CHAPTER 8 - FATE OF ELEMENTS DURING INCINERATION

The municipal solid waste stream consists of components containing an almost unlimited number of chemical compounds and virtually every element. The intent of burning this waste is to destroy the organic constituents and to convert the inorganic species into essentially inert materials. Since all chemical processes are controlled by equilibria, complete conversion may not be achievable in some cases. Furthermore, side-reactions may take place causing the production of unwanted by-products.

Many transformations in the combustion chamber or in the resulting residues from an incinerator may produce compounds which have the potential to impact on the environment through contamination of air, soil or groundwater. These reactions have to be minimised by appropriate control of the combustion process and all other processes associated with MSW incineration and/or by adequate treatment of post-combustion residues.

To develop suitable technical measures to minimise the potential environmental impact, the behaviour of the elemental species in each part of the incinerator should be understood. This chapter is a compilation of the present knowledge in this field. Much of the focus has been placed on the elements which are of greatest concern, either because of their concentration or their toxicity. The elements have been classified based on their partitioning between the different residue streams of an incinerator facility.

Matrix or lithophilic elements are those elements which are considered tightly fixed in the waste fuel. Although they may undergo chemical or geochemical changes on the grate during combustion, the greatest proportion appears in the bottom ash.

Volatile elements are subdivided into two groups: elements forming acid gases, like halogens or sulphur, and volatile trace metals. Both these groups of elements account for the major release of contaminants into the flue gas stream.

The difference between matrix or volatile elements is caused by the different vapour pressure curves of the individual elements or their compounds, which implies that the most dominant influence in ash chemistry is the temperature in the fuel bed.

A third group is represented by the organic compounds. Due to their thermal instability, organics are virtually totally destroyed during combustion. However, special trace by-products may have the ability to synthesise new compounds during the cooling phase of the flue gases and thus may cause difficulties with contamination of the different output streams of an incinerator.

Much of the data presented here are gleaned from several research programs or investigations of full scale incinerators. The attempt is made to interpret the observed effects based on the chemical and physico-chemical properties of the elements and on the temperature dependent vapour pressure equilibria.

8.1 MECHANISMS CONTROLLING THE FATE OF ELEMENTS

8.1.1 Fundamentals

In order to adequately describe the chemical reactions and physico-chemical transformations which control the behaviour of elements and compounds during incineration, a fundamental knowledge of the physical parameters, chemical concentrations and the speciation of elements is required. Although most of the important physical parameters, such as temperature and pressure can be measured, not all of them can be measured to the degree of accuracy needed for physico-chemical calculations. Much of the attention given here is to the measurement of temperature, since it controls nearly all other physical parameters, especially the essential vapour pressures, as well as the chemical equilibria and the kinetics of chemical reactions.

Temperatures in the gas phase of combustion chambers are well documented and are subject to legislative regulations. The bed temperature and the pertinent residence time of the bed material are the most important measurements for calculating the release rates of thermally mobile species. Both parameters influence the extent of immobilisation of elemental phases in the bottom ash. Unfortunately, there is a dearth of accurate data of fuel bed temperatures which are required to understand some of the reactions which take place. Although recent speciation data suggest that localised areas of the fuel bed can reach substantially higher temperatures than 1,000°C (Eighmy, 1993), we have assumed that average temperatures on the burning section of the grate of a modern mass burning MSW incinerator is between 800 and 1,000°C.

Nearly all chemical compounds of importance are well characterised. Their behaviour is controlled by natural laws and can be predicted if certain parameters are established. The current knowledge is based on investigations in ideal systems, i.e., low quantities of one or a few compounds in well-defined closed systems. If concentrations or numbers of reactants or both increase, the exact correlations fail and the measured effects can only be approached by introduction of activity coefficients that try to describe unknown interactions.

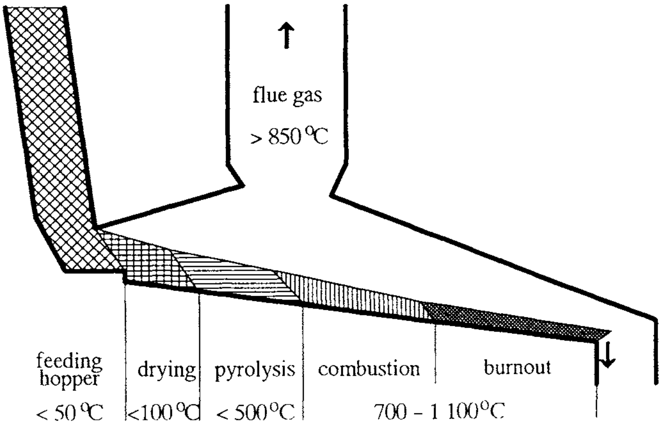
The concentrations of elements, especially their local distribution, show substantial variations. Waste is not only a physically but also a chemically inhomogeneous material. Consequently, the application of chemical and physical laws on elements in the field of municipal solid waste incineration is limited. Most of the following is based on best practical knowledge.

8.1.2 Processes in the Combustion Chamber

Physical Parameters

As described in Chapter 3, there are a great variety of incineration technologies in use today, all sharing some common processes. In most systems, the temperature of the untreated waste charged to the furnace is similar to the ambient temperature of the storage pit. As the waste moves down the grate, it heats up to temperatures above the point of ignition. The schematic in Figure 8.1 illustrates the pronounced temperature profile established along the grate and also between the top and bottom of the fuel bed on the grate. In most countries, the minimum gas temperature must exceed 800 to 850°C, although the maximum temperature is normally kept below 1,100°C to prevent corrosion of the walls of the combustion chamber and the heat recovery system.

Figure 8.1 Temperature Zones on the Grate



The radiant heat emitted from the hot furnace walls and burning waste causes a temperature profile across the depth of the fuel bed with higher temperatures on top and lower temperatures at the bottom. As the waste is exposed to these temperatures, the moisture is driven off into the flue gas. Further heating of the dried waste increases the temperature of the fuel to some 100°C and pyrolysis of organic compounds starts. At about 500°C, the ignition temperature is reached and the waste combusts. The remaining part of the grate is used to achieve a good burnout by extending the residence time of the waste to high temperatures.

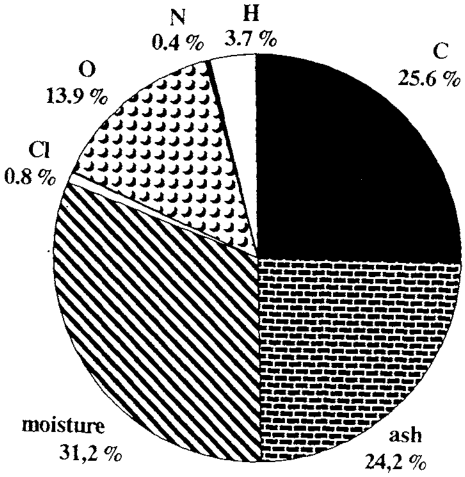
The maximum temperature in the fuel bed is generally found at the transition zone between the combustion and burnout zone. The maximum temperature in the gas phase is just above the top of the flame bed, downstream of the secondary air injection ports. For safety reasons, the combustion chamber is designed to operate under a slightly negative pressure. Since all of the physico-chemical parameters are a function of pressure, the following calculations are based on standard pressure as a first approximation.

Chemical Reactions

Reactions of Main Waste Components

The energy production in the combustion chamber is essentially caused by the exothermic oxidation of the carbon and the hydrogen inventory of the waste. An ultimate analysis of municipal solid waste is seen in Figure 8.2

Figure 8.2 Ultimate Analysis of Waste



Adapted from Environment Canada, 1988

In the drying zone of the grate, no chemical reactions of importance are to be expected. The mean humidity of waste is in the order of 30% and the evaporated water adds about 60 g/Rm^3 to the water content of the flue gas. While the temperature increases, highly volatile organic and/or inorganic compounds may be transferred into the gas phase. However, these products will not survive when they pass through the hot zones of the incinerator and thus will not appear in the flue gas in their initial gas phase form.

In the pyrolysis zone at temperatures above 200°C, most organic compounds start to disintegrate. The decomposition products are volatile or semi-volatile organic compounds, tar, and elementary carbon. The volatile species are oxidised in the gas phase, at least in the post-combustion region and can account for the major energy release in the furnace. The fixed carbon is burned on the grate in the combustion zone. Due to the overall oxygen surplus and the high stability of oxides of most elements, oxidation processes will be the predominant reactions in the fuel bed and in the gas phase of the combustion chamber.

The most important oxidation reactions are those of carbon and organic carbon compounds. The most stable oxidation product up to very high temperatures is CO_2. In all cases, the first oxidation step results in the intermediate product CO which has to be suppressed and will be oxidised to CO_2 if an oxygen surplus can be maintained. As an example, the oxidation of graphitic carbon is given:

$$2\ C_{graphite} + O_2 \rightleftharpoons 2\ CO \qquad (8.1)$$

$$2\ CO + O_2 \rightleftharpoons 2\ CO_2 \qquad (8.2)$$

The equilibrium between CO and CO_2 [equation (8.2)] is shifted toward CO with increasing temperature, but at 1,200°C (commonly not exceeded in waste combustion) only about 0.03% of the CO_2 molecules are dissociated (Remy, 1961).

Another process, the Boudouard reaction, may be responsible for enhanced CO concentrations in the flue gas:

$$C_{solid} + CO_2 \rightleftharpoons 2\ CO \qquad (8.3)$$

If equilibrium could be reached at 900°C, about 97% of the gaseous compounds would be present as CO. Fortunately this reaction is kinetically hampered and at temperatures below 800°C, without the presence of catalysts, reaction rates cannot be measured. However, in ash deposits in the boiler where diffusiophoresis (see Chapter 10) is a controlling factor, long residence times in combination with catalytic ingredients of the ashes may be responsible for a certain portion of the CO production.

The equilibrium in equations (8.2) and (8.3) indicate that the production of CO can be minimised if care is taken to ensure proper oxygen distribution in the combustion zone and if the release of particulate carbon into the flue gas can be avoided. Under these conditions, virtually all of the carbon in the waste (about 25%) should be transformed to CO_2 and result in concentrations of about 130 g/Rm^3 in the flue gas. In properly operated MSW incinerators, the CO emissions can easily be kept below 50 mg/Rm^3.

The next most important element due to its concentration is hydrogen. Hydrogen is present in all organic compounds. The total inventory is transformed into the only stable oxidation product, H_2O. To quantify the production, a mean hydrogen concentration in the waste of about 36 kg/tonne (see Figure 8.2) corresponds with a C/H-ratio of about 7.5 (Tillman et al., 1989; Behrendt, 1992). The resulting water concentration in the flue gas is in the order of 65 g/Rm^3 which adds to the 60 g/Rm^3 of water evaporated in the drying zone of the grate.

The third most important element (compare Figure 8.2) is chlorine, which cannot be oxidised due to the similarity of its electronegativity to that of oxygen. During incineration, the chlorine favours the oxidation state of -1. The chlorine compounds leaving the combustion chamber are inorganic chlorides, or HCl. Since there is no elementary hydrogen available in the combustion chamber, the HCl is formed by secondary reactions like hydrolysis.

Reactions Controlling the Alkalinity

The water formed during incineration may be very aggressive to other compounds not altered by the oxygen attack resulting in secondary hydrolytic reactions. In most cases, those reactions result in the formation of hydroxides which contribute to the alkalinity of the solid residues. These reactions have a major influence on the fate of alkali and earth-alkali elements. Normally, the chlorides of these elemental groups are thermally very stable. However, in the presence of water, hydrolysis takes place. The earth-alkali chlorides are less stable than the alkali salts. $CaCl_2$*6 H_2O can even be hydrolysed by its own crystal water at temperatures above 260°C if it is heated rapidly:

$$CaCl_2 + H_2O \rightleftharpoons CaO + 2\,HCl \qquad (8.4)$$

The product CaO is a strong base if brought into contact with water.

Many compounds, especially heavy metal salts, are also sensitive to hydrolytic reaction at elevated temperatures. Other inorganic salts in the waste do not survive the combustion process due to their limited thermal stability. A well-known example in the building industry is the burning of lime:

$$CaCO_3 \rightleftharpoons CaO + CO_2 \qquad (8.5)$$

With the exception of the alkali compounds, all other carbonates are sensitive to thermal decomposition, forming CO_2 and the respective oxide. In the case of the earth-alkali carbonates, the thermal stability increases with the atomic number. $MgCO_3$ and $CaCO_3$ decompose at about 550°C and 897°C respectively, whereas more than 1,400°C is required to destroy $BaCO_3$. This is another reaction which may contribute to the alkalinity of the combustion residues.

Sulphates (with the exemption of the alkali compounds) can be thermally decomposed, forming SO_x compounds in the flue gas. The most sensitive sulphates are those of trivalent metals, such as Al or Fe:

$$2\,Al_2(SO_4)_3 \rightleftharpoons 2\,Al_2O_3 + 6\,SO_3 \qquad (8.6)$$

The disintegration temperatures of $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ are about 750°C and 720°C, respectively. If water is present in the flue gas of the combustion chamber, hydrolytic attack is also observed and the decay of these compounds may start at about 550°C.

In some cases, the high temperatures decompose sulphates and form SO_2 and O_2, instead of SO_3.

In the cooling regions on the grate, or in the flue gas stream, many of the described equilibria shift back, forming the original compounds. In most cases, however, the gaseous reaction product is no longer present and the reaction cannot be reversed.

Oxides or hydroxides released as dust particles from the fuel bed have a certain probability to react with acid gas components like HCl, SO_2, and CO_2. Generally, the high concentration of CO_2 drives the reaction toward the formation of carbonates, and hence provides a level of buffering capacity to the residues. This is consistent with evidence that ash particles from different ash streams (that have short residence times in the flue gas stream) have acid neutralisation capacities within the same order of magnitude (Sawell and Constable, 1988).

Reactions of Heavy Metals

The complex behaviour of heavy metals and other trace elements during incineration has been modelled qualitatively based on Gibbs' fundamental equation (Borchers, 1989):

$$G = H - T * S \tag{8.7}$$

where:
G = molar free enthalpy H = molar enthalpy
T = temperature S = molar entropy

Using thermodynamic data, the temperature dependencies of the standard formation enthalpies (ΔG^0) can be calculated using the Gibbs-Helmholtz equation:

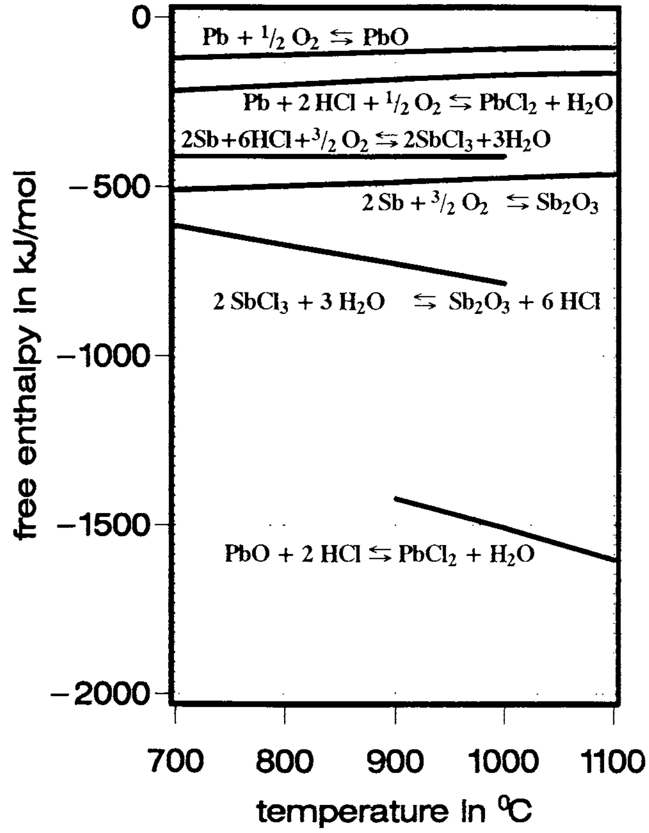
$$\Delta G^0 T = \Delta H^0_{298} + \int \Delta c_p \, dT - T \, \Delta S0_{298} - T \int \Delta c_p / T \, dT \tag{8.8}$$

where: c_p = molar heat at constant pressure.

The calculation must include all compounds of an element which can theoretically be formed under the respective conditions. The basic data needed for the calculation can be found in the literature (Barin, 1993). It is assumed that the residence time allows the system to reach equilibrium.

The comparison of the calculated free enthalpies gives an indication of which compound is the most stable and will drive the thermochemical reactions. For example, the calculated free formation enthalpies of reactions for elemental lead and antimony in the temperature range between 700 and 1,100°C are shown in Figure 8.3. To concentrate on the most important reactants in the combustion chamber, only reactions with oxygen, H_2O and HCl have been taken into account. Clearly, metallic lead and lead oxide prefer to react with HCl. $PbCl_2$ is the most stable combustion product in the temperature range illustrated. Although these calculations explain the behaviour of these lead compounds, similar calculations have to be carried out using all other species of lead present in the waste to provide an overall indication of the element's behaviour.

Figure 8.3 Free Formation Enthalpies of Some Pb and Sb Compounds



In the case of antimony, the differences in formation enthalpies are not as high as lead, and therefore the prediction of its behaviour is more difficult. The enthalpies of the reactions with O_2 and with Cl are similar. The resulting $SbCl_3$ may be hydrolysed, however, the actual residence times and the kinetics will limit the importance of this reaction. It must be assumed that $SbCl_3$ and Sb_2O_3 will be the most dominant products of combustion.

There is another type of reaction in the fuel bed with the potential to form volatile species. This is the solid state reaction between inorganic salts involving the exchange of cations. For example:

$$2\ NaCl + ZnSO_4 \rightleftharpoons ZnCl_2 + Na_2SO_4 \qquad (8.9)$$

The reaction given in Eq. (8.9) transforms the immobile $ZnSO_4$ into $ZnCl_2$ which can be vaporised in the combustion chamber. The formation enthalpy of this reaction is in the order of 8 kJ/mole at 400°C (Lieser and Elias, 1962). The probability of such reactions can hardly be calculated due to the unknown speciation as well as the unknown local distribution of these species. If the respective species come into contact, however, the yield will be high due to the long residence time on the grate. It should be mentioned that this type of reaction can also take place in the heat recovery system and in other parts of the flue gas system where elevated temperatures prevail.

Thermodynamic data are useful to estimate the integral reactions. It must be emphasised that limitations arise because there is a lack of data about the kinetics of the reactions and the conditions for the chemical reactions (i.e. temperature and local concentrations) change substantially down the burning grate. A great deal of complex information would be required to accurately model the reactions which do occur under the variable conditions.

Most reactions are prevented from reaching equilibrium. For example, if a solid piece of oxidisable metal is present in the combustion chamber, the oxidation starts at the surface by forming an oxide layer. If oxidation is to continue, the oxygen must reach the surface of the elemental metal first, which can only be facilitated by diffusion. Since the oxide layer is a dense structure, it inhibits the diffusion and thus protects the metal from further oxidation. Consequently, many metals and alloys, especially in bulky form, pass through the combustion chamber virtually unaltered by the process. Aluminum, antimony, copper, iron, nickel, titanium and lead all belong to this group.

Although this is true for most metals, metals with relatively low melting points present an even more complicated set of reactions. For example, the respective melting point temperatures of aluminum and lead are 660.4°C and 327.5°C. Even if a dense protective oxidised layer forms, the metallic nucleus may melt prior to further oxidation and result in molten material dropping through the grates to solidify as a metallic mass in the under-grate hoppers. A substantial amount of metallic aluminum and lead can be observed in grate siftings (Environment Canada, 1991; WASTE Program, 1993).

The presence of metallic aluminum in grate siftings has two potentially detrimental affects. The first is that mixing grate siftings with bottom ash in the quench tank results in the formation of aluminum hydroxide and the liberation of hydrogen from the quench tank. As a result, most facilities provide adequate ventilation above the quench tank to avoid a dangerous build-up of the gas. The second potential problem occurs when grate siftings end up in a utilisation scenario, such as in a road base. The formation of aluminum hydroxide results in an expansion of the material, which could cause undesirable heaving in localised areas. These disadvantages support recommendations suggesting that grate siftings be collected separately from bottom ash, especially if bottom ash is to be utilised (Vehlow et al., 1990).

If the primary combustion products are stable at the temperatures in the combustion chamber, the shape of their vapour pressure curves will ultimately dictate their further behaviour. The nonvolatile products may be incorporated into either the ashes in their original species or they may undergo further reactions forming compounds of greater stability. In most cases, these are reactions between metals and nonmetallic oxides, or solid phase reactions, which are controlled by solid state diffusion and have moderate velocities even at elevated temperatures. Nevertheless, they contribute substantially to the chemical stability of bottom ash.

Volatile species are released from the fuel bed into the gas phase. Among these are pure metals which have low boiling points or at least vapour pressures high enough to be evaporated. Such is the case for aluminum. This is evident from the liberation of hydrogen from filter ashes contacted with acids or even with water (Oberste-Padberg and Schweden, 1990). A very simple example of the transfer of pure metals into fly ash is the burning of aluminum foil which results in entrainment of small pieces of foil in the flue gas stream.

Pure metals such as cadmium (b.p. 765°C), mercury (b.p. 356.6°C) and zinc (b.p. 907°C), are very likely to be volatilised during incineration. Although these metals should not be stable in the metallic state at high temperatures, a small fraction of metal vapour might survive and condensate on the dust particles at lower temperatures. The same is true for lead, however, the vapour pressure is about 1 hPa at a temperature of 950°C, and volatilisation is less likely to occur.

Another reason which might explain the presence of metallic forms of metals on the surfaces of fly ash is that these volatile compounds may decompose into radicals and/or atoms when passing the regions of highest temperature in the gas phase. Some iodides of heavy metals, some oxides (e.g. Pb_3O_4) and carbonyls (e.g. $Ni(CO)_4$) are, to a substantial degree, thermally dissociated into the metals and other ionic or radical groups. In the case of iodides and carbonyls, quick condensation onto particles may enable some of the metals to be absorbed in the metallic state on appropriate surfaces.

All these reactions are dependent on a number of variables, including the localised temperature in the fuel bed, the local distribution of the element and the speciation of reactants. The inhomogeneity prevents the adjustment of chemical equilibria and thus only allows the prediction of gross trends. These trends, based on extended laboratory, semi-technical and full scale research programs as well as operational experience, are discussed in more detail for selected elements later in this chapter.

Sintering and Related Processes

The conditions in the combustion chamber control the chemical reactions, which in turn dictate the reactivity or stability of the combustion products. To a certain extent, changes in the stability of solid residues can be achieved alone by changes in physico-chemical parameters without changing the nature of the chemical bond. The best-known cases are phase transfers in single phase materials, induced by changes in temperature. For example, the sequence of stable SiO_2 modifications with increasing temperature is:

$$\alpha\text{-quartz} \overset{575^{\circ}C}{\rightleftharpoons} \beta\text{-quartz} \overset{870^{\circ}C}{\rightleftharpoons} \beta\text{-tridymite} \overset{1470^{\circ}C}{\rightleftharpoons} \beta\text{-cristobalite}$$

If the cooling down of those materials is fast, as in the case of bottom ash quenching, some high temperature modifications can be frozen.

Residues from waste incineration are in most cases multi-phase, multi-component products. This applies especially to bottom ash. Although the temperatures in the fuel bed are generally below the melting points of the main constituents of bottom ash, a certain proportion of annealing can take place, resulting in changes to the physical and chemical properties of ash.

