CHAPTER 11 - CHARACTERISATION OF AIR POLLUTION CONTROL RESIDUES

11.1 INTRODUCTION

The most dramatic change in incinerator technology over the past decade has been related to the air pollution control (APC) systems. The desire to reduce the emissions of undesirable contaminants to the atmosphere has resulted in the development of a wide variety of APC systems. In turn, this has affected the characteristics and quantity of residues (and liquid waste streams) generated from these systems. In Europe, both dry/semi-dry and wet scrubber systems are commonly in use, whereas in North America, only dry and semi-dry APC systems have gained widespread use.

The information presented in this chapter builds upon the concepts discussed in Chapters 4, 8 and 10. The amount of information available on the properties of APC residues from MSW incineration is not as extensive as that available on bottom ash (see Chapter 9). This is probably partly due to the fact that APC residues generally are "newer" than bottom ash, and partly due to the apparently more limited potential of APC residues for utilisation. Therefore, most of the available information on APC residues is related to disposal or to APC system performance. In addition to illustrating the different physical and chemical characteristics of the various types of APC system residues, the contrast between residue composition and properties in relation to the APC process, as well as type of incinerator technology and operation are discussed. As a final note, all dry and semi-dry APC system residues referred to in this chapter are from mass burn incinerators and contain fly ash unless otherwise indicated.

11.1.1 Terminology

Historically, the term "fly ash" has been used as a generic descriptor for all types of finely-sized ash and sorbent material collected in APC systems. However, due to the very different chemical and physical properties of the different residue streams generated in an APC system, it is prudent, and much more accurate to use specific terms for residue streams to avoid any potential confusion. Generally, the residue is best described by the type of unit where the residue has been collected.

Fly Ash

As mentioned in Chapter 10, the specific term "fly ash" refers to the particulate matter carried over from the combustion chamber and removed from the flue gas stream prior to the addition of any type of sorbent material (such as at facilities without acid gas cleaning systems or from particulate removal systems which are located prior to the acid gas cleaning equipment). Although fly ash is an acceptable term, it is more accurate to identify the ash based on the type of unit the ash was collected in, such as cyclone arrestor ash or ESP ash. For acid gas cleaning processes without upstream removal of particulate, the term fly ash is used to describe the portion of the residue corresponding to the original particulate matter carried over from the boiler and is

generally mixed with the other components of the APC residue (reaction products and surplus reactants).

Dry System Residues

"Dry" lime-based APC systems operate by injecting powdered lime into the flue gas stream, either in conjunction with humidification of the flue gas stream, or alone. The injection is performed in a reactor chamber (dry reactor - DR) before the particles entrained in the flue gas stream pass into a separate dust collection unit, such as an ESP or fabric filter (FF). The residue generated from these APC processes (DP residues) usually consists of a fine-powdered mixture of fly ash, reaction products (predominantly calcium chloride) and unreacted lime, and is generally referred to as dry scrubber (DS) or fabric filter (FF) residue. Since there is usually no upstream removal of particulate, in most cases the fly ash can make up a substantial proportion of the collected residues. In some facilities, a portion of the collected residue may be recycled as a substitute for a portion of the injected fresh lime in order to improve the reaction stoichiometry. In some cases, sodium sulphide or activated carbon is added to the lime reagent in order to enhance mercury removal. In all of cases, it is important to convey as much information as possible when identifying the residue stream.

Semi-dry System Residues

"Semi-dry" APC systems operate in much the same manner as dry systems, however, the lime is usually mixed with water and is injected into the flue gas stream as a slurry. Residues from semi-dry processes (SDP residue) resemble the residue from dry processes, although there is usually a lower content of unreacted lime due to a better reaction stoichiometry. Although it is not common, part of the collected residue may be recycled through the reactor in order to improve the reaction stoichiometry. In some cases sodium sulphide or activated carbon is added to the lime reagent in order to improve mercury removal.

Wet Scrubber Sludge

Wet process (WP) residue is a sludge resulting from the treatment of the wastewater from a one-stage or two-stage wet scrubber system with lime and organic sulphides (often trimercaptotriazine or TMT). The wet scrubber process produces a stream of fly ash which is collected upstream of the acid gas cleaning process (either a cyclone or ESP unit), and a stream of acid scrubber effluent which is contaminated with inorganic salts (predominantly calcium and/or sodium chloride) and trace elements/heavy metals. The content of trace elements/heavy metals in the saline scrubber effluent must be reduced prior to discharge (to a sewer system or a surface water body), e.g. by lime precipitation and subsequent polishing with TMT.

In a two-stage wet scrubber process, the scrubbing liquid in the second scrubbing stage is kept nearly neutral, usually by the addition of sodium or calcium hydroxide, in

order to enhance SO_X removal efficiency. In the latter case, gypsum can be produced from this residue stream. Direct mixing of the two wastewater streams may cause problems due to precipitation of calcium sulphate (gypsum) and in some cases are treated or pre-treated separately. The (dewatered) sludge from the treatment of the wastewater stream(s) is often mixed with the fly ash prior to disposal. This chapter presents information on the properties of the wastewater treatment sludges from the wet scrubber process both with and without fly ash. Examples are also given of the composition of treated and untreated wet scrubber effluents.

11.2 MAJOR FACTORS INFLUENCING THE CHARACTERISTICS OF APC RESIDUES

Although the APC technology is the single most important factor influencing the characteristics of the APC residues, several other factors also play a role. Beginning with the type of waste feed to the incinerator, everything which occurs prior to, and during, the collection of the APC residues may affect the characteristics and quantities of the captured residues (see Chapters 3, 4 and 8).

Typical ranges of the amounts of residues and wastewater produced from the three major APC processes at mass burn systems under Danish/German conditions (typical averages: 5.2 Nm^3 of stack gas per kg of waste at 10% O_2, removal of 700 mg HCl/Nm^3) are presented in Table 11.1.

Table 11.1
Approximate Quantities of Residues and Wastewater Produced per Tonne of Refuse

		APC Process		
Waste Stream/Residue	Unit	Dry	Semi-dry	Wet
Fly ash	kg DM	(10 - 30)	(10 - 30)	10 - 30
Dry residue, including fly ash	kg DM	20 - 50	15 - 40	
Sludge from wastewater treatment	kg DM			1 - 3
Treated wastewater	m^3			0.3 - 0.5
Chloride content in treated wastewater	kg DM			3.5 - 10

DM : Dry matter

Hjelmar et al., 1990; Rasmussen et al., 1993; Vehlow, 1993

Another major factor which influences the characteristics and volume of APC residue collected is the type of incinerator system. For example, average uncontrolled particulate levels in the flue gas stream of RDF stoker units have been measured at >3,000 mg/Rm^3 (dry @ 25°C, 101.3 kPa & 11% O_2) prior to a fabric filter (Environment Canada, 1991), whereas particulate levels of <2,200 and <300 mg/Rm^3 have been recorded for mass burn and two-stage systems (CCME, 1989). Consequently, the volume of APC residue collected in RDF stoker systems is far greater per tonne of refuse burned than in mass burn systems, which in turn, is greater than in two-stage combustion systems.

These factors should be considered when attempting to compare data on APC residues from different types of incinerator and APC systems.

11.3 PHYSICAL CHARACTERISTICS OF APC RESIDUES

11.3.1 General Appearance and Behaviour

Freshly collected fly ash, as well as dry and semi-dry process residues, appear as fine, dusty materials with practically no water content. The colour may vary from almost white through various shades of grey and brown to almost black, depending on the composition and (for dry and semi-dry process residues) the content of fly ash and how well it has been combusted. Since $CaCl_2$ is the major constituent of dry and semi-dry process residues, the material has hygroscopic properties, and therefore will gradually sorb moisture from the ambient air. Residues with high contents of calcium chloride may even "liquify" due to excessive uptake of water vapour.

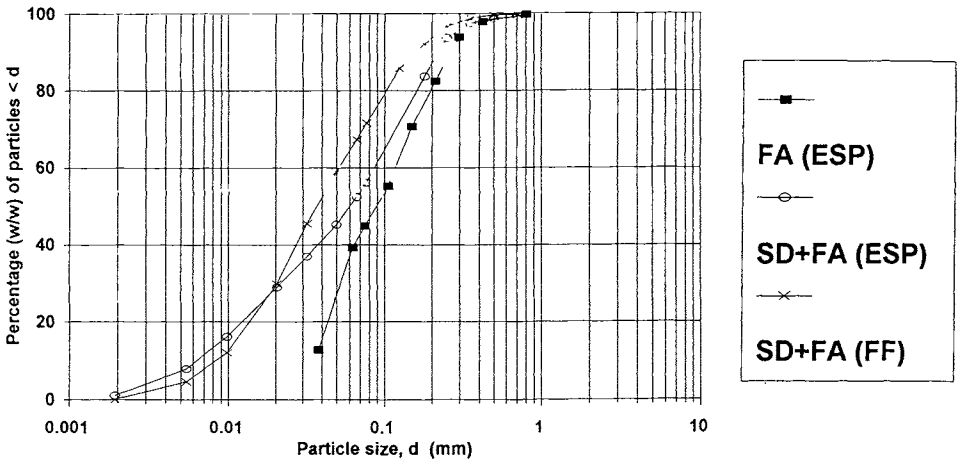
The residue from the wet scrubber process(es) appears as a wastewater treatment sludge which is usually dark brown in colour. The water content may vary widely and depends upon the dewatering equipment used (e.g. filter press, band filter, centrifuge). Typical water contents of filter cakes are 65 - 75% (w/w), (Rasmussen et al., 1993). Effectively dewatered filter cakes are easily handled whereas insufficiently dewatered sludge may create handling problems, in some cases even if it is combined with the fly ash collected prior to the wet scrubber.

11.3.2 Particle Size Distribution

Typical particle size distributions of fly ash and dry/semi-dry APC process residues from mass burn incinerators are shown in Figure 11.1. The dry and semi-dry process residues generally contain a higher proportion of fine material than fly ash without acid gas cleaning residue. Because fabric filters are more efficient at removing submicron size particles than ESPs, the proportion of fine material in fabric filter residues will be higher than in residues collected in ESPs (e.g. Environment Canada, 1986 and 1988; Carlsson, 1988; Hjelmar, 1992). Results have also indicated that semi-dry APC systems (lime slurry spray) generate residues with a finer particle size distribution than

dry systems where lime powder is injected (Hjelmar, 1992). Determination of particle size distribution is usually not relevant for the sludge-like residues from the wet scrubber APC processes.

Figure 11.1 Typical Particle Size Distribution for APC Residues



As an example, the particle size distribution data determined by weight for dry scrubber reactor (DSR) and fabric filter (FF) residues collected from a modern mass-burning incinerator are given in Table 11.2. The optically determined frequency of the particles for the different size ranges is also given. The data indicate the particle size distribution (by mass) for the dry scrubber reactor residue is in the 40 to >200 micron size range, whereas the fabric filter residue is predominantly 10 to 40 microns in diameter. Furthermore, although the most prevalent residue particle size by frequency is the range 2 to 5 microns, the greatest proportion of particle mass was in the 10 - 40 micron size fraction. The inverse relationship of the lowest population of particles representing the greatest proportion by weight is similar to findings on boiler ashes (see Chapter 10). It should also be noted that the amount of residue collected in the DSR normally represents only a small fraction of the total amount of residue captured within the entire APC system.

