CHAPTER 16 - LEACHING DATA

16.1 INTRODUCTION

16.1.1 Overview

The leaching of contaminants into the environment is the major concern associated with the management of incinerator residues (Chapter 1). Many types of leaching tests have been used for regulatory and research purposes to evaluate the leaching behaviour of residues. It is the apparently highly variable results from these different tests, and the misinterpretation of these results, which has resulted in a substantial portion of the controversy over incinerator residues. With the exception of research programs, the majority of leaching data that has been generated globally has been based on regulatory leach tests. These tests generally control the laboratory extraction conditions to simulate the various leaching conditions anticipated at disposal sites, and test results are compared to specified performance criteria. Consequently, ash has been labelled a "toxic" material without the benefit of understanding the intrinsic properties of the ash, the underlying mechanisms causing a particularly high or low release, nor an understanding of how the disposal or utilisation scenarios for the residues may effect environmental impact.

The information presented in this chapter builds on the information presented in the previous four chapters and focuses on contaminant leachability data. Test results from a wide variety of test conditions have been compared to provide a uniform basis for data interpretation. The large amount of information collected to date allows a more rigorous treatment of data to generate a generic picture of residue leachability. The data evaluated was obtained from tests on ash collected at MSW incinerators in many different countries and facilities of varying design. Thus, the data set represents a global range of residue properties.

16.1.2 Data Sources

Bottom ash represents the bulk of the total residue stream generated by an incinerator (Chapter 8) and is also the most heterogeneous stream (Chapter 9). Leaching considerations are important to both disposal and to the utilisation of bottom ash in construction applications. In this chapter, results obtained by a wide variety of test methods applied in different jurisdictions have been collected to generate a better understanding of bottom ash leaching characteristics.

Although there is a substantial amount of leaching data on bottom ash presented, it is important to recognise that "bottom ash" samples are generally a mixture of bottom ash, grate siftings and sometimes heat recovery system ash (dependent on the configuration of the incinerator). The presence or absence of these individual ash streams in a "bottom ash" sample may effect the leachability of some elements because of differences in the chemical characteristics of these streams. In addition, the refuse feed stock for a particular incinerator facility may include or exclude components normally found in MSW, and thus have an effect on the leachability of elements in ash.

The generation, collection and composition of different types of APC residues has been discussed in detail in Chapter 4 and 11. The data presented in this chapter represent data on different air pollution control (APC) residues including filter ash (electrostatic precipitator ash and fabric filter ash) and residues from acid gas cleaning (dry scrubbing, semi-dry and wet systems) (Born, 1993; Eighmy, 1993, Hjelmar, 1993, Environment Canada, 1993). The limited information which is available for heat recovery ashes is gleaned from some of these same studies.

16.1.3 Data Transformation

Leaching test results can be expressed either as leachate concentration (mg/l) or as constituent release (mg/kg residue). The basis selected for expressing leaching results should be based on the type of data comparison which is desired. Regulatory test results most often are expressed as leachate concentrations for comparison to performance criteria values (e.g., groundwater, drinking water), but do not consider the underlying basis for release phenomena which are observed. Results expressed as a concentration permits a comparison of contaminant solubility which reflects the chemical speciation of the elements and leaching solution conditions (e.g., pH). Transformation of measured concentrations into units of release is necessary for comparison of the data obtained at different liquid-to-solid (L/S) ratios and determination of availability. Release is defined as the ratio of the mass of a contaminant dissolved to the mass of residue leached (Environment Canada, 1986). Currently, there is a shift in some jurisdictions toward regulatory limits based on release, rather than leachate concentration, for evaluation of environmental impacts. Release fluxes (e.g., $mg/m^2/yr$) describe release of a constituent as a function of geometric surface area and time. Much of the data presented in this chapter has been transformed from its originally reported basis into either leachate concentrations or release to facilitate valid comparison of the data.

16.2 TOTAL SOLUBLE FRACTION AND AVAILABILITY OF ELEMENTS

16.2.1 Total Soluble Fraction

The total soluble fraction of a residue is an important consideration for evaluating potential groundwater impacts from disposal and the physical and environmental suitability for utilisation.