In masses of powders and compacted porous material, the application of heat causes bonding of particles and diffusion transport of material across particle surfaces, ultimately resulting in:

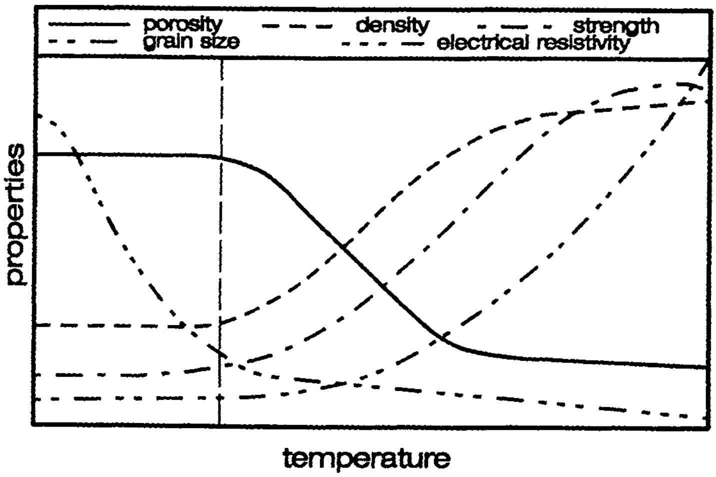
- changes in pore structure and porosity
- strengthening
- densification
- crystal grain growth ("Oswald ripening")
- changes in electrical resistivity and other parameters.

A fundamental scheme of the changes that can occur for some physical parameters is illustrated in Figure 8.4. In a porous or powdery material, the porosity starts to decrease at a certain temperature. Simultaneously the density and strength increase. Other effects, like the electrical resistivity, start to vary substantially, even at lower temperatures. This effect is called "sintering" and it is used industrially in (metal) powder technology and in the production of special ceramics.

The definitions of sintering vary considerably between authors because of the complexity of the process, the different mechanisms which cause sintering and the different properties which are affected (Hausner, 1979). Furthermore, there are a number of different types of sintering, including cold sintering, pre-sintering, high sintering, pressure sintering, solid state sintering, liquid phase sintering, etc. This discussion will focus on sintering effects which are essential factors in the solid state reactions on the grate.

If the original material is chemically homogeneous, sintering affects only the crystal lattice via self-diffusion of atoms or molecules across the boundaries of adjacent grains. However, if it consists of different chemical phases, solid state reactions between single components have to be considered.

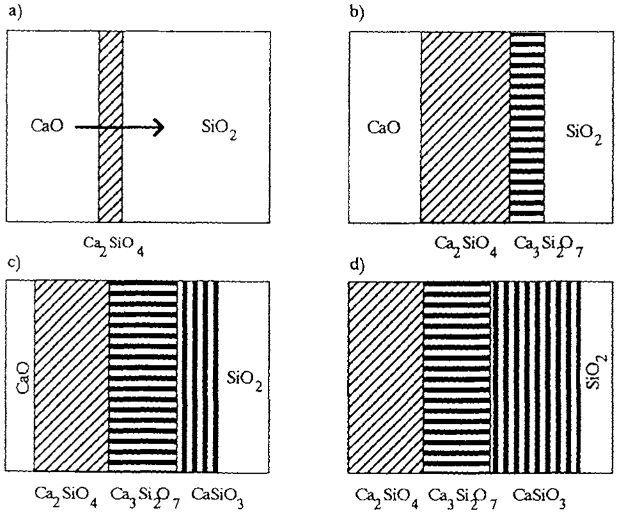
Figure 8.4 Changes of Physical Properties versus Temperature



Hausner, 1979

The stepwise formation of silicates from a mixture of the single components CaO and SiO_2 is provided in Figure 8.5 as an example of the fundamental sintering process. These compounds are by far the most common components in bottom ashes. The concentration of SiO_2 in bottom ashes is in the order of 35 to 55%, whereas the concentration of CaO varies between 5 and 20% (Baccini and Brunner, 1985; Hjelmar, 1987; Eighmy et al., 1987; Löffler, 1989; Vehlow et al., 1992).

Figure 8.5 Progress of Reaction Between CaO and SiO_2



The diffusion coefficient of CaO is higher than that of SiO_2 and thus enables CaO to migrate into the SiO_2, forming different phases. The first step is always the formation of the ortho-silicate Ca_2SiO_4. Depending on the local ratio of components, new phases may be formed. The final product is the most stable phase, the meta-silicate $CaSiO_3$. The number of phases present in an equilibrium is regulated according to Gibbs' phase law and depends on the number and the molar ratio of the initial components.

Although calcium is the predominant cation in bottom ash, other cations of earth-alkali and alkali metals can neutralise silicate anions. Thus, the principal reaction shown in Figure 8.5 produces a series of different silicates and meta-silicates with mainly calcium, magnesium, sodium and potassium. Aluminum and iron can also act as carriers of the positive charge.

The different silicates are distinguished by different crystal lattices depending on the radii of the single ions. These radii and their ratios determine the coordination number and thus the type of lattice. Crystallographic investigations using microscopic and X-ray diffraction methods have revealed well-defined crystals of several silicates generated during combustion (see Bottom Ash Characteristics).

In all defined crystals, the components of the lattice can be replaced by other ions if:

- these have a corresponding chemical behaviour.
- the ionic radii are similar.
- they have the same chemical valence.
- they tend to crystallise in the same type of lattice.

Consequently, many trace metals can be incorporated into stable matrices. The data in Table 8.1 is a compilation of crystal ionic radii from the literature (e.g. Pauling, 1969; Handbook of Chemistry and Physics, 1992) which indicates the important heavy metals which could replace the main constituents in silicates. For example, cadmium may replace the calcium found in carbonates or silicates.

Table 8.1
Crystal Ionic Radii (nm)

Na^+ 0.097	K^+ 0.133	Ca^{2+} 0.099	Fe^{2+} 0.074	Fe^{3+} 0.064
Cu^+ 0.096	In^+ 0.132	Ti^{2+} 0.094	Mg^{2+} 0.066	Cr^{3+} 0.063
	Tl^+ 0.140	Cd^{2+} 0.097	Co^{2+} 0.072	Mn^{3+} 0.066
			Ni^{2+} 0.072	Co^{3+} 0.063
			Cu^{2+} 0.072	Ni^{3+} 0.062
			Zn^{2+} 0.074	

Adapted from Pauling, 1969; Handbook of Chemistry and Physics, 1993

The tetravalent Si^{4+} ion in the silicate lattice has a crystal radius of 0.042 nm and can be replaced by Al^{3+} ions with a radius of 0.051 nm to form aluminosilicate. These compounds are widespread in the lithosphere. The most common group is the feldspars, found in bottom ash in concentrations between 5 and 10% (Vehlow et al., 1992). The same study measured other aluminosilicate, such as the melilithes, in concentrations above 10%. At the other end of the scale, some aluminosilicate found in bottom ash are artificial compounds that can only be formed within very small temperature ranges. This can be used to estimate the maximum temperatures in the fuel bed. To a certain extent, trace elements can also be incorporated into silicates (as well as other lattices) as impurities, bond to lattice defects or precipitate onto grain boundaries.

Many silicates, especially double silicates consisting of sodium and calcium, show no defined transformation temperature when cooled down and do not crystallise, but convert into a glassy state. Glasses are defined by non-periodic lattices which have large areas without any symmetry. Nevertheless, their atoms are grouped and exhibit the same coordination number in their neighbouring spheres as they do in crystals.

The mean composition of a "normal" glass can be defined with the formula:

$$Na_2O * CaO * 6\ SiO_2$$

Glasses generated on the grate during the combustion process are characterised by typical streak patterns and bubbles, which can be found in bottom ash in relatively large proportions of more than 10 % (Vehlow et al., 1992). Glasses have a greater potential to incorporate trace metal ions than crystals, mainly due to their lack of symmetry and the normal inhomogeneity of their structure. Substantial concentrations of metals in glass are generally denoted by distinct colours. Metals may also become embedded with small particles of other materials in the glass. If these particles become totally encapsulated, the potential for mobility through leaching is reduced significantly.

Single oxides of metals are also present in bottom ash. Magnetite (Fe_3O_4) is the most prevalent compound (up to 10%). Fe_2O_3, FeO, Cr_2O_3 and Al_2O_3 are also present, but in concentrations below 5%. A special type of mixed oxide consisting of bivalent and trivalent metals is represented by the group of spinelles. These form defined crystals with the representative molecular formula:

$$A\ B_2\ O_4$$

where:

A = bivalent metal
B = trivalent metal.

Common spinelles can contain the trivalent ions of Al, Cr and Fe, and the bivalent ions of Mg, Mn, Fe, and Zn. Trace elements can be substituted for some of the main components and thus become fixed in the solid phase. Many different spinelles have been observed in bottom ash, however, they typically represent only a small fraction of the total of mineral phases.

In general, chemical reactions in the combustion chamber produce thermodynamically stable compounds. The elements which remain in the fuel bed and form bottom ash are mainly bound to Si, Al, and O. Similar mineral matrices can also be found in fly ash particles entrained in the flue gas stream (Hundesrügge, 1990). The quantity of fly ash generated is influenced by the type of grate and the control of air flow within the combustion chamber. Modern incinerator technologies are based on combustion with lower air velocities through the fuel bed and enhanced mixing of the gas stream in the furnace which severely limits entrainment of particulates. This also has the benefit of reducing the production of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) in the heat recovery and APC systems.

Physicochemical Transformations

Most substances can exist as solids, liquids or gases, depending on the actual temperature, however, there are some notable exceptions. For instance, the liquid phase of iodine, carbon or carbon dioxide cannot be achieved under normal pressure conditions. Other compounds, such as all organics, heavy metal carbonates, several oxides (e.g., Pb_3O_4, HgO), and heavy metal sulphates, will simply decompose if the temperature is too high.

In most substances, the transition between solid and liquid phases takes place at one defined temperature, the melting point, which is a function of pressure. Although solid and liquid phases of a species can only be in equilibrium at one defined temperature, both phases are in permanent equilibrium with the gas phase. Due to the statistical distribution of oscillation energy in the lattice or of kinetic energy in the liquid, some atoms or molecules are able to cross the interface and evaporate into the gas phase. This transition is stimulated by increasing temperature, until the substance reaches its boiling or sublimation point above which all molecules are present in the gas phase. Consequently, the gas phase will always contain molecules of all species present in the system, even at very low temperatures. These gas molecules move freely through the gas volume and have the potential to impinge on the surface of the liquid or solid and return, or condense back into the original matrix. Condensation is a function of the concentration of the respective molecules in the gas phase.

Equilibrium is reached if the number of particles crossing the interface to evaporate is exactly the same as the number of particles striking the interface and returning into the condensed phase. The equilibrium is, like all chemical equilibria, a function of temperature and pressure. At each temperature, the equilibrium concentration of the chemical species in question causes a defined partial pressure of this species in the gas phase. The temperature dependency of this partial pressure, called the vapour pressure of the species, can be described using fundamental physico-chemical properties of the species. The conditions for equilibrium between a condensate and a gaseous phase are based on :

$$R\ \log\frac{P}{P^{\circ}}=\frac{G^{\circ_{cond}}(T)}{T}-\frac{G^{\circ_{gas}}(T)}{T}=-\frac{\delta G^{\circ}(T)}{T} \qquad (8.10)$$

where: R = gas constant p = (vapour) pressure
G = molar free enthalpy T = temperature
° = standard conditions

Using the definition of free enthalpy given in equation (8.7):

$$G = H - T S$$

Equation (8.10) can be transformed to:

$$R\ \log\frac{P}{P^{0}}=-\frac{H^{0_{gas}}(T)-H^{0_{cond}}(T)}{T}+S^{\circ_{gas}}(T)-S^{\circ_{cond}}(T)=-\frac{\delta H^{\circ}(T)}{T}+\delta S^{\circ}(T) \qquad (8.11)$$

using:

$$S_{gas}(T)=c_{p_{gas}}\log T+\int_{0}^{T}\frac{C_{o_{gas}}}{T}dt+D_{1} \qquad (8.12)$$

and:

$$S_{cond}(T)=\int_{0}^{T}\frac{C_{p_{cond}}}{T}dt+D_{1} \qquad (8.13)$$

where c_p = molar heat under constant pressure
c_0 = molar oscillation heat
D = constant

Simplified, the molar enthalpies and the integrals can be described by the linear functions of T (only valid for limited temperature ranges), and the temperature dependency of the vapour pressure can be approached by:

$$\log p=-\frac{A}{T}+B+C\log T+DT \qquad (8.14)$$

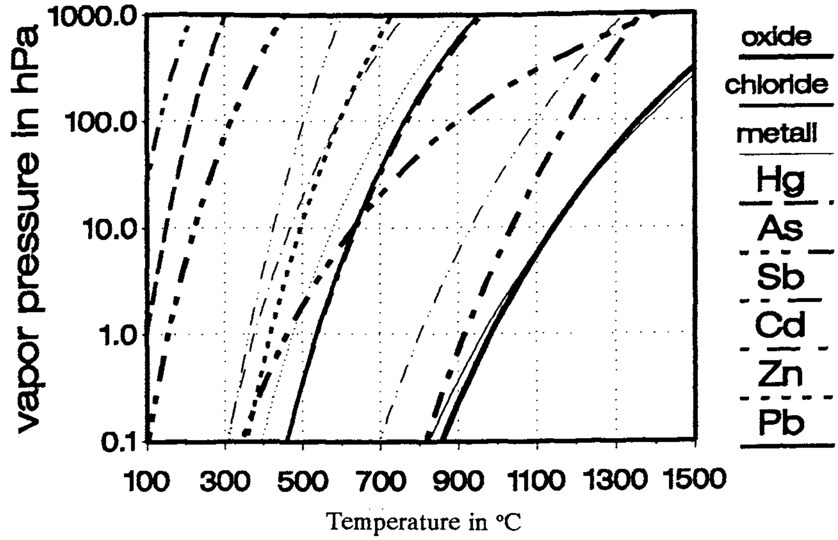
where A, B, C, D = constant.

This is the type of equation used to interpolate experimentally obtained vapour pressure data. In small temperature ranges the equation can be even further simplified to:

$$\log p = -\frac{A}{T} + B \tag{8.15}$$

Figure 8.6 compiles the vapour pressure curves for selected species of some elements which are known to be more or less mobile during incineration. The curves are calculated using vapour pressure formulas from Bartels et al. (1960).

Figure 8.6 Vapour Pressure Curves for Selected Metals in the Metal, Oxide and Chloride State



If the exact chemical formula of a species in the gas phase at a given temperature is known, by means of the fundamental gas equation:

$$pV = nRT \tag{8.16}$$

where n = number of moles.

The equilibrium concentration of this species in the gas phase can be calculated, providing an estimate of the potential partitioning.

In a limited volume of gas, achieving vapour pressure equilibrium is a relatively rapid process. The major controlling factor is the time the evaporated atoms or molecules need to establish a uniform concentration in the gas phase by diffusion. In the combustion chamber of an incinerator, equilibrium will normally not be reached, due to the large volume of fresh air used to maintain the combustion process. Hence, the quantity of evaporated substances cannot be calculated precisely, even if all concentrations and the temperature distribution in the combustion chamber were known. Nevertheless, the shape of vapour pressure curves allows an estimate of the degree of evaporation of a substance, and thus indicates the potential partitioning of a substance between the bottom ash and flue gas stream.

8.1.3 Mechanisms in the Boiler

Condensation

The hot flue gases from the furnace enter the boiler at temperatures of <800°C and are cooled rapidly to about 200°C or lower. The decrease in temperature across the boiler prompts condensation of many gaseous species entrained in the flue gases. Condensation is also controlled by vapour pressure. The condensation process in a dust-free gas phase starts as soon as the temperature falls below the boiling point by forming a condensation nucleus. However, the condensation process is kinetically inhibited in a saturated atmosphere and nuclei begin to form at lower temperatures.

Supersaturation of the flue gas stream is minimised due to the loading of dust particles which act as condensation nuclei. Condensation takes place mainly at the surface of dust particles. Since smaller particles have higher specific surface areas, the finest fraction of fly ash particles is generally the most enriched with condensated material. Furthermore, the enrichment of special compounds in the fine dust fraction indicates the thermal mobility of these compounds under the operating conditions present in the combustion chamber.

There are indications that fly ash from modern MSW incinerators is characteristic of enhanced enrichment of volatile species compared to fly ash from older facilities. The enhanced enrichment is probably due to a combination of high bed temperature, which promotes the vaporisation of volatile compounds, and a more "soft" combustion which causes a reduction in the overall mass of inert material carried over from the combustion chamber (e.g., Sawell and Constable, 1989; Horch, 1990).

Although the boiler's primary function is to act as a heat exchanger, it also acts to a limited extent as a dust removal system. Particles which are either coarse enough or dense enough to fall out of suspension in the flue gas stream collect in the bottom of the boiler chambers. These ash particles are not as enriched with volatile substances as residue collected in APC systems. The main reasons for the difference are:

- The higher temperature of the flue gas in the boiler limits condensation of volatile components.
- The condensation reaction favours enrichment of finer sized particles, namely the APC residues rather than the relatively larger sized boiler ash particles.

Although reactions between the acid gases and alkaline dust particles take place in the boiler, they do not cause substantial changes in the overall partitioning of elements. However, some evaporated species may undergo special reactions with other reactants during transport through the boiler, resulting in a difference in speciation of the condensated compounds compared to those remaining in the flue gas. For example, H_2O concentrations in the flue gas can reach values up to 170 g/Rm^3 and in cases of soot blowing of the boiler tubes using steam, levels can reach above 200 g/Rm^3. At the comparably high temperatures in the boiler, this water may cause hydrolytic reactions with organic compounds, but also with inorganic salts (see above: Reactions Controlling the Alkalinity).

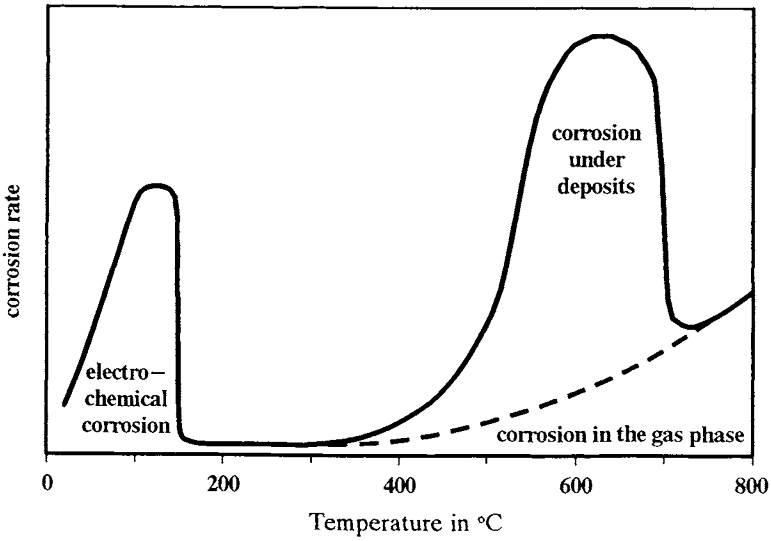
Corrosion

Another reaction which is often neglected with respect to the mass transfer, but is of vital importance for the maintenance of the boiler, is corrosion attack of gases and salts on the heat exchanger tubes (Fäßler et al., 1968). The materials used for the tubing are non-alloy or low alloy steels. Waterwall tubes are often coated with a castable refractory like SiC. In the superheater region, sometimes high alloyed austenitic steels have been used (Reichel and Schirmer, 1989). Principally two temperature regions can be identified where severe corrosion of the ferrous tubing material is observed. Figure 8.7 depicts the dependency of the corrosion rate as a function of the wall temperature of the tubes. At temperatures below 150°C, condensation of acids takes place and the low alloy steels suffer tremendous electrochemical corrosion attack. High alloy steels show pit corrosion and due to a combination of acid attack and mechanical stress loading, corrosion cracking may occur.

This so-called "standstill" corrosion can be avoided by diluting the flue gases during shutdown procedures with air or by controlled cooling down of the incinerator using fuels with low chlorine and sulphur levels.

A second region of potential corrosion attack is observed at temperatures above 300°C with increasing effects at increasing temperatures. The waterwall tubes in the combustion chamber and the superheater tubing are especially at risk. The flue gas temperature may exceed 800°C at these locations and the wall temperatures in the superheater sometimes reach values above 500°C.

Figure 8.7 Schematic Dependency of Corrosion Rates on Wall Temperature



Although there are substantial amounts of corrosive gases present in the flue gas, corrosion effects caused by direct interaction with gaseous HCl or SO_2 can only take place during the start up of a new boiler. After a short period of operation, the heat exchanger tubes are normally covered by layers of ash (see Chapter 10) and there is no free access of gases to the tube surfaces. The dotted curve in Figure 8.7 compares qualitatively the corrosion rates caused by pure gas corrosion with the corrosion rates actually found in boilers. Within the temperature regime in the boiler, corrosion attack on the covered tubes exceeds that which would be expected by gas corrosion. These corrosion effects must be induced by ingredients of or by reactions in the surface deposit layers.

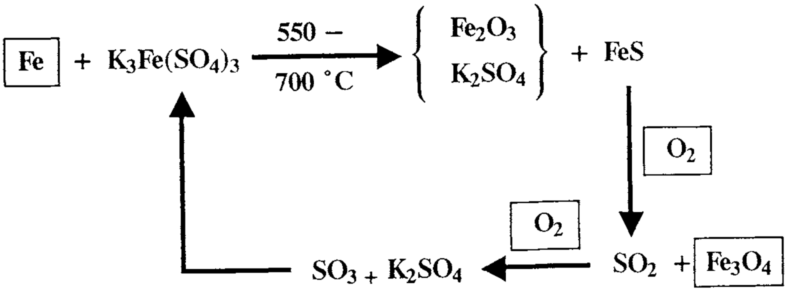
The deposits on the heat exchanger tube surfaces contain salts which may produce corrosive species by disintegration or by reaction with components of the flue gas. One example may be the formation of SO_3 close to the tube walls by thermal decay of sulphates [equation (8.6)]. The theoretical production rate should be very low and no major corrosion damage could directly be traced back to this component.

Sulphates with low melting points, especially complex alkali-iron sulphates can be formed in the temperature range 320 to 450°C following the reaction (Corey et al., 1965):

$$Fe_2O_3 + 3\ K_2SO_4 + 3\ SO_3 \rightleftharpoons 2\ K_3Fe(SO_4)_3 \qquad (8.17)$$

This reaction has been blamed for severe corrosion attack since it may induce a mechanism which recycles the corrosive agent (Figure 8.8).

Figure 8.8 Mechanism of High Temperature Sulphate Corrosion



Nelson and Cain, 1960

Although a small proportion of corrosion damage may be explained by this mechanism, in most cases it is difficult to measure the respective corrosion products (Fäßler et al., 1968). Furthermore, the formation of the complex sulphates requires SO_3 concentrations exceeding 250 mg/Rm^3, which is far above normal levels in the flue gas (<50 mg/Rm^3).

