0.001 for 1,2,3,7,8 pentachlorodibenzofuran.

For a gas that contains a mixture of different dioxins and furanes the PCDD/F concentration is calculated in toxic equivalents (TEQ, or I-TEQ when using the table above):

$$\text{PCDD/F (TEQ)} = \sum (\text{concentration dioxin or furan})_i \times (\text{TEF})_i \quad (7-2)$$

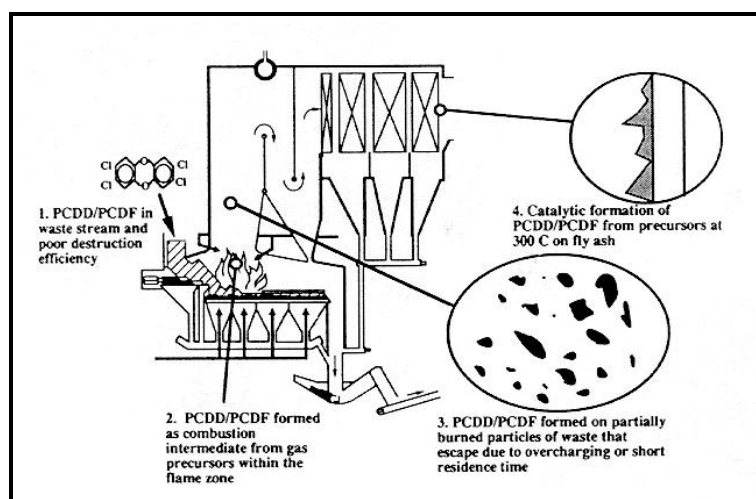


Figure 7.14 Mechanisms for PCDD/F formation during waste combustion (picture from Seeker, 1990)

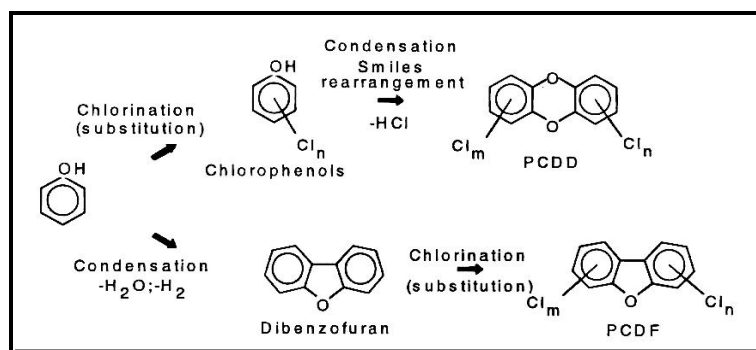


Figure 7.15 Possible scheme for PCDD/F formation from phenol (picture from Cains *et al.*, 1997)

Seeker (1990) distinguished four major mechanisms for PCDD/F formation during the incineration of wastes, as shown in Figure 7.14. A first source may be PCDD/F that enters with the input waste and is not destroyed in the process. In Finland, this was found to occur when firing biomasses: PCDD/Fs from earlier emissions may be dispersed once more. The second mechanism is a gas-phase formation from carbon and chlorine species such as phenol and HCl. Indeed, relations were found between PCDD/F emissions and polychloro-benzenes and phenols in the flue gas. An example of such chemical routes is given in Figure 7.15.

Chemical routes like these are highly uncertain and are widely questioned. The same holds for the third mechanism which is connected to partially burnt matter in the combustion zone. Most tests show that unburned matter that is entrained from the high temperature zones is more important to PCDD/F emissions than condensation reaction mechanisms are. These three "high temperature" formation mechanisms must strongly compete with destruction mechanisms since PCDD/Fs are not stable above 800-850EC.

The fourth mechanism in Figure 7.14, referred to as *de novo* formation of PCDD/Fs takes place in the flue gas duct in the temperature range 250-450EC. Depending on five factors, being 1) the cooling rate of the gas at 300-400EC, 2) the presence of oxygen, 3) the amount of fly ash particles, 4) the presence of trace elements such as Cu and Pb and 5) the carbon and chlorine content in the fly ash and the flue gas the PCDD/Fs can be formed, at a temperature where destruction mechanisms are too slow. A scheme of chemical routes that lead to PCDD/Fs is given in Figure 7.16.