Bottom ash is not highly soluble in water. Results from batch tests at a liquid-to-solid (L/S) ratio of 20 indicate that approximately 6% of bottom ash (including grate siftings) from mass burn and RDF incinerator systems can be readily solubilised in water. The majority of the constituents solubilised from bottom ash are potassium, sodium and calcium chlorides and sulphates (see Chapter 11). This data is corroborated by data from column studies which indicate that the major components of percolated leachate are readily soluble salts which are flushed from the columns within 1 - 2 pore volumes without any noticeable retention.

Bottom ash from two-stage systems appears to be slightly less soluble (3%). The reduced total soluble fraction most likely results from the higher content of uncombusted material which acts to dilute the salt concentrations remaining in the bottom ash. In addition, the char can act as a sorptive medium for potentially soluble metals. After conversion to mass leached relative to total mass of waste input, the overall quantities of total salts leached from two-stage, mass burn and RDF incinerators are similar.

The high total soluble fraction of APC residues is a critical factor in management of these materials. In contrast with bottom ash, the total soluble fraction of APC residues, particularly scrubber residues, range from 30 to greater than 65%. This high solubility also is a major factor of environmental concern. In leaching experiments, the resulting high concentrations of dissolved can cause analytical problems (see Chapter 7).

16.2.2 Availability

Availability for leaching is defined as the maximum quantity or soluble fraction of a residue constituent that can be released into solution under aggressive leaching conditions (NEN 7341, 1994). These conditions, in theory, should provide an estimate of the maximum mass of material that could leach under a 1,000 to 10,000 year time frame, except for mobile species such as highly soluble salts (e.g., sodium chloride) for which the availability can be reached in a matter of years. Under availability controlled conditions, the resulting solution is at a concentration less than the saturation condition for the element or species of interest. For example, availability in bottom ash typically excludes elemental species which are tightly bound in glassy matrices and in geologically stable mineral forms such as Si in SiO_2 (quartz), Ca in $Ca_2Al_2SiO_7$ (gehlenite), and Mg in $MgCa_2Si_2O_7$ (åkermanite). Thus, the availability of a specific element can be significantly less than the total content of that element (e.g., Pb) or may be approximately equal to the total content (e.g., Cl). Determination of availability, however, does not indicate whether or not this maximum quantity of a particular constituent will be released, or over what precise time interval the release will occur for the environmental exposure scenario of interest.

NEN 7341 (formerly NVN 2508, 1987) was developed to quantify the availability of constituents in inorganic wastes and combustion residues. This leaching procedure is based on a pH-controlled extraction at pH=7 and 4, successively, using a total liquid to solid ratio (L/S) of 100. These conditions generally prevent solubility limitations during extraction.

The data obtained from the availability test assessed is not directly applicable for evaluation of actual environmental impact because the entire available fraction may not be released under specific environmental exposure scenarios or in realistic time scales. However, it does represent the mass transfer driving force for leaching and has been proven useful in modelling. (NEN7345, 1994). One exception to this is with respect to some amphoteric metal compounds, particularly Pb-based compounds. In some instances, the availability test data can underestimate the quantity of metals, such as lead, which are available for leaching under highly alkaline conditions.

Table 16.1 summarises the ranges for total composition and availability for bottom ashes from USA, Canada, Denmark, Germany, Sweden and the Netherlands (Chapter 9). The availability for several constituents (e.g. Si, Al, Cr) is an order of magnitude less than the total content. When the availability of a specific constituent is very low with respect to the potential for environmental impact, further evaluation of the release of that constituent from environmental point of view is unnecessary. Availability results indicate that B, Ca, Cd, Cl, Cu, Pb, Mo, SO_4 and Zn are important constituents in bottom ash which warrant further evaluation.

Table 16.1
Ranges of Total Content and Availability for Bottom Ash

Element	Total content (mg/kg)		Availability (mg/kg)		Fraction available (-)	
	Min	Max	Min	Max	Min	Max
Major						
Ca	50000	90000	20000	70000	0.4	0.8
Cl	1000	3000	1000	3000	1	1
K	7000	20000	1000	4000	0.14	0.2
Mg	10000	30000	1000	6000	0.1	0.2
SO_4	12000	30000	8000	18000	0.6	0.7
Trace						
As	5	40	0.3	5	0.06	0.13
B	80	300	50	200	0.6	0.7
Ba	500	1800	50	200	0.1	0.15
Cd	2	25	0.5	5	0.2	0.25
Cr	200	1000	2	10	0.01	0.01
Cu	1200	2500	50	200	0.04	0.08
Hg	0.5	1	0.01	0.1	0.02	0.1
Mo	5	30	1	4	0.1	0.2
Pb	1500	3000	50	300	0.03	0.1
Sb	30	200	1	2	0.01	0.03
Zn	2000	4000	50	500	0.03	0.13