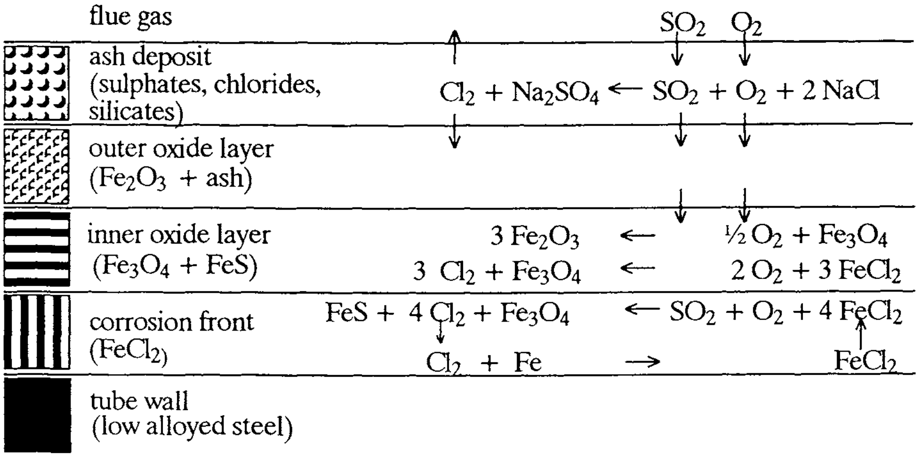
The high corrosion damage in boilers of MSW incinerators compared with those in coal fired power plants can be explained by the higher chlorine inventory in MSW than coal. The higher chlorine content of MSW flue gases has prompted development of a corrosion mechanism based on the reactivity of chlorine compounds, including elementary chlorine which is shown schematically in Figure 8.9.

The basic corrosion reaction in the mechanism postulated above is the formation of $FeCl_2$ at the metal surface and the direct recycling of elementary chlorine. Its presence at the corrosion front prevents the growth of the tightly bound, protective oxide layers and thus is responsible for the relatively high corrosion rates.

According to this corrosion model, chlorides are the essential components in the deposits. The formation of elementary chlorine by sulphation is favoured at high temperatures. A second mechanism (Equation 8.18), is also a primary step in the de-novo synthesis of PCDD and PCDF (the Deacon Process), which is initiated at temperatures >350°C:

$$\begin{aligned} 2\,CuCl_2 + O_2 &\rightleftharpoons 2\,CuO + 2\,Cl_2 \\ 2\,CuO + 4\,HCl &\rightleftharpoons 2\,CuCl_2 + 2\,H_2O \end{aligned} \qquad (8.18)$$

Figure 8.9 Chlorine Induced Mechanism of High Temperature Corrosion



Reichel and Schirmer, 1989

However, due to the much higher concentration of alkali chlorides compared to $CuCl_2$, this reaction should contribute little corrosive chlorine at the higher temperatures.

8.1.4 Mechanisms in the Dust Removal System

As mentioned in Chapter 3, the most commonly used dust removal system, if dry or semi-dry scrubbing is applied, is the fabric filter (baghouse), especially in North America. In European countries where very strict emission guidelines are in place, wet scrubbing is prevalent and dedusting is generally facilitated using electrostatic precipitators. In addition, cyclones are sometimes still used as an initial dust removal device prior to modern APC equipment.

In most existing MSW incinerators, filter residues consist not only of the original particulate released from the grate, but also of additional substances which have been added for gas cleaning purposes. If dry or semi-dry scrubbing is applied, or if in wet systems the flue gas scrubbing solution is evaporated by spray drying upstream of the filter system, the dust particles are combined with these APC residues. Similarly, in other MSW incinerators, charcoal is injected into the flue gas for sorption of PCDD/PCDF and mercury, and subsequent removal in the APC system.

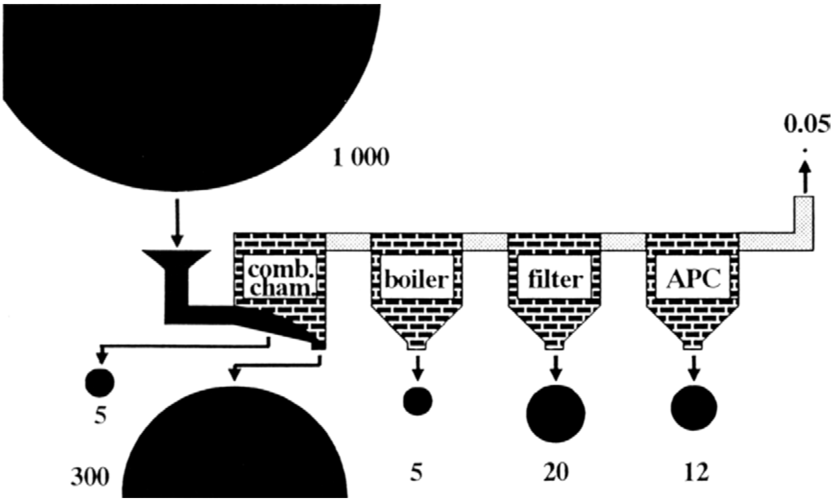
8.1.5 Mechanisms in the Air Pollution Control System

This system is installed to remove volatile species from the flue gas by means of chemical reactions which are described in detail in Chapter 4. In all following calculations of mass streams for solid matter or single elements, only the stoichiometric quantities are taken into account, regardless of the scrubbing technology.

8.2 MASS STREAMS IN A MUNICIPAL SOLID WASTE INCINERATOR

To estimate the partitioning of elements, data from the literature were used, despite the differences in quality. These data have been generated in different countries at different times and thus reflect different waste qualities, technological standards and operation parameters. The basic requirement of the calculations is the knowledge of the different mass streams. Figure 8.10 shows mean data for these streams which are compiled from modern mass burning systems (Baccini and Brunner, 1985; Schneider, 1986; Environment Canada, 1988; Reimann, 1989; Barniske and Johnke, 1990; Göttlicher and Anton, 1990; Mühlenweg and Brasser, 1990).

Figure 8.10 Streams of Solid Masses in MSW Incinerators



The anticipated air consumption of this typical mass burn system is estimated to be about 5,000 m^3 per Mg of waste. Old incinerators operated more in the region of 6,000 m^3/tonne, whereas new installations are about 4,000 to 4,500 m^3/tonne.

The bottom ash production rates differ substantially, between 250 and 420 kg/tonne of waste. These data include the grate siftings, which are generally combined with the bottom ash. The fraction of siftings is a function of the type of waste fuel and the type and age of grate being used. The generation rates for grate siftings are seldom measured, consequently there is a dearth of data. Observations from the WASTE Program (1993) estimate that grate siftings contributed about 3.8% of the total mass flux from a modern mass burn incinerator. Siftings from some facilities may increase the amount of unburnt matter and metallic phases in the bottom ash and consequently are collected separately and fed back into the combustion chamber (Vehlow et al., 1990). However, the recent WASTE Program data indicates that there is very little unburnt matter in grate siftings (<2% loss on ignition).

Although recent data indicate that grate siftings contain enriched levels of metals such as aluminum, copper, lead and zinc, the concentrations of most metals are similar to the concentrations in bottom ashes (Schneider, 1986). For the purposes of this section, the grate siftings mass stream has not been accounted for in the valuation of element partitioning. The exceptions will be noted later in the chapter.

As mentioned in Chapter 3, the quantity of boiler ash generated depends on the type of boiler and on the amount of particulate originally released from the grate. The variation of this mass stream is estimated between 2 and 12 kg/tonne of waste. In many MSW incinerators, the boiler ash is still combined with the bottom ash in the quench tank. In the future it should be treated together with the APC residues since its chemical characteristics are more similar to APC residues than to bottom ash. In some countries, this is already enforced by legislative regulations.

Although the estimated mass flux of filter ashes used here is about 25 kg/tonne of waste, (based on a particulate loading of 5 g/Rm^3), the operating conditions at most modern incinerators promote lower particulate loading (<2 g/Rm^3) (Environment Canada, 1988; Vogg et al., 1990 & 1991; Reeck et al., 1991), with corresponding APC residue production rates of about 10 kg/tonne (Faulstich et al., 1990).

The mass of APC residues shows the highest variation of all residue streams. The 12 kg/tonne listed is a mean value for wet systems which operate near stoichiometry. The value includes the amount of dry neutral sludge (2 to 4 kg/tonne) and the soluble salts (5 to 12 kg/tonne). In semi-dry or dry systems, the amount increases because of unreacted additives which are removed along with the residues. In the calculated mass balances presented in the following sections, the residue streams from wet systems will be used. This limitation will not influence the balances substantially, since all existing scrubbing systems achieve about the same emission limits and remove about the same fraction of the specific species from the flue gas.

For calculating stack emissions, the residual particulate loads of about 10 mg/Rm^3 are used to comply with the emission limits of many countries. Modern MSW incinerators achieve emissions below 1 mg/Rm^3. In the following balances of single elements, the German emission limits are used, which are similar to those in many other countries (Bundesministerium, 1990).

8.3 LITHOPHILIC ELEMENTS

8.3.1 Fundamentals

Some elements and their most common compounds have boiling points far above 1,500°C. Consequently, these materials will remain in the bottom ash. However, this does not mean that they do not undergo changes in chemical speciation during the combustion process. In some cases, it can be expected that they gain stability, either through sintering or incorporation into other stable matrices (as discussed above).

The most important members of this group are silicon and aluminum, which form very stable oxides and anions, i.e. the silicates and aluminosilicate. These are the major matrix compounds of bottom ashes, since they are relatively "heat stable". Their presence in APC residues is due to particulate matter carried over from the furnace in the flue gases. Some theoretically stable volatile compounds of metals are not formed under the conditions of waste combustion due to energetic or kinetic hindrance. These metals are preferably fixed in the crystal structures of silicates and aluminosilicate, or they may be transformed into more stable oxidic compounds during the quenching or condensation. The latter is true for chromium, manganese, iron and nickel, which are distinguished by similar crystal radii and are included under the category of lithophilic elements.

Some metals form stable volatile compounds in the combustion chamber but the fraction actually vaporised is very low. Although these metals can exhibit a significant enrichment in the fine particle fraction of the APC residues, much of the material remains in the bottom ash, and therefore has been categorised here with the lithophilic elements. Copper is an example of a lithophilic element with volatilised species of importance for other reactions, i.e. its chlorides play an important role since they act as catalysts in the dioxin synthesis (Vogg and Stieglitz, 1986; Stieglitz and Vogg, 1987; Hagenmaier et al., 1987).

Other members of this group are the alkali metals which are responsible for the alkalinity of the bottom and fly ashes. A certain proportion of these elements are also associated with the silicates, where they act as neutralising cations. The predominant metal in this group is calcium.

8.3.2 Alkali Metals

Sodium, potassium and to a lesser extent rubidium are considered major alkali metals present in ash. All these elements prefer the oxidation state +1 and exhibit a pronounced electropositive character, designated by very high negative potentials against a hydrogen electrode. Due to their high reactivity these metals are present in nature, and in the waste, bound to electronegative elements.

The inorganic salts are relatively thermally stable, i.e. the boiling points are far above 1,000°C. In the case of chlorides, the boiling points decrease with increasing atomic number: NaCl boils at 1,730°C, KCl at 1,411°C, RbCl at 1,383°C, and CsCl at 1,303°C. The extremely high transfer temperature of NaCl will only allow a very limited fraction to be volatilised in the combustion chamber. A large proportion of sodium and potassium are bonded to silicates, and hence partitions mainly to the bottom ash. This fraction is higher for sodium than for potassium. Although the concentration of sodium does not differ much in the various residue streams, filter ashes might show a certain enrichment, thus indicating a small transport of Na via the gas phase (Angenend, 1990).

The thermodynamic data of the other alkali chlorides, especially the slopes of their vapour pressure curves, indicate a much more distinct volatilisation at temperatures found in the combustion chamber. This explains the pronounced concentration of potassium and rubidium in the fine fractions of filter ashes (see Clean Gas Dust column in Table 8.2)

Table 8.2
Mean Concentrations of Alkaline Elements in the Waste and in Solid Residues (mg/g)

Element	Waste	Bottom Ash	Boiler Ash	Fly Ash	Clean Gas Dust
Na	3 - 15	8 - 40	8 - 40	10 - 40	20 - 50
K	5	2 - 15	15 - 40	4 - 40	100
Rb	0.04	0.125	0.10	0.16	0.45

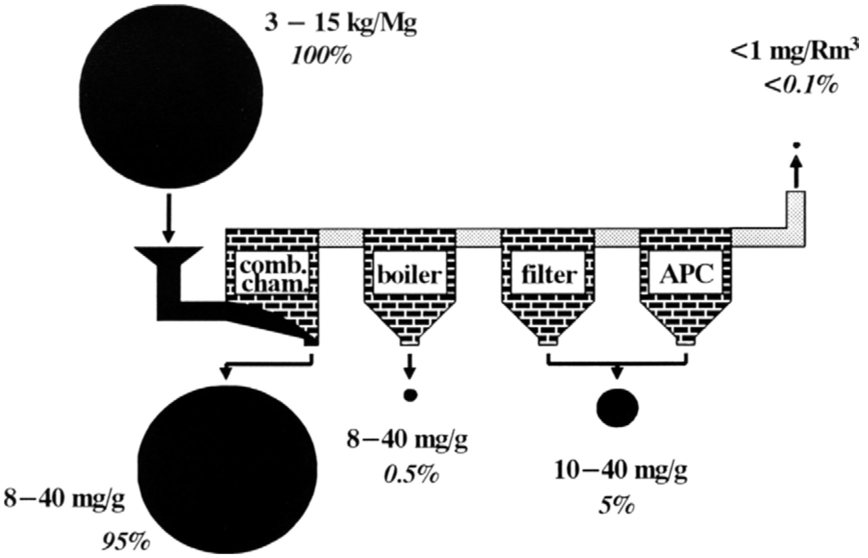
Data taken from literature, see respective chapters

Organic alkali compounds decompose during incineration, with the primary products being Na_2O_2 for sodium and K_2O or K_2O_4 for potassium. Since these compounds are not stable in a reactive environment, reactions with other species present in the fuel will take place. The final products can include the respective chlorides, sulphates, carbonates and eventually hydroxides. The latter two compounds add to the alkalinity of the residues.

The alkali elements sodium and potassium are ubiquitous and show similar abundance in the lithosphere with about 2.6 and 2.4% respectively. Both are essential physiological elements and act to maintain the osmotic pressure of cells. The daily intake for humans is about 3 to 7 g of sodium and about 2 to 4 g of potassium.

In the waste, the concentration of Na is about 10 to 15 kg/tonne, which is much higher than that of potassium (about 5 kg/tonne) (Schneider, 1986). In Figure 8.11, the partitioning of sodium is depicted on the basis of the cited data set. The concentration is more or less equal in all residue streams and compares favourably to data in other publications (Hjelmar, 1987; Angenend, 1990).

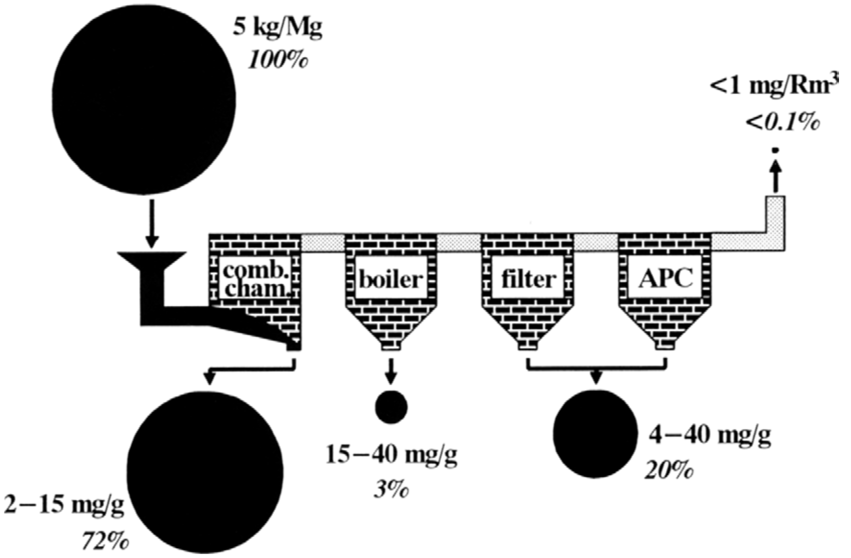
Figure 8.11 Concentrations and Percent Partitioning of Na



As has been mentioned above, the fraction of volatilised chlorides should be higher for the heavier alkali metals than for sodium. The compilation of concentrations in the residue streams given in Table 8.2 supports this hypothesis for potassium. The only available data set which provides values for all residue streams depict a substantial fraction of potassium partitioning to the fly ash stream (Figure 8.12).

It can be expected that the alkali metals rubidium and cesium behave more like potassium than like sodium. The key point seems to be the speciation of these alkali metals in the feed. If they are mainly bound to silicates, they will not volatilise. Volatilisation can only occur with the organic matter or chloride bound metals.

Figure 8.12 Concentrations and Percent Partitioning of K



8.3.3 Earth-Alkali Metals

The group of earth-alkali metals consists of beryllium, magnesium, calcium, strontium, barium and radium. With the exception of beryllium and radium, which are very rare in nature and in the waste, the earth-alkalis are among the most abundant elements in the lithosphere.

The chemical properties of magnesium are more similar to those of aluminum than those of calcium, strontium and barium. The latter metals are the typical earth-alkalis and are always found in the oxidation state +2 and bound to electronegative elements. Generally, no earth-alkali salts can be thermally mobilised at the temperatures inherent in waste incinerators.

The reactivity of earth-alkali salts is somewhat higher than that of alkali salts. During incineration, many earth-alkali compounds present in the waste are subject to hydrolysis or thermal decomposition. The primary reaction products are oxides or hydroxides which can be transformed into carbonates by the high levels of CO_2 in the atmosphere. Hence, the earth-alkali metals can substantially contribute to the alkalinity and buffering capacity of the bottom ash stream.

The lithosphere contains about 3.6% calcium, mainly bound to carbonates like limestone, $CaCO_3$, or to sulphates like gypsum, $CaSO_4 \bullet 2H_2O$. These calcium compounds are often found together with salts of other earth-alkali metals. A considerable amount of calcium can be found in the putrescible waste fraction contributing alkalinity to the bottom ash stream. Calcium is physiologically important with respect to bone structure, i.e. about 1.2 kg of calcium are present in the human skeleton.

Although calcium is among the most abundant elements, there is a dearth of analytical data on its behaviour during incineration. The partitioning of calcium shown in Figure 8.13 is calculated from two data sets (Schneider, 1986; Belevi, 1993). Since no calcium compounds can be volatilised, it has to be concluded that the concentrations of calcium reflect the proportion of ash generated in each stream. However, if lime scrubbing APC systems are utilised, the calcium content in the APC residue will increase dramatically. Magnesium, strontium and barium behave in a manner similar to calcium (see Table 8.3).

Table 8.3
Mean Concentrations of Earth-Alkali Elements in the Waste and in Solid Residues (mg/g)

Element	Waste	Bottom Ash	Boiler Ash	Fly Ash	Clean Gas Dust
Mg		5 - 20		10 - 40	
Ca	10 - 35	50 - 100	100	50 - 100	50
Sr	0.12	0.20 - 1.0	0.50	0.65	0.45
Ba	0.73	0.50 - 2.5	2.5	2.5 - 3.5	1.30

Data taken from literature, see respective chapters

8.3.4 Heavy Metals

Most heavy metals in the group of lithophilic elements are present in the waste in relatively high concentrations (>100 g/tonne), however, some trace elements also belong in this category. Similar to other elements, there is a paucity of valid data sets for all residue streams containing these metals. Table 8.4 contains the mean concentrations of iron and other lithophilic elements in the waste input and in residue streams, taken from the literature.

Figure 8.13 Concentration and Percent Partitioning of Ca

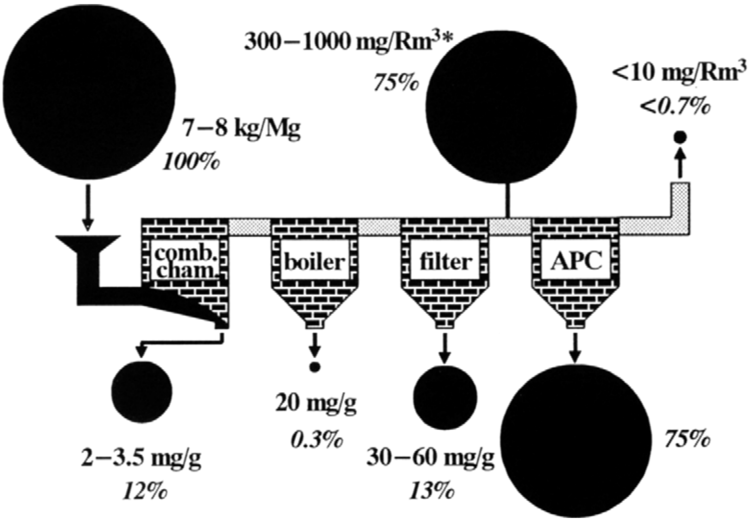


Table 8.4
Mean Concentrations of Elements in Waste and Solid Residues (µg/g except * = %)

Element	Waste	Bottom Ash	Boiler Ash	Fly Ash	Clean Gas Dust
Ti	1300	3500 - 8000	6500	7000 - 9000	4000
Cr	40 - 400	100 - 1200	200 - 800	100 - 1000	200 - 800
Mn	200 - 500	400 - 1000	700 - 1200	800 - 1500	900
Fe*	2.5 - 5.0	5 - 15	3.0 - 5.0	3.0 - 6.0	4.0
Ni	20 - 130	50 - 800	100 - 300	100 - 300	100 - 200
Cu	200 - 1000	250 - 4500	300 - 1500	50 - 5000	300 - 3000

Data taken from literature, see respective chapters

Iron

Iron is another common element in the lithosphere, as well as in municipal solid waste. The concentration of iron in the waste feed has been well documented in the order of 25 to 50 kg/tonne (Brunner and Zobrist, 1983; Dobberstein, 1983; Brunner and Ernst, 1986; Schneider, 1986; Perrier-Rosset, 1989; Belevi, 1993). Today, the iron in most incinerators is introduced by the metallic fraction. Modern waste management strategies, however, promote metal recycling and this will reduce the input of metallic iron in future.

The most stable iron compounds are the oxides (Fe_2O_3 and Fe_3O_4) which can be found by mineralogical examination of bottom ash (Vehlow et al., 1992) and fly ash (Hundesrügge, 1990). There are two iron chlorides which can theoretically be volatilised in the combustion chamber. The $FeCl_2$ sublimates at 1,026°C and has a high vapour pressure at relatively low temperatures, but it can only exist in a reducing environment (compare the corrosion mechanism in Figure 8.9). $FeCl_3$ has a very low boiling point of 319°C, but is immediately converted into Fe_2O_3 as soon as H_2O is present. Therefore, both compounds do not contribute substantially to the transport of iron to the fly ashes. Since fly ashes show no enrichment of iron in the fine fractions, the iron is originally bound to particles carried over from the furnace. However, it should be noted that chlorides of iron can be formed in certain parts of the incinerator, (i.e. in the boiler), by the same types of reactions given in equation (8.9) or in the corrosion mechanisms outlined in Figure 8.9.

Metallic iron present in the waste fuel cannot be oxidised easily. The relatively small surface area-to-volume ratio of larger particles prevents the rapid reaction. It is often protected against corrosion by zinc, tin or cadmium layers which will volatilise first. Consequently, ferrous material passes through the incinerator relatively unscathed.