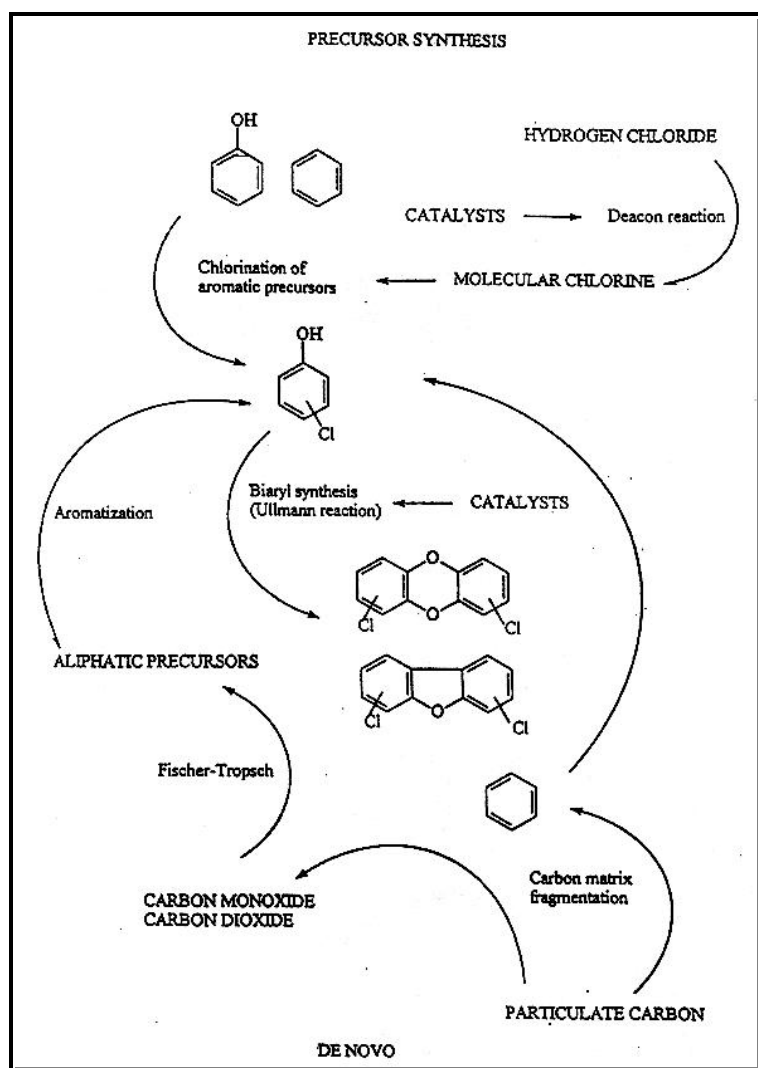
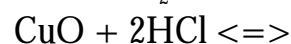
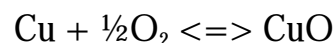


Figure 7.16 PCDD/F formation routes (picture from Tuppurainen *et al.*, 1998)

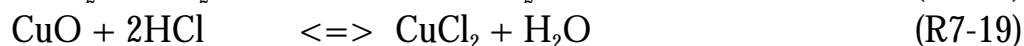
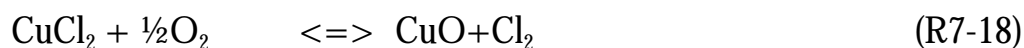
Here is the Deacon reaction (R7-6) which is catalysed by a number of metals (Cu, Pb, Zn, Sn, Fe) and alkali is most important (*e.g.* Olie *et al.*, 1997, Ruuskanen *et al.*, 1994).

Also important is sulphur: it was shown repeatedly that the presence of SO<sub>2</sub> reduces emissions of PCDD/Fs. It is assumed that this is due to the oxidation of SO<sub>2</sub> to SO<sub>3</sub> by Cl<sub>2</sub> (reaction R7-15), which reduces the possibility for Cl<sub>2</sub> to participate in dioxin/furan formation. The Deacon reaction for Cl<sub>2</sub> production may actually be a two-step reaction:



(R7-16,17)

(Ruokojärvi *et al.*, 1998), or



(Olie *et al.*, 1998) that depends highly on the chemical form of Cu. Therefore it may also happen that SO<sub>2</sub> reduces PCDD/F emissions by reacting with the Cu to form CuSO<sub>4</sub>, which does not support Cl<sub>2</sub> formation via the Deacon reaction.

For the low temperature *de novo* mechanism the maximum rate of PCDD/F formation is at a temperature near 400°C based on data from several sources - see Figure 7.17.

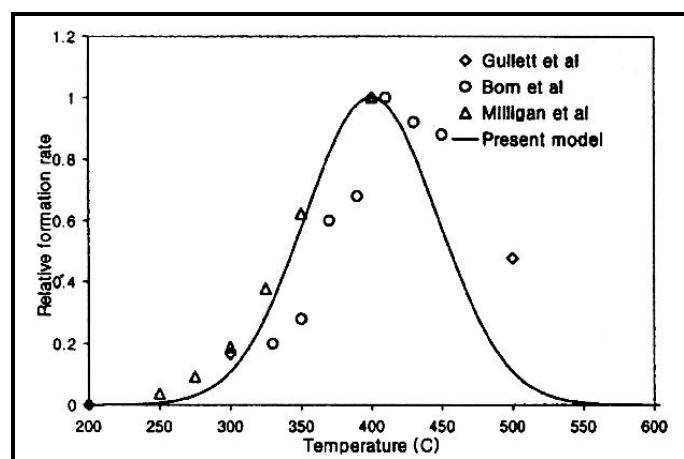


Figure 7.17 Rate of *de novo* PCDD/F formation relative to rate at 400EC (picture from Shin *et al.*, 1999)

Much dispute is ongoing on the role of organic or inorganic precursors, catalysts and the role of NaCl, PVC and other organo-halogen compounds in fuel or waste. Several recent studies have shown that there is no significant difference between how NaCl or PVC contribute to dioxin/furan formation during waste incineration (Yasuhara *et al.*, 2001, Hatanaka *et al.*, 2000). PVC decomposes into HCl and a

chlorine-free hydrocarbon residue at temperatures between 250 and 350EC (Zevenhoven *et al.*, 2001), whilst NaCl eventually reacts with water to form HCl as well:



Huotari and Vesterinen (1996) reported that for co-combustion of refuse-derived fuel (RDF) with wood, coal or peat in FBC the gas phase PCDD/Fs correlates with CO and PAHs such as PCB, polychlorinated benzenes (PCBzs), and polychlorinated phenols (PCPhs), Cu in fly ash, fuel-Cl and fuel Cl/S ratio. Particle bound PCDD/Fs, *i.e.* found in ESP fly ash, increased when amounts of unburned hydrocarbon, Cl, or 1,2,4- trichlorobenzene in the fly ash increased.