Using a similar approach as for bottom ash, the availability of constituents from APC residues has been determined (Kosson et al., 1993; Versluijs et al., 1990; Hjelmar, 1993; Whitehead, 1990). Table 16.2 presents data on total composition and availability for filter ashes, scrubber residues and combined APC residues. In general, the availability is high (50%) for Pb, Zn, Ca, Mg and approaches 100% for several constituents (Cd, Na, K, Ca, Cl, SO_4). This indicates a potential risk posed by this type of residue if disposed in a landfill without adequate design considerations.

Table 16.2
Ranges of Total Content and Availability for APC Residues

Element	Total content (mg/kg)		Availability (mg/kg)		Fraction leached (-)	
	Min	Max	Min	Max	Min	Max
Ca	50000	200000	50000	100000	0.5	1
Cl	8000	60000	80000	60000	1	1
K	20000	40000	10000	25000	0.5	0.6
Mg	10000	30000	4000	15000	0.4	0.5
SO_4	30000	90000	30000	80000	0.7	1
As	30	100	1	2	0.02	0.03
B	30	200	30	150	0.6	1
Ba	100	3000	30	80	0.02	0.05
Cd	100	900	100	900	1	1
Cr	100	800	5	50	0.05	0.15
Cu	300	3000	1	20	0.01	0.05
Hg	5	20	4	10	0.5	0.9
Pb	4000	20000	100	5000	0.1	0.4
Sb	50	950	0.5	1	0.02	0.05
Zn	5000	40000	4000	20000	1	1

16.2.3 Sequential Chemical Extractions

The sequential chemical extraction (SCE) procedure was originally derived to identify the association of trace contaminants with particular chemical phases in sediments (Tessier et al., 1979). The extractions are operationally defined and the test results do not necessarily reflect an association with the claimed phases (carbonate phase, iron and manganese bound, organic degradable or reducing phase) as shown by Gruebel et al., (1988). However, under the NITEP Program, a modified SCE procedure was used on incinerator residues (WTC, 1993; based on Fraser and Lum, 1983). Moreover, the emphasis on interpretation of the SCE data shifted away from the associated chemical phases toward association with different leaching conditions within an MSW landfill over time (see Table 16.3). Results are usually expressed as a percentage contribution to the five operationally defined extraction steps. The procedure does provide a qualitative indication of the matrix association of specific elements. In Figure 16.1, SCE results for bottom ash, filter ash and economiser ash from the NITEP study (Sawell et al., 1988) are presented. In bottom ash, substantial fractions of the total element content are found in the fractions considered unavailable for leaching. This agrees with the observations made in the availability test.

Table 16.3
Interpretation of the Sequential Chemical Extraction Procedure

Fraction	Interpretation
A	Immediately available for leaching
B	Potentially available for leaching under acidic conditions
C	Potentially available for leaching under severe reducing conditions
D	Unavailable for leaching under normal leaching conditions
E	Unavailable for leaching

16.3 SOLUBILITY AND RELEASE OF ELEMENTS

Measurement of solubility requires that sufficient contact time be allowed for the solution and solid phases to approach equilibrium. The most common time frame used in laboratory testing is 18 to 24 hours. Time dependent leaching studies have shown that equilibrium is approached for most constituents after about 24 hours for a particle size of less than 3 mm (Comans et al., 1993). For some constituents (Mg, Zn) equilibrium was not reached within 200 hours. In general, the time required to reach equilibrium may be shortened through reductions in particle size.

The most dominant factor influencing the solubility of most elements from ash, especially trace metals, is the pH of the leaching environment. Numerous studies have underscored the importance of the endpoint pH of the leaching medium on the release of trace metals (DiPietro et al., 1989; Sawell et al., 1987, 1988 & 1989; US EPA, 1988; De Groot et al., 1987; van der Sloot et al., 1989, 1991a, 1991b; Kosson et al, 1993).