In addition to the type of APC system and the type of particulate removal system, the particle size distribution of APC system residues can depend on other factors including:

- waste feed composition
- incinerator type
- operating conditions
- presence of a heat recovery system

Table 11.2
Particle Size Distribution of Dry Scrubber Reactor (DSR) and Fabric Filter (FF) Residues from a Mass Burning Incinerator

		% of Particles in Each Size Range (microns)				
Test	Sample	2 - 5	5 - 10	10 - 20	20 - 40	40 - +200
By Mass	DS	0	0	0	11	89
		0	0	2	11	87
		0	0	0	11	89
	FF	12	7	81	0	0
		2	2	17	78	0
		11	10	79	0	0
By Freq	DS	70	13	0	9	9
		50	18	15	9	9
		43	0	0	29	29
	FF	92	3	5	0	0
		87	5	5	3	0
		90	5	5	0	0
Avg Mass	DS	0	0	1	11	88
	FF	8	6	59	26	0
Avg Freq	DS	54	10	5	16	16
	FF	90	4	5	1	0

WASTE Program, 1993

The proportion of fine sized or dust-like material in the waste can influence the ratio of particle sizes carried over in the flue gas stream. For example, higher ratios of fines, soil or construction debris may increase the ratio of finer to coarser particles collected in the APC system, since this type of material may be readily suspended in the furnace by the turbulence created by primary and secondary air injection.

As mentioned earlier, the type of incinerator system would also act to influence the range of particle sizes normally entrained in the flue gas. Because of the semi-pyrolytic combustion conditions in the primary chamber of a two-stage system, the flue-gas velocities in the primary chamber are relatively low, hence granular sized particles are not likely to be carried over, even to the boiler. Conversely, because of the semi-suspension combustion of RDF, there is a greater potential for carry-over of a greater proportion of larger sized particles than in a mass burn system.

Changes in operating conditions can also affect the particle size distribution. For example, in mass burn systems, an increase in the under-fire air pressure and decrease in the depth of the fuel bed can increase the potential for carry-over of larger sized particles compared to normal operating conditions. Conversely, a decrease in the under-fire air would result in a smaller proportion of larger sized particles being present in the APC system.

The presence of a heat recovery system will also influence the particle size distribution of APC system residues. Since the heat recovery system will act to remove a great deal of the larger sized particles entrained in the flue gas via the deposition mechanisms mentioned in Chapter 10, the proportion of finer sized particles carried through to the APC system would increase.

11.3.3 Geotechnical Properties

The geotechnical properties of the APC system residues are important both in relation to the physical feasibility of storage and disposal, and in relation to the potential environmental impacts resulting from these activities. Geotechnical properties include:

- Compaction properties
- Density
- Hydraulic conductivity
- Compressive strength

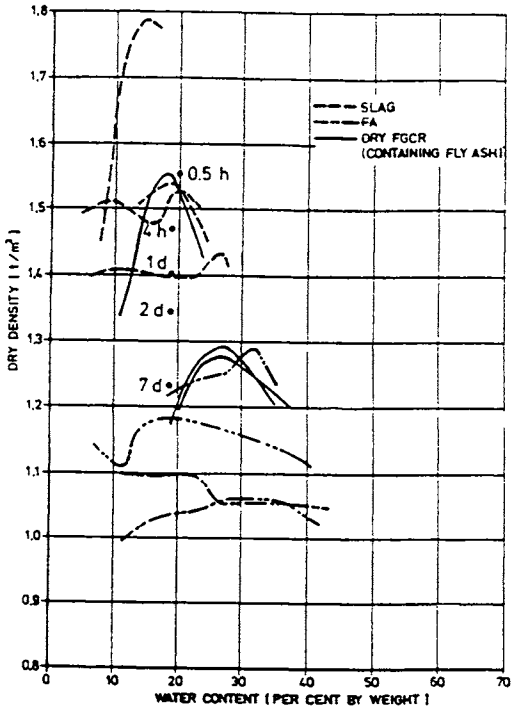
Most of these properties are interrelated and will be addressed together. For example, higher compaction is often associated with higher density and lower hydraulic conductivity.

Proctor tests carried out on dry and semi-dry APC system residues from mass burn incinerators indicated that densities of 1.22 - 1.43 tonnes/m^3 could be attained at optimum water contents (30 - 40% (w/w)) (Hjelmar 1992), whereas uncompacted densities of dry and semi-dry APC residues can range between 0.65 and 0.75 tonnes/m^3 (Sawell and Constable, 1988; Sawell et al., 1989a, 1991).

Kullberg & Fällman (1989) and Hartlén & Elander (1986) have investigated the geotechnical properties of ESP fly ash and semi-dry APC process residues. Their results are shown in Figure 11.2 and are compared to similar observations for bottom ash. Semi-dry APC residues began hardening immediately after it was moistened, and tests showed that the compaction properties deteriorated and became poorer the longer the moistened residue had been stored prior to compaction (see Figure 11.2 and Table 11.3). The data in Table 11.3 indicate that the compressive strength decreased and the saturated hydraulic conductivity increased with decreasing compaction. This may have significant implications for a landfilling operation for semi-dry/dry APC system residues.

Field measurements (using double ring infiltrometers) on landfilled and compacted semi-dry APC process residues at various depths gave infiltration rates of 7.6×10^{-6} m/s - 1.3×10^{-7} (VKI 1992). The ranges of hydraulic conductivity of fly ash, dry and wet APC process residues, bottom ash (slag) and various other ashes observed by Kullberg et al. (1989) are presented in Figure 11.3.

Figure 11.2 Compaction Densities of Various MSWI Residues, Including Bottom Ash or Slag



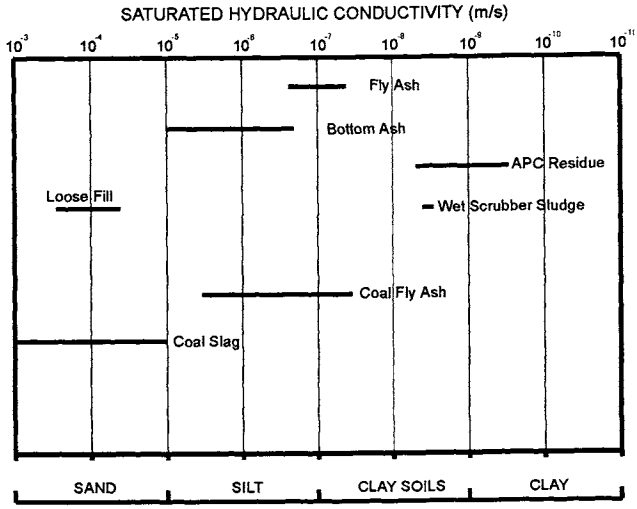
Kullberg and Fällman, 1989

Table 11.3
Influence of Storage Time on Compressibility, Unconfined Compressive Strength (UCS) and Hydraulic Conductivity of Semi-dry APC System Residue

Time hrs	Dry density tonnes/m^3	Water content weight %	UCS kPa	Saturated hydraulic conductivity m/s
0.5	1.55	20	2200	1×10^{-9}
4	1.47	19	1380	1×10^{-9}
24	1.40	19	2100	2×10^{-9}
48	1.34	19	900	2×10^{-8}
168	1.23	19	660	4×10^{-8}

Kullberg and Fällman, 1989

Figure 11.3 Saturated Hydraulic Conductivity (Permeability) of Various APC System Residues and Other Ash Types



Kullberg et al., 1989

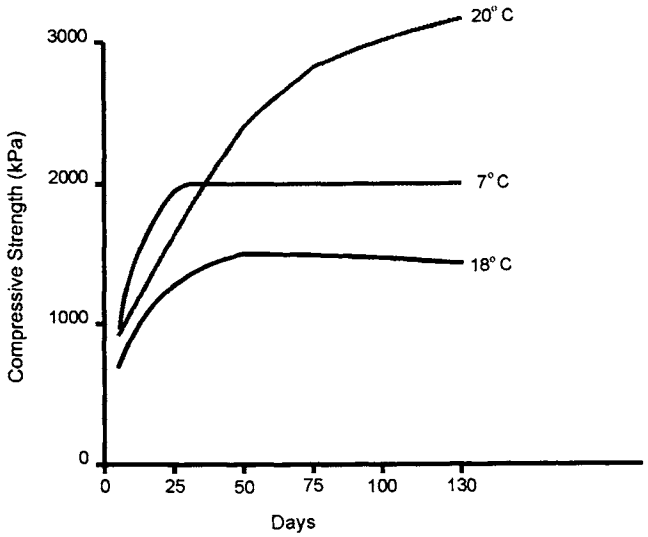
Kullberg et al. (1989) have tested the unconfined compressive strength (UCS) of molds made from dry APC system residues mixed with 45% (w/w) water and stored at different temperatures.

The results are presented in Figure 11.4 and indicate that the UCS increases with increasing temperature during the first 28 days at all temperatures between -18 and 20°C. No further strength development was observed at -18 and 7°C, whereas the UCS continued to increase through day 130 at 20°C.

It is uncertain which chemical or physical-chemical reactions within the residues are responsible for the strength development and the other observed changes occurring with time. Considering the high content of soluble chlorides (20 - 40 % (w/w)), pozzolanic reactions are not likely to occur, and attempts at detecting possible pozzolanic activity have proven negative (e.g. Kosson et al., 1993, Hjelmar 1992). Some of the cohesive properties of the dry/semi-dry APC process residues may be explained by the high content of calcium chloride and the excess lime present. When moisture is added to the dry residue, $CaCl_2 \cdot 4H_2O$ may be formed in the porewater. The addition of water also causes a strongly exothermic hydration of any excess CaO still in the residue, which may generate high temperatures (local boiling of water has been observed). $CaCl_2 \cdot 4H_2O$ has a melting point of 29.9°C, and may be first crystallised and then melted during the hydration of CaO. When the residue begins to cool off, melted

$CaCl_2 \cdot 4H_2O$ will fill the pores and subsequently solidify, thereby providing some mechanical strength to the residue (Hjelmar, 1993). This could also explain why the compaction properties deteriorate if moistened residues are stored prior to compaction.

Figure 11.4 Unconfined Compressive Strength of Testbodies of Dry APC System Residue (45% of Water) as a Function of Time and Temperature



Kullberg et al., 1989

11.4 PARTICLE MORPHOLOGY AND MINERALOGY

During the WASTE Program (1993), qualitative analysis was conducted on some of the dry APC system fabric filter residue samples using scanning electron microscopy (SEM) to determine the morphology of the particles. The particles were categorised into the 5 types listed in Table 11.4.

In addition to the identification exercise, the relative percentage of the different particle types was determined optically (Table 11.4). The most common particle types in the dry scrubber residue were the polycrystalline and opaque irregular shaped particles, whereas the overwhelming majority of the fabric filter residue were polycrystalline in structure. The dry scrubber residue characteristics were very similar to those of heat recovery system ash (see Chapter 10), whereas the morphology of the fabric filter residue was dominated by the powdered lime particles encrusted with flue gas condensation/reaction products.