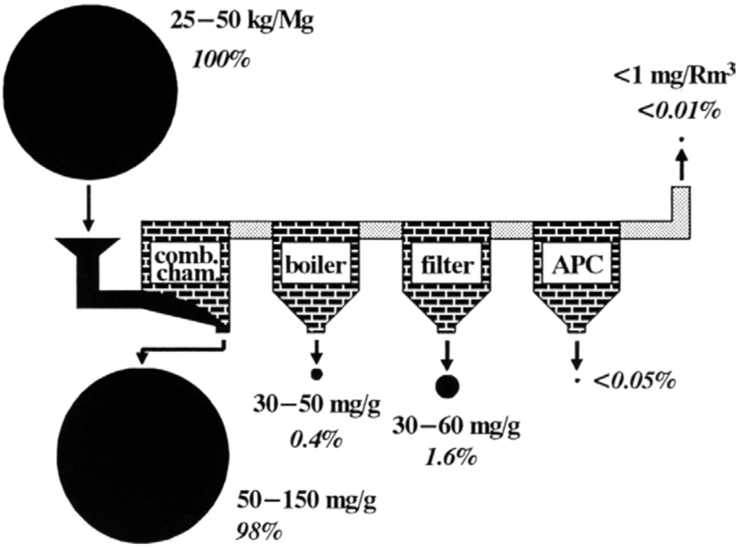
Concentrations of iron in bottom ash can vary widely for a number of reasons, including:

- if primary material was or was not removed from the sample prior to sample preparation and analysis
- if the sample was collected prior to or after magnetic separation of ferrous from the ash
- the effectiveness of source separation schemes for the waste fuel.

The quantity of magnetically separated iron from bottom ash can reach 12 to 15% of the total weight of the ash (Pietrzeniuk, 1985). Typical iron concentrations in bottom ash from mass burn systems can vary between 9 and 15% (Hjelmar, 1987; Eighmy et al., 1987; Schneider, 1986; Belevi, 1993), although concentrations of up to 24% have also been reported (Baccini and Brunner, 1985; Brunner and Mönch, 1986; Cernuschi et al., 1987). Concentrations in boiler ash are in the order of 3 to 5% (Schneider, 1986) and mean values of 3 to 6% have been recorded for fly ash (Brunner and Zobrist, 1983; Baccini and Brunner, 1985; Schneider, 1986; Environment Canada, 1988).

Figure 8.14 provides the partitioning of iron during incineration based on three different sets of data (Schneider, 1986; Brunner and Mönch, 1986; Belevi, 1993), which are consistent with the information provided above for individual residue streams. Virtually all of the iron in the waste remains in the bottom ash. Only negligible amounts (1 to 2%) are transferred in the fly ash particles and, if excellent dedusting is achieved, less than 0.01% of the total input is emitted through the stack.

Figure 8.14 Concentration and Percent Partitioning of Fe



Chromium

Chromium is an abundant element in the lithosphere and an essential additive in all stainless steel alloys. In addition, layers of chromium are used for corrosion protection of iron materials. Chromium is an element of environmental concern, since its hexavalent compounds are distinguished by high oxidation potentials as well as by high solubility in water.

The waste fractions with the highest enrichment of chromium include the metal fractions, batteries, green glass, construction debris and textiles (especially leather due to the tanning process) (WASTE Program, 1993). Significant concentrations have also been measured in wood and rubber fractions (Lorber, 1983). The overall concentration of chromium in waste is in the order of 40 to 400 mg/tonne (Schneider, 1986; Environment Canada, 1988; Reimann, 1989; Angenend, 1990).

Chromium compounds are not considered thermally mobile during incineration and therefore should remain mainly in the bottom ash stream. A survey of the literature indicates that the chromium concentrations in the bottom ash are slightly higher than with other streams: up to 1% (Baccini and Brunner, 1985; Eighmy et al., 1987; Sawell and Constable; 1993). The raw particulate carried over from the furnace, even clean gas flue dust, contain substantial concentrations (100 - 1,200 µg/g) (Schneider, 1986; Environment Canada, 1988; Reimann, 1989; Vogg et al., 1991; Sawell and Constable 1993), however, there is little evidence of significant enrichment in the fine fraction (compare Table 8.4). The partitioning of chromium is similar to that of iron (compare Figure 8.14).

Nickel

Nickel is a very common element and is used as an alloying component in stainless steel and other nickel-based alloys. Fine nickel powder (Raney nickel) is utilised as a catalyst in the mineral oil and chemical industry, and large quantities are used in rechargeable Ni-Cd batteries. Inhalation of nickel compound dusts or aerosols represent a potential cancer risk.

The highest input of nickel into the waste is in the ferrous and nonferrous metal fractions. The partitioning is similar to that of chromium and iron (Table 8.4). The overall input concentrations are in the order of 100 g/tonne of waste (Schneider, 1986; Environment Canada, 1988; Brunner and Zobrist, 1983; Reimann, 1989; WASTE Program, 1993). There is one nickel compound [$Ni(CO)_4$] which is gaseous at ambient temperature and which might theoretically be formed under the conditions in the combustion chamber. However, at the present time there is no data to support this hypothesis, since it is easily hydrolised.

The experimental results categorise nickel as a lithophilic element. The concentrations in all solid residue streams are about 50 to 300 µg/g (Baccini and Brunner, 1985; Schneider, 1986; Environment Canada, 1988; Reimann, 1989; Angenend, 1990).

Copper

Copper is considered a half-noble metal and has a strong resistance to oxidation. As a result, copper and copper alloys (with tin and zinc) are used for kitchen utensils and other tools. About 40% of the copper produced is used in apparatus and instrument construction today. Its ability to conduct electricity readily makes it an important material in the electronics industry. Furthermore, copper compounds are applied as pigments, catalysts, stabilisers and for acetate rayon production. Copper and its compounds are potentially toxic to special plants and microbes so they are used in herbicides and wood preservatives (e.g. copper arsenate).

The copper concentration in waste is reported to be about 200 to 1,000 mg/tonne of waste (Brunner and Zobrist, 1983; Schneider, 1986; Brunner and Mönch, 1986; Reimann, 1989; Tobler, 1988; Angenend, 1990; Belevi, 1993; Dalager, 1993) and is generally enriched in the organic, electrical and paper board fractions (Lorber, 1983; Waste Program, 1993).

The behaviour of copper during incineration is similar to that of iron, chromium and nickel. The only thermally mobile compound is $CuCl_2$, which has a boiling point of 993°C. This decomposes into CuCl which has a boiling point of 1,490°C. Consequently, $CuCl_2$ does not contribute substantially to the transfer of copper into the gas phase.

The mean concentration of copper in the individual residue streams is highly variable, especially in the bottom ash, but the mean concentrations are in the order of 1,000 µg/g

(Table 8.4) (Baccini and Brunner, 1985; Schneider, 1986; Reimann, 1989; Brunner and Mönch, 1986; Tobler, 1988; Angenend, 1990; Sawell and Constable, 1993; Dalager, 1993).

Investigations on the distribution of copper in fly ashes indicate a significant increase in concentration in the fine particle fractions, which in turn indicates a certain degree of volatilisation of either pure metal, copper chloride compounds or copper-based compounds in wood preservative (Vehlow, 1993). $CuCl_2$ is thought to play an important role in the de-novo synthesis of PCDD/PCDF in the boiler (Vogg and Stieglitz, 1987; Stieglitz and Vogg, 1987; Hagenmaier et al., 1987).

8.4 VOLATILE ELEMENTS

Many nonmetallic elements present in the waste are converted by the combustion process into compounds which form acids if contacted with water. Those compounds may be oxides, as for sulphur (SO_2 and to a lesser extent SO_3), or nitrogen (mainly NO). Other elements such as halogens have a strong tendency to react with hydrogen and are preferably converted into hydrides by the combustion process. Theoretically, hydrogen compounds may also exist in association with sulphur, selenium, tellurium, arsenic or antimony. Although these compounds should be of interest because of their toxicity, the limited data in literature indicate that the actual quantity of those compounds is probably very low.

8.4.1 Halogens

The predominant and most stable oxidation state of the halogens is -1. Due to their reactivity, the respective hydrohalogenic acids are not found in nature. Instead, the natural form is as an alkali or earth-alkali halogenide. Most halogens are also essential elements for all plants and animals. During MSW incineration, the prevailing products are the acid hydrogen halides, which are treated in the APC systems.

The stability of hydrogen halides against thermic dissociation according to:

$$2\,HX \rightleftharpoons H_2 + X_2 \qquad (8.19)$$

where X = halogen

decreases with increasing atomic number. Hydrogen fluoride cannot be decomposed. The degree of thermal dissociation of the other hydrogen halides is given in Table 8.5. The data demonstrate clearly that virtually all HCl is present as a molecule in the flue gas, whereas HBr and HI are to a substantial degree dissociated at elevated temperatures and may be involved in other reactions, especially bromination or iodation of organic compounds.

Table 8.5
Thermal Dissociation of Hydrogen Halides (%)

Temperature °C	HCl	HBr	HI
300	0.3×10^{-6}	0.003	19
1,000	0.014	0.5	33

The halogens enter the incinerator in various chemical forms. In inorganic materials they are present as hydrohalogenic salts. The alkali and earth-alkali salts, especially those of fluorine and chlorine, are very stable and possess high boiling points >1,400°C. This limits their volatilisation from the grate, however, if H_2O is present, hydrolysis may take place at much lower temperatures forming hydrogen halides. In most organic materials, such as plastics or textiles, the halogens are present in the form of covalent bonds. This permits formation of hydrohalogenic acid gases in the combustion chamber.

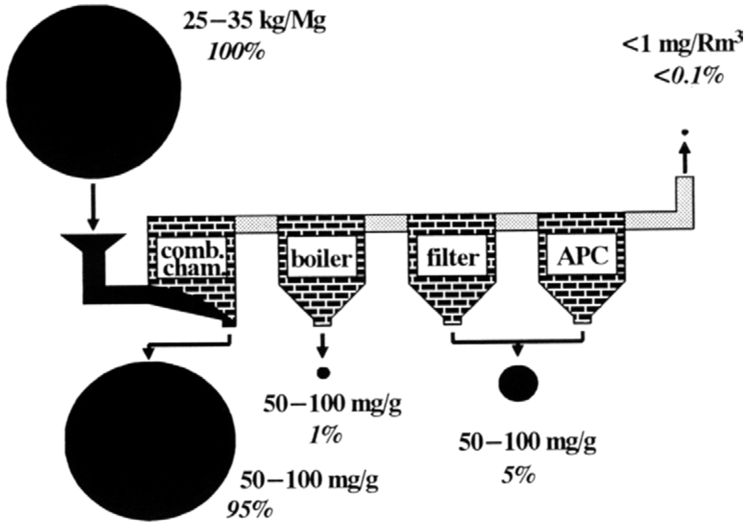
Chlorine

Chlorine is classified as a major element. Its concentration in the lithosphere is similar to that of carbon or chromium. Chloride ions are ubiquitous and essential to life on earth. Sea water contains about 2% chloride ions. The human body contains about 0.12 % chlorine, most of it in the form of chloride.

Organic bound chlorine is converted at comparably low temperatures into HCl. Even from plastics, such as PVC, HCl is evolved at temperatures above 230°C. Some inorganic chlorides tend to undergo hydrolytic decomposition at temperatures above 500°C. In residues, organic compounds containing chlorine are present, namely, polychlorinated dibenzo-p-dioxins, dibenzofurans, benzenes, phenols and biphenyls. More detailed information on these compounds is included later in this chapter.

Based on six data sets, the partitioning of Cl in MSW incinerator residues is illustrated in Figure 8.15 (Brunner and Mönch, 1986; Schneider, 1986; Reimann, 1989; Angenend, 1990; Belevi, 1993; Dalager, 1993). Parts of the data given there, for example the concentrations in the gas phase, are consistent with other publications, not being referenced with respect to their almost unlimited number. On the basis of these data sets the partitioning of Cl in a municipal solid waste incinerator is compiled in Figure 8.15. The chlorine concentration in the input is estimated to be 6.9 to 7.7 kg/tonne. Plastics, especially PVC, may contribute up to 50% to this value (Toetsch and Gaensslen, 1990).

Figure 8.15 Concentrations and Percent Partitioning of Cl



(* = raw gas concentrations)

Chloride concentrations in bottom ash range from about 2,000 to 3,500 µg/g. Approximately 8 to 13% of the chloride partitions to the bottom ash stream and the remaining fraction is entrained in the flue gas leaving the combustion chamber (Figure 8.15). Depending on the length of time the ash is exposed to the flue gas stream, chloride concentrations in boiler ash can reach upwards of about 20,000 µg/g [median concentration for mass burn facility (Environment Canada, 1988)], representing only 0.3% of the total chlorine mass flux. Raw particulate from the flue gas stream has been found to contain up to 11% chloride (based on particulate loading of 1 to 2 g/m^3) (Horch et al., 1990; Vogg et al., 1991).

Typical HCl concentrations in the raw flue gas stream are in the order of 1,000 mg/Rm^3. New regulations in some countries set HCl emission limits down to 10 mg/Rm^3. This stringent target can be achieved with modern APC systems, resulting in <1% of the chlorine input being emitted through the stack to the atmosphere. The balance of the HCl is trapped in the APC system. In wet scrubbing systems, about 50% of the chloride which was fed to the incinerator is discharged with the wastewater effluent (Dalager, 1993).

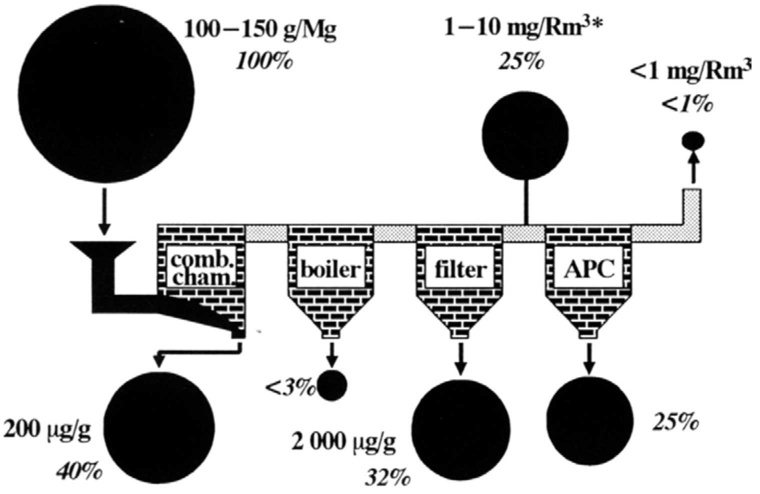
Fluorine

Due to its extremely high electronegativity, fluorine is a very reactive element. The only stable oxidation state is -1. Hydrofluoric acid is very aggressive and can dissolve SiO_2

and other stable silicates. Fluorides are used to a limited extent in some industrial processes, however, the importance of the element has increased since 1955, when the production of fluorine containing organic compounds and plastics began. Large quantities of chlorofluorocarbons (CFCs) were used (and subsequently banned) as propellants for sprays, as refrigerants and as thermal insulating gases in polyurethane and polystyrene foams. Now, new plastics containing fluorine are being produced, such as PTFE, and higher concentrations should be expected in the waste. Organic fluorine compounds start to disintegrate at temperatures above 250°C, forming HF. Only very high concentrations of fluoride prove harmful to humans.

The only two data sets available on fluorine concentration in MSW were used to generate the mass balance given in Figure 8.16 (Brunner and Mönch, 1986; Reimann, 1989). Both studies found similar input concentrations of 140±60 g/tonne and 103 g/tonne. The bulk of fluorine is typically bound to alkali metals. Only a minor fraction is currently contributed by organic compounds, such as PTFE.

Figure 8.16 Concentrations and Percent Partitioning of F



(* = raw gas concentrations)

Bottom ash concentrations were measured at about 200 µg/g. Although Reimann (1989) describes a washing process for bottom ashes using a quench tank, only about 1% of the fluorine inventory was separated. This indicates that fluorine in bottom ash is tightly bound to earth-alkali elements which have very low solubilities in water.

The fluorine content in gas path residue streams varied substantially. Reimann (1989) measured concentrations of 45 - 62 µg/g in boiler ash and about 100 µg/g in fly ash. Brunner and Mönch (1986) measured concentrations up to 2,000 µg/g in fly ash. There is no discernable reason based on facility type, operation or sampling methods which could account for the discrepancy. It is speculated that one major source of error could have been the digestion and analysis of special fluorides, especially those of calcium or iron, however, this cannot be confirmed.

The HF concentrations measured in the gas phase are consistent with each other, ranging from 3 to 5 mg/Rm^3. This is also consistent with other findings in the range of 1 to 10 mg/Rm^3 (Jochem, 1989; Ruytenbeek and Braams, 1989; Vehlow et al., 1992). Regulations in several countries limit HF emissions to 1 mg/Rm^3 which can be met by modern air pollution control equipment (Reeck et al., 1991; Environment Canada, 1986), even if the HF concentration in the raw gas is substantially increased (Vehlow et al., 1992). Typically less than 1% of the total fluorine input is emitted to the atmosphere.

Bromine and Iodine

Bromine and iodine are much less abundant than chlorine, although bromine typically is found associated with chlorine. The general properties of both elements are similar to those of chlorine. In sea water, the concentration of bromine is 200 times lower than the concentration of chlorine. The concentration of iodine is 2000 times lower. Bromine compounds are often used in plastics as flame retardants. Although chlorine and bromine are mainly present as halogenides, iodine is more frequently found in covalent bonds in organic compounds. Little is known about the behaviour of both elements during incineration, however, it is speculated that the main combustion products are hydrogen halides.

Schneider (1986) reports a bromine concentration of 6.5 g/tonne in MSW. The concentration of bromine in bottom ash is, as expected, very low (<10 µg/g). The major portion is captured in the APC residues, where concentrations of about 250 µg/g were measured. On a comparative basis, the partitioning of bromine will be similar to chlorine. Unfortunately, no data were available for iodine in MSW or ashes.

Since HBr and HI will be present at very low concentrations in the flue gas and the partitioning is similar to HCl, no problems are foreseen with respect to their emission to the atmosphere. No emission limits exist for these compounds.

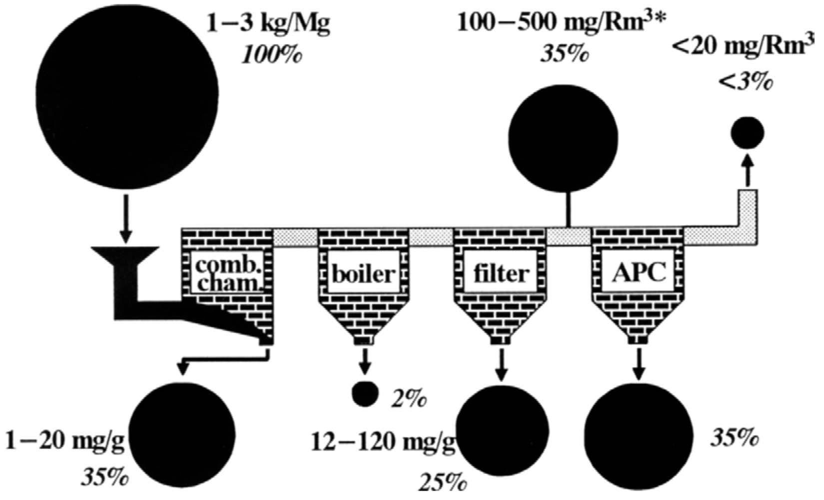
Sulphur

About 80% of global sulphur production is used to produce sulphuric acid in the chemical and fertiliser industry. Elementary sulphur is also used in the tyre industry for vulcanisation of rubber. Sulphur can form a series of different organic and inorganic compounds. The most stable inorganic compounds are sulphates. The gaseous oxide

SO_2 is by far the most prevalent combustion product of elementary sulphur, sulphides or organic sulphur compounds present in MSW. The formation of SO_2 in the combustion chamber depends on the temperature in the fuel bed. Elementary, organic, and sulphidic bound sulphur is converted into SO_2 at temperatures of about 300°C, whereas sulphates of trivalent metals like iron and aluminum start to disintegrate at temperatures of more than 550°C (see 8.2.3). Sulphates of alkali or earth-alkali metals are stable at temperatures up to about 1,000°C. Hence, the formation of SO_2 from sulphates increases with increasing temperature, and the concentration of sulphates in bottom ash decreases.

A rough estimate of sulphur partitioning during incineration compiled from several sources is depicted in Figure 8.17 (Baccini and Brunner, 1985; Hjelmar, 1987; Eighmy et al., 1987; Brunner and Mönch, 1986; Lorber, 1983; Roffman, 1991; Environment Canada, 1988; Jochem, 1989; Ruytenbeek and Braams, 1989; Belevi, 1993; Dalager, 1993). About 30% of the 1 to 3 kg/tonne of sulphur in MSW originates from the organic fraction and the remaining 70% is found in paper, paperboard, plastics and fines.

Figure 8.17 Concentrations and Percent Partitioning of S



(Concentrations in the gas phase given for SO_2, the solid residue for SO_4^{2-})
* = raw gas concentration

Sulphur will be present in all ash streams in the oxidation state +6, which means sulphates of mainly alkali and earth-alkali metals. Sulphate concentrations in bottom ash have been recorded ranging from 1,000 to 20,000 µg/g. Based on these results, about 35% of the sulphur input remains in the bottom ash. Sulphur concentrations in boiler ash do not differ significantly from those in the fly ashes, although the length of time the ash is exposed to the flue gas will significantly influence the concentration (see Chapter 10). SO_4^{2-} concentrations ranging from 12,000 to 120,000 µg/g have been recorded in fly ashes. These data indicate that about 2% of the sulphur input partitions to the boiler ashes and about 25% partitions to the fly ash.

Less than 40% of the sulphur input is released as sulphur dioxide into the flue gas. The corresponding SO_2 concentration in the raw gas is about 200 to 500 mg/Rm^3. Most modern APC systems guarantee SO_2 emissions of <20 mg/Rm^3 (Reeck et al., 1991; Environment Canada, 1986), thus emitting less than 5% of the total sulphur input.

Nitrogen

The oxidation product of nitrogen is NO, which is relatively chemically stable. During pyrolysis, amines, ammonia and other compounds can also be released, which are subject to further reactions in the hot zones of the combustion chamber. In dry MSW, the nitrogen content is about 1%. Complete oxidation of all the nitrogen in the waste fuel to NO would result in concentrations of about 1,500 mg/Rm^3 in the flue gas. However, the normal NO load is only in the order of 200 to 300 mg/Rm^3. It is speculated that the NO formed is produced only by the nitrogen compounds present in the waste. This is supported by data generated under different oxygen concentrations in the flue gas and at different combustion temperatures (Horch, 1987). NO emissions are limited in several countries to 50 to 200 mg/Rm^3. These limits cannot be achieved without additional post-combustion abatement (see Chapter 4). Since NO is virtually insoluble in water, wet gas cleaning systems have very limited effects on the NOx levels in the flue gas. The addition of the Fe^{2+} complex with the organic compound EDTA enhances the solubility, and if sulphites are present, NO can be reduced to N_2 (Schuster, 1984). However, this process is no longer used since it is detrimental to achieving adequate control of mercury emissions.

Studies indicate that amines and ammonia are able to react with NO to produce elementary nitrogen (de Soete, 1975). This process can be adapted for selective non-catalytic NOx reduction (SNCR) in MSW incinerators by means of ammonia injection (Hurst, 1983). There are some technical challenges in all SNCR processes:

- to inject the agent at the proper temperature
- to achieve a uniform distribution across the gas stream
- to guarantee a sufficient residence time in the appropriate temperature regime.

On the other hand, ammonia injection has the advantage of being performed at the front end of the flue gas system, and does not require special reactors or reheating of the gas. Although ammonia slip is a real problem, it can be minimised by the application of special organic nitrogen compounds (Dransfeld et al., 1992).

Most applied or proposed abatement processes are selective catalytic reduction processes (SCR) using metal oxide catalysts often based on TiO_2. Much of the drive for improvement of this technology has been in areas with chronic urban smog problems, especially Japan (Ando, 1985). Oxidative processes producing nitrates have been tested but are of little use since nitrates are water soluble and therefore are substances which are subject to landfill disposal regulations. Moreover, their contamination with heavy metals and other compounds precludes their use as fertilisers.