Presentation of leachate concentrations as a function of pH is useful when solubility in the solution phase is limiting release (solubility control). This presentation also can be used to visualise the effects of complexation reactions of constituents and effects of reducing conditions.

Figure 16.1 Sequential Chemical Extraction (SCE) Results for Bottom Ash for Selected Metals

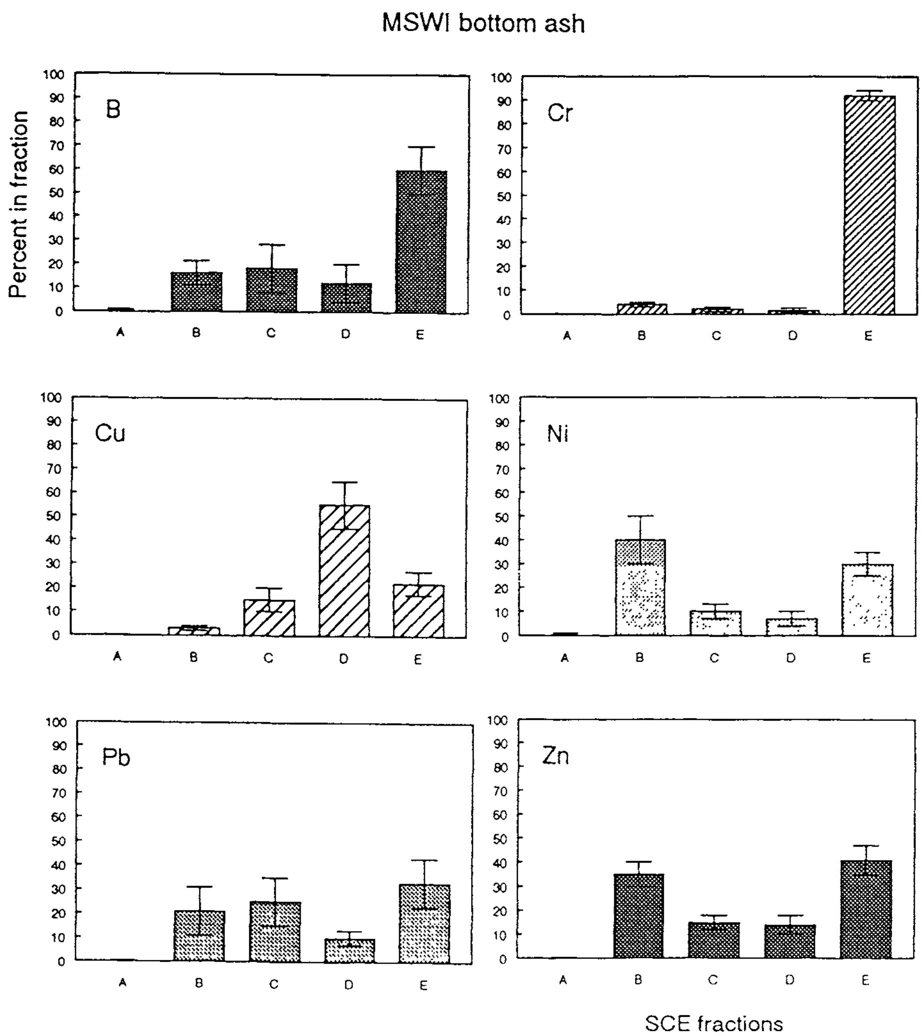


Figure 16.1 Continued

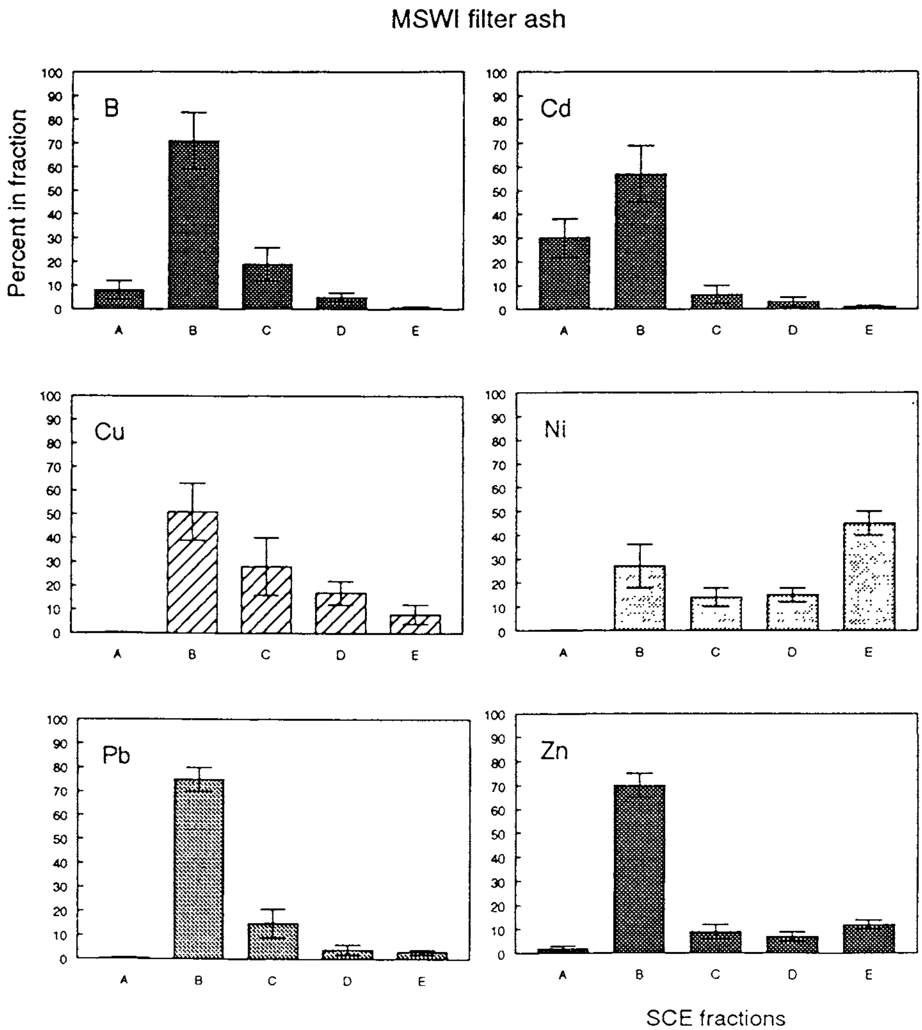
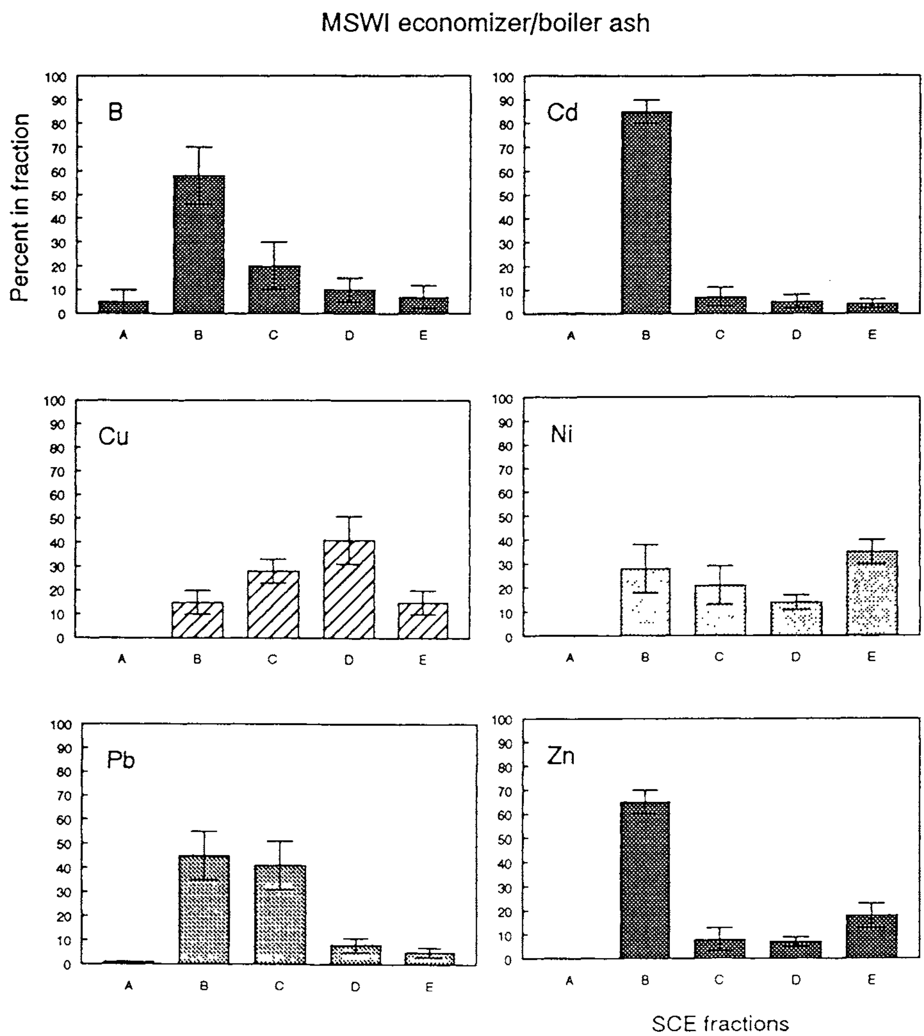