Table 11.4
Summary of Morphological Characteristics and Estimated Relative Percentages of Particle Types in Dry APC System Residues

Morphology	Estimated Relative %		Size Range	
	DS	FF	DS	FF
Fused Spheres	15	5	5 - 150	5 - 60
Crystalline	10	<5	5 - 150	10 - 40
Polycrystalline	30	80	5 - 200	2 - 90
Opaque	30	5	5 - 200	5 - 40
Char	15	<5	160 - 240	60 - 500

Fused Spheres: Spheroids of various colours with particulate or gaseous inclusions
Crystals: Irregular in shape, similar to soil-like particles of calcite or quartz
Polycrystallines: Dense agglomeration of irregular shaped particles
Opaques: Single, large irregular shaped particles (<300 microns)
Char: Black fibrous particles

WASTE Program, 1993

Oberste-Padtberg and Schweden (1990) have shown that fly ash and dry/semi-dry APC system residues may contain elemental Al particles. When the residues are contacted with water, a highly alkaline leachate will occur and react with the elemental aluminum to form hydrogen according to the following reaction (see also Equation 9.1):

$$Al + OH^- + 3H_2O \rightarrow [Al(OH)_4]^- + 15H_2 \qquad [11.1]$$

Hydrogen evolution has indeed been observed, both during laboratory batch leaching tests at low L/S ratios with fly ash and dry/semi-dry APC system residues, and in connection with full scale conditioning of semi-dry APC system residues with water. In the latter case, it caused explosions which were subsequently prevented by ventilation of the conditioning equipment (Hjelmar 1993).

The mineralogical characteristics of APC residues play an important role in determining their leaching behaviour, and hence a thorough understanding of the mineralogy of APC residues may be essential to the development of an environmentally sustainable long-term APC residue management strategy. Specific mineralogical phases have been shown to control the leachability of key contaminant trace elements from incinerator ash (Comans et al., 1993), and the mineralogy of an ESP fly ash (without scrubber residue) has been investigated by Eighmy et al. (1993). Both studies used X-ray powder diffraction (XRPD) on fly ash before and after leaching, and observed that some of the more soluble phases (e.g. K_2ZnCl_4, NaCl, $CaClO_4$, $MgSO_4 \cdot 5H_2O$) were removed from the residue during leaching, (see Table 11.5). Hjelmar (1992) and Eighmy (1993) have reported XRPD data on semi-dry APC system residues (including fly ash) and the results are given in Table 11.5. Both sets of data appear to indicate that two of the major components, $CaCl_2$ and the excess reagent calcium oxide/hydroxide, occur partly as various double salts. In a study of two semi-dry APC

system residues (Stuart, 1993), CaClOH, $CaCO_3$, $CaSO_4$, KCl, NaCl, SiO_2, and PbO_2 were identified using XRPD. It should be noted that the data represents only a portion of the crystalline minerals that may be present in APC system residues. The presence of several other "exotic" or less common minerals have also been detected, but not confirmed. Further research using XRDP and other techniques (see e.g. Chapter 7.3) is needed to reach a better understanding of APC system residue mineralogy.

Table 11.5
Likely Mineral Phases of APC System Residues Based on Interpretation of X-Ray Powder Diffraction Data

ESP fly ash (Eighmy et al., 1993)		Semi-dry APC process residue	
Unleached ash	Leached ash	Hjelmar (1992)	Eighmy (1993)
Likely minerals		Likely minerals	
K_2ZnCl_4	$KAl(SO_4)_2$	$CaCl_2Ca(OH)_2•H_2O$	CaClOH
$K_2H_2P_2O_5$	$(Sr,Ba)SO_4$	NaCl	$Ca(ClO)_2•4H_2O$
NaCl	(Mg_2SnO_4)	KCl	$Ca(OH)_2$
$KClO_4$	$Ba_{0.5}Sr_{0.5}SO_4$	$Na_2SO_4•10H_2O$	NaCl
$CaAl_4O_7$	TiO_2	$CaSO_4$	$(Pb_2Sb_2O_7)$
$Ca_3Al_6Si_2O_{16}$	$Ca_3Al_2O_6$		$NaAsO_2$
$CaAl_2Si_2O_8$	Na_2CrO_4		$CaTiSiO_5$
$MgSO_4•5H_2O$	$PbSO_4$		
$CaSO_3$	$Pb_5(PO_4)_3Cl$		
$KAlSi_3O_8$			

11.5 WATER SOLUBILITY

Water solubility is a very important property of APC system residues because it strongly influences the options available for treatment, disposal and possible utilisation of the residues. Generally, APC system residues contain a much higher proportion of soluble components than fly ash or bottom ash. The bulk of the soluble portion of combined fly ash and dry and semi-dry APC system residues consist of inorganic salts, which are acid-gas reaction products (most notably the highly soluble calcium chloride), surplus reactants and flue-gas condensation products. A certain proportion of most of the minor components, such as trace elements, are also soluble. This may be particularly true at low L/S ratios where solubility is enhanced for several components due to high ionic strength.

Dry and semi-dry APC residues without fly ash are typically extremely soluble, whereas the pre-collected fly ash will be only moderately to very soluble in water. For residues from the wet scrubber process, the water soluble part primarily consists of gypsum and salt containing water retained in the pores of the filter cake. If the wet residue is mixed with the fly ash, the combined residue will contain more soluble salts which originated from the fly ash.

Total water solubility of the APC system residues should be determined at high L/S ratios (e.g. 100 -200 l/kg) and preferably in a two-step procedure in order to minimise solubility restraints caused by interference between the dissolved components. When such data are not available, column leaching data or multiple batch leaching data covering a reasonably broad L/S range may be used.

For mass burn systems, water solubilities of 21 - 23% (w/w) for fly ash from ESPs, 27 - 38 % (w/w) for dry and semi-dry APC process residues and 14 % (w/w) for a wet scrubber APC sludge mixed with fly ash, have been measured (Hjelmar, 1992 and 1993). Conversely, water solubilities of up to 65% (w/w) have been observed for ESP ashes, and dry/semi-dry APC process residues from both mass burn and two-stage systems (Sawell and Constable, 1988; Sawell et al., 1989a & 1991; WASTE Program, 1993). In one of these studies, the relatively small corresponding proportion of residue collected in the dry scrubber reactor was only about 20% (w/w) water soluble due to the higher proportion of coarser fly ash present in the residue.

11.6 LOSS ON IGNITION

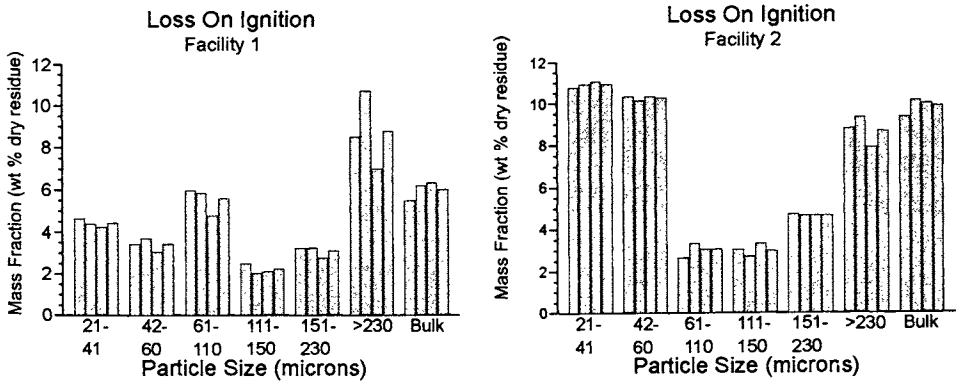
Loss on ignition (LOI) is defined as the weight fraction (expressed as a percentage) of material that is lost by heating at 550°C. LOI values for APC residues vary depending on type of APC system as well as on incinerator type and operation. Although LOI is an important indicator of the degree of burnout for bottom ash (see Chapter 9), the parameter is more difficult to interpret for APC residues. Comparisons between LOI and total organic carbon (TOC) indicate that the largest portion of the LOI for APC system residues containing acid gas cleaning residues must be attributed to loss of chemically bound water, such as dehydration of calcium chloride and excess calcium hydroxide at 550 °C, other flue-gas condensation products and possibly to loss of inorganic carbon (char). For fly ash collected upstream of the acid gas cleaning system, the LOI may be considered an indicator of carbon content, although the content of condensation products would depend on the temperatures within the collection unit.

ESP fly ash from modern mass burn facilities can contain a relatively low LOI content of 1.1 - 1.3% (w/w) (Hjelmar, 1993). However, higher values (3 - 6% w/w) have been reported for ESP fly ash from older or retrofitted mass burn facilities (Hartlén & Elander, 1986; Sawell and Constable 1988). LOI values of 2.8 - 4.9% (w/w) have been observed for dry and semi-dry APC system residues (Hartlén & Elander, 1986; Hjelmar, 1992), whereas the data from the NITEP Program indicated a wide variation of 2.1 - 12% (w/w) under a variety of operating conditions (Environment Canada, 1993). An LOI of 11% (w/w) has been observed for a sludge/fly ash mixture from a mass burn incinerator equipped with a wet APC system (Hjelmar, 1992). The differences underscore the influence that incinerator operating conditions have on APC residues.

Stuart (1993) investigated LOI as a function of particle size for 2 semi-dry APC process residues from mass burn systems with bulk LOI values of 6.0 and 9.7%. The results are shown in Figure 11.5 and indicate that the larger particles (often char) generally

have the largest LOI values. The fine particles in one of the residues also had a high LOI, however, this was attributed to loss of water of hydration and calcination (Stuart, 1993).

Figure 11.5 LOI as a Function of Particle Size for Two Semi-Dry APC System Residues from North American Mass Burning Incinerators



Stuart, 1993

LOI values ranging between 5.9 - 10% (w/w) have been recorded for dry/semi-dry APC system residue from two-stage incinerators (Environment Canada, 1993). In addition, older RDF semi-suspension incinerators were found to generate dry/semi-dry APC residues containing higher LOI values (11% w/w) compared to values ranging between 4.1 - 7.9 % (w/w) for similar residues from a modern RDF incinerator (Environment Canada, 1993).

11.7 CHEMICAL CHARACTERISTICS

Knowledge of the chemical characteristics, i.e. pH and acid neutralisation capacity and the chemical composition of the APC system residues and their dependency on various variables, is necessary for an understanding of the behaviour of these residues during handling, treatment, disposal and/or utilisation. In order to provide an overview of the chemical characteristics of the various types of APC system residues, a data base has been compiled using data from incinerators in Canada (6 facilities), Denmark (7 facilities), Germany (4 facilities), Jersey, Channel Islands (1), the Netherlands (6 facilities), Sweden (7 facilities) and the USA (8 facilities). In all, information has been collected on APC system residue chemical characteristics from 39 incineration facilities. Some background on the origin of the data is given in Tables 11.6, 11.7, 11.8 and 11.9.

Table 11.6
Origin of Data on Composition of Fly Ash (FA) from Mass Burning (BM) Incinerators

Country	Type of Residue	Incinerator	Sampling Point	Year Sampled	Reference
Canada	FA	MB, Quebec City	ESP	1991	Eighmy, 1992
	FA	MB, Quebec City	ESP	1986	Sawell & Constable, 1988
Denmark	FA	MB, Vestforbrænding	ESP	1985+92	Hjelmar, 1987 & 1993
	FA	MB, Amagerforbrænding	ESP	1985	Hjelmar, 1987
	FA	MB, Kolding II	ESP	1992	Hjelmar, 1993
	FA	MB, Fasan	ESP	1992	Hjelmar, 1993
Germany	FA	MB, Bamberg	ESP	1982	Schneider et al., 1983
	FA	MB, Göppingen	ESP	1982	Schneider et al., 1983
	FA	MB, Göppingen	ESP	1984	Schneider, 1986
	FA	MB, Oberhausen	ESP	1987	Vehlow, 1988
Jersey, Channel Is.	FA	MB, Bellozane	ESP	1988	Hjelmar et al., 1993
The Netherlands	FA	MB, Amsterdam	ESP	1985/86	Versluijs et al., 1990
	FA	MB, Rotterdam	ESP	1985/86	Versluijs et al., 1990
	FA	MB, den Haag	ESP	1985/86	Versluijs et al., 1990
Sweden	FA	MB, GRAAB, Göteborg	ESP	1988	SGI data base, 1993
	FA	MB, Uppsala	ESP	1988	SGI data base, 1993
	FA	MB, Avesta	ESP	1988	SGI data base, 1993
USA	FA	MB, Glen Cove, LI	ESP	1987	LIRPB, 1993
	FA	MB, Saugus, Mass.	ESP	1989	Hjelmar et al., 1993

ESP = Electrostatic Precipitator

The data have been divided into groups representing ESP fly ash from mass burn incinerators (see box plots Table 11.6), dry and semi-dry APC system residues from mass burn incinerators (Table 11.7), wet scrubber APC system residues from mass burn incinerators (Table 11.8) and dry/semi-dry APC system residues from two-stage incinerators and RDF-fed incinerators (Table 11.9).