**Table 7.8 PCDD/Fs in gas and particulate phase for RDF combustion in FBC (data from Frankenhaeuser *et al.*, 1994)**

ng/m <sup>3</sup> <sub>STP</sub> I-TEQ, @ 11 % O <sub>2</sub> , dry	gas phase without/ with limestone	particle phase without / with limestone
after cyclone	0.004 / 0.009	0.009 / 0.038
after boiler	0.006 / 0.005	0.011 / 0.071
after ESP	0.014 / 0.006	0.0005 / 0.003

The distribution of PCDD/Fs over the gas phase and the particulate phase along flue gas line and particulate control system was studied by Frankenhaeuser *et al.* (1994) for FBC co-firing of used packaging waste co-fired with coal or peat. For three positions

in the flue gas line the distribution of PCDD/Fs is given in Table 7.8, for combustion with and without calcium-based sorbent for sulphur and chlorine control. Limestone addition has a significant effect on particle phase PCDD/Fs, which are effectively removed by the ESP.

The effect of calcium on dioxin/furan emissions was also reported by Tagashira *et al.*, (1999) as illustrated by Figure 7.18.  $\text{Ca}(\text{OH})_2$  was fed to a CFBC waste incinerator, fired at  $\sim 850^\circ\text{C}$ , at  $\text{Ca}/(\text{S} + \frac{1}{2}\text{Cl})$  ratio 2. Reduced formation of PCDD/Fs in the furnace and increased decomposition in the flue gas duct were the positive results.

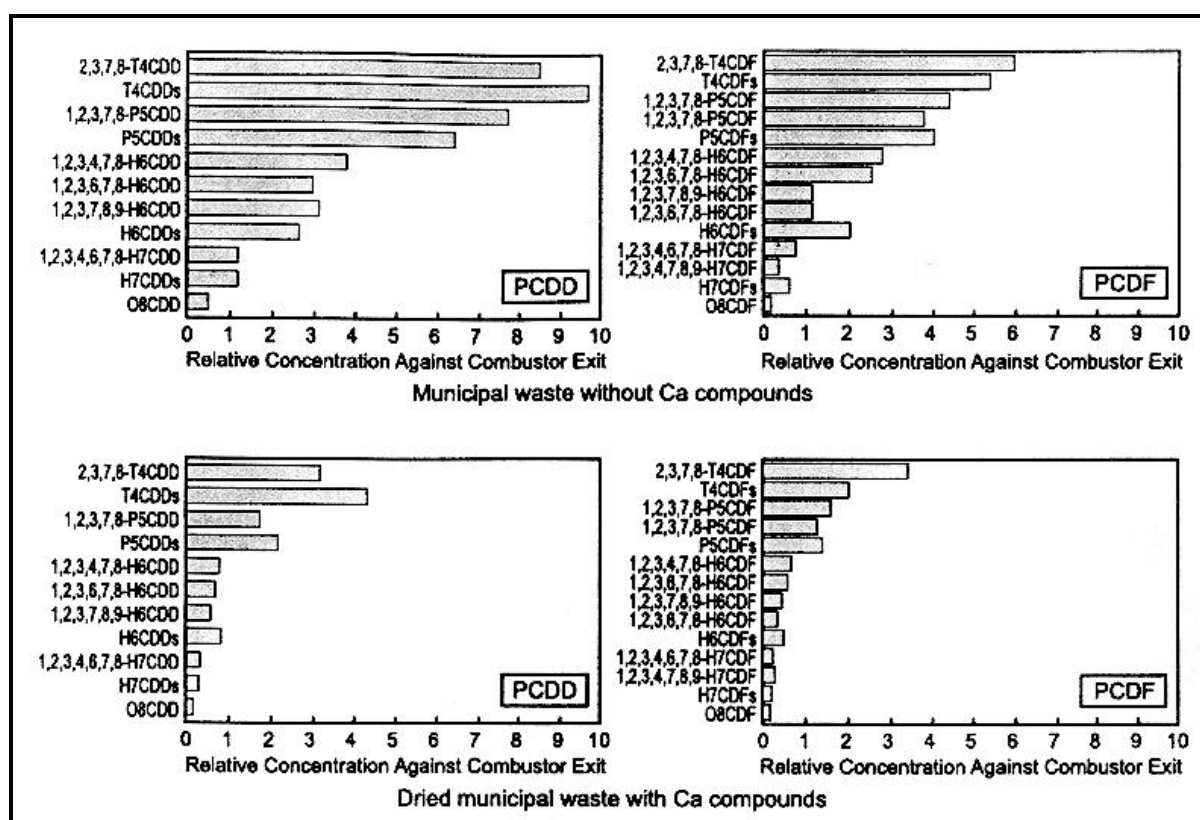


Figure 7.18 Effect of calcium-based sorbents on the increase of PCDD/Fs concentrations in the flue gas duct, relative to combustor outlet (picture from Tagashira *et al.*, 1999)