The occurrence of oxidised nitrogen compounds in bottom and fly ashes is unlikely and has not been reported. The ammonia slip in SNCR and SCR processes may cause problems in APC residues, and more research needs to be conducted on the extent of the influence de-NOx systems have on ash quality.

8.4.2 Volatile Metals

The main property of this group of metals is their volatility during incineration. The metals included in this group are not only those compounds of which vaporise readily, such as mercury, but also those semi-volatiles which cause a significant enrichment in fly ash even though a substantial portion may remain in the bottom ash stream. Reported concentrations of volatile metals in the waste stream and the residue streams are compiled in Table 8.6.

Table 8.6
Mean Concentrations of Volatile Metals in Waste and Ash

Element	Waste g/Mg	Bottom Ash µg/g	Boiler Ash µg/g	Fly Ash µg/g	Emissions µg/Rm^3
Sb	10 - 60	10 - 80	20 - 60	40 - 120	<5
As	3 - 9	1 - 80	20 - 60	40 - 120	<50
Cd	5 - 15	<0.5 - 10	50 - 150	50 - 1,000	<10
Pb	400 - 1,000	350 - 5,000	2,000 - 8,000	2,500 - 12,000	<50
Hg	0.5 - 5	<1	<5	1 - 30	<50
Se	0.8	0.4 - 1	4	10 - 20	<2
Sn	120	250	500	1700	-
Tl	0.2	<0.5	<0.5	<0.5	<1
Zn	600 - 2000	800 - 6,000	5,000 - 10,000	5,000 - 80,000	<5

Mercury

Mercury is a rare noble metal, and most of its compounds are distinguished by their relatively high vapour pressures. Mercury is used in thermometers, barometers, diffusion pumps, batteries, fluorescent light tubes, electric switches and relays, and as cathodes in chlorine-alkali electrolysis. Other applications include dental alloys, dyes and herbicides. Mercury is considered to be potentially highly toxic and the use of Hg is quickly becoming restricted in most countries.

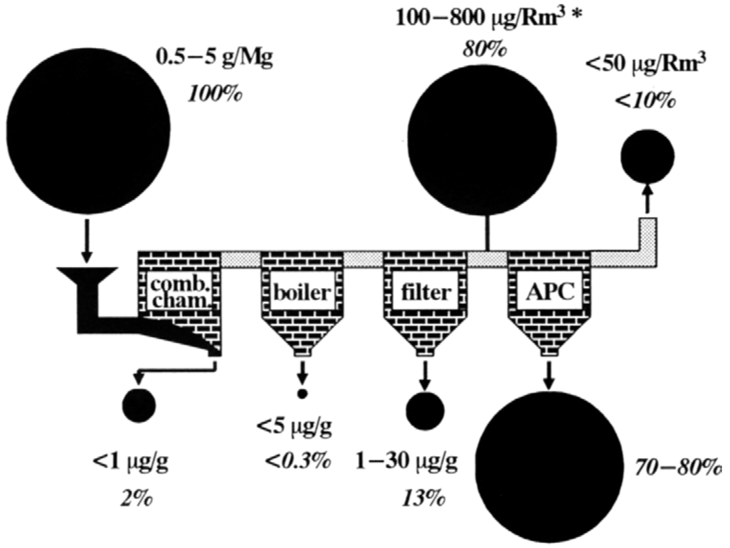
Mercury is by far the most thermally mobile trace metal and mercury compounds can remain in the gas phase at temperatures <180°C. This poses a unique problem with respect to MSW incineration, even though the concentration in the waste is very low (only 0.5 to 5 g/tonne) (Bergström and Sundquist, 1984; Environment Canada, 1985 & 1988; Schneider, 1986; Brunner and Ernst, 1986; Reimann, 1989; WASTE Program, 1993). The mechanisms of release and removal for mercury have been studied in great detail (e.g. Lindquist et al., 1986; Nagase et al., 1986; Braun et al., 1986 & 1988; Metzger and Braun, 1987; Teller and Quimby, 1991; Guest and Knizek, 1992; Reimann, 1989; Richman et al., 1993).

The mercury input depicted in Figure 8.18 is compiled from four of the data sets (Reimann, 1989; Brunner and Mönch, 1986; Angenend, 1990; Dalager, 1993). The mass balance indicates that almost no mercury remains in the bottom ash, since the reported mercury concentrations are normally <1 µg/g (Baccini and Brunner, 1985; Hjelmar, 1987; Eighmy et al., 1987; Schneider, 1987; Environment Canada, 1988; Ruytenbeek and Braams, 1989; Reimann, 1989; Angenend, 1990; Roffman, 1991; Sawell and Constable, 1993). In the combustion chamber, virtually all the mercury and its compounds are transformed into $HgCl_2$, which has a boiling point of only 304°C. Boiler ashes contain less than 5 µg/g of Hg and the concentrations in fly ash is also very low (1 - 30 µg/g). Therefore, the partitioning of mercury in the incinerator is about 2% in bottom ash and about 13% in fly ash.

Concentrations of mercury in the raw gas have been measured at several hundred $\mu g/Rm^3$ (Environment Canada, 1986 and 1988; Braun et al., 1986; Reimann, 1989; Brna, 1991). It is estimated that about 70 to 80% of the mercury inventory in MSW is present in vapour form at the entrance to the APC system, and as outlined in Chapter 4, there are several methods of mercury removal. Since mercury has a very strong preference to adsorb to particulate carbon, most modern incinerators (with characteristically low carbon particulate content in the flue gas stream) must rely on special mercury removal methods.

In dry or semi-dry systems the temperatures are kept below 150°C and the injection of activated carbon or sodium sulphide is recommended to guarantee sufficient removal. In the case of wet scrubbing systems, the acidity of the first scrubber has to be kept well below a pH of 1 to ensure adequate absorption of mercury as complex $(HgCl_4)^{2-}$ ions. Reducing compounds in the scrubbing solution may cause a partial reduction of the Hg^{2+} to Hg^{1+}, which is absorbed in the acid environment, but also undergoes spontaneous dissociation into Hg^{2+} and Hg^0 (Braun et al., 1986 & 1988). Metallic mercury can only be removed from the flue gas by means of activated carbon.

Figure 8.18 Concentrations and Percent Partitioning of Hg



(* = raw gas concentrations)

Additional problems arise in wet scrubbing systems when effluents have to be cleaned in wastewater treatment plants. The mercury concentrations in the order of 5 to 10 mg/l must be reduced to about 0.05 to 0.02 mg/L. Although this process is well established, it needs careful monitoring.

Irrespective of the APC system, mercury emissions from modern MSW incinerators can be kept below 0.05 µg/Rm³, which means that <10% of the mercury input is emitted to the atmosphere (Reeck et al., 1991; Brna, 1991; Braun and Gerig, 1990).

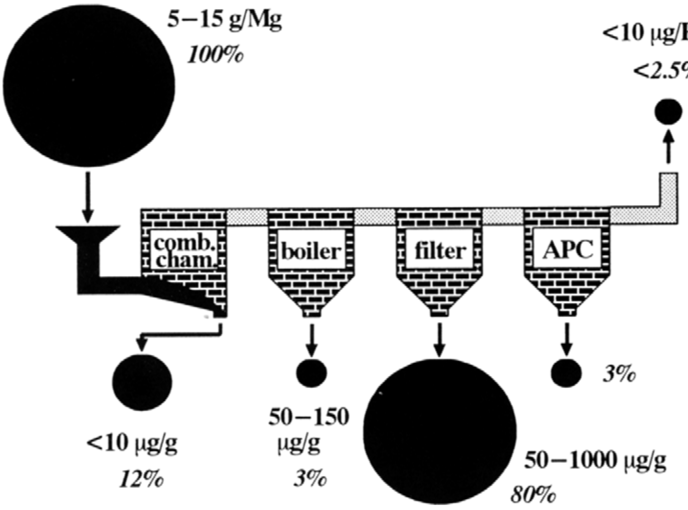
Cadmium

Environmental concerns over cadmium arise over its thermal mobility, potential solubility and toxicity in aquatic systems. It is classified as a rare element, and its chemical properties are very similar to those of zinc. In fact, cadmium is always present as a trace contaminant in zinc applications. Because of its corrosion resistance, cadmium is used in the metallic state as a corrosion protection layer on screws and other ferrous materials. A substantial amount of cadmium is also used in the manufacturing of rechargeable Ni-Cd batteries, as pigments in dyes and plastics, and as chloride scavengers in certain plastics. In some countries, applications of cadmium compounds are restricted, suggesting that concentrations in MSW will decrease in the near future.

According to thermodynamic calculations, cadmium and cadmium oxide are preferentially converted into $CdCl_2$ during combustion (Borchers, 1989). Furthermore, Figure 8.6 indicates that not only the metal itself, but cadmium chloride and to a limited extent cadmium oxide can be vaporised during incineration. Consequently, the bulk of cadmium entering the incinerator will be entrained in the flue gas stream. Since the boiling point of $CdCl_2$ is about 975°C and the flue gas contains high levels of HCl, virtually all of the cadmium found in the flue gas downstream of the boiler will be found in the particulate matter as $CdCl_2$.

The partitioning of cadmium is given in Figure 8.19. It is based mainly on five different sets of data (Brunner and Mönch, 1986; Schneider, 1986; Reimann, 1989; Dalager, 1993; Belevi, 1993).

Figure 8.19 Concentrations and Percent Partitioning of Cd



The concentration of cadmium in MSW ranges from 5 to 15 g/tonne in earlier studies (Schneider, 1986; Brunner and Zobrist, 1983; Dobberstein, 1983; Brunner and Ernst, 1986; Bergström and Lindquist, 1984; Reimann, 1989; Angenend, 1990; Belevi, 1993; Dalager, 1993), whereas two recent studies indicate that the quantities may have increased slightly (up to 13.6 g/tonne). Data indicate that although Ni-Cd batteries are a major source of the cadmium in the waste stream, plastic and organic fractions also contribute substantial proportions (20 to 50%) (Lorber, 1983; WASTE Program, 1993).

Cadmium concentrations in the bottom ash are normally well below 10 µg/g (Baccini and Brunner, 1985; Brunner and Mönch, 1986; Ruytenbeek and Braams, 1989; Reimann, 1990; Sawell and Constable, 1993; Belevi, 1993; WASTE Program, 1993), which represents less than 15% of the total input. Concentrations in any of the fly ash streams can range widely from 50 to almost 1,000 µg/g (Baccini and Brunner, 1985; Brunner and Mönch, 1986; Schneider, 1986; Hjelmar, 1987; Eighmy et al., 1987; Reimann, 1989; Horch et al., 1990; Angenend, 1990; Sawell and Constable, 1993; WASTE Program, 1993), depending on the length of time the ash remains exposed to the flue gas. The bulk of the cadmium fed into the incinerator partitions to the fly ash streams (about 80%).

The quality of the dust removal system dictates the emissions of cadmium to the atmosphere. As mentioned above, volatile species are enriched in the finer size fractions of the APC residue. For example, concentrations of cadmium in clean gas dust range from 100 to 4,000 µg/g (Brunner and Zobrist, 1983; Schneider, 1986; Brna, 1991; Vogg et al., 1991). Although these fine particles are difficult to capture, modern APC equipment can easily meet the most stringent emission limits for cadmium (e.g. values <10 µg/Rm^3 have been reported by Reeck et al., 1991; Brna, 1991; Vogg et al., 1991). Based on these emission limits, less than 1% of the cadmium inventory in MSW is emitted into the atmosphere.

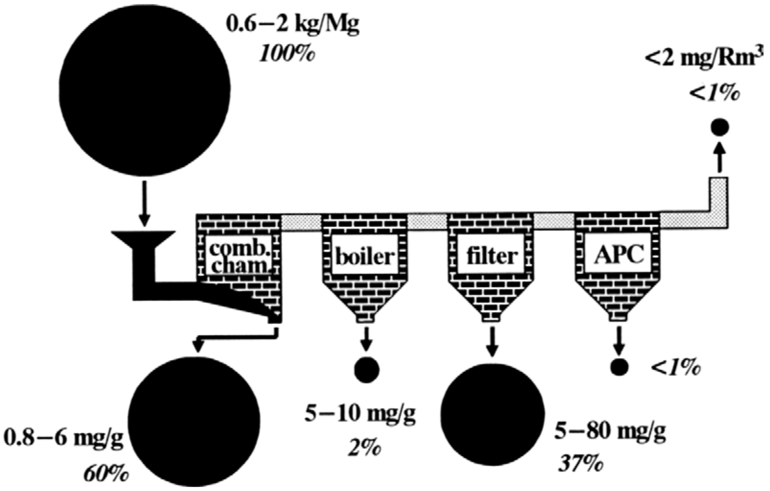
Zinc

In nature, zinc is often found in ores together with lead and cadmium. The greatest quantity of zinc produced is used to galvanise steel. Zinc is also an essential alloying element in brass and other alloys. Zinc oxide and other zinc compounds are used widely, for example in paper production, filler materials and pigments and catalysts in plastics. Zinc is generally not considered a toxicological concern.

Zinc is not as volatile as mercury or cadmium. Figure 8.20 illustrates the partitioning of zinc during incineration. Although zinc is fairly ubiquitous in waste components, nonferrous, organic, plastic, fines, wood and paper materials contribute substantial proportions to the remarkably high concentration of zinc in MSW (Lorber, 1983; Beek et al., 1989; WASTE Program, 1993). Concentrations in the overall waste stream range between 600 and 2,000 g/tonne (Brunner and Zobrist, 1983; Bergström and Lindquist, 1984; Schneider, 1986; Brunner and Mönch, 1986; Horch, 1987; Environment Canada, 1988; Reimann, 1989; Angenend, 1990; Beveli, 1993; Dalager, 1993; WASTE Program, 1993).

In the combustion chamber, zinc can either be transformed into an oxide or a chloride (Borchers, 1989). Due to the oxidative nature of the burn, the first reaction will be an almost complete oxidation. The second step, chlorination, is a relatively slow process. Since a substantial amount of the zinc is already present in the waste in the oxide form, the conversion into $ZnCl_2$ will be limited. Nevertheless, zinc shows the typical properties of a thermally mobile metal with enrichment on finer fly ash particles.

Figure 8.20 Concentration and Percent Partitioning of Zn



Although the $ZnCl_2$ and eventually traces of metallic zinc are volatilised in the combustion chamber (see Figure 8.6), the bulk of the zinc remains in the bottom ash. Concentrations range from about 800 to 6,000 µg/g (Brunner and Mönch, 1986; Schneider 1986; Hjelmar, 1987; Eighmy et al., 1987; Reimann, 1989; Angenend, 1990; Sawell and Constable, 1993; Beveli, 1993; WASTE Program, 1993). Estimates on the basis of these values result in approximately 65% of the zinc inventory staying in the bottom ash.

The volatilised zinc species begin to condense onto the surfaces of fly ash particles in the boiler. Zinc concentrations in fly ash streams range between 5,000 and almost 60,000 µg/g, depending on the length of time the ash remains exposed to the flue gas (Brunner and Mönch, 1986; Schneider, 1986; Reimann, 1989; Angenend, 1990; Sawell and Constable, 1993; WASTE Program, 1993). As is expected for a thermally mobile metal, zinc enrichment increases with decreasing particle size. It is estimated that about 30% of the zinc is partitioned into the fly ash streams. The emissions of zinc can be kept very low (down to less than 5 µg/Rm³) if an efficiently operating filter is installed (Vogg et al., 1991).

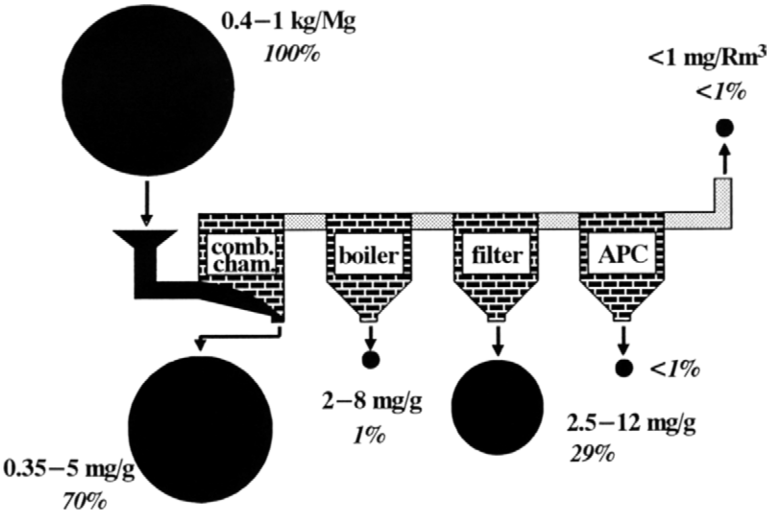
Lead

Lead is a relatively rare element, but it is enriched in nature in some large deposits, and because it can easily be reduced to the metallic form, it has been in use for centuries. Today, the main use of lead is in lead acid batteries (approximately 45% by weight), however, recent studies indicate that most of these are recycled. Lead is also used as a pigment and a stabilising agent in plastics. Dust and soil in MSW are typically contaminated with lead from its use as an anti-knocking agent in gasoline [$Pb(C_2H_5)_4$], although the quantities of leaded gas being sold globally are decreasing annually. Furthermore, the use of lead in paints has been phased out. All mobile species of lead are potentially toxic.

As indicated in Figure 8.3, the most preferential reaction for lead during the incineration process is to produce $PbCl_2$ (Borchers, 1989), then vaporise. Although the metallic form itself is potentially volatile, it is speculated that the metal melts and drips through the grates before reaching the vaporisation temperature (WASTE Program, 1993). Lead is an amphoteric metal, which is soluble in acidic or highly alkaline media. These phenomena must be considered when developing disposal strategies for MSW incinerator ash.

Partitioning of lead during incineration is given in Figure 8.21. Older studies have reported data which vary between 400 and 1,000 g/tonne in MSW (Dobberstein, 1983; Brunner and Mönch, 1986; Schneider, 1986; Reimann, 1989), however, more recent studies indicate that lead in MSW is decreasing (see Chapter 2 and Angenend, 1990; Beveli, 1993; Dalager, 1993). In spite of the thermal mobility of the lead and lead chloride, relatively high concentrations of lead ranging up to 5,000 µg/g were measured in bottom ash (Schneider, 1986; Hjelmar, 1987; Eighmy et al., 1987; Brunner and Mönch, 1986; Reimann, 1989), although more recent studies have indicated that these levels are decreasing (see Chapter 9). Nevertheless, bottom ash combined with grate siftings still contains the bulk of the lead (about 70%) which enters the facility and indicates that the chlorination reaction is kinetically hampered.

Figure 8.21 Concentrations and Percent Partitioning of Pb



About 30% of the lead input is vaporised from the grate, but all lead compounds formed in the combustion process condense onto dust particles in the temperature ranges downstream of the boiler. Boiler ashes can contain lead concentrations between 2,000 and 8,000 µg/g depending on the residence time in the boiler, or about 1% of the lead inventory (see Chapter 10).

Lead concentrations between 2,500 and 12,000 µg/g have been recorded in fly ashes (Baccini and Brunner, 1985; Horch, 1990; Reimann, 1989; Sawell and Constable, 1993; WASTE Program, 1993), representing about 30% of the total input. Clean gas dust can be highly enriched in lead (up to 10%) but modern APC systems are capable of limiting emissions to <50 µg/Rm^3 (Brna, 1991).

Arsenic

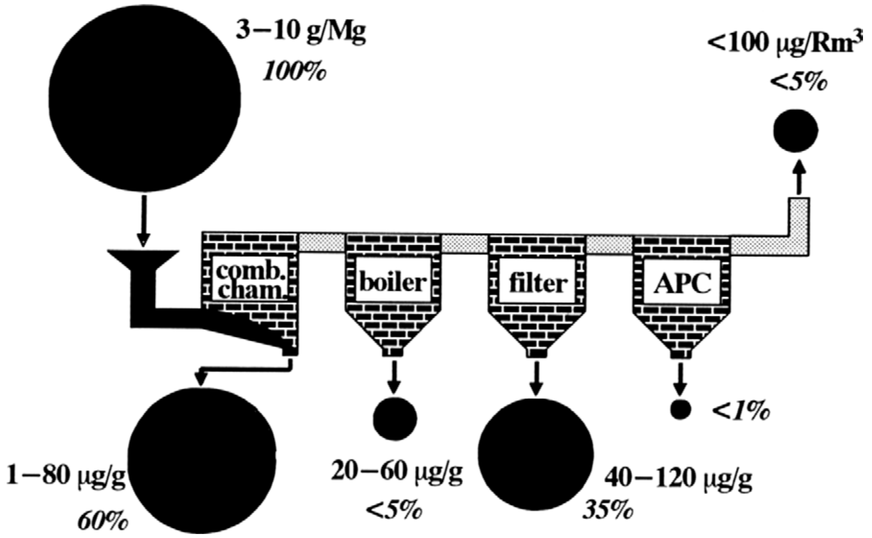
Arsenic is classified as a semi-metal and is most stable in the +3 oxidation state. Its industrial use has been reduced to some special applications, such as an alloying additive and as a component of special semiconductors. In many countries the application of arsenic compounds in herbicides or drugs is prohibited, however, copper arsenate is still used as an antifungal treatment for wood. Due to the poisonous nature of all of its compounds, arsenic is an element of concern in MSW incinerator ash. Many compounds (e.g. chlorides and oxides) are distinguished by a high thermal mobility, but should not be affected in the fuel bed if present in the anionic state.

The behaviour of arsenic during incineration is not as well documented as other metals. Three data sets have been used as the basis for the partitioning diagram in Figure 8.22 (Schneider, 1986; Angenend, 1990; Sawell and Constable, 1993). Since arsenic always creates analytical problems in the low concentration range, the given values should be regarded as first estimates.

The waste concentration is reported to be between 3 and 9 g/tonne. This is surprisingly low given that the background concentration in natural soils is 2 g/tonne (Taggart, 1948). Concentrations in the bottom ash vary between 8 µg/g and 32 µg/g which is consistent with the variability reported for some Danish and U.S. ashes (1.3 to 80 µg/g) (Hjelmar, 1987; Roffman, 1991). It is estimated that about 60% of the arsenic input remains in the bottom ash. Concentrations of arsenic in boiler ash and fly ash (including APC residues) are slightly enriched compared to bottom ash, varying from 20 to 60 µg/g and from 40 to 120 µg/g respectively. The overwhelming majority of the arsenic vaporised in the furnace condenses onto the finer fly ash particles which are trapped out by the APC control system.

These data indicate that there are no gaseous arsenic compounds to be found in the temperature range below 200°C. Based on a study of a modern incinerator, the cumulative emission of arsenic, cobalt, nickel, selenium and tellurium was about 60 µg/Rm^3 with total dust emissions of 12.8 mg/Rm^3 (Reeck et al., 1991), indicating that air emissions of arsenic do not pose a health risk.