Box plots depict all of the data that is available in the data base for each type of residue. The central box for the elements in each plot extends from the first quartile to the third quartile, with a horizontal line across the box to indicate the median value. The first quartile denotes the twenty-fifth percentile, the median denotes the fiftieth percentile and the third quartile denotes the seventy-fifth percentile. The height of the box equals the interquartile range. Lines are sometimes drawn out from the quartiles to adjacent values, defined as those data points less than 1.5 times the interquartile range beyond the first or third quartiles. Values farther than 1.5 times the interquartile range from the box are considered outliers and are denoted by individual circles in each of the plots. The width of each box in a plot is proportional to the number of observations it represents.

Table 11.7
Origin of Data on the Composition of Dry(DP) and Semi-dry (SDP) APC System Residues from Mass Burn (MB) Incinerators

Country	Residue	Incinerator	Sampling Point	Year Sampled	Reference
Canada	DP + FA	MB, GVRD	FF	1991	Eighmy, 1992
	DP + FA	MB, GVRD	FF	1988	Sawell et al., 1990
	DP + FA	MB, GVRD	FF	1991	WASTE Program, 1993
	DP + FA	MB, Flakt/QUC	FF	1986	Sawell et al., 1987
	SP + FA	MB, Flakt/QUC	FF	1986	Sawell et al., 1987
Denmark	DP + FA	MB, Nordforb.	FF	1989	Hjelmar, 1992
	DP + FA	MB, REFA	ESP	1989	Hjelmar, 1992
	SP + FA	MB, Amagerforbrænding	FF	1989/92	Hjelmar, 1992 & 1993
	SP + FA	MB, KARA	ESP	1989	Hjelmar, 1992
Germany	SP + FA	MB, Düsseldorf	ESP	1982	Schneider et al., 1983
Netherlands	DP (-FA)	MB, Incinerator 1			van der Sloot, 1992
Sweden	DP + FA	MB, Högdalen	FF	1985/88	SGI database, 1993
	SP + FA	MB, Sysav	CY	1988	SGI database, 1993
	SP + FA	MB, Linköping		1988	SGI database, 1993
		MB, Karlstad		1988	SGI database, 1993
USA	DP + FA	MB, "Dry Scrubber 1"		1988	LIRPB, 1993
	DP + FA	MB, "Dry Scrubber 2"		1988/89	LIRPB, 1993
	SP + FA	MB, 3x750 tpd	FF	1989	Kosson et al., 1993
	SP + FA	MB, "Dry Scrubber 3"		1988/89	LIRPB, 1993
	SP + FA	MB, 500 tpd	FF		Stuart, 1993

(-FA) : Without fly ash (precollected) FF : Fabric filter
+ FA : Including the fly ash CY : Cyclone system
ESP : Electrostatic precipitator(s)

Table 11.8
Origin of Data on the Composition of Wet Scrubber Residues from Mass Burning (MB) Incinerators

Country	Residue	Incinerator	Sampling Point	Year Sampled	Reference
The Netherlands	WP (-FA)	MB, Incinerator 2	WWT	1990/91	van der Sloot, 1992
	WP (-FA)	MB, Incinerator 3	WWT		van der Sloot, 1992
Sweden	WP (-FA)	MB, GRAAB, Göteborg	WWT	1988	SGI database, 1993
	WP (-FA)	MB, GRAAB, Göteborg	WWT	1989	Hjelmar, 1994
	WP + FA	MB, GRAAB, Göteborg	WWT	1989	Hjelmar, 1994
	WP (-FA)	MB, Uppsala	WWT	1988	SGI database, 1993

WP: Wet scrubber process residue + FA: Mixed with the precollected fly ash
WWT: Wastewater treatment system (-FA): Not mixed with the precollected fly ash

Table 11.9
Origin of Data on the Composition of Dry APC System Residues from Two-Stage Mass Burn (MB) Incinerators and an RDF-fed Semi-Suspension Incinerator

Country	Residue	Incinerator	Sampling Point	Year Sampled	Reference
Canada	DP + FA	MB, 2-stage, Inc. A	CT/FF	1992	PRRI, 1992
	DP + F	MB, 2-stage, Inc. B	CT/FF	1988	Sawell et al., 1990
	DP + FA	MB, 2-stage, LVH	CT/FF	1988	Sawell et al., 1989b
USA	DP + FA	SS, RDF, Inc. 1	CT/FF	1990	Sawell et al., 1991

CT/FF : Combined residue from conditioning tower and fabric filter
SS : Semi-suspension
RDF : Refuse-derived fuel

The use of box plots allows the reader to compare the data bases that are available for each type of residue. Several of the data sets have outliers that denote a skewness in the data. Such skewness means that the data is not normally distributed.

As can be seen from Tables 11.8 and 11.9, data are available on fly ash and dry/semi-dry APC system residues from six or seven countries, covering both Europe and North America. In contrast, information on wet scrubber system residues is only available from Europe (Table 11.8) and information on APC system residues for two-stage and RDF-fed systems is only available from North America (Table 11.9).

Only a few data sets are available on the characteristics of dry/semi-dry APC residues from systems with pre-collection of fly ash. Studies have shown that the content of most trace elements in the acid gas cleaning residues is very low and primarily originating from the lime or the process water if a very effective fabric filter precollection system for fly ash is employed upstream of the acid gas cleaning system (Vehlow, 1993).

11.7.1 pH and Acid Neutralisation Capacity

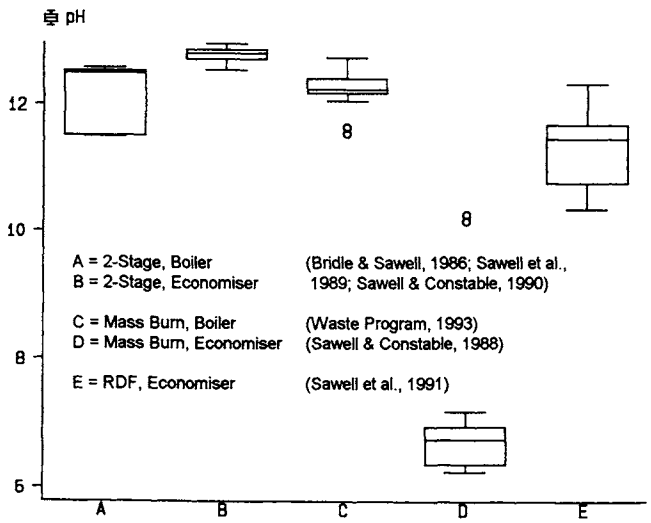
The pH resulting from contact of an APC system residue with water is the most important factor controlling the solubility of various heavy metals and trace elements from these residues. Since the pH may change with time due to interaction with the surroundings (acid/base reactions and transport), the buffering capacity of a residue plays an important role in maintaining a certain pH level, or determines the rate of change of pH with time. Most APC system residues are highly alkaline (pH 11-12.5) and the buffering capacity is generally equal to the alkalinity.

The pH of a residue is normally measured in a distilled water suspension at L/S ratios between 20 and 100. Based on a contact time of 0.5 hrs at 100:1 L/S ratio, pH ranges

of 7.0 - 11.3 for ESP fly ashes, 12.1 - 12.5 for dry and semi-dry APC system residues, and 10.5 for wet APC system sludge mixed with fly ash have been recorded (Hjelmar, 1993). All these residues were from mass burn incinerators. Figure 11.6 shows pH ranges measured in leachates generated with water at L/S = 20 from ESP fly ash and dry/semi-dry APC system residues from mass burn incinerators, and dry/semi-dry APC system residues from a two-stage and a semi-suspension (RDF) incinerator (Sawell & Constable, 1988; Sawell et al., 1991; WASTE Program, 1993). All the dry/semi-dry APC residues are seen to be highly alkaline, whereas the ESP fly ash ranged from slightly acidic to moderately alkaline.

Practically all dry/semi-dry APC system residues are highly alkaline due to the presence of excess lime. Normally, ESP fly ash also contains enough alkaline material (e.g. oxides and carbonates of calcium, sodium and potassium carried over from the boiler) to create an alkaline pH in equilibrium with water. The alkaline core of the ESP ash particles is, however, often coated by sorbed acidic condensation products. The relative amount of acidic condensation products to alkaline material depends on the conditions and temperatures in the ESP. In some cases an ESP ash generates an initially acidic pH when contacted with water, after which the pH gradually increases to an alkaline level (Hjelmar, 1987; Sawell & Constable, 1988). In other cases, the amount of alkaline material is insufficient to neutralise the acidic condensation products, resulting in a neutral or slightly acidic pH (as in Figure 11.6).

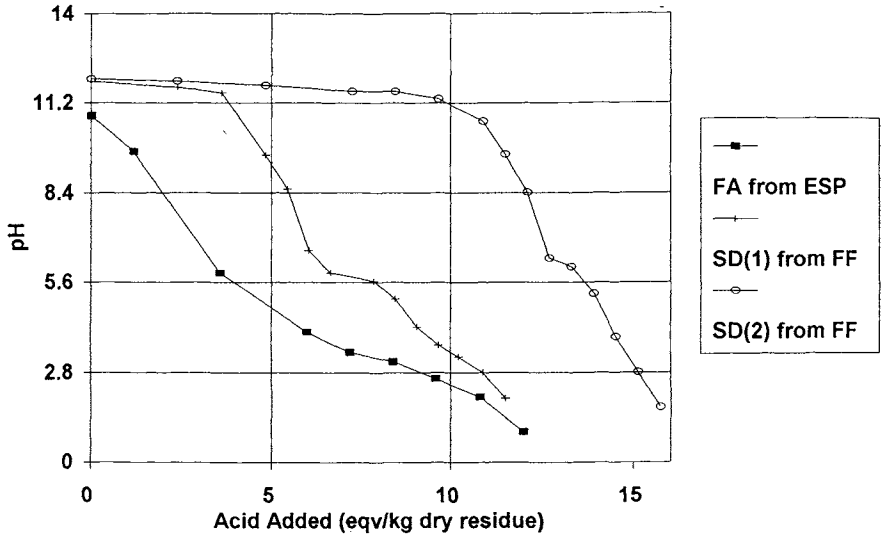
Figure 11.6 Boxplots of pH at L/S = 20 for ESP Fly Ash and Various Dry APC System Residues



In column leaching tests with dry and semi-dry APC system residues, an initial depression of pH (9.7 - 10.8) in the first leachate has been observed, even under equilibrium conditions with high amounts of excess lime (Hjelmar, 1992). This was probably caused by the very unusual solubility conditions imposed by the high ionic strength (>10 moles/litre or up to 500 g dissolved salts/litre). At higher L/S ratios and lower ionic strengths, the pH reached a level of 12.1 - 12.5.