Suppressing the formation of PCDD/Fs may be the best way to control their emissions. Optimisation of the combustion process, *i.e.* turbulent mixing, residence times in combustion and post-combustion zones, scale-up, or flue gas recirculation are an option. A second method is based on lowering the chlorine content of the fuel/waste or removing chlorine altogether: washing out NaCl or PVC dehydrochlorination (Zevenhoven *et al.*, 2000). A third approach is based on the injection of gaseous inhibitors for PCDD/F formation, such as ammonia, dimethylamine, methylmercaptane, sodium sulphide, or EDTA. These are injected

in the flue gas duct at 300-600EC. Especially particle-phase PCDD/F emissions can be significantly lowered by this method, which seems mainly based on deactivating potential catalysts for the Deacon reaction (Ruokojärvi *et al.* 1998, Addink *et al.*, 1996). The most powerful method, though, may be to switch to gasification of chlorine-containing fuels or wastes: absence of oxygen effectively blocks PCDD/F formation routes.

### 7.7 Control of dioxins/furans (PCDD/Fs)

Dioxins and furans can be removed from flue gases by several methods which are mainly based on adsorption on carbon-based materials or on catalytic oxidation, *e.g.* by H<sub>2</sub>O<sub>2</sub> or the SCR system for NO<sub>x</sub> control (UN, 1998). Table 7.9 summarises some approaches to MSW or RDF incineration emissions.

**Table 7.9 Dioxins and furans control for several waste combustion processes (data from Huotari and Vesterinen, 1995)**

process	PCDD/Fs from furnace ng/m <sup>3</sup> <sub>STP</sub>	gas clean-up system	PCDD/Fs removal efficiency %
5 incinerators for RDF or MSW	43 - 2157	wet scrubber + fabric filter	> 95.7
3 incinerators for MSW	28 - 783	SCR + wet scrubber + fabric filter	87.7 - 99.6
pilot incinerator for MSW	87 - 2277	sorbent injection + fabric filter	> 99.55
MSW incinerator	170	wet scrubber + ESP	64.3

Particle-bound PCDD/Fs are most effectively removed by dust control systems. Water injection may reduce mainly gaseous PCDD/F emissions somewhat, probably due to a cooling effect. Activated carbon beds such as the STEAG/a/c/t adsorber (7 Figure 6.4), operated at 100-150EC remove PCDD/Fs to below 0.03 ng/m<sup>3</sup><sub>STP</sub> TEQ (Brüggendick and Gilgen, 1996).

Recently, Tagashira *et al.* (1999) found a relation between baghouse filter removal efficiency for PCDD/Fs and filter entrance temperature, as shown in Figure 7.19: above ~ 180EC the efficiency starts to drop. This was explained by a larger fraction of gaseous PCDD/Fs at higher temperature, which pass the filter more easily. Earlier, Brna (1988) reported that a spray dryer absorber + ESP system may remove dioxins

by 48 % (TCDD) to 89 % (OCDD) and furans by 65 % (TCDF) to 85 % (OCDF). The higher chlorinated PCDD/Fs are probably removed more easily: apparently with increasing melting and boiling points a larger fraction is found in the particle phase.

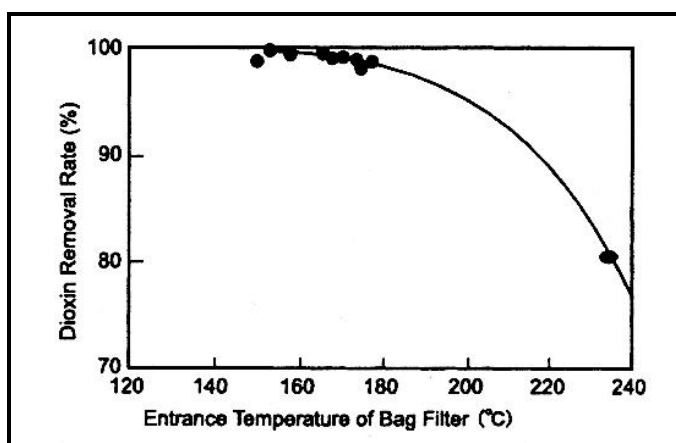


Figure 7.19 PCDD/F removal by a bag filter versus filter entrance temperature (Tagashira *et al.*, 1999)

Werther (1999) gave a comparison of dioxin and furan control options for waste incinerator flue gas clean-up as given in Table 7.10. An SCR for DeNO<sub>x</sub> provides both the ammonia that may deactivate potential Deacon reaction catalysts and the strong oxidation catalyst that may destroy PCDD/Fs. Also SNCR involves injection of nitrogen species that inhibit PCDD/F formation at lower temperatures. Methods based on solids injection rely partly on solid removal downstream by the dust control system. A mixture of 5 % carbon with lime was found to remove PCDD/Fs to below 0.1 ng/m<sup>3</sup><sub>STP</sub> TEQ during co-firing of packaging plastics with MSW on a grate (Mark and Vehlow, 1999).