Figure 16.1 Continued



16.3.1 Bottom Ash

Unified curves presenting the pH dependent solubility of various elements in bottom ash have been developed based on compilation of the data from a wide variety of sources (Versluijs et al, 1990; Sawell et al., 1987, 1989; Eighmy et al., 1989, Eighmy, 1993; Hjelmar,1991; Kosson et al., 1993; Kosson, 1992; Fällman et al., 1992; Wahlström, 1992; VVAV, 1988,1992; WASTE Program, 1993; van der Sloot et al., 1987, 1991a, 1991b, Comans et al., 1993; Sakai, 1995). Data from the following test procedures (see Chapter 14) have been included:

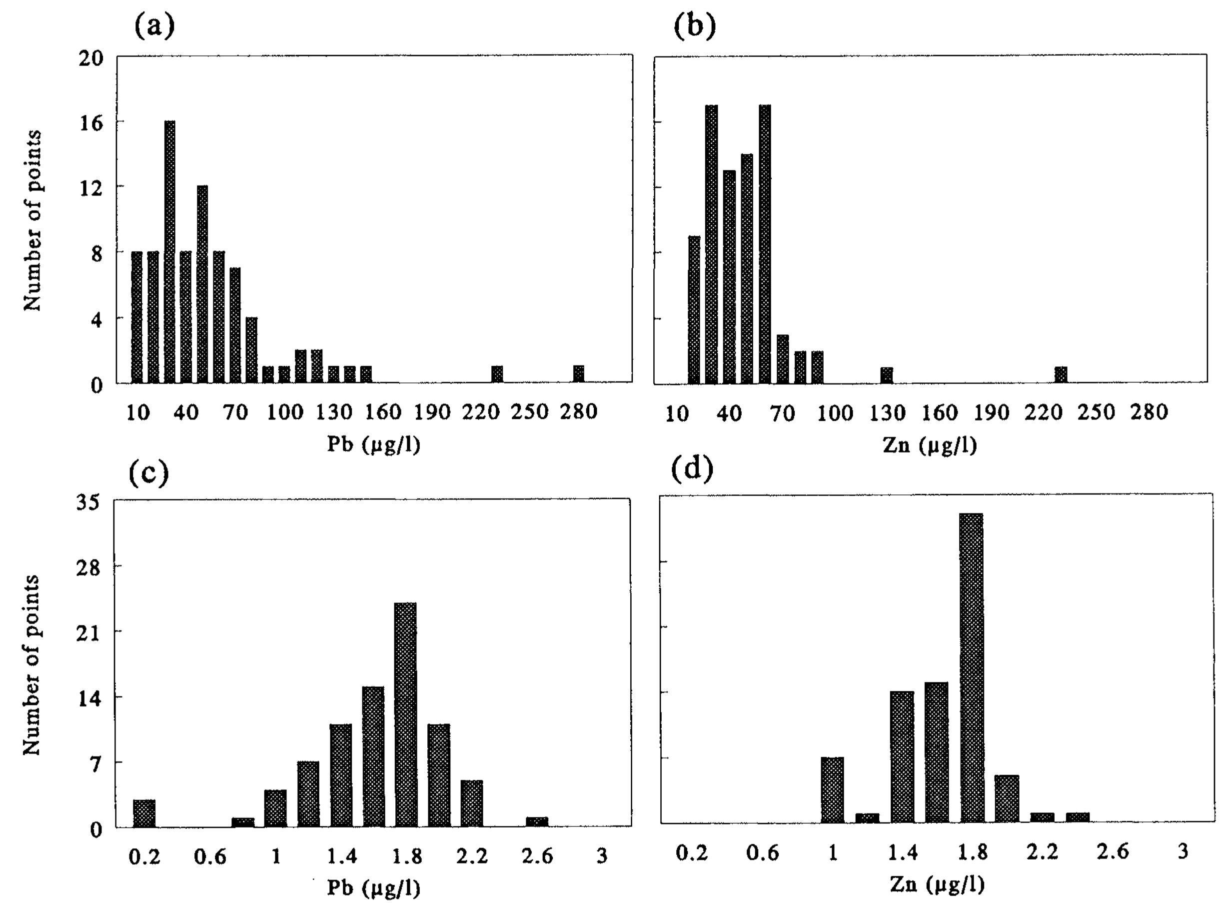
- Acid Neutralisation Capacity Test
- DEV S4
- Distilled Water Leach Test
- EP Toxicity
- MOE Regulation 309 (now 347) Leach Procedure
- pH Stat Test
- Serial Batch Tests (NVN 2508, now 7349)
- Swiss TVA
- TCLP
- California WET Test
- Japanese JLT-13