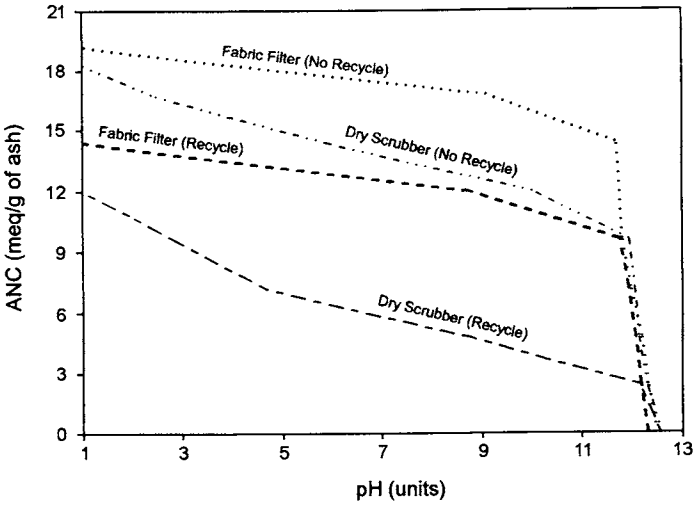
The alkalinity or the acid neutralisation capacity (ANC) of the residues may be measured either as a full titration curve (see Chapter 7), or as the amount of acid equivalents used to titrate the residue to a fixed endpoint, usually pH = 7 or 4.4. Some typical ANC titration curves for APC system residues are presented in Figure 11.7. Hjelmar (1992 and 1993) has reported ANC values (titration to pH = 7) for ESP fly ashes of 2.5 - 3.5 eqv/kg, for dry and semi-dry APC system residues of 5.6 - 12 eqv/kg, and for a wet APC system sludge mixed with fly ash of 4.5. This corresponds with the values shown in Figure 11.7. The ANC of the dry and semi-dry APC system residues reflect the amount of excess lime present which again reflects the operating conditions (i.e. the stoichiometric ratio of lime addition or whether or not the residue is recycled). The influence of recycling on the ANC of dry scrubber residues from the scrubber reactor and the fabric filters (the bulk of the material) is illustrated in Figure 11.8. The data indicate that the concentration of acid gas reaction products increases with increased exposure to the flue gas stream, thereby reducing the ANC.

Figure 11.7 ANC Titration Curves for an ESP Fly Ash (FA) and Two Semi-Dry APC System Residues (SD) from Fabric Filters



Stuart, 1993; Hjelmar, 1994

Figure 11.8 Comparison of ANC Values for Dry APC System Residues with and without Lime Recycle



Sawell and Constable, 1992

11.7.2 Chemical Composition: Inorganic Constituents

Although the compiled data base on elemental composition of APC system residues contains more than 100 individual data sets, the diversity of the APC residues due to differences in incinerator type and APC system technology is such that a statistically justifiable comparison of APC system residues by country similar to that shown for bottom ash in Chapter 9 cannot be made. Instead, the elemental compositions of APC system residues are compared by type irrespective of the country of origin, as shown in Table 11.10. The differences in composition between residues/products from the semi-dry (SP) and the dry (DP) APC processes are small, and these residues are therefore treated as one single category (SP/DP).

One of the main criteria for acceptance of analytical data into the data base has been based on the analytical methods applied. The use of a total quantification technique, e.g. neutron activation, x-ray fluorescence or total digestion followed by some spectrophotometric quantification, was required. However, due to the limited availability of data, it has been necessary to accept data on the trace element composition of wet APC process residues without fly ash which were determined after aqua regia digestion rather than total digestion. The difference between trace element analyses based on total digestion and aqua regia digestion, respectively, is probably minor for this particular type of residue in which the trace elements primarily are associated with calcium or TMT-based precipitates rather than silicates.

Table 11.10
Categories of APC System Residues Considered

Type of incinerator	Type of APC residue
Mass burn	FA from ESP (no scrubber residue)
Mass burn	SP/DP from ESP and FF (with fly ash)
Mass burn	DP from FF (without fly ash)
Mass burn	WP (without fly ash)
Mass burn	WP (mixed with fly ash)
Mass burn, 2-stage	DP from CT/FF (with fly ash)
RDF, semi-suspension	DP from CT/FF (with fly ash)

Ranges of Elemental Composition of APC System Residues
Based on the data base, the total ranges of elemental composition of the various categories of APC system residues are presented in Tables 11.11, 11.12 and 11.13.

Table 11.11 shows the ranges of composition for fly ash, for dry/semi-dry APC system residues (with fly ash) and for wet APC system residues without and with fly ash, all from mass burn incinerators.

In Table 11.12, the ranges of elemental composition of dry APC system residues from an incinerator equipped with an upstream ESP are compared with the corresponding ranges of composition for SP/DP without pre-collection of fly ash (from Table 11.11) for a limited amount of elements. Table 11.12 shows that, with the exception of Hg, most of the trace elements are primarily associated with the fly ash. For most of the elements analysed, a substantial enrichment is seen in the residues containing fly ash relative to the fly ash free residues.

Table 11.13 shows ranges of elemental composition of dry APC system residues from two-stage and RDF semi-suspension incinerators. The number of elements presented in each of the tables reflects both the availability of analytical methods, and the degree and contaminants of environmental concern. Traditionally, much emphasis has been placed on trace metals, therefore, trace metal analyses are available for nearly all types of APC system residues. Less interest has been directed at understanding the role of the major constituents, including the soluble salts which may indeed be the most important and problematic constituents, both in relation to environmental risk and to the options available for management/treatment prior to disposal/utilisation. Due to this lack of interest, comprehensive information on the contents of all relevant major elements and soluble salt is not available for all types of APC system residues.

Similar to the treatment of the bottom ash data in Chapter 9, the elements have been divided into three groups, namely, those present in one or more of the APC system residue types as major constituents (>10,000 mg/kg), minor constituents (>1,000 mg/kg but <10,000 mg/kg), and trace constituents (<1,000 mg/kg). For some of the elements

Table 11.11
Composition of Fly Ash, Dry/Semi-Dry and Wet APC System Residues from Mass Burn Incinerators

Element	Range for Fly Ash (mg/kg)	Range for Dry/Semi-dry APC System Residues (mg/kg)	Range for Wet APC System Residue without Fly Ash (mg/kg)	Range for Wet APC System Residue/Fly Ash Mixture (mg/kg)
Ag	2.3 - 100	0.9 - 60	-	53
Al	49,000 - 90,000	12,000 - 83,000	21,000 - 39,000	71,000 - 81,000
As	37 - 320	18 - 530	41 - 210	130 - 190
Ba	330 - 3,100	51 - 14,000	55 - 1,600	330 - 1,900
Be	-	0.5 - 0.9	-	1.5 - 1.9
C	-	-	-	-
Ca	74,000 - 130,000	110,000 - 350,000	87,000 - 200,000	93,000 - 110,000
Cd	50 - 450	140 - 300	150 - 1,400	220 - 270
Cl	29,000 - 210,000	62,000 - 380,000	17,000 - 51,000	48,000 - 71,000
Co	13 - 87	4 - 300	0.5 - 20	14 - 22
Cr	140 - 1,100	73 - 570	80 - 560	390 - 660
Cu	600 - 3,200	16 - 1,700	440 - 2,400	1,000 - 1,400
Fe	12,000 - 44,000	2,600 - 71,000	20,000 - 97,000	15,000 - 18,000
Hg	0.7 - 30	0.1 - 51	2.2 - 2,300	38 - 390
K	22,000 - 62,000	5,900 - 40,000	810 - 8,600	35,000 - 58,000
Mg	11,000 - 19,000	5,100 - 14,000	19,000 - 170,000	18,000 - 23,000
Mn	800 - 1,900	200 - 900	5,000 - 12,000	1,400 - 2,400
Mo	15 - 150	9.3 - 29	1.8 - 44	20 - 38
N	-	-	1,600	-
Na	15,000 - 57,000	7,600 - 29,000	720 - 3,400	28,000 - 33,000
Ni	60 - 260	19 - 710	20 - 310	67 - 110
O	-	-	-	-
P	4,800 - 9,600	1,700 - 4,600	-	6,000 - 7,400
Pb	5,300 - 26,000	2,500 - 10,000	3,300 - 22,000	5,900 - 8,300
S	11,000 - 45,000	1,400 - 25,000	2,700 - 6,000	11,000 - 26,000
Sb	260 - 1,100	300 - 1,100	80 - 200	-
Se	0.4 - 31	0.7 - 29	-	12
Si	95,000 - 210,000	36,000 - 120,000	78,000	120,000
Sn	550 - 2,000	620 - 1,400	340 - 450	1,000
Sr	40 - 640	400 - 500	5 - 300	200
Ti	6,800 - 14,000	700 - 5,700	1,400 - 4,300	5,300 - 8,400
V	29 - 150	8 - 62	25 - 86	62
Zn	9,000 - 70,000	7,000 - 20,000	8,100 - 53,000	20,000 - 23,000

Table 11.12
Comparison of Trace Element Content of Dry/Semi-Dry APC System Residues with and without Prior Removal of Fly Ash

Element	Range for Dry APC System Residue without Fly Ash from Mass Burn Incinerator (mg/kg)	Range for Semi-dry/Dry APC System Residue with Fly Ash from Mass Burn Incinerators (mg/kg)
As	1.5 - 3	18 - 530
Ba	44 - 48	51 - 14,000
Cd	10 - 15	140 - 300
Co	1	4 - 300
Cr	3 - 5	73 - 670
Cu	13 - 25	16 - 1,700
Hg	9.5 - 24	0.1 - 51
Mo	6	9.3 - 29
Ni	1	19 - 710
Pb	110 - 270	2,500 - 10,000
Zn	220 - 680	7,000 - 20,000

Table 11.13
Concentration of Selected Elements in Dry APC System Residues from Two-Stage Mass Burn Incinerators and From an RDF-fed Semi-Suspension Incinerator

Element	Range for Dry APC System Residue from Mass Burn 2-Stage Incinerators (mg/kg)	Range for Dry APC System Residue from RDF-fed Semi-Suspension Incinerator (mg/kg)
Al	1,000 - 17,000	43,000 - 53,000
As	< 0.3 - 140	6.3 - 7.6
B	35 - 360	200 - 240
Ba	57 - 210	640 - 1,200
Cd	100 - 820	75 - 160
Cl	97,000 - 280,000	83,000 - 120,000
Co	14 - 18	32 - 67
Cr	21 - 190	240 - 420
Cu	130 - 630	620 - 760
Hg	0.3 - 54	34 - 84
Mn	110 - 370	890 - 1,500
Ni	17 - 47	280 - 650
Pb	1,900 - 13,000	2,800 - 5,200
Sb	150 - 1,100	330 - 580
Se	< 0.2 - 10	0.69 - 1.3
Zn	5,100 - 47,000	5,000 - 8,900

this means that even though they are listed as major elements due to their typical concentration levels in one or more types of APC residues, they may in fact be minor or even trace constituents in other types of APC residues. The elements in each group are discussed in approximate order of decreasing abundance in the residues.

Major Elements (>10,000 mg/kg): O,Cl,Ca,Si,Mg,Fe,Al,K,Na,Zn,S,Pb
A comparison with section 9.4.2 on bottom ash shows that the number of major elements is larger for APC system residues than for bottom ash. This is partly due to the greater diversity of APC residues, i.e. the major elements may vary between the residues from different types of APC systems.