**Table 7.10 Typical PCDD/F concentrations after various waste incinerator flue gas cleaning methods (data from Werther, 1999)**

Gas clean-up system	Exit PCDD/F concentration (ng/m <sup>3</sup> <sub>STP</sub> I-TEQ)
carbon injection	0.004 - 0.006
fixed bed char filter + SNCR	0.024 - 0.05
lime + char absorption	0.004 - 0.006
SCR catalytic oxidation	0.02 - 0.05
SNCR + carbon injection	~ 0.004
SCR + carbon injection	0.002 - 0.02

The residuals from PCDD/F control such as spent carbon filters or polluted catalysts are often classified as highly toxic hazardous wastes that need special after-treatment.

## 7.8 Other halogen compounds (HF, HBr, PBDD/Fs)

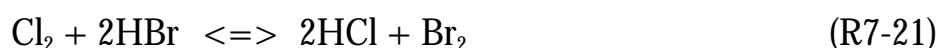
HF and HBr are the main fluorine and bromine species from thermal processing of fluorine or bromine containing fuels or wastes. They may be removed from gases simultaneously with, or using methods similar to, the removal of HCl although the removal efficiency is somewhat lower. Around 50-70 % HF removal and ~ 90% HBr removal were measured (against ~ 98% HCl removal) in an acid scrubber (pH=1) for flue gas cleaning for CFC containing insulation foam plastics incineration (Mark and Vehlow, 1999). Specific for fluorine was that it attacked silicates, hence not all fluorine was found in the flue gas. Recently also Yang (2000) reported that HF attacked silica oxides in baghouse filter bags, which became more serious with increasing condensation of moisture. Brna (1988) compared the removal of HCl and HF by various control systems as given in Table 7.11.

**Table 7.11 Control systems for HF and HCl (data from Brna, 1988)**

Process*	Temperature at outlet EC	HF removal %	HCl removal %
dry sorbent injection + fabric filter	160 - 180	98	80
spray dryer absorber + ESP	140 - 160	99	> 95
spray dryer absorber + fabric filter	140 - 160	99	> 95
spray dryer absorber + dry sorbent injection + ESP or fabric filter	~ 200	99	> 95
ESP + wet scrubber	104 - 122	99	> 95
spray dryer + wet scrubber + ESP or fabric filter	104 - 122	99	> 95

\* sorbent = sodium- or calcium- based sorbent

Bromine is found as flame retardants such as PBB (the bromine-analogue of PCB) PBDPE and TBBA (see Figure 7.1) in electric and electronic equipment. Upon incineration of brominated compounds the bromine will distribute over bottom ash, fly ash and flue gas as ~ 2%, ~ 20% and ~ 78% respectively. Removal of bromine is either as HBr by adsorption in water or by neutralisation with sodium or calcium hydroxide, forming NaBr or CaBr<sub>2</sub>. The first process is more feasible from a bromine recycling point of view (PBKD, 1999). These processes involve the risk of Br<sub>2</sub> emissions that needs further processing, for example when chlorine is present as well:



Finally, brominated dioxins and furans (PBDD/Fs) can be formed similar to their chlorinated analogues. Very little is known about their toxicity. For flame retardants such as polybrominated diphenylethers (PBDE) the chemical routes to PBDD/Fs are very short, as seen in Figure 7.20.

Experiments showed that up to 10% of the bromine from PBDEs can form PBDD/Fs when heated

to 510-630°C, giving *e.g.* concentrations of ~ 15 ppmw in deposits near a burned-out TV set after a residential fire (Stevens and Mann, 1999).

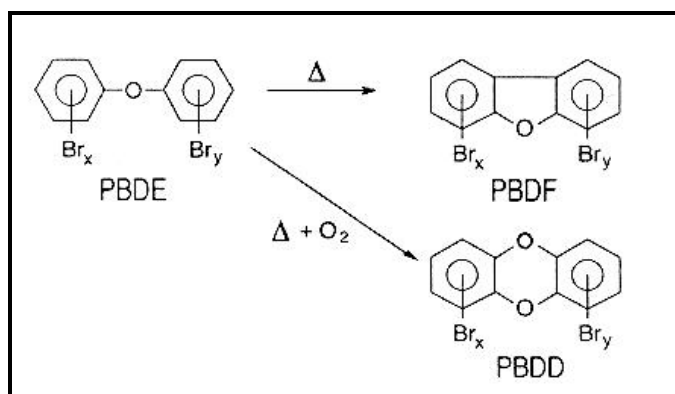


Figure 7.20 Formation of PBDD/Fs from PBDE flame retardants  $x+y=5,8$ , or 10 (picture from Scheirs and Camino, 1996)

Regarding the similarities between PBDD/Fs and PCDD/Fs, similar methods for their removal from gases (7 section 7.7) may be most suitable.