Figure 8.22 Concentrations and Percent Partitioning of As



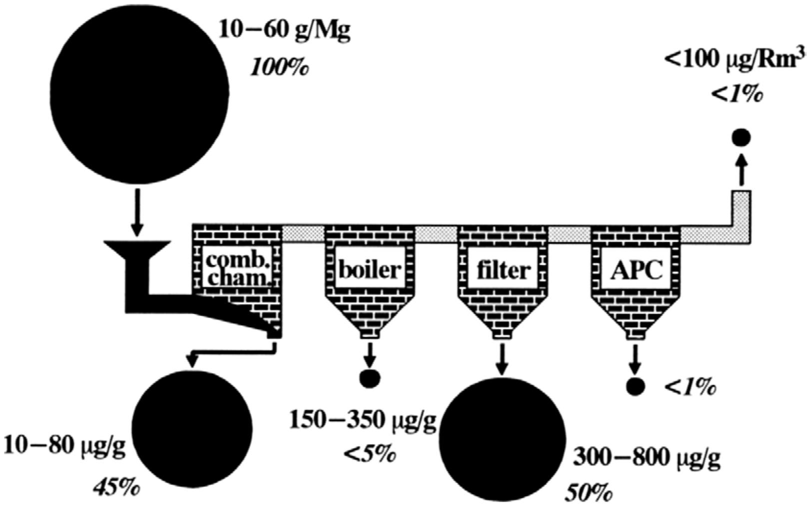
Antimony

Arsenic and antimony are closely related elements with respect to their chemical properties. Antimony is considered a semi-metal, however, it is also stable in its metallic form. In nature antimony is often found together with arsenic in copper, lead or silver ores. Antimony is used in special alloys and some of its compounds are used for pharmaceutical purposes. The toxicity of antimony is not as clearly defined as arsenic, but its compounds appear to be less harmful.

The formation enthalpies of antimony compounds are shown in Figure 8.3, and indicate that antimony is converted in the combustion chamber to Sb_2O_3 and $SbCl_3$ (Borchers, 1989). Although $SbCl_3$ has a relatively low boiling point and is the only compound which could potentially be vaporised, it is also sensitive to hydrolysis and can ultimately be oxidised (Sb_2O_3).

In nature, antimony is much less abundant than arsenic, by a factor of 10 to 20 (Taggart, 1948). In waste, however, the opposite is true. Concentrations of antimony in MSW are reported to be between 10 and 60 g/tonne (Schneider, 1986; Environment Canada, 1988). The partitioning of antimony is depicted in Figure 8.23, and indicates an almost equal distribution of antimony between the bottom ash and fly ash streams. Hence, kinetic factors may promote chlorination of antimony and hamper its oxidation and/or hydrolysis.

Figure 8.23 Concentrations and Percent Partitioning of Sb



Other Volatile Elements
There are other elements which are known to show significant enrichment in the fine particle fraction and hence are classified as volatile elements. Among these elements, tin, thallium, selenium and tellurium are present in quantifiable concentrations in MSW incinerator ash. Unfortunately, there is a dearth of data on their behaviour during incineration, which needs to be addressed in future research initiatives.

8.5 CARBON AND SELECTED CARBON COMPOUNDS

8.5.1 Total Carbon

Carbon is one of the key elements in MSW incineration. It not only contributes to the heating value of the waste, but it is also highly reactive and responsible for the generation of many by-products of combustion.

An ultimate analysis of waste (see Figure 8.2) indicates that approximately 250 kg/tonne of waste is carbon (CCME, 1989). At the beginning of this chapter, a description of the oxidation reaction and resulting products of carbon (CO_2 and to a limited extent CO) was given. This section builds on those reactions and addresses the issue of products of incomplete combustion.

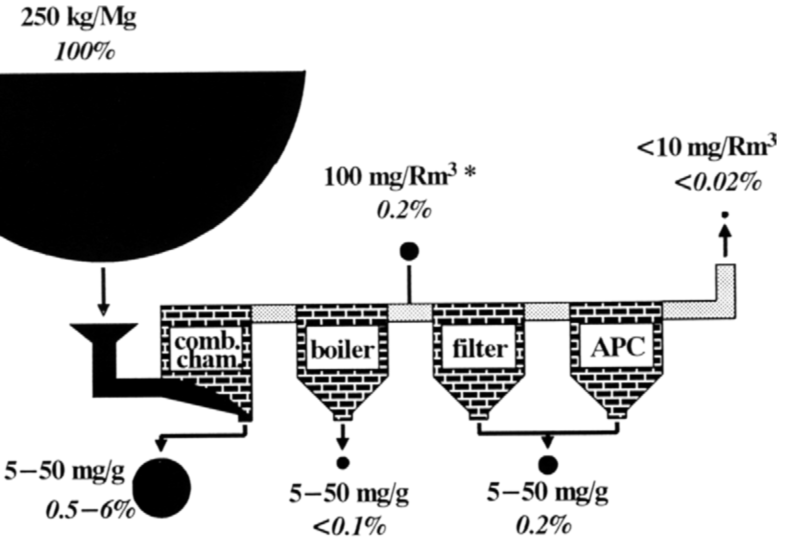
The concentrations of particulate carbon in bottom ash are in the order of 0.5 to 5%, depending on the combustion efficiency of the incinerator (Faulstich, 1991; Horch and Schneider, 1991; Vehlow et al., 1992). Fly ash concentrations also range from 0.5 to

5% (Vogg, 1984; Vogg et al., 1987; Faulstich, 1991; Horch and Schneider, 1991). These data indicate that at least 95% of the carbon compounds entering an incinerator should be thermally destroyed. Moreover, in modern incinerators, improved combustion conditions should result in even greater destruction efficiency.

In modern incinerators with dust emissions of <10 mg/Rm^3, CO and organic compounds are the major forms of emitted carbon. If an emission standard of 10 mg/Rm^3 for the organic carbon and 50 mg/Rm^3 for CO is taken as a basis, about 300 g/tonne or 0.12% of the total input of carbon would be emitted via the stack in these forms. However, the application of the latest combustion technology guarantees a combined total emission of CO and organic carbon of <10 mg/Rm^3, representing less than 0.02% of the total carbon input (Reeck et al., 1991).

On the basis of these data, a carbon balance for products of incomplete combustion (i.e. not counting CO_2) has been calculated and is depicted in Figure 8.24. The information provided in the Figures given in this section for organic compounds is based on a recently published overview paper (Vehlow and Vogg, 1991).

Figure 8.24 Concentrations and Balance of C



(without CO_2, * = raw gas concentration)

8.5.2 Polychlorinated Dibenzo-p-Dioxins and Furans

Unfortunately, not all carbon compounds present in incinerator ash or stack emissions are in the form of CO, particulate carbon or short chain hydrocarbons like methane. In 1977, the presence of polychlorinated dibenzo-p-dioxins and dibenzofurans was detected in fly ash from an MSW incinerator (Olie et al., 1977). This finding contributed considerably to the passionate discussions about the acceptability of MSW incinerators, a discussion which is still steeped in controversy.

This group of compounds is symbolised by the catchword "dioxins" and consists of 75 isomers of polychlorinated dibenzo-p-dioxins and 135 isomers of polychlorinated dibenzofurans. All of the isomers which contain chlorine atoms in positions 2, 3, 7 and 8 are considered toxic, with the tetra isomer ranking the most toxic. Although PCDD/PCDF compounds are susceptible to photodegradation, they are persistent under normal environmental conditions and tend to bio-accumulate in fatty tissues of animals (Poiger and Schlatter, 1986).

To compare PCDD/PCDF data on the basis of their toxicity, toxic equivalency factor (TEF) units are calculated based on weighting of the potential toxicity of each specific isomer in relation to 2,3,7,8 - tetrachloro-dibenzo-p-dioxin. Although the basic weighting is the same, there are several differences in the schemes between the several methods, including the Eadon, U.S. EPA, California, Canadian, German and Nordic methods. To avoid any confusion, an international scheme was presented by an expert group (NATO 1988) and tends to replace all other proposals. Table 8.7 summarises the international toxic equivalent factors (I/TEF) together with some other TEF schemes. The "tolerable daily intake" for humans is 1 to 10 pg (TE)/kilogram of body weight/day (WHO, 1987).

In all residues from waste incineration the isomer distribution of PCDD/PCDF is more or less the same. The toxic equivalents are dominated by PCDF, especially the 2,3,4,7,8 -pentachloro-dibenzofuran, due its high equivalency factor. About 70% of the TE concentration is normally contributed by PCDFs, whereas only 30% is actually derived from PCDDs. Based on these considerations, the information provided here will focus on the major trends. In many cases, especially for data from old MSW incinerators where isomer specific concentrations of PCDD and PCDF are not available, the TE is estimated using the following approximation based on Vogg et al., (1989):

$$E = 0.01\ x\ \Sigma PCDD + 0.02\ x\ \Sigma PCDF\ \text{for}\ \Sigma PCDD/PCDF > 1.5 \qquad (8.20$$

$$E = 0.005\ x\ \Sigma PCDD + 0.02\ x\ \Sigma PCDF\ \text{for}\ \Sigma PCDD/PCDF < 1.5 \qquad (8.21$$

Table 8.7
Summary of Various Toxic Equivalent Factors

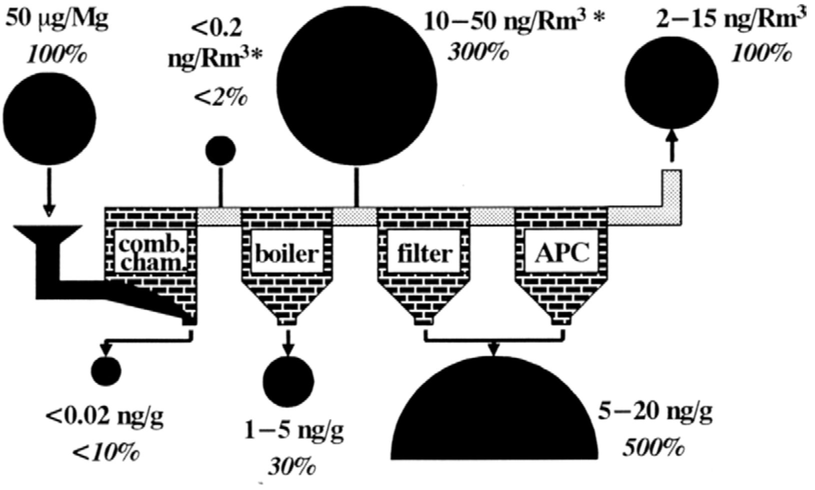
Isomer	I/TEF	Eadon	EPA	BGA	Nordic
2,3,7,8 - TetraCDD	1	1	1	1	1
1,2,3,7,8 - PentaCDD	0.5	1	0.2	0.1	0.5
1,2,3,4,7,8 - HexaCDD	0.1	0.03	0.04	0.1	0.1
1,2,3,6,7,8 - HexaCDD	0.1	0.03	0.04	0.1	0.1
1,2,3,7,8,9 - HexaCDD	0.1	0.03	0.04	0.1	0.1
1,2,3,4,6,7,8 - HeptaCDD	0.01	0	0	0.01	0.01
Octa CDD	0.001	0	0	0.001	0.001
2,3,7,8 - TetraCDF	0.1	0.33	0.1	0.1	0.1
1,2,3,7,8 - PentaCDF	0.05	0.33	0.1	0.1	0.01
1,2,3,4,7,8 - PentaCDF	0.5	0.33	0.1	0.1	0.5
1,2,3,4,7,8 - HexaCDF	0.1	0.01	0.01	0.1	0.1
1,2,3,6,7,8 - HexaCDF	0.1	0.01	0.01	0.1	0.1
1,2,3,7,8,9 - HexaCDF	0.1	0.01	0.01	0.1	0.1
2,3,4,6,7,8 - HexaCDF	0.1	0.01	0.01	0.1	0.1
1,2,3,4,6,7,8 - HeptaCDF	0.01	0	0.001	0.01	0.01
1,2,3,4,7,8,9 - HeptaCDF	0.01	0	0.001	0.01	0.01
OctaCDF	0.001	0	0	0.001	0.001
Other PCDD/PCDF	0	0	0-0.01	0.001-0.01	0

Adapted from: NATO, 1988; Barnes et al., 1986; BGA, 1985; and Ahlborg, 1989

Although PCDDs and PCDFs are ubiquitous (formed during burning of any material), in the environment their concentrations are very low. Industrial and thermal processes have increased the potential for PCDD/PCDF contamination of air, water and soils. Consequently, the waste entering an incinerator is contaminated with PCDD/PCDF as well. Published data consistently indicate that concentrations in waste are about 50 µg(TE)/tonne (Environment Canada, 1985 & 1988; Tosine, 1985; Hagenmaier, 1989; Fricke et al., 1989; Lahl et al., 1991; Johnke and Stelzner, 1992).

Although uncontrolled waste incineration plants were considered to be among the major sources of PCDD/PCDF loading to the environment, the situation during the last five to ten years has changed dramatically. The understanding of formation and decomposition reactions for PCDD/PCDF has resulted in a reduction of these emissions from MSW incinerators by a factor of 10 to 100. In addition, methods to destroy PCDD/PCDF in APC residues have been developed to further reduce the potential problem. The PCDD/PCDF partitioning in old MSW incinerators (Figure 8.25) is based on mean data from numerous publications which have been checked for consistency (Vehlow and Vogg, 1991).

Figure 8.25 Concentrations (TE) and Partitioning of PCDD/PCDF in an Old MSW Incinerator



(* = raw gas concentrations)

The most important reactions and conditions for the production of PCDD/PCDF in MSW incinerators have been studied in great detail (Rghei and Eiceman, 1982; Griffin, 1986; Vogg and Stieglitz, 1986; Stieglitz and Vogg, 1987; Hagenmaier et al., 1987; Hinton and Lane, 1991). The findings can be summarised:

- PCDD and PCDF are formed mainly by heterogeneous oxichlorination of particulate carbon.
- The chlorine is supplied by alkali and earth-alkali chlorides.
- An oxygen surplus in the atmosphere is essential.

- Copper and to a minor extent other metal compounds act as catalysts.
- The temperature range is 250 to 450°C.

The critical temperature range for this de-novo synthesis occurs in the flue gases passing through the boiler and economiser, and consequently is the principal area for PCDD/PCDF formation. This mechanism has been confirmed not only in laboratory experiments, but also by the results of a great number of field tests. Investigations on full scale incinerators demonstrated a strong correlation between PCDD/PCDF levels and particulate carbon. Based on these findings, it was deduced that a reduction of the PCDD/PCDF levels in raw flue gas can be facilitated by excellent burnout of the waste. The formation of PCDD/PCDF in the coolest area of the boiler was verified by the analysis of flue gas sampled at different points across the boiler in a full scale incinerator (Düwel et al., 1990; Nottrodt et al., 1990) and by data on boiler ash discharged via separate hoppers at different temperature levels (Vogg et al., 1987; Mariani et al., 1990).

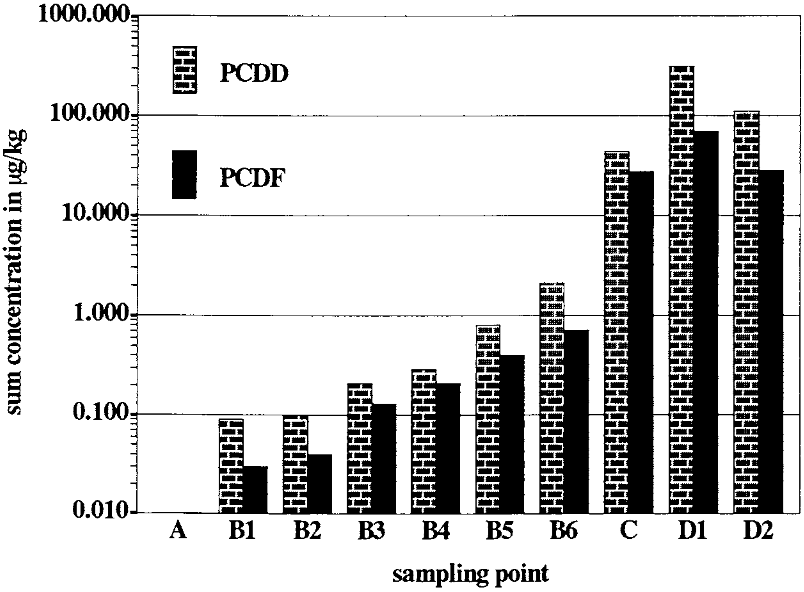
An analysis of ashes sampled at different areas of an incinerator and an electrostatic precipitator elucidates the increase in PCDD/PCDF concentration with decreasing temperatures (Figure 8.26). The inlet temperature to the boiler was 950°C, and the outlet temperature was 270°C. No temperature profile across the boiler was reported.

Only very low concentrations of PCDD/PCDF are present in the flue gas stream exiting the combustion chamber (<0.2 ng(TE)/Rm^3) (Environment Canada, 1985; Löffler, 1989; Düwel et al., 1990; Mariani et al., 1990; Nottrodt et al., 1990). Concentrations in bottom ash from well-operated incinerators are typically <0.02 ng(TE)/g (Roffman, 1991; Johnke and Stelzner, 1992; Morselli et al., 1989; Sawell and Constable, 1993).

Less than 5 µg(TE)/tonne of the combusted waste partitions to the bottom ash stream and less than 1 µg(TE)/tonne of waste is released into the flue gas. This means that at least 90% of the PCDD/PCDF fed into incinerators with the waste are destroyed by the combustion process. There is no data currently available on whether or not PCDD/PCDF formation can occur in the bottom ash as it cools, although a survey of PCDD/PCDF levels in German reports indicates that concentrations in quench tank water vary between 1 and 98 ng(TE)/L (Johnke and Stelzner, 1992). It should be noted that no details were given with respect to the operation of the incinerator or the quench tank (i.e. make up water addition). Furthermore, these concentrations may be the result of measuring the PCDD/PCDF content of suspended carbon particles introduced into the quench tank by the boiler ashes and accumulated during long periods of operation.

In the raw flue gas of old incinerators sampled directly downstream of the boiler, mean PCDD/PCDF levels of about 30 ng(TE)/m^3 have been measured (Environment Canada, 1985, 1986 & 1988; Merz et al., 1989; Düwel et al., 1990; Mariani et al., 1990; Nottrodt, 1990; Vogg et al, 1990; Johnke and Stelzner, 1991; Vogg et al., 1991). Based on these data, PCDD/PCDF loading of 150 µg(TEF)/tonne of waste can be calculated, which in turn means that the raw flue gas downstream of the boiler carries three times more PCDD/PCDF than was fed into the incinerator. The PCDD/PCDF concentrations in the boiler ashes given in the cited studies ranged from about 0.1 to 5 ng(TEF)/g of ash.

Figure 8.26 PCDD/PCDF in Ashes Sampled from Different Points of an MSW Incinerator



Since most of the PCDD/PCDF load present in the raw gas of older incinerators is bound to particulate matter, especially to carbon particles, it will be partitioned to the APC system residues. A sampling program in different German MSW incinerators resulted in a mean value of 10 ng(TEF)/g of ash, i.e. about 250 µg(TE)/tonne of waste combusted (Hagenmaier, 1989; Johnke and Stelzner, 1992). Highly chlorinated isomers are typically formed over the lesser chlorinated isomers. These data are consistent with other data found in the literature.

Although temperature is the most important controlling factor for trace metal condensation, the types of dust removal system and the operating temperature are both important considerations when examining organic compounds. In the past, electrostatic precipitators were often operated at temperatures in the region of 300°C. This obviously resulted in increased PCDD/PCDF formation, which has been confirmed by several studies (see below). As an example, a 20 tonne per hour incinerator fitted with an electrostatic precipitator operated at a temperature of 320°C, resulted in an increase of seven times the PCDD/PCDF concentrations measured in the entrance to the precipitator (Vogg et al., 1989).

Recently published studies provide evidence that in some cases there may be another mechanism for PCDD/PCDF production in lower temperature precipitators as well (200 to 220°C) (Hanay et al., 1986; Vogg et al., 1990; Kilgroe et al., 1991; Hiraoka et al., 1991). The underlying reaction is not yet fully known, however, it may be the influence of the electromagnetic charges which enhance formation in the device. The net formation of PCDD/PCDF between the boiler exit and the APC ash discharge hopper, given in Figure 8.25, should reflect these effects if an electrostatic precipitator is in use.

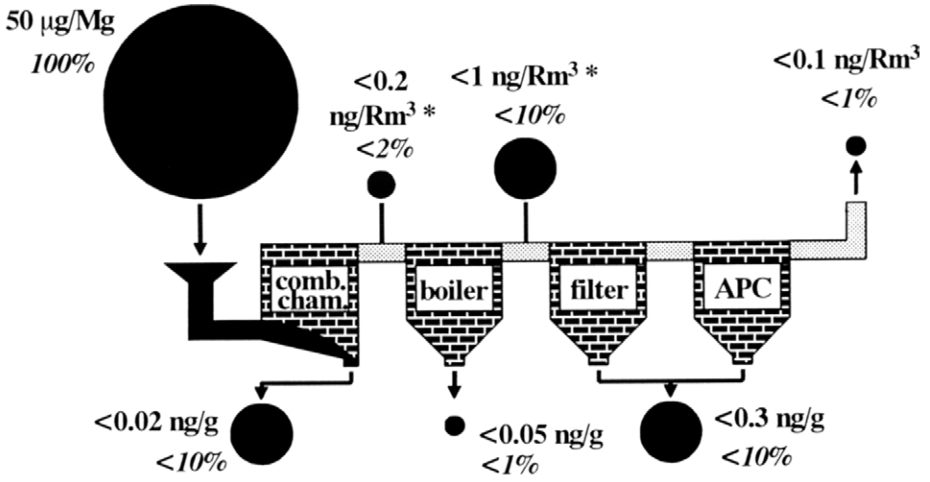
The minimisation of PCDD/PCDF formation has been investigated as extensively as the formation mechanisms. Much of the data in this area point to improved combustion conditions. In addition, new designs to combustion chambers were found to be successful in limiting formation of the compounds. Now proper operating conditions and modern furnace designs are capable of reducing raw flue gas concentrations of PCDD/PCDF to <0.2 ng(TE)/m^3 (Environment Canada, 1988; Horch, 1990; Reeck et al., 1991). A few years ago, this value was impossible to achieve even in clean gas of old facilities. Moreover, the concentrations in the different ash streams were also considered very low, i.e. bottom ashes 0.007 ng/g, boiler ashes 0.023 ng(TE)/g, and APC ashes 0.213 ng/g.

Although proper operating conditions and adequate design of the furnace are requisites for reduced PCDD/PCDF formation, efficient removal and/or destruction technologies are also warranted. Spray absorbers in combination with fabric filters (Environment Canada, 1986) and even electrostatic precipitators (Nielsen and Møller, 1989) have been optimised. Activated charcoal filters have been developed with a high absorption potential (Dannecker and Hemschemeier, 1990). Similarly, activated carbon is now injected into the flue gas to sorb PCDD/PCDF and mercury (Mosch and Gottschalk, 1991; Regler, 1991) and catalytic oxidation has been successfully demonstrated (Hiraoka et al., 1989; Hagenmaier and Mittelbach, 1990; Fahlenkamp et al., 1991). The use of different reactive additives injected into the flue gas has also been examined in a semi-technical test facility (Lenoir and Hutzinger, 1989; Vogg et al., 1990^a).

Figure 8.27 illustrates the partitioning of PCDD/PCDF during incineration, based on a state-of-the-art incinerator facility. The contamination of bottom ashes is generally lower than levels found in some soils (about 5 ng/kg). Moreover, the gaseous emissions do not add substantially to today's background concentrations in ambient air (50 to 300 fg/Rm^3).

Furthermore, the PCDD/PCDF discharged with the boiler and filter ashes can be thermally destroyed by various treatment methods. Two processes have been developed and tested, and both guarantee excellent destruction (>99%). The first one applies a thermal treatment in a rotary kiln at about 400°C under oxygen deficient conditions, then copper salts are added as catalysts. A full scale facility is in operation (Schetter et al., 1990). A second process, the 3R Process, utilises the combustion chamber of the incinerator itself to decompose PCDD/PCDF in extracted and compacted filter ashes (Merz et al., 1989). All vitrification processes proposed for APC residues may also be appropriate for treatment of PCDD/PCDF as well.