Figure 11.9 is a grouping of box plots depicting the concentration of the major elements in three types of APC residues from mass burn incinerators, fly ash without scrubber residue (FA), semi-dry/dry APC system products including fly ash (SP/DP), and wet scrubber products without fly ash (WP).

Oxygen is one of the most prevalent elements in all APC system residues. It is present as oxides of several of the other major, minor and trace elements, most notably silicon, calcium, magnesium, iron, aluminum, sodium, potassium, sulphur and carbon. Few analytical determinations of the total oxygen content of APC system residues are available. Based on a variety of alternative analytical methods, the oxygen contents of fly ash from an ESP ranged from 60,000 mg/kg (AES), to 120,000 mg/kg (XPS) to 480,000 mg/kg (SEM/EDS) (Eighmy et al., 1993).

Table 11.14 shows the mean and median values as well as the 25-75 percentile ranges of the concentrations of the major components Cl, Ca, Si, Mg, Fe, Al, K, Na, Zn, S and Pb in fly ash (FA), semi-dry/dry APC products (SP/DP) and wet scrubber products (WP) from mass burn incinerators.

Calcium is present both as one of the major matrix constituents of the particulate FA carried over from the boiler and as part of the major reaction product in SP/DP, calcium chloride. It may also be present as unreacted calcium oxide/hydroxide. Therefore, calcium is most abundant in SP/DP and least abundant in the FA-free WP.

Chloride is present as a major condensation product on FA particles and as part of the major reaction product in SP/DP, calcium chloride. The chloride concentration of SD/DP is therefore generally 2-3 times higher than that of FA without scrubber residue. The chloride content of the wet APC system product (WP) is much lower because the chlorides from a wet scrubber is discharged with (or recovered from) the wastewater stream.

Numerous studies have shown that the chloride concentration in FA and SP/DP is a function of temperature in the APC system (e.g., Environment Canada, 1986 and 1988; Carlsson, 1988; Ettehadiah and Lee, 1989; Itaya et al., 1989; Chang et al., 1989;

Figure 11.9 Major Element Concentrations in Fly Ash (FA), Semi-Dry APC Products with Fly Ash (SP/DP) and Wet Scrubber Products without Fly Ash (WP-FA)

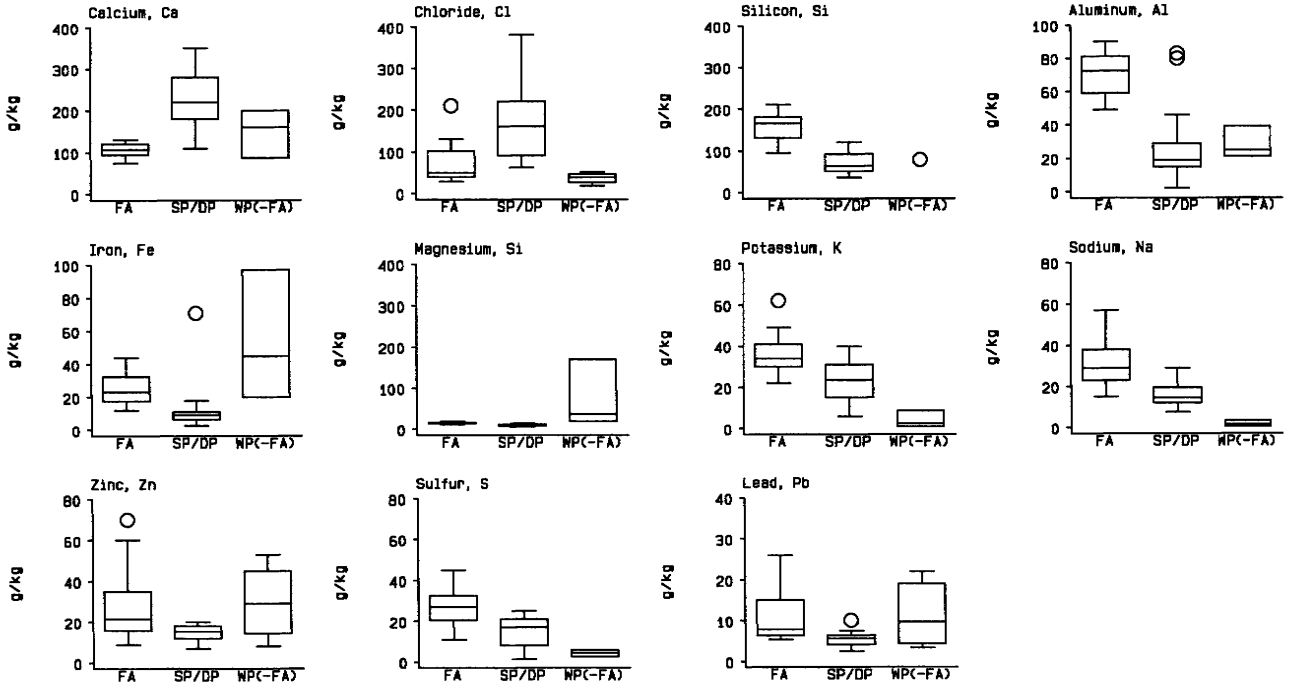


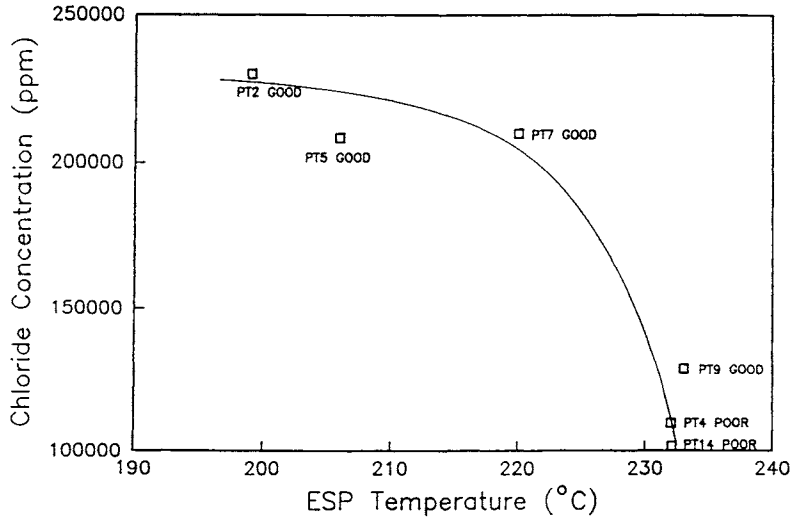
Table 11.14
Concentrations of Major Elements (>1000,000 mg/kg) Measured in APC Residues from Mass Burn Incinerators

Residue	Element	Mean (mg/kg)	Median (mg/kg)	25-75 percentile range (mg/kg)	n
FA	Ca	107,000	107,000	95,000 - 120,000	20
	Cl	74,000	50,000	40,000 - 102,000	24
	Si	160,000	170,000	130,000 - 180,000	14
	Mg	15,000	15,000	14,000 - 17,000	15
	Fe	25,000	23,000	18,000 - 33,000	20
	Al	71,000	73,000	59,000 - 81,000	18
	K	36,000	34,000	30,000 - 41,000	19
	Na	31,000	29,000	23,000 - 38,000	17
	Zn	28,000	22,000	16,000 - 35,000	26
	S	26,000	27,000	21,000 - 33,000	20
	Pb	11,000	7,800	6,300 - 15,000	25
SP/DP	Ca	230,000	220,000	180,000 - 280,000	19
	Cl	180,000	160,000	91,000 - 220,000	23
	Si	69,000	63,000	51,000 - 92,000	12
	Mg	9,400	8,800	7,400 - 12,000	16
	Fe	12,000	9,100	63,000 - 11,000	19
	Al	26,000	19,000	15,000 - 29,000	27
	K	23,000	24,000	15,000 - 31,000	18
	Na	17,000	15,000	12,000 - 20,000	16
	Zn	15,000	16,000	12,000 - 18,000	28
	S	15,000	17,000	8,200 - 21,000	18
	Pb	5,400	5,600	4,100 - 63,000	27
WP	Ca	150,000	160,003	87,000 - 200,000	3
	Cl	36,000	38,000	26,000 - 47,000	4
	Si	78,000	-	-	1
	Mg	75,000	36,000	19,000 - 170,000	3
	Fe	54,000	45,000	20,000 - 97,000	3
	Al	28,000	25,000	21,000 - 39,000	3
	K	3,900	2,300	810 - 8,600	3
	Na	1,900	1,700	720 - 3,400	3
	Zn	31,000	29,000	15,000 - 45,000	12
	S	4,400	-	2,700 - 6,000	2
	Pb	11,000	9,700	4,400 - 19,000	12

FA: Fly ash
WP: Wet sludge without FA
SD/DP: Semi-dry/dry APC process products with fly ash
n: Number of residues analysed

Klingspor et al., 1989;). This trend is illustrated in Figure 11.10 by the increase in chloride concentration of ESP ash with decreasing flue gas temperatures. The data is taken from a study at a mass burn incinerator and shows a marked difference in chloride concentrations with the inflection point between 220°C and 230°C (Sawell and Constable, 1988). It is important to note that there was no lime injection prior to the ESP unit.

Figure 11.10 Influence of Temperature on Chloride Concentrations in ESP Ash



From Figure 11.9 it can be seen that calcium and chloride are the only major elements which are more abundant in SP/DP than in FA. The content of very soluble calcium chloride, which may account for up to 60 percent of the total mass of semi-dry/dry APC system residues (without prior removal of fly ash), is responsible for many of the difficulties involved in the management of these residues. Not only do the very high concentrations of calcium chloride in the leachate pose a risk to potable water, but it may also increase the solubility of other potential contaminants such as trace metals (see Chapter 13). Furthermore, the solubility and thermal instability of the calcium chloride are serious obstacles to solidification and thermal stabilisation of the residues without prior removal of the soluble salts (see Chapters 18 and 19). A substantial amount of the sulphur in APC residues is present as sulphate and sulphite. Between 46,000 - 80,000 ppm of SO_4^{2-} and 13,000 - 35,000 ppm of SO_3^{2-} have been measured in semi-dry and dry APC system residues, and 110,000 ppm of SO_4^{2-} and 9,000 ppm of SO_3^{2-} in a wet APC system residue mixed with fly ash (Hjelmar, 1992). The sulphite is thermodynamically unstable under oxidising conditions, and if the APC residue is exposed to oxygen (e.g. atmospheric air), will gradually be oxidised to sulphate. In wet scrubber residues, part of the sulphur content is present in the form of organic

sulphides (e.g. trimercaptotriazine, TMT). The long-term stability of these sulphides is not known.

Both Pb and Zn are present as major constituents in APC system residues. Because of its increased solubility at high pH values, high ionic strength and high chloride concentrations, Pb is of particular concern in relation to disposal and utilisation of APC system residues.