## 7.9 References

- Addink, R., Paulus, R.H.W.L., Olie, K. (1996) "Prevention of polychlorinated dibenzo-p-dioxins/furans formation on municipal waste incinerator fly ash using nitrogen and sulphur compounds" *Environ. Sci. Technol.* **30** 2350-2354
- Alderliesten, P.T. *et al.* (1990) "Systeemstudie hoge temperatuur gasreiniging bij KV-STEG systemen", ECN/KEMA/TNO-M&E/TU Delft, report ref. nr. 90-310 NOVEM Sittard (the Netherlands)
- Anthony, E.J., Bulewicz, E.M., Preto, F. (1994) "The combustion of halogenated wastes in FBC systems", *Proc. of the 49<sup>th</sup> Purdue Industrial Waste Conf.*, Lewis Publ. Chelsea (MI), pp. 673-679
- Anthony, E.J., Bulewicz, E.M., Preto, F. (1993) "The effect of halogens on FBC systems", *Proc. of the 12<sup>th</sup> Int. Conf. on FBC*, San Diego (CA), May 1993, L.N. Rybow (Ed.), ASME, New York, pp. 41-52
- ASME (1995) Rigo, H.G., Chandler, A.J., Lanier, W.S. "Relationship between chlorine in waste streams and dioxin emissions from combustors of the ASME Research Committee on industrial and municipal wastes" Report CRTD-Vol 36, ASME New York
- Björkman, E., Strömberg, B. (1997) "Release of chlorine from biomass at pyrolysis and gasification conditions", *Energy & Fuels* **11** 1026-1032
- Brna, T.G. (1988) "State-of-the-art flue gas cleaning technologies for MSW incineration" *AIChE Symp. Series* **265(84)** 127-140
- Bryers, R.W. (Ed.) (1991) "Incinerating municipal and industrial waste" Hemisphere Publ., New York

- Bryers, R.W. (1996) "Fireside slagging, fouling and high temperature corrosion of heat-transfer surfaces due to impurities in steam-raising fuels", *Prog. Energy Combust. Sci.*, **22** 29-120
- Brüggendick, H., Gilgen, R. (1996) "Adsorption technology brings waste incinerators into compliance - STEAG's /a/c/t™ process in European facilities" ACS Division of Fuel chemistry, Vol. 41 No. 1 (211<sup>th</sup> ACS National Meeting, New Orleans (LA), March 1996) pp. 399-403
- Cains, P.W., McCausland, Fernandes, A.R., Dyke, P. (1997) "Polychlorinated dibenzo-p-dioxines and dibenzofurans in incineration: effects of fly ash and carbon source" *Environ. Sci. Technol.* **31** 776-785
- Chlorophiles (1996) "Chlorine emissions and dioxin emissions"
- Christholm, P.N., Rochelle, G.T. (1999) "Dry adsorption of HCl and SO<sub>2</sub> with hydrated lime from humified flue gas", *Ind. & Eng. Chem. Res.* **38** 4068-4080
- CIEMAT (1998?) "Flue gas cleaning" European Commission DG XVII Clean Coal Technology Handbook, Section 5, Madrid/Brussels
- CLPSD (1998) Contract Laboratory Program Statistical Database, Viar & Co Alexandria (VA) USA
- Davidson, R.M. (1996) "Chlorine and other halogens in coal" IEA Coal Research, Report IEAPER/28, London
- Desroches-Ducarne, E., Dolgnier, J.C., Marty, E., Martin, G., Delfosse, L. (1998) "Modelling of gaseous pollutants emissions in circulating fluidised bed combustion of municipal refuse", *Fuel* **77** 1399-1410
- Desroches-Ducarne, E. (1997) "Étude de devenir des polluants gazeux lors de 'incinération d'ordures ménagères en lit fluidisé circulant" Ph.D. thesis, Université de Haute Alsace, France
- Duo, W., Kirby, N.F., Seville, J.P.K., Kiel, J.H.A., Bos, A., den Uil, H. (1996) "Kinetics of HCl reactions with calcium and sodium sorbents for IGCC fuel gas cleaning", *Chem. Eng. Sci.* **51(11)** 2541-2546
- Düsenberg, Harz, Helmers, Röpe, Rizk, Scheffknecht (1997) "Operational reliability, advantages and potentials for improvement of the fluidised bed combustion for coal", in: *The future of fluidised bed combustion*, VGB report TW 212e, VGB-Kraftwerkstechnik GmbH, Essen, Germany
- ETSU (1998) "Integrated hot fuel-gas cleaning for advanced gasification with combined cycle processes", Project summary 166, ETSU, Harwell, UK
- Finland (1994) Government decision 626/1994 (1.8.1994)
- Fonseca, A.M., Órfão, J.J., Salcedo, R.L. (1998) "Kinetic modelling of the reaction between HCl and solid lime at low temperatures" *Ind. & Eng. Chem. Res.* **37** 4570-4576
- Foster Wheeler (1997) *Heat Engineering*, Spring 1997
- Frankenhaeuser, M., Hiltunen, M., Manninen, H., Palonen, J., Ruuskanen, J., Vartiainen, T. (1994) "Emissions from co-combustion of used packaging with peat and coal" *Chemosphere* **29(9-11)** 2057-2066
- Greenpeace (1997) Costner, P. "PVC - The poison plastic - The burning question Chlorine and dioxin" <http://www.greenpeaceusa.org/reports/toxics/PVC/burning/rigotoc.html>
- Gullett, B.K., Jozewicz, W., Stefanski, L.A. (1992) "Reaction kinetics of Ca-based sorbents with HCl" *Ind. & Eng. Chem. Res.* **31** 2437-2446
- Gupta, R.P., O'Brien, W.S. (2000) "Desulphurisation of hot syngas containing hydrogen chloride vapors using zinc titanate sorbents" *Ind. & Eng. Chem. Res.* **39** 610-619