Figure 8.27 Concentrations (TE) and Partitioning of PCDD/PCDF in a Modern Incinerator



Based on the information given above, a modern MSW incinerator which is well operated and equipped with adequate APC devices is capable of meeting the most stringent emission regulations for PCDD/PCDF. In some European countries, this limit is 0.1 ng(TE)/Rm^3, however, even lower limits have been achieved during recent pilot plant studies (<0.01 ng/Rm^3) (Cleve, 1989; Vicinius and Knoche, 1991). Overall, modern incinerators act as net destroyers of PCDD/PCDF.

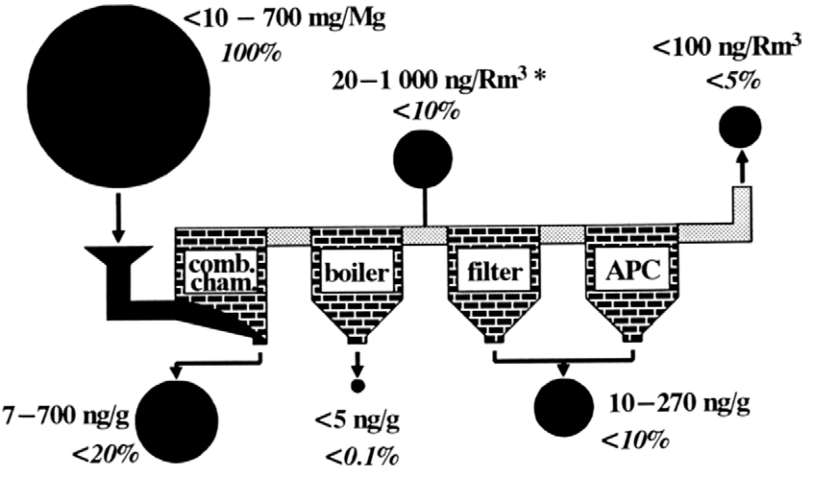
8.5.3 Polychlorinated Biphenyls (PCBs)

PCBs are a class of noncorroding, highly stable, nonflammable chemical compounds which were used widely in electrical transformers, other electric applications, heat exchange equipment and to a lesser degree in inks, oils, sealants and caulking compounds. Their use was banned in 1977 due to their persistence and their propensity to bio-accumulate in fatty tissues of animals (Government of Canada, 1990). Although PCBs are suspected of being toxic, the toxicity is much lower than PCDD/PCDFs. In 1983, the estimated mean intake rate per person in industrialised countries was about 350 ng/kg of body weight/day (Bennett, 1983).

There has been a tendency to extend the toxicity equivalent factor defined for PCDD/PCDFs to these compounds (Bol et al., 1989; Safe, 1990) and first estimates suggest that emissions and residues from MSW incineration might increase the toxicity equivalence proposed for PCDD by approximately 10% (van Bavel et al., 1992). Data for PCB concentrations in MSW have ranged widely from below detection to 700 mg/tonne of waste, reflecting the sporadic presence in MSW. (Environment Canada, 1985, 1988, & 1992; Tosine et al., 1985; Fricke et al., 1989; Lahl et al., 1991).

Concentrations in bottom ashes are very low, typically below detection limits (Environment Canada, 1993). The concentrations depicted in Figure 8.28, which attempts to provide an idea of partitioning for PCBs, are compiled from Italian and U.S. data and might overestimate the residual burden of these compounds (Morselli, 1989; Roffman, 1991). Although PCBs have not been detected in boiler ash (<5 ng/g) (Environment Canada, 1993), concentrations in the raw flue gas downstream of the boiler range between 20 ng/Rm^3 and 1,000 ng/Rm^3 in mass burner systems (Environment Canada, 1986 & 1988). In well operated incinerators, concentrations <12 ng/Rm^3 could be achieved (Reeck et al., 1991). The levels reported for filter ashes of 10 to 270 ng/g are consistent with the raw flue gas concentrations (Sawell and Constable, 1993; Gonzales et al., 1991).

Figure 8.28 Concentrations and Partitioning of Polychlorinated Biphenyls



(* = raw gas concentration)

The partitioning of PCBs during incineration indicates that modern incinerators are net destroyers of PCBs. Based on the fact that these compounds have been banned from use and their concentrations should decrease in the future, this group of compounds does not pose a potential problem with regard to MSW incineration. The concentrations of emissions from well-operated incinerators are typically <100 ng/Rm^3 (Environment Canada, 1986; Cleve, 1989; Morselli et al., 1989; Reeck et al., 1991), which means that these emissions are insignificant and do not add a substantial portion of PCB to the background intake.

8.5.4 Polychlorinated Benzenes

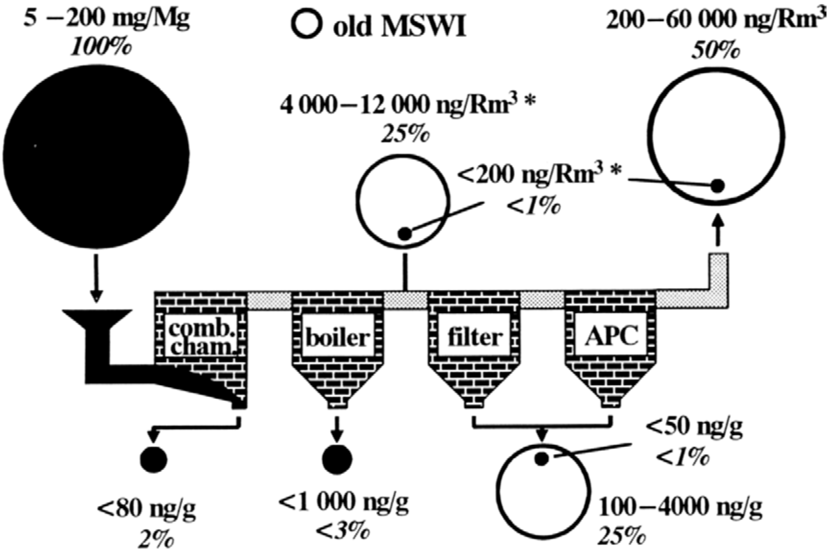
Polychlorinated benzenes (CBs) are widely used in the chemical industry as intermediate products in special syntheses and as solvents for fats and resins. CBs are among the most thermally stable organic compounds. Under the specific conditions of elevated temperatures in the presence of water vapour, they can form PCDDs and PCDFs, hence they have a certain relevance in the waste incineration. These compounds are of relatively low toxicity, however, they bio-accumulate in fatty tissue of humans and animals. The acceptable daily intake of hexachlorobenzene for humans is in the order of 4 µg/kg of body weight/day which is far greater than any possible dose which could be received through exposure to MSW incinerator emissions or ash (Greim, 1990).

Since CBs are ubiquitous in the environment, they are present in MSW. The data from three separate studies indicate that concentrations in waste vary widely, e.g. 5 to 200 mg/tonne of waste (Environment Canada, 1985 & 1986; Tosine et al., 1985). Data on bottom ash concentrations from Environment Canada's NITEP Program (Environment Canada, 1993) and one American facility investigation (Roffman, 1991) are relatively consistent ranging from below detection to 80 ng/g. CBs can be formed at boiler outlet by the same type of de-novo synthesis which is responsible for PCDD/PCDF formation (Schwarz et al., 1990). Concentrations in the flue gas downstream of the boiler measured in mass burn units during the NITEP Program ranged from 4 to 12 µg/Rm^3 (Environment Canada, 1985 and 1986). In a new German incinerator, the concentration was only 15 ng/Rm^3 (Reeck et al., 1991). The partitioning of CBs during incineration (during good and poor operation) is given in Figure 8.29.

Concentrations in boiler ash and APC residues ranged from below detection to 4.2 µg/g (Environment Canada, 1985; Sawell and Constable, 1993). The data included samples collected during a wide range of operating conditions. "Good" operating conditions generally resulted in much lower concentrations of CBs being measured in all ash streams (Environment Canada, 1985, 1986, 1988 and 1991).

Similar to the phenomenon of enhanced PCDD/PCDF formation in electrostatic precipitators, the concentrations of CBs also appear to increase due to the electrical charges (Hanay, 1986). Concentrations downstream of the precipitator increased by a factor of about five. The partitioning of CBs during proper operating conditions indicates that modern MSW incinerators are net destroyers of these organic compounds.

Figure 8.29 Concentration and Partitioning of Polychlorinated Benzenes



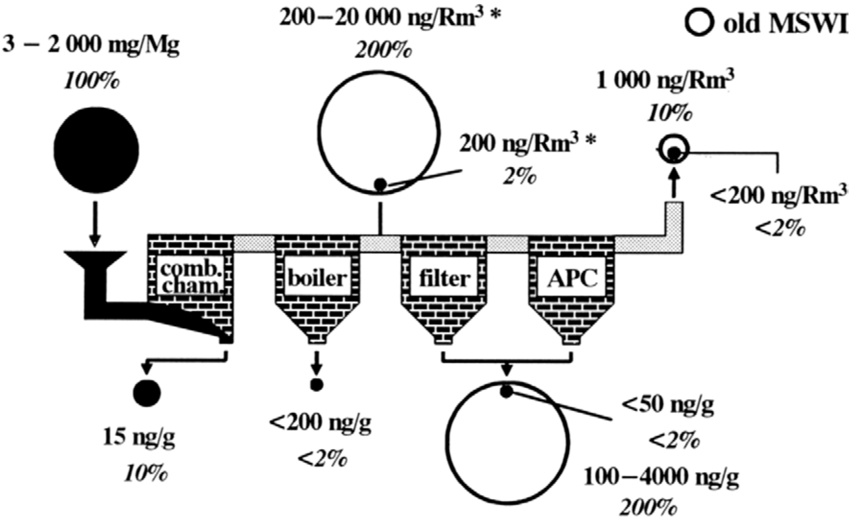
(* = raw gas concentration)

8.5.5 Polychlorinated Phenols

The properties of polychlorinated phenols (CPs) are similar to those of polychlorinated benzenes. They are thermally stable and are used mostly as biocides, herbicides and fungicides, and bio-accumulate in fatty tissue. The partitioning of CPs during incineration is given in Figure 8.30.

Concentrations of CPs in MSW between 3 and 2,000 mg/tonne of waste have been reported (Environment Canada, 1985, 1986, 1988 and 1991). Like PCDD/PCDFs and CBs, CPs can be formed at the boiler outlet and a second formation mechanism may occur in an electrostatic precipitator. Emissions can be kept far below 200 ng/Rm^3, especially if the best available technology is applied. Although carcinogenic effects can be realised at very high doses, the emissions from incinerators pose no significant health risk (Greim, 1990).

Figure 8.30 Concentrations and Partitioning of Polychlorinated Phenols



(* = raw gas concentration)

8.5.6 Brominated Hydrocarbons

Since the chemical properties of chlorine and bromine are similar, the same mechanisms that form chlorinated organic compounds should also form brominated and mixed brominated/chlorinated compounds during incineration. The stability of hydrogen halides decreases with increasing atomic number (see Table 8.5), making it easier to produce elementary bromine from HBr or bromides than it is to form chlorine from HCl or chlorides. Although oxybromination might be a favoured reaction over oxychlorination, bromine concentrations are only 0.5% that of chlorine, hence the overwhelming bulk of formation compounds will be chlorinated.

Brominated compounds, even brominated dibenzo-p-dioxins and dibenzofurans, have been detected in fly ash (Schäfer and Ballschmiter, 1986; Oehme et al., 1987; Schwind et al., 1988). There are 3,500 isomers of mixed halogenated dibenzo-p-dioxins and dibenzofurans, and appropriate standards are only available for a few isomers making quantitative analysis of these compounds extremely difficult.

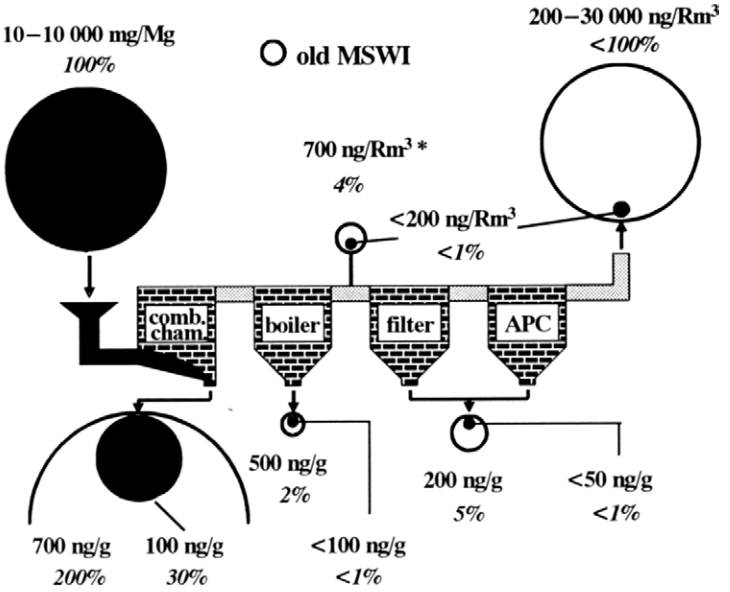
8.5.7 Polycyclic Aromatic Hydrocarbons (PAH)

The group of polycyclic aromatic hydrocarbons (PAHs) consists of 16 planar condensated aromatic compounds, eight of which are suspected of being carcinogenic

(Menzie et al., 1992). PAHs are formed in all kinds of smouldering or pyrolytic reactions, thus their presence is an indicator of poor combustion conditions. The main sources of PAHs in the environment include car exhausts, domestic heating and atmospheric emissions from industry and sewage sludge.

Figure 8.31 illustrates the partitioning of PAHs during incineration. Similar to the other organic compounds, concentration of compounds in the waste, the type of incinerator and the operating conditions under which the samples were collected will all greatly influence the concentrations of PAHs measured in the ash and the flue gases. Consequently, the data from the NITEP Program are widely scattered. The concentrations of PAHs in the waste varied from 10 to 10,000 mg/tonne of waste (Environment Canada, 1985, 1986, 1988 & 1991). Data from a German study indicate about 100 mg/tonne (Fricke et al., 1989).

Figure 8.31 Concentrations and Partitioning of Polycyclic Aromatic Hydrocarbons



(* = raw gas concentration)

Since PAHs are considered semi-volatile, the highest concentrations are generally measured in bottom ash. Concentrations as low as 100 ng/g seem to be achievable with modern grate systems (Fricke et al., 1989). Concentrations of up to 700 ng/g have been measured in mass burn systems (Sawell and Constable, 1988; Morselli et al., 1989), up to almost 7 µg/g in modular incinerators (Environment Canada, 1985) and 19 µg/g in old RDF systems (Environment Canada, 1993). Boiler ash is normally only moderately contaminated with PAHs (20 to 500 ng/g) and concentrations measured in APC residues are typically even lower (Environment Canada, 1985 and 1988). Although a recent study has focused on the potential mobility of these compounds after deposition of ash by means of a special extraction procedure (Bauw et al., 1991), the low solubility of the compounds indicates these compounds do not pose a risk of contaminating groundwater.

Although relatively high emissions (5 to 30 µg/Rm^3) have been measured during interrupted operation of an incinerator (Benestad et al., 1990), well-operated MSW incinerators are capable of achieving emissions of PAHs below 200 ng/Rm^3 (Environment Canada, 1985, 1986, 1988 & 1991). PAH concentrations measured in stack gases during a test run of a charcoal filter were only 12 ng/Rm^3. The partitioning of PAHs during incineration indicates that although these semi-volatile compounds behave differently from the other chlorinated compounds discussed earlier, modern MSW incinerators act as a net destroyer of PAHs.

REFERENCES

Ahlborg, U.G. "Nordic Risk Assessment of PCDDs and PCDFs." Chemosphere 19: 603, 1989.

Ando, J. "Review of Japanese NOx Abatement Technology for Stationary Sources." NO_X-Symposion Karlsruhe 1985, Proceedings Edited by O. Rentz, F. Ißle and M. Weibel. Universität (TH), Karlsruhe, A1, 1985.

Angenend, F.J. and L. Trondt. "Schadstoffinput - Schadstoffoutput." VGB Kraftwerkstechnik 70: 36-42, 1990.

Baccini, P. and P.H. Brunner. "Behandlung und Endlagerung von Reststoffen aus Kehrichtverbrennungsanlagen." Gaz - Eaux - Eaux usees 65: 403, 1985.

Barin, J. Thermochemical Properties of Inorganic Substances. Springer-Verlag, Berlin-Göttingen-Heidelberg, 1993.

Barnes, D.G., J. Bellin and D. Cleverly. "Interim Procedure for Estimating Risks Associated with Exposures to Mixtures of Chlorinated Dibenzodioxins and Dibenzofurans (CDDs and CDFs)." Chemosphere 15:, 1985, 1986.

Barniske, L. and B. Johnke. "Die Abfallverbrennung im Spannungsfeld einer modernen Abfallentsorgung." Müllverbrennung und Umwelt 4 Edited by K.J. Thomé-Kozmiensky. EF-Verlag, Berlin, 15, 1990.

Bartels, J., P. ten Bruggencate, H. Hausen, K.H. Hellwege, Kl. Schafer and E. Schmidt Landolt-Börnstein. Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik, sechste Auflage, II: Band: Eigenschaften der Materie in ihren Aggregatzuständen, 2. Teil: Gleichgewichte außer Schmelzgleichgewichten. Springer-Verlag, Berlin - Göttingen - Heidelberg: 1, 1960.

Bauw, D.H., G.A. de Wilde, G.A. Rood and T.G. Aalbers. "A Standard Leaching Test, Including Solid Phase Extraction, for the Determination of PAH Leachability from Waste Materials", Chemosphere 22: 713, 1991.

Beek, A.I.M. van de, A.A.J. Cornelissen and Th.G. Aalbers. Fysisch en Chemisch Onderzoek aan Huishoudelijk Afval, Pub. Rijksinstituut Voor Volksgezondheid en Milieuhygiene Bilthoven, Rapportnr. 738505005, June, 1988.

Behrendt, Th., H. Dittrich and A. Lubecki. "Modellansätze zum Betriebsverhalten einer Rostfeuerung am Beispiel TAMARA." Symposium 25 Jahre LIT, 5 Jahre TAMARA, KfK report 5000: 38, 1992.

Belevi, H. "Wie wird die Schlacke erzeugt?" Entwicklung und Umsetzung neuer Qualitätsanforderungen in der Abfallwirtschaft Kartause Ittingen, September 14-16, 1993. Dokumentation Vertiefungskurs V1/93, EAWAG, Zürich: 54-74, 1993.

Benestad, C., L. Hagen, A. Jebens, M. Oehme and H. Ramdahl. "Emissions of Organic Micropollutants from Discontinuously Operated Municipal Solid Waste Incinerators." Waste Management and Research 8: 193, 1990.

Bennett, B.G. "Exposure of Man to Environmental PCBs - an Exposure Commitment Assessment." The Science of the Total Environment 29: 101, 1983.

Bergström, J. and J. Sundquist. "Emission Control for Municipal Solid Waste Incineration in Sweden." EWPCA-ISWA '84, 6th European Sewage and Refuse Symposium EWPCA Munich, 21 to 25 May 1984, Documentation, EWPCA, Ed., GFA, St. Augustin: 885, 1984.

BGA. "Sachstand Dioxine." Bericht des Umweltbundesamtes 5/85: 264, 1985.

Bol, J., M. van den Berg and W. Seinem. "Interactive effects of PCDDs, PCDFs and PCBs as Assessed by the E.L.S.-Bioassay." Chemosphere 19: 899, 1989.

Borchers, H.-W. "Thermal Behaviour of Heavy Metals in Exhausts of Waste Burning Plants." Recycling International Edited by K.J. Thomé Kozmiensky. Berlin EF-Verlag: 1461, 1989.

Braun, H. and A. Gerig. "Mercury Emission Monitoring on Municipal Waste Combustion." Municipal Waste Combustion, Conference Papers and Abstracts from the 2nd Annual International Speciality Conference Tampa, FL April 15 - 19. Air and Waste Management Association, Pittsburgh, PA: 798, 1991.

Braun, H., H. Metzger and H. Vogg. "Zur Problematik der Quecksilber-Abscheidung aus Rauchgasen von Müllverbrennungsanlagen." 1. Teil, Müll und Abfall 18: 62, 1986. 2. Teil, Müll und Abfall 18: 89, 1986.

Braun, H., H. Metzger and H. Vogg. "Die Verbesserung der Abscheidung von Quecksilber aus Rauchgasen der Müllverbrennung." Chemie-Ingenieur-Technik 60: 135, 1988.

Braun, H. and A. Gerig. "Entwicklung eines Quecksilberanalysators zur kontinuierlichen Messung in Rauchgasen." AbfallwirtschaftsJournal 2: 819, 1990.

Brna, Th.G. "Toxic Metal Emissions from MWCs and their Control." Municipal Waste Combustion, Conference Papers and Abstracts, Tampa, FL, April 15 - 19, 1991. Air and Waste Management Association, Pittsburgh, PA: 145, 1991.

Brunner, P.H. and J. Zobrist. "Die Müllverbrennung als Quelle von Metallen in der Umwelt." Müll und Abfall 15: 221, 1983.

Brunner, P.H. and W.R. Ernst. "Alternative Methods for the Analysis of Municipal Solid Waste." Waste Management & Research 4: 147, 1986.

Brunner, P.H. and H. Mönch. "The Flux of Metals through Municipal Solid Waste Incinerators." Waste Management and Research 4: 105, 1986.

Bundesministerium für Umwelt. "Naturschutz und Reaktorsicherheit 17." Verordnung zur Durchführung des Bundesimmissionsschutzgesetzes, (17. BImSchV), Bundesgesetzblatt, Teil 1, 2: 545, 2: 832, 1990.

Canadian Council of Ministers of the Environment (CCME). Operating and Emission Guidelines for Municipal Solid Waste Incinerators Report CCME-TS/WM-TRE003, June 1989.

Cernuschi, S., M. Giuliani and R. Marforio. "Kurzfristiges Umweltverhalten von Flugasche und Schlacke aus städtischen Festmüllverbrennungsanlagen." Messen und Analysieren an Abfallbehandlungsanlagen, Edited by K.J. Thomé-Kozmiensky. EF-Verlag, Berlin: 308, 1987.

Cleve, U. "Stand of Technical and Economical Application of Activated Carbon for Flue Gas Washing Plants with Waste Incineration." Recycling International Edited by K.J. Thomé-Kozmiensky. EF-Verlag, Berlin: 1265, 1989.

Corey, R.C., B.J. Cross and W.T. Reid. "External Corrosion of Furnace-Wall-Tubes-II. Significance of Sulfate Deposits and Sulphur Trioxide in Corrosion Mechanism." Transactions ASME 67: 289, 1965.

Dalager, S. "Danske Massebalanceundersøgelser." Konference om affaldsforbrænding under nye betingelser, Kopenhagen, September 3, 1993.

Dannecker, W. and H. Hemschemeier. "Level of Activated-Coke Technology for Flue Gas Dust Collection Behind Refuse Destruction Plants Looking at the Problem from the Special Aspects of Dioxin Separation." In Organohalogen Compounds, Vol. 4, Dioxin 90 - EPRI-Seminar Edited by O. Hutzinger and H. Fiedler. Ecoinforma Press, Bayreuth: 267, 1990.

de Soete, G.G. 15th Symposium Int. on Combustion, Tokyo, August 1974. Proceedings: 1093, 1975.