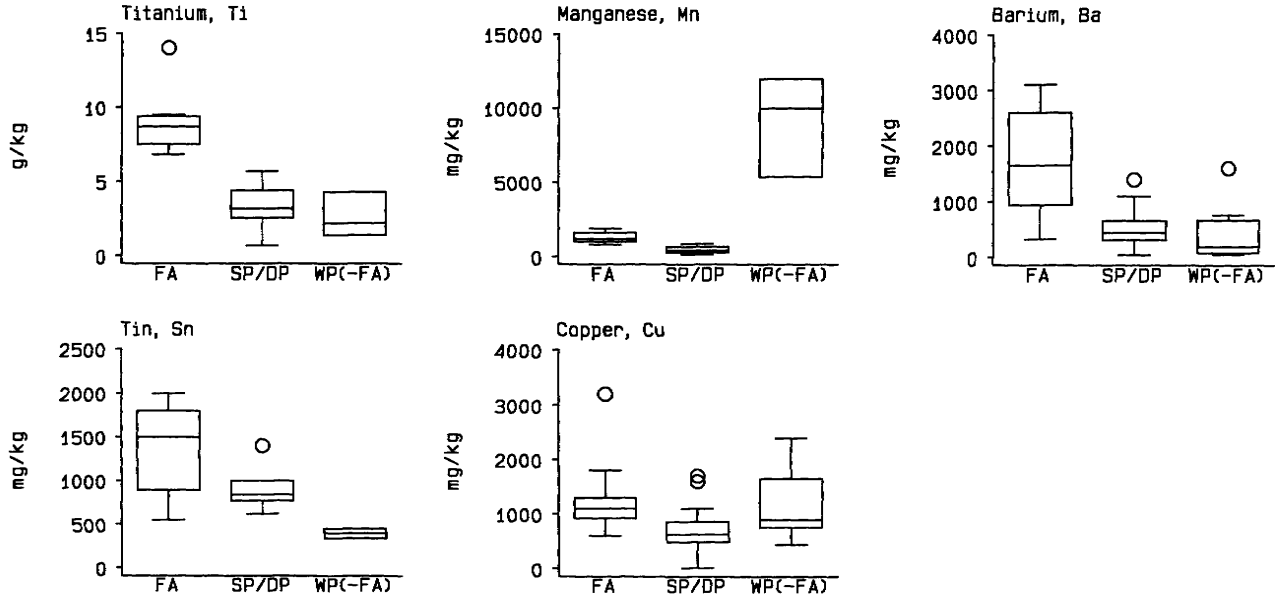
Figure 11.11 presents box plots depicting the concentrations of the minor elements in APC system residues (FA, SP/DP and WP) from mass burn incinerators. Table 11.15 gives the mean and median values as well as the 25-75 percentile ranges of the concentrations of the minor components Ti, Mn, Ba, Sn and Cu for the three types of residues.

Table 11.15
Concentrations of Minor Elements (1,000 - 10,000 mg/kg) Measured in APC Residues from Mass Burn Incinerators

Residue	Element	Mean (mg/kg)	Median (mg/kg)	25-75 percentile range (mg/kg)	n
FA	Ti	8,700	8,700	7,500 - 9,400	17
	Mn	1,300	1,200	1,000 - 1,600	19
	Ba	1,700	1,700	940 - 2,600	18
	Sn	1,400	1,500	890 - 1,800	15
	Cu	1,200	1,100	930 - 1,300	25
SP/DP	Ti	3,300	3,200	2,600 - 4,400	17
	Mn	480	440	280 - 680	19
	Ba	540	450	320 - 660	18
	Sn	890	840	770 - 1,000	15
	Cu	710	630	490 - 860	25
WP	Ti	2,600	2,200	1,400 - 4,300	3
	Mn	9,100	10,000	5,400 - 12,000	3
	Ba	460	200	87 - 670	11
	Sn	400	-	340 - 450	2
	Cu	1,200	900	760 - 1,700	12

FA: Fly ash
SD/DP: Semi-dry/dry APC process products with fly ash
WP: Wet scrubber products without fly ash
n: Number of residues analysed

Figure 11.11 Minor Element Concentrations in Fly Ash (FA), Semi-Dry/Dry APC Products with Fly Ash (SP/DP) and Wet Scrubber Products Without Fly Ash (WP-FA)



Inorganic carbon in the form of carbonate is also one of the minor elements. Total concentrations between 16,000 - 33,000 ppm for CO_3^{2-} in SP/DP and a value of 19,000 ppm for CO_3^{2-} in WP have been reported (Hjelmar, 1992). Carbon is also present in APC system residues as elementary C (soot or char) carried over from the boiler. In addition, activated carbon may be injected with the sorbent in some dry/semi-dry APC systems in order to enhance mercury adsorption.

Trace Elements (< 1,000 mg/kg): Hg,Cd,Sb,Cr,Sr,Ni,As,V,Ag,Co,Mo,Se

Figure 11.12 presents box plots showing the distribution of some trace elements in APC system residues (FA, SP/DP and WP) from mass burn incinerators. Table 11.16 shows the mean and median values as well as the 25-75 percentile ranges of the concentrations of the trace elements Hg, Cd, Sb, Cr, Sr, Ni, As, V, Ag, Co, Mo and Se for the three types of residues.

The concentration of mercury is substantially higher in WP than in SP/DP, which in turn has a higher concentration of mercury than FA. Trimercaptotriazine (TMT) which is most commonly used for wet scrubber wastewater treatment is particularly effective for removal of mercury and is ultimately concentrated in the sludge. Several facilities equipped with dry or semi-dry APC systems inject sodium sulphide, or as mentioned above, activated carbon with the sorbent to increase the sorption of mercury vapour. Without mercury control, mercury tends to condense out as Hg_2Cl_2 (mercuric II chloride) (Metzger and Braun, 1987). Mercury in this form can undergo either reduction or methylation on fly ash, and that elevated temperatures can greatly increase the speed of the reduction reaction (Lindquist et al., 1986). Nagase et al., (1986) observed that methylation of Hg_2Cl_2 can occur at normal temperatures on fly ash.

Several studies have been conducted on the removal efficiency of mercury from flue gas based on temperatures at the outlet of the APC system (e.g., Moller and Christiansen, 1985; Clarke, 1986; Carlsson, 1986; Environment Canada, 1986). All of the studies demonstrated that the increased efficiency of mercury removal was achieved (>91% capture) at temperatures below 150 - 160°C. At temperatures over 200°C, mercury removal efficiency was negligible, if not nonexistent. However, the use of activated carbon or sodium sulphide has been demonstrated as effective control reagents for mercury (Guest and Knizek, 1991).

Sodium sulphide injection results in effective formation of stable HgS. Consequently, mercury (as well as sulphate) concentrations are increased in the residues. Conversely, it has been speculated that mercury sorbed onto activated carbon is not as stable, since it is susceptible to reduction by carbon. Although this has not been confirmed, further study into the phenomenon should be conducted to ensure that there is no substantial release of elemental mercury into the atmosphere through reduction, or methylation reactions.

Figure 11.12 Trace Element Concentrations in Fly Ash (FA), Semi-Dry/Dry APC Products with Fly Ash (SP/DP) and Wet Scrubber Products without Fly Ash (WP-FA)

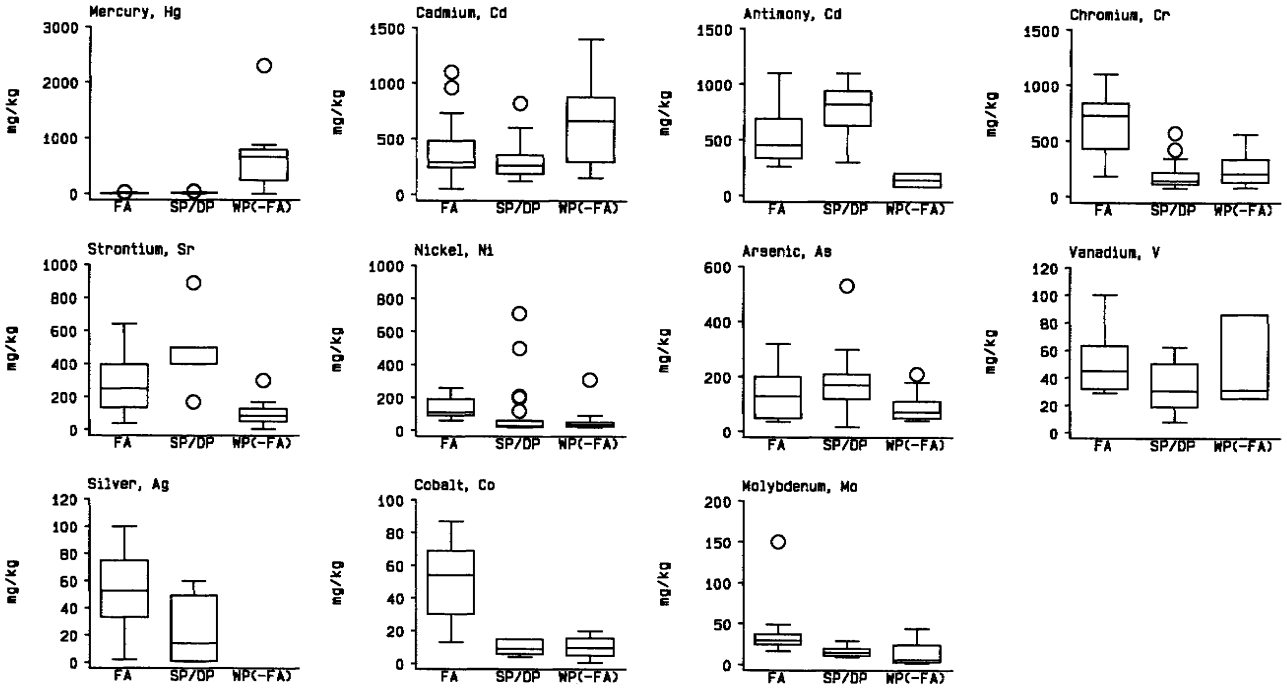


Table 11.16
Trace Elements (<1,000 mg/kg) Measured in APC Residues from Mass Burn Incinerators

Residue	Element	Mean (mg/kg)	Median (mg/kg)	25-75 percentile range (mg/kg)	n
FA	Hg	8.0	6.0	2.3 - 10	17
	Cd	390	290	240 - 480	26
	Sb	530	450	340 - 690	12
	Cr	650	730	430 - 840	26
	Sr	280	250	140 - 400	12
	Ni	140	110	91 - 110	25
	As	130	130	49 - 200	17
	V	51	45	32 - 63	15
	Ag	55	53	33 - 75	10
	Co	51	54	30 - 69	17
	Mo	40	30	25 - 37	13
	Se	14	12	11 - 18	12
SP/DP	Hg	15	12	8.4 - 18	28
	Cd	300	260	190 - 360	28
	Sb	790	820	630 - 940	13
	Cr	180	140	110 - 220	28
	Sr	460	400	400 - 500	6
	Ni	94	30	23 - 60	25
	As	170	170	120 - 210	26
	V	33	31	19 - 50	6
	Ag	22	14	1.1 - 49	11
	Co	9.6	9.0	6.0 - 15	11
	Mo	15	15	11 - 20	11
	Se	8.2	7.0	4.8 - 11	23
WP	Hg	650	660	240 - 790	12
	Cd	630	660	290 - 880	12
	Sb	140	-	80 - 200	2
	Cr	240	210	130 - 340	12
	Sr	104	85	52 - 130	10
	Ni	62	36	26 - 53	12
	As	89	72	49 - 110	12
	V	47	31	25 - 86	3
	Co	9.8	9.7	4.8 - 16	12
	Mo	12	6.0	3.0 - 24	11

FA: Fly ash
SD/DP: Semi-dry/dry APC process products with fly ash
WP: Wet scrubber products without fly ash
n: Number of residues analysed

11.7.3 Role of Particle Size in Element Distribution

Researchers (e.g. Ontiveros et al., 1989; Stuart, 1993) have investigated the variation of element distribution in fly ash and semi-dry APC system residues as a function of particle size. Based on acid extraction data, Ontiveros et al. (1989) have shown that more volatile elements such as cadmium and lead are enriched substantially in the smaller particle sizes of fly ash, whereas the opposite is true for the matrix elements, such as aluminum, barium, iron, manganese, nickel and potassium. The enrichment is ascribed to condensation of volatile metals on the surface of the smaller particles, since the small particles have larger surface area to volume ratios than larger particles. Similar results have been obtained by Stuart (1993) for semi-dry APC system residues when the results are corrected for the dilution effects caused by soluble acid gas cleaning reaction products. Stuart also found that a high percentage of the bulk APC residues investigated consisted of calcium complex species, which preferentially partitioned to the smallest size fractions. A significant increase in the concentration levels of cadmium, lead and zinc with decreasing grain size below 200 microns has been observed in ESP fly ashes (Hundesrügge, 1990). However, between 600 and 1,000 microns (usually a small fraction), an increase in concentration with increasing grain size was observed for the same elements. This was ascribed to increased adsorption due to the high carbon content in this fraction.