- Harrison, D.P. (1993) "Control of gaseous contaminants in IGCC processes, an overview", in Proc. of the 12<sup>th</sup> Ann. Int. Pittsburgh Coal Conf., S.-H. Chiang (Ed.), Pittsburgh (PA), Sept. 1995 pp. 1047-1052
- Hatanaka, T., Imagawa, T., Takeuchi, M. (2000) "Formation of PCDD/Fs in artificial solid waste incineration in a laboratory-scale fluidised-bed reactor: influence of contents and forms of chlorine sources in high-temperature combustion" *Environ. Sci. Technol.* **34** 3920-3924
- Hedemalm, P., Carlsson, P., Palm, V. (1995) "Waste from electrical and electronic products", Nordic Council of Ministers, Report TemaNord 1995:554, Copenhagen Denmark
- Hong, C.C., Opatrny, J.C., Sanyal, A., Sommer, T.M., Folsom, B.A., May, T.J., Krueger (1993) "HCl-HF removal by sorbent injection" Proc. of the 10th Ann. Int. Pittsburgh Coal Conf., S.-H. Chiang (Ed.), Pittsburgh (PA) 838-845
- Huotari, J., Vesterinen, R. (1995) "Muut polton päästöt", Chapter 11 in: "Poltto ja palaminen", R. Raiko, *et al.*, (Eds.), IFRF Finland, Gummerus, Jyväskylä, Finland
- Huotari, J., Vesterinen R. (1996) "PCDD/F emissions from co-combustion of RDF with peat, wood waste, and coal in FBC boilers" *Hazardous Waste & Hazardous Materials* **13**(1) 1-10
- Julien, S., Brereton, C.M.H., Lim, C.J., Grace, J.R., Anthony, E.J. (1996) "The effect of halides on emissions from circulating fluidised bed combustion of fossil fuels", *Fuel* **75**(14) 1655-1663
- Kiel, J.H.A. (1997) "Dry halides removal process for entrained-flow gasification based IGCC concepts", presented at the UK-DTI Workshop "Removal of gaseous contaminants from hot fuel gases", Milan, Italy (February 1997)
- Krishnan, G.N., Gupta, R.P., Canizales, A., Shelukar, S., Ayala. R. (1996a) "Removal of hydrogen chloride from hot coal gas streams", in: High temperature gas cleaning, R. Schmidt *et al.*, (Eds.), Karlsruhe, 405-414
- Krishnan, G.N., Gupta, R.P., Canizales, A., Ayala. R. (1996b) "Development of disposable sorbents for chloride removal from high-temperature coal-derived gases" *Adv. Coal-fired Power Systems Review Meeting '96*, Morgantown, (WV), June 1996
- Krupp VDM (1999?) "Thermische Abfallverwertung - Verfahren - Werkstoffe - Case Histories" Krupp VDM, Werdohl, Germany
- Liang, D.T., Anthony, E.J., Loewen, B.K., Yates, D.J. (1991) Proc. of the 11<sup>th</sup> Int. Conf. on FBC, Montreal, Canada, May 1991, E.J. Anthony (Ed.), ASME, New York, pp. 917-922
- Liu, K., Pan, W.-P., Riley, J.T. (2000) "A study on chlorine behaviour in a simulated fluidised bed combustion system" *Fuel* **79** 1115-1124
- Mark, F., Vehlow, J. (1999) "Co-combustion of end of life plastics in MSW incinerators", APME, Brussels
- Murena, F., Schioppa, E., Gioia, F. (2000) "Catalytic hydrodechlorination of a PCB dielectric oil", *Environ. Sci. Technol.* **34** 4382-4385
- Nielsen, H.P., Frandsen, F.J., Dam-Johansen, K., Baxter, L.L. (2000) "The implications of chlorine-associated corrosion on the operation of biomass-fired boilers" *Progr. Energy Combust. Sci.* **26** 283-298
- Nieminen, M., Kangasmaa, K., Laatikainen-Luntama, J., Kurkela, E. (1997) "Integrated hot fuel gas cleaning for advanced gasification combined cycle: halogen control in integrated hot gas cleaning", Final Report EU Joule II contract JOU2-CT93-0431
- Nunokawa, M., Kobayashi, M., Shirai, H. (1999) "Hydrogen chloride removal from hot coal-derived gas with sodium-based sorbents" in: "High temperature gas cleaning", Vol. II, 1999, A. Dittler, G. Hemmler, G. Kasper (Eds.), University of Karlsruhe, Germany, pp. 627-640