Dobberstein, J. "Energie und Schadstoffe im Hausmüll." Müll und Abfall 15: 305, 1983.

Dransfeld, P., H. Hunsinger and H. Vogg. "Die thermische NO_X-Emissionsminderung mit Melamin und verwandten Verbindungen bei Müllverbrennungsanlagen." VGB Kraftwerkstechnik 72: 995, 1992.

Düwel, U., A. Nottrodt and K. Ballschmiter. "Simultaneous Sampling of PCDD/PCDF Inside the Combustion Chamber and on Four Boiler Levels of a Waste Incineration Plant." Chemosphere 20: 1839, 1990.

Eighmy, T.T., M.A. Guay, S.A. McHugh, P.H. Thompson, N.E. Kinner and T.P. Ballestero. "Codisposal of Municipal Solid Waste Bottom Ash and Wastewater sludges." Municipal Waste Incineration, Proceedings, October 1 - 2, 1987, Montreal, Quebec. Edited by Environment Canada. 349, 1987.

Eighmy, T.T. Personal communication concerning petrographic data from the WASTE Program, Phase II, Speciation of Elements in MSW and Incinerator Residues, Progress Review, August 1993.

Environment Canada. The National Incinerator Testing and Evaluation Program: Two-stage Combustion (Prince Edward Island) Environment Canada Report EPS 3/UP/1, 1985.

Environment Canada. The National Incinerator Testing and Evaluation Program: Air Pollution Control Technology Environment Canada Report EPS 3/UP/2,, 1986.

Environment Canada. National Incinerator Testing and Evaluation Program: Environmental Characterization of Mass Burning Incinerator Technology at Quebec City, Summary Report. Environment Canada Report EPS 3/UP/5, 1988.

Environment Canada. The Environmental Characterization of RDF Combustion Technology, Summary Report Environment Canada Report, 1991.

Environment Canada. The National Incinerator Testing and Evaluation Program: A Summary of the Characterization and Treatment Studies on Residues from Municipal Solid Waste Incineration Prepared by S.E. Sawell and T.W. Constable for Waste Management Branch. Environment Canada Report, 1993.

Fahlenkamp, H., G. Mittelbach and H. Hagenmaier. "Katalytische Zerstörung von Dioxinen." Müllverbrennung und Umwelt 5 Edited by K.J. Thomé-Kozmiensky. EF-Verlag, Berlin: 469, 1991.

Fäßler, K., H. Leib and H. Spähn. "Korrosionen an Müllverbrennungskesseln." Mitteilungen der VGB 48: 126, 1968.

Faulstich, M., A. Freudenberg, G. Kley and P. Köcher. "Thermodynamische und mineralogische Überlegungen zur Inertisierung fester Rückstände aus der Abfallverbrennung." Müllverbrennung und Umwelt 4 Edited by K.J. Thomé-Kozmiensky. EF-Verlag, Berlin: 339, 1990.

Faulstich, M. "Feste Rückstände aus Abfallverbrennung und Rauchgasreinigung." Müllverbrennung und Umwelt 5 Edited by K.J. Thomé-Kozmiensky. EF-Verlag, Berlin: 297, 1991.

Fricke, K., H. Vogtmann, J. Jager and M. Wilken. "Organische Schadstoffe in Bioabfallkomposten." Müll und Abfall 21: 472, 1989.

Gonzales, M., M. Fernandez, L. Jimenez and L. Hernandez. "Application of Multivariate Analysis to the Determination of PCB in Fly Ash from Municipal Incinerators." Chemosphere 18: 2213, 1989.

Göttlicher, R. and P. Anton. "Reststoffe aus der Müllverbrennung." AbfallwirtschaftsJournal 2: 376, 1990.

Government of Canada. PCB Fact Sheets Health and Welfare Canada, 1990.

Greim, H. "Toxicological Evaluation of Emissions from Modern Municipal Waste Incinerators." Chemosphere 20: 317, 1990.

Griffin, R.D. "A New Theory of Dioxin Formation in Municipal Solid Waste Combustion." Chemosphere 15, 1987, 1986.

Guest, T. and O. Knizek. Mercury Control at Burnaby's Municipal Waste Incinerator, 1992.

Hagenmaier, H., M. Kraft, H. Brunner and R. Haag. "Catalytic Effects of Fly Ash from Waste Incineration Facilities on the Formation and Decomposition of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans." Environmental Science and Technology 21: 1080, 1987.

Hagenmaier, H. "Polychlorierte Dibenzodioxine und polychlorierte Dibenzofurane - Bestandsaufnahme und Handlungsbedarf." In Halogenierte organische Verbindungen in der Umwelt, VDI-Berichte VDI-Verlag, Düsseldorf. 745: 939, 1989.

Hagenmaier, H. and G. Mittelbach. "Versuche zum katalytischen NO_X- and Dioxinabbau im Abgas einer Hausmüllverbrennungsanlage." VGB Kraftwerkstechnik 70: 491, 1990.

Hanay, Y., T. Katou and H. Ide. "Chlorination Process in the Refuse Incinerator's Equipment." Yokohama Kokuritsu Daigaku Kankyo Kagaku Kenkyu Senta Kiyo 13: 37, 1986.

Handbook of Chemistry and Physics 72nd Edition. CRC Press, Cleveland, OH, 1992.

Hausner, H.H. "Discussion of the definition of the term 'sintering'." Materials Science Monographs, 4, Sintering - New Developments Edited by M.M. Ristic. Amsterdam, Oxford, New York, 1979.

Hinton, W.S. and A.M. Lane. "Characteristics of Municipal Solid Waste Incinerator Fly Ash Promoting the Formation of Polychlorinated Dioxins." Chemosphere 22: 473, 1991.

Hiraoka, M., N. Takeda, S. Okajima, T. Kasakura and Y. Imoto. "Catalytic destruction of PCDDs in flue gas." Chemosphere 19: 361, 1989.

Hiraoka, M., T. Fujii, K. Kashiwabara, K. Teyama and M. Kondo. "The Removal Efficiency of Dioxin in Flue Gas of MSW Incinerator - Comparision of a Fabric Filter with an Electrostatic Precipitator." Chemosphere 23: 1439, 1991.

Hjelmar, O. "Leachate from incinerator ash disposal sites." Municipal Waste Incineration, Proceedings, October 1 - 2, 1987, Montreal, Quebec. Edited by Environment Canada. 287, 1987.

Horch, K. "Optimierung von Feuerungen mit dem Ziel der Schadstoffminderung." Thermische Abfallbehandlung in Entsorgungskonzepten VDI-Berichte Nr. 637, VDI-Verlag, Düsseldorf, 173, 1987.

Horch, K., A. Christmann and G. Schetter. "Zukunftorientiertes Feuerungskonzept zur Abfallverwertung." Müll und Abfall 22: 288, 1990.

Horch, K. and D. Schneider. "Das Brenn-Schmelz-Verfahren - Verglasen von Rückständen aus der Abfallverbrennung." Müllverbrennung und Umwelt 5 Edited by K.J. Thomé-Kozmiensky. EF-Verlag, Berlin: 341, 1991.

Hundesrügge, T. "Phasenanalytische Untersuchungen an Filteraschen aus Müllverbrennungsanlagen." Aufschluß 41: 281, 1990.

Hurst, B.E. Technology Advances in Selective Non-Catalytic NO_X-Reduction (Thermal DeNOx) Exxon Research and Engineering Company, Houston, TX, 1983.

Jochem, M. "Stand der Rostfeuerungstechnik und Entwicklungstendenzen." Entsorgungspraxis Spezial No. 10: 28, 1989.

Johnke, B. and E. Stelzner. "Results of the German Dioxin Measurement Programme at MSW Incinerators." Chemosphere 10: 345-355, 1992.

Kautz, K. "Korrosionsursachen in Hausmüllverbrennungsanlagen." Mitteilungen der VGB 51: 398, 1975.

Kilgroe, J.D., W.S. Lanier and T.R. van Alten. "Montgomery County South Incinerator Test Project: Formation, Emission and Control of Organic Pollutants." Municipal Waste Combustion, Conference Papers and Abstracts, Tampa, FL, April 15 - 19, 1991. Air and Waste Management Association, Pittsburgh, PA: 190, 1991.

Lahl, U., L. Wilken, B. Zeschmar-Lahl and J. Jager. "PCDD/PCDF Balance of Different Municipal Waste Management Methods." Chemosphere 23: 1481, 1991.

Lenoir, D. and O. Hutzinger. "PCDD/F: Verhinderung der Entstehung chlorierter Dibenzodioxine und -furane bei der Müllverbrennung." UWSF-Z. Umweltchem. Ökotox 4: 3, 1989.

Lieser, K.H. and H. Elias. Z. Anorg. Allg. Chem. 316: 208, 1962.

Lindquist, O., K. Puromaki and P. Schager. "Mercury from Waste Combustion." Appendix to Residues from Waste Incineration - Chemical and Physical Properties by J. Hartlén and P. Elander, Swedish Geotechnical Institute, 1986.

Löffler, H. "Wiener Anforderungen an eine umweltverträgliche Entsorgung von MVA-Reststoffen." In Reststoffe aus der thermischen Abfallbehandlung, VDI-Berichte Nr. 753, VDI-Verlag, Düsseldorf: 51, 1989.

Löffler, H. "Müllverbrennungsanlagen und polychlorierte Dioxine und Furane." Beiträge zum Umweltschutz Heft 19, Magistrat der Stadt Wien, 1989.

Lorber, K.E. "Die Zusammensetzung des Mülls und die durch Müllverbrennungsanlagen emittierten Schadstoffe." Müllverbrennung und Rauchgasreinigung Edited by K.J. Thomé-Kozmiensky. EF-Verlag, Berlin: 559, 1983.

Mariani, G., E. Benfenati and R. Fanelli. "Concentrations of PCDD and PCDF in Different Points of a Modern Refuse Incinerator." Chemosphere 21: 507, 1990.

Menzie, C.A., B.B. Potocki and J. Santodonato. "Exposure to Carcinogenic PAHs in the Environment." Environmental Science and Technology 26: 1278, 1992.

Merz, A., K. Horch, J. Schneider, L. Stieglitz, J. Vehlow and H. Vogg. "Thermal Destruction of PCDD/PCDF Compounds by 3R Product Recycling into the Solid Incineration Furnace." International Conference on Municipal Waste Combustion, Hollywood, FL, April 11 - 18, 1989. Vol. 2, Supply and Services Canada, 7A/37, 1989.

Metzger, M. and H. Braun. "In-situ Mercury Speciation in Flue Gas By Liquid and Solid Sorption Systems." Chemosphere Volume 16: No. 4, 1987.

Morselli, L., S. Zappoli, A. Liberti, M. Rotatori and E. Brancaleoni. "Evaluation and Comparision of Organic and Inorganic Compounds between Emission and Immission Samples from Municipal Solid Waste Incinerators." Chemosphere 18: 2263, 1989.

Mosch, H. and J. Gottschalk. "Filsorption - Kombinierte Filtration und Sorption bei Gesamtkonzepten für die Rauchgasreinigung." Müllverbrennung und Umwelt 5 Edited by K.J. Thomé-Kozmiensky. EF-Verlag, Berlin: 227, 1991.

Mühlenweg, U. and Th. Brasser. "Reststoffe bei der Hausmüllverbrennung." Müll und Abfall 22: 53, 1990.

Nagase, H., Y. Ose, T. Sato and M. Yamada. "Mercury Methylation by Ash from Refuse Incineration." Science of the Total Environment No. 53, 1986.

NATO, CCMS. "International Toxicity Equivalency Factors (I/TEF) Method of Risk Assessment for Complex Mixtures of Dioxins and Related Compounds." Report 178, December 1988.

Nelson, W. and C. Cain. "Corrosion of Superheaters and Reheaters of Pulverized Coal-Fired Boilers. part 1." Transactions ASME Series A, 83: 194, 1960. Part 2, Transactions ASME Series A, 84: 468, 1960.

Nielsen, K.K. and J.T. Møller. "Reduction of Chlorinated Dioxins and Furans in the Flue Gas from Incinerators with Spray Absorbers and Electrostatic Precipitators." Chemosphere 19: 367, 1989.

Nottrodt, A., U. Düwel and K. Ballschmiter. "The Influence of Increased Excess Air on the Formation of PCDD/PCDF in a Municipal Waste Incineration Plant." Chemosphere 20: 1847, 1990.

Oberste-Padberg, R. and K. Schweden. "Zur Freisetzung von Wasserstoff aus Mörtlen mit MVA-Reststoffen." Wasser, Luft und Boden 6: 61, 1990.

Oehme, M., S. Manø and A. Mikalsen. "Formation and Presence of Polyhalogenated and Polycyclic Compounds in the Emissions of Small and Large Scale Municipal Waste Incinerators." Chemosphere 16: 143, 1987.

Olie, K., P.L. Vermeulen and O. Hutzinger. "Chlorodibenzo-p-Dioxins and Chlorodibenzofurans are Trace Components of Fly Ash and Flue Gas of Some Municipal Incinerators in the Netherlands." Chemosphere 6: 455, 1977.

Pauling, L. The Nature of the Chemical Bond, 3rd Ed. Cornell University Press, 1969.

Perrier-Rosset, A. "Valorization or Disposal of Incineration Residues in France." SARDINIA 89, Second International Landfill Symposium, Porto Conte (Alghero), Italy. Proceedings - Vol.I, C.I.P.A.s.r.l., Milan. LIX 1, October 9-13, 1989.

Pietrzeniuk, H.J. "Stand der Verwertung der Rückstände aus Müllverbrennungsanlagen." Thermische Verfahren der Abfallwirtschaft Statusbericht 1985, VDI-Gesellschaft Energietechnik, Düsseldorf: 153, 1985.

Poiger, H. and C. Schlatter. "Pharmacokinetics of 2, 3, 7, 8-TCDD in Man." Chemosphere 15: 1489, 1986.

Reeck, G., W. Schröder and G. Schetter. "Zukunftsorientierte Abfallverbrennung in der MVA Ludwigshafen." Müll und Abfall 23: 661, 1991.

Regler, H. "Flugstromverfahren mit Kalk-Aktivkoks-Gemischen." Müllverbrennung und Umwelt 5 Edited by K.J. Thomé-Kozmiensky. EF-Verlag, Berlin: 245, 1991.

Reichel, H.H. and U. Schirmer. "Waste Incineration Plants in the FRG: Construction, Materials, Investigation on Cases of Corrosion." Werkstoffe und Korrosion 40: 135, 1989.

Reimann, D.O. "Heavy Metals in Domestic Refuse and Their Distribution in Incinerator Residues." Waste Management and Research 7: 57-62, 1989.

Remy, H. Lehrbuch der Anorganischen Chemie, Vol. II Akademische Verlagsgesellschaft Geest, and Portig KG, Leipzig: 883, 1961.

Rghei, H.O. and G.A. Eiceman. "Adsorption and Thermal Reactions of 1, 2, 3, 4-Tetrachlorodibenzo-p-Dioxin on Fly Ash from a Municipal Incinerator." Chemosphere 11: 569, 1982.

Richman, M., D. Fickling and J. Hahn. "Mercury Removal Studies at a Municipal Waste Combustor in Marion County, Oregon." Report by Ogden Martin Systems Inc., 1993.

Roffman, H. "Major Findings of the U.S. EPA/CORRE MWC-Ash Study." Municipal Waste Combustion, Conference Papers and Abstracts Tampa, FL, April 15 - 19, 1991. Air and Waste Management Association, Pittsburgh, PA: 96, 1991.

Ruytenbeek, A. and P.M. Braams. "Einfluß der Vorwegnahme von organischen Abfällen auf die Abfallverbrennung." Müllverbrennung und Umwelt 3 Edited by K.J. Thomé-Kozmiensky. EF-Verlag, Berlin: 85, 1989.

Safe, S. "Polychlorinated Biphenyls (PCBs), Dibenzo-p-Dioxins (PCDDs), Dibenzofurans (PCDFs), and Related Compounds: Environmental and Mechanistic Considerations Which Support the Development of Toxic Equivalency Factors (TEFs)." CRC Crit. Rev. Toxicol. 21: 51, 1990.

Sawell, S.E. and T.W. Constable. The National Incinerator Testing and Evaluation Program: the Combustion Characterization of Mass Burning Incinerator Technology Quebec City, Volume VI, Assessment of Contaminant Leachability from Residues Environment Canada Report, Manuscript Series: IP-82, 1988.

Sawell, S.E. and T.W. Constable. "The National Incinerator Testing and Evaluation Program: Characterisation of Residues from a Refuse Derived Fuel Combustion System and a Modular Municipal Waste Incinerator." Proceedings of the International Conference on Municipal Waste Combustion Hollywood, FL, 1989.

Schäfer, W. and K. Ballschmiter. "Monobromo-polychloro-derivates of Benzene, Biphenyl, Dibenzofurane and Dibenzodioxin Found in Chemical-Waste Burning." Chemosphere 15: 755, 1986.

Schetter, G., K. Horch, R. Stutzle, H. Brunner and H. Hagenmaier. "Low Temperature Thermal Treatment of Filter Ash from Municipal Solid Waste Incinerators for Dioxin Decomposition on a Technical Scale." Organohalogen Compounds Vol. 3, Dioxin 90 - EPRI-Seminar. Edited by O. Hutzinger and H. Fiedler. Ecoinforma Press, Bayreuth: 165, 1990.

Schneider, J. "Determination of Elemental Waste Composition by Analysis of Incineration Residues." Recycling International Vol. 1.1. Edited by K.J. Thomé-Kozmiensky. EF-Verlag, Berlin: 318, 1986.

Schuster, H. "Minderung der NO_X-Emissionen aus Kraftwerksfeuerungen." VDI-Berichte Nr. 495 VDI-Verlag, Düsseldorf: 143, 1984.

Schwarz, G., L. Stieglitz and W. Roth. "Formation Conditions of Several Polychlorinated Compound Classes on Fly Ash of a Municipal Waste Incinerator." Organohalogen Compounds Vol. 3, Dioxin 90 - EPRI Seminar. Edited by O. Hutzinger and H. Fiedler. Ecoinforma Press, Bayreuth: 169, 1990.

Schwind, K.-H., J. Hosseinpour and H. Thoma. "Brominated/Chlorinated Dibenzo-p-Dioxins and Dibenzofurans. Part 1: Brominated/Chlorinated and Brominated Dibenzo-p-Dioxins and Dibenzofurans in Fly Ash from a Municipal Waste Incinerator." Chemosphere 17: 1875, 1988.

Stieglitz, L. and H. Vogg. "On Formation Conditions of PCDD/PCDF in Fly Ash from Municipal Waste Incinerators." Chemosphere 16: 1917, 1987.

Taggart, A. Handbook of Mineral Dressing, Ores and Industrial Minerals J. Wiley, New York, 1948.

Teller, A.J. and J.M. Quimby. "Mercury Removal from Incinerator Flue Gas", 1991.

Tillman, D.A., A.J. Rossi, and K.M. Vick. Incineration of Municipal and Hazardous Solid Wastes Academic Press: 29, 1989.

Tobler, H.P. "Behandlung und Verfestigung von Rückständen aus Müllverbrennungsanlagen in der Schweiz" Entsorgungspraxis Special 1988 188, 1988.

Toetsch, W. and H. Gaensslen. Polyvinylchlorid Verlag TÜV Rheinland, Köln: 78, 1990.

Tosine, H.M., R.E. Clement, V. Ozwacic and G. Wong. "Levels of PCDD/PCDF and other Chlorinated Organics in Municipal Refuse." Chemosphere 14: 821, 1985.

van Bavel, B., I. Fangmark, S. Marklund, G. Soderstrom, K. Ljung and C. Rappe. "Quantitative Analysis of Organic Trace Compounds by Isotope Dilution: Formation of the Non-ortho PCBs 77, 126, 169 during Incineration." Organohalogen Compounds 8: 225, 1992.

Vehlow, J., H. Braun, K. Horch, A. Merz, J. Schneider, L. Stieglitz and H. Vogg. "Semi-Technical Demonstration of the 3R Process." Waste Management and Research 8: 461, 1990.

Vehlow, J. and H. Vogg. "Thermische Zerstörung organischer Verbindungen." Müllverbrennung und Umwelt 5 Edited by K.J. Thomé-Kozmiensky. EF-Verlag, Berlin: 447, 1991.

Vehlow, J., K. Jay, C. Rittmeyer, L. Stieglitz and W. Vielohr. "Disposal of Rigid PUR Foams in Municipal Waste Incinerators." Alternatives to CFCs and Halons, International Conference Berlin, 24th to 26th February 1992. Organized by BMU, Umweltbundesamt, U.S. EPA. Proceedings, Umweltbundesamt, Berlin: 543, 1992.

Vehlow, J., G. Pfrang-Stotz and J. Schneider. "Reststoffe - Charakterisierung, Behandlung, Verwertung." Symposium 25 Jahre LIT, 5 Jahre TAMARA, KfK report 5000: 124, 1992.

Vicinius, J. and R. Knoche. "Abscheidung von Dioxinen, Furanen und Schwermetallen in einer Gasreinigung." Müll und Abfall 23: 229, 1991.

Vogg, H. "Verhalten von, (Schwer-)Metallen bei der Verbrennung kommunaler Abfälle." Chemie-Ingenieur-Technik 60: 740, 1984.

Vogg, H. and L. Stieglitz. "Thermal Behaviour of PCDD/PCDF in Fly Ash from Municipal Incinerators." Chemosphere 15: 1373, 1986.

Vogg, H., A. Christmann and K. Wiese. "Das 3R-Verfahren, ein Baustein zur Schadstoffminderung bei der Abfallverbrennung." Recycling von Haushaltsabfällen Edited by K.J. Thomé-Kozmiensky. EF-Verlag, Berlin, Vol. I: 471, 1987.

Vogg, H., M. Metzger and L. Stieglitz. "Recent Findings on the Formation and Decomposition of PCDD/PCDF." Municipal Solid Waste Incineration, Waste Management and Research 5: 285, 1987.

Vogg, H., A. Merz, L. Stieglitz and J. Vehlow. "Chemical Process Engineering Aspects of Dioxin Reduction in Waste Incineration Processes." VGB Kraftwerkstechnik 69: 795, 1989.

Vogg, H., H. Hunsinger and L. Stieglitz. "Contribution to Solving the Problem of Dioxins Generated during Waste Incineration". Chemical Engineering Technology 13: 221, 1990.

Vogg, H.,A. Merz, L, Stieglitz, F. Albert and G. Blattner. "Zur Rolle des Elektrofilters bei der Dioxin-Bildung in Abfallverbrennungsanlagen." AbfallwirtschaftsJournal 2: 529, 1990.

Vogg, H., H. Hunsinger, A. Merz, L. Stieglitz and J. Vehlow. "Head-end-Techniken zur Dioxinminderung." Prozeßführung und Verfahrenstechnik der Müllverbrennung VDI Berichte Nr. 895, VDI-Verlag, Düsseldorf: 193, 1991.

Vogg, H., A. Merz and E. Becker, E. "Permanent Monitoring of the Emission of Highly Ecotoxic Substances from Waste Incineration Plants." Proceedings of the 1991 Incineration Conference Knoxville, TN: 555, May 1991.

WASTE Program. Effects of Waste Stream Characteristics on MSW Incineration: The Fate and Behaviour of Metals, Final Report Report prepared for Environment Canada, U.S. Environmental Protection Agency and International Lead Zinc Research Organization, 1993.

WHO. Dioxins and Furans from Municipal Incinerators Environmental Health Series 17, World Health Organization, Regional Office for Europe, Copenhagen: 25, 1987.