11.7.4 Chemical Composition: Organic Constituents

Organics Present in APC System Residues

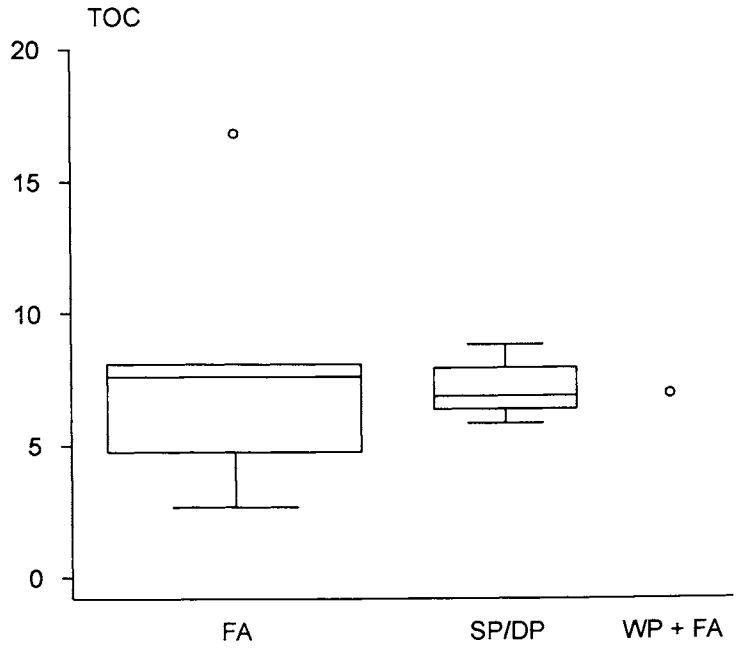
A number of studies have been performed using APC residues either to develop analytical techniques or to assess the formation of organic compounds during incineration, especially PCDD/PCDF. However, some of these studies contain insufficient information about the origin of the residues, incinerator and APC system technology, and sampling techniques. Other studies have addressed APC system residues only as a constituent of combined ash. Therefore, only a few selected data sets are presented, mostly in the form of concentration ranges. Most of these are based on the data base described in Tables 11.6, 11.7, 11.8 and 11.9.

The data on total organic carbon (TOC) concentrations in APC system residues are presented in the box plots in Figure 11.13. The specific nature of the bulk portion of the TOC in the APC system residues has not been investigated. Median values for TOC of 7.7 g/kg and a total range of 2.7 - 17 g/kg for ESP fly ash from mass burn incinerators have been recorded (Hjelmar, 1987 and 1993; Hjelmar et al., 1992). A median value of 7 g/kg and a total range of 6 - 9 g/kg of TOC for semi-dry/dry APC system residues from mass burn incinerators have also been reported, whereas a single value of 7 g/kg was measured for a wet APC system residue mixed with fly ash from a mass burn incinerator.

Some trace organics of potential concern for human health have been quantified in the various types of APC system residues. These include the polychlorinated dibenzo-p-

dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) as well as potential precursors for these compounds under certain reaction conditions. The potential precursors are chlorinated benzenes (CBs), chlorinated phenols (CPs), and polychlorinated biphenyls (PCBs). Another group of potentially toxic compounds that have been identified in APC system residues consists of condensed polycyclic aromatic hydrocarbons (PAHs). In addition, a limited amount of information is also available on the concentration of phthalates in some APC system residues. The presence of most the above-mentioned trace organics in combustion residuals and their fate during combustion is thoroughly discussed in Chapter 8. Table 11.17 summarises the data on trace organic concentrations in APC system residues.

Figure 11.13 Concentrations of Total Organic Carbon (TOC) in Selected APC System Residues from Mass Burn Incinerators



Chlorinated Benzenes and Phenols

Table 11.17 indicates that total CB and CP concentrations are available for fly ash and dry APC residue from mass burn incinerators, dry APC residue from a two-stage mass burn incinerator and an RDF-fed semi-suspension incinerator. The values which range from 220 - 1,900 ng/g for CB and 860 - 3,200 ng/g for CP are 1 to 2 orders of magnitude higher than those found for bottom ash (see Table 9.20).

Table 11.17
Trace Organic Concentrations in APC System Residues (ng/g)

Parameter	Mass Burn Incinerators (MB)				MB, 2-Stage	RDF,SS
	FA	SP/DP	WP	WP+FA	DP	DP
CB	890[a] 800-1,900[b]	0.03-0.4[j]			220[c]	1,600[d]
CP	1,800[a] 1,500-3,200[b]	50-200[j]			860[c]	860[d]
PCB	Nd[a] 6-16[b] <20[i]	ND[j]	<20[i]		< 40[c]	270[d]
PAH	110[a] 450-1,050[b]	30[j]			65[c]	260[d]
PCDD	580[a] 590-1,040[b] 115-140[f]	14-32[e] 0.7-3.6[j]		260	60[c]	390[d]
PCDF	190[a] 190-280[b] 48-69[f]	25-73[e] 1.4-9.7[j]		120	53[c]	120[d]
TCDD-EQ	1.5-2.5[f]	0.8-2.0[e]		2.8		
Phthalates	<500-4,200[i]		1,600-10,000[i]			

FA : Fly ash (from electrostatic precipitator)
SP/DP : Semi-dry/dry APC system residue (with FA)
WP : Wet APC system residue (without FA)
WP+FA : Wet PC system residue (mixed with FA)
RDF : Refused derived fuel
SS : Semi-suspension combustion technology

a : Klicius et al., 1988
b : Sawell & Constable, 1988
c : Sawell et al., 1989a
d : Sawell et al., 1989b
e : Hjelmar, 1992
f : Hjelmar et al., 1993
g : Hjelmar, 1987
h : Hjelmar, 1993
i : Miljøstyrelsen, 1993
j : Sawell et al., 1990

Polychlorinated Biphenyls
Determinations of concentrations of PCB in fly ash, dry APC residue and a wet scrubber product from mass burn incinerators, dry APC system residues from a two-stage mass burn incinerator and an RDF-fed semi-suspension incinerator are shown in Table 11.17. The concentrations of PCBs are generally small or below the detection limit, except in the DP from an RDF-fed semi-suspension incinerator which has a PCB concentration of 270 ng/g. The lowest PCB concentration is found in the dry APC residue from the two-stage incinerator. This is probably a result of the very high temperature level in the secondary combustion chamber. In contrast, the bottom ash from these incinerators is generally poorly combusted and contains relatively high concentrations of PAHs.

Polycyclic Aromatic Hydrocarbons
PAHs are to a large extent a measure of the quality of the combustion process. For example, the higher the concentration, the poorer the combustion. The values found range from 65 to 1,050 ng/g.

Dioxins and Furans
The TCDD equivalents have been calculated according to Eadon's method. The ranges of concentrations of PCDDs and PCDFs in the APC system residues are between 1 - 1,040 n/g and 1.4 -280 ng/g, respectively. The data does not allow a clear distinction between PCDD and PCDF concentrations for the different types of APC system residues, although there is data available which indicates that ESPs can enhance PCDD/PCDF formation (see Chapter 8). The concentrations of PCDDs and PCDFs in APC system residues are generally several orders of magnitude higher than that in bottom ash (See Chapter 9).

Phthalates
One study has included a determination of the concentrations of phthalates in fly ash and wet APC system residues from a Danish mass burn incinerator (Miljøstyrelsen 1993). As shown in Table 11.17, a phthalate concentration range of <500 - 4200 ng/g was found for the fly ash and a range of 1,600 -10,000 was found for the wet scrubber residue. The dominant phthalates were di-n-butylphthalate and di(2-ethylhexyl)-phthalate.

11.8 COMPOSITION OF WASTEWATER FROM WET SCRUBBER APC SYSTEMS

The wastewater from wet scrubbing systems normally has a high content of salts and a moderate to high content of metals and other trace elements. Table 11.18 shows the concentrations of metals in the wastewater streams from the first (acidic) and second (neutral) scrubbing stages of a two-stage wet scrubber system on a 4 x 12 tph mass burn incinerator (Vestforbrænding 1993, Rasmussen et al., 1993).

The two wastewater streams constitute about 0.4 m^3/tonne of the waste from stage 1, and 0.1 m^3/tonne of the waste from stage 2. These are treated in the wastewater treatment system shown in Figure 4.10 in Chapter 4. The treatment consists of an initial adjustment of the acidic scrubber water to pH = 1.8 with limestone (calcium carbonate) followed by adjustment of the combined streams to pH = 8.8 with lime slurry (calcium hydroxide), addition of organic sulphide (TMT) to bind heavy metals and polymer to aid settling, separation of the suspended particulate matter in a lamellae tank separator, and sand filtration prior to discharge to the sewer system. The settled sludge is mixed with the ESP fly ash and landfilled. Bottom ash quench discharge water is used for slaking, and a stream of the treated wastewater is recycled and used for bottom ash quenching. The composition of the treated wastewater stream is presented in Table 11.18 in terms of ranges and average parameter values based on monthly sampling and analysis over a 12 month period (1993).

Table 11.18
Composition of Untreated and Treated Wastewater from a Two-Stage Wet Scrubber APC System (mg/L)

Parameter	Wastewater from the first stage* (acidic)	Wastewater from the second stage* (neutral/alkaline)	Treated wastewater (combined from both stages)	
			Range	Mean
Temperature	-	-	35 - 43	-
(°C)	0 - 1	Approx. 7	6.9 - 10.2	-
pH (units)	-	-	620 - 1,050	840
Sulphate	-	-	7,000 - 12,000	9,600
Chloride	-	-	15 - 110	53
SS	0.12	0.037	< 0.02	-
Ag	0.41	0.25	< 0.001 - 0.020	0.008
Cd	< 0.004	< 0.004	-	-
Co	0.25	0.031	0.14 - 0.36	0.23
Cr	3.2	0.74	0.10 - 0.47	0.19
Cu	3.0	0.79	0.002 - 0.015	0.005
Hg	0.051	0.020	0.03 - 0.27	0.10
Ni	34	2.0	<0.02 - 0.68	0.18
Pb	2.6	0.46	< 0.10 - 0.21	-
Sn	83	22	0.20 - 3.2	0.90
Zn	-	-	< 0.01 - 0.11	0.05
Cyanide	-	-	< 0.05 - 0.53	-
Phenols				

* = single determinations

Vestforbrænding, 1993; Rasmussen et al., 1993

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