- Olie, K., Addink, R., Schoonenboom, M. (1997) "Metals as catalysts during the formation and decomposition of chlorinated dioxins and furans in incineration processes" *J. Air & Waste Manage. Assoc.* **48** 101-105
- PBKD (1999) "Recovery of bromine & energy from waste electrical & electronic equipment containing bromine in European Union", PB Kennedy & Donkin Ltd, Report BECCH074.1071, May 1999, Chester, UK
- Procaccini, C., Bozzelli, J.W., Longwell, J., Smith, K.A., Sarofim, A.F. (2000) "Presence of chlorine radicals and formation of molecular chlorine in the post-flame region of chlorocarbon combustion" *Environ. Sci. Technol.* **34** 4565-4570
- Ruokojärvi, P.H., Halonen, I.A., Tuppurainen, K., Tarhanen, J., Ruuskanen, J. (1998) "Effect of inhibitors on PCDD/F formation" *Environ. Sci. Technol.* **32** 3099-3103
- Rutkowksi, M.D., Klett, M.G., Zaharchuk, R. (1996) "Assessment of hot gas contaminant control", *Adv. Coal fired Power Systems '96 Review Meeting*, Morgantown (WV), June 1996
- Ruuskanen, J., Vartiainen, T., Kojo, I., Manninen, H., Oksanen, J., Frankenhaeuser, M. (1994) "Formation of polychlorinated dibenzo-p-dioxines and dibenzofurans in co-combustion of mixed plastics with coal: exploratory principal component analysis" *Chemosphere* **28**(11) 1989-1999
- Ryan, J.V., Gullett, B.K. (2000) "On-road emission sampling of a heavy-duty diesel vehicle for polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans" *Environ. Sci. Technol.* **34** 4483-4489
- Scheirs, J., Camino, G. (1996) "Effect of contamination on recycling of polymers" in: *Recycling of PVC and mixed plastics waste*, F.P. LaMantia (Ed.) ChemTec Publ., Toronto, Canada, pp. 167-183
- Seeker, Wm. R. (1990) "Waste incineration", *Proc. of the Combustion Institute*, The Combustion Institute, Pittsburgh (PA) 867-885
- Shao, D., Hutchinson, E.J., Cao, H., Pan, W.-P., Chou, C.-L. (1994) "Behaviour of chlorine during coal pyrolysis" *Energy & Fuels* **8** 399-401
- Shin, D., Choi, S., Oh, J.-E., Chang, Y.-S. (1999) "Evaluation of polychlorinated dibenzo-p-dioxin /dibenzofuran (PCDD/F) emission in municipal solid waste incinerators" *Environ. Sci. Technol.* **33** 2657-2666
- Stevens, G.C., Mann, A.H. (1999) "Risks and benefits in the use of flame retardants in consumer plastics" report URN98/1026 for UK DTI/Consumer Safety, University of Surrey, Guildford, UK
- Tagashira, K. *et al.* (1999) "Combustion characteristics and dioxin behavior of waste fired CFB" *Chem. Eng. Sci.* **54** 5599-5607
- Tuppurainen, K., Halonen, I., Ruokojärvi, P., Tarhanen, J., Ruuskanen, J. (1998) "Formation of PCDDs and PCDFs in municipal waste incineration and its inhibiting mechanisms: a review", *Chemosphere* **36**(7) 1493-1511
- UN (1998) "Draft protocol to the convention of long-range transboundary air pollution on persistent organic pollutants" United Nations, Economic and social council, report EB.AIR/1998/2, Århus, Denmark, June 24, 1998
- Vassilev, S.V., Eskenazy, G.M., Vassileva, C.G. (2000a) "Contents, modes of occurrence and origin of chlorine and bromine in coal" *Fuel* **79** 903-921

- Vassilev, S.V., Eskenazy, G.M., Vassileva, C.G. (2000b) "Contents, modes of occurrence and behaviour of chlorine and chlorine in combustion wastes from coal-power stations" *Fuel* **79** 923-937
- Weinell, C.E., Jensen, P.I., Dam-Johansen, K., Livbjerg, H. (1992) "Hydrogen chloride reaction with lime and limestone: kinetics and sorption capacity" *Ind. & Eng. Chem. Res* **31** 164-171
- Werther, J. (1999) "Legal requirements on gaseous emissions from waste combustion and are these fulfilled?" lecture at 1999 Finnish Waste-to-Energy course, Part 2, Turku, Finland Oct. 1999
- WHO (1996) "Updating and revision of the air quality guidelines for Europe"; World Health Organisation, Regional office for Europe, Copenhagen, Denmark, Report EUR/ICP/EHAZ 94 05/MT12
- Wilén, C. (1999) "Production of refuse-derived fuels" lecture at 1999 Finnish Waste-to-Energy course, Part 1, Espoo, Finland, Oct. 1999
- Xie, W., Liu, K., Pan, W.-P., Riley, J.T. (1999) "Interaction between emissions of SO<sub>2</sub> and HCl in fluidised bed combustors" *Fuel* **78** 1425-1436
- Xu, J., Xiw, W., Han, W., Dicken, L., Riley, J.T., Pan, W.-P. (1998) "The effect of chloride on emissions from atmospheric fluidised bed combustors" *Proc. of the 215 ACS National Meeting*, March-April 1998, Dallas (TX), Vol. 43 No. 1 pp. 152-156
- Yang, Z. (2000) "The effects on baghouse filter bags during the incineration of high-fluoride wastes" *Powder Technol.* **108** 160-163
- Yasuhara, A., Katami, T., Okuda, T., Ohno, N., Shibamoto, T. (2001) "Formation of dioxins during the combustion of newspapers in the presence of sodium chloride and polyvinyl chloride" *Environ. Sci. Technol.* **35**(7) 1373-1378
- Zevenhoven, R., Axelsen, E.-P., Hupa, M. (2001) "Pyrolysis of waste-derived fuel mixtures containing PVC" *Fuel* *submitted*
- Zevenhoven, R., Saeed, L., Fogelholm, C.-J. (2000) "Optimisation of a two-stage combustion process for high-PVC solid waste with HCl recovery", in: *Proc. of ECOS 2000, Int. Conf. on Efficiency, Cost, Optimisation, Simulation and Environmental Aspects of Energy and Energy Systems*, Enschede, the Netherlands, July 2000, Vol. 4 pp. 1959-1970