The data have been selected from studies in which either a wide range of materials was studied or in which particular focus was placed on the pH sensitivity of leaching. The pH related data compiled here does not represent the natural pH range of ash in the environment. Although aged bottom ash can exhibit a neutral to mildly alkaline pH in the environment, acidic to strongly acidic pH's on the solubility curve are strictly a function of the quantity of acid added during the test. It should also be noted that acidic to strongly acidic leaching conditions (pH <4.5) are not normally found in the environment.

The results have been presented in the form of aqueous concentration as a function of pH to emphasise solubility control. The data used are all based on extractions at L/S =5, 10 or 20. No distinction was made with respect to incinerator manufacturer or type of grate, because such variations appeared to be of limited importance in comparison with the variability in the feed stock to the facilities. Care has been taken to select only data for bottom ash from mass-burn facilities, but the bottom ash may include grate siftings, depending on the facility and sampling protocol. Data from RDF facilities and other related installations are discussed in Section 16.4.4.

The resulting leaching data set was sorted according to increasing pH and obvious outliers were omitted. Figure 16.2 presents the histograms for untransformed and log-transformed Pb and Zn data over a small pH interval. The results clearly indicate that the overall data set should be treated as log-normally distributed. Data over increments of 0.1 pH units were log-normalised, averaged and the standard deviation

Figure 16.2 Histograms of Raw (a,b) and Log Transformed Data (c,d) for Zn and Pb from Laboratory Batch Extractions Between pH 11.4 and 11.6



was determined. Figure 16.3 presents polynomial curves fit to the mean and +/- 1 standard deviation of data which has been log-transformed and averaged. Coefficients for the polynomial curves are provided in Table 16.4. All leaching data, with the exception of the California WET data and the Swiss TVA data, were omitted during regression. Data for As, Cd, Cr, Cu, Mo, Pb, Ni and Zn are presented. These curves indicate very consistent and well defined pH dependent leaching behaviour for the different elements studied.

Table 16.4
Polynomial Coefficients for Unified pH Curves

Coeff.	Cd	Cr	Cu	Mo	Ni	Pb	Zn
a0	0.59975	1.31282	2.19662	-4.99936	0.30126	2.31369	2.89268
a1	-0.17105	-0.16596	0.29699	0.23601	0.37705	-0.17839	-0.60674
a2	0.26699	0.05870	-0.59716	0.36681	-0.42432	0.08597	0.51484
a3	-0.11127	-0.06533	0.15578	-0.1285	0.15610	-0.05557	-0.14276
a4	0.01573	0.01204	-0.01681	0.01861	-0.02478	0.00736	0.01489
a5	-0.00100	-0.00082	0.00079	-0.00123	0.00170	-0.00036	-0.00070
a6	0.000024	0.000019	-1.3E-05	0.00003	-4.2E-05	6.1E-06	0.000014
R	0.994	0.996	0.990	0.989	0.989	0.988	0.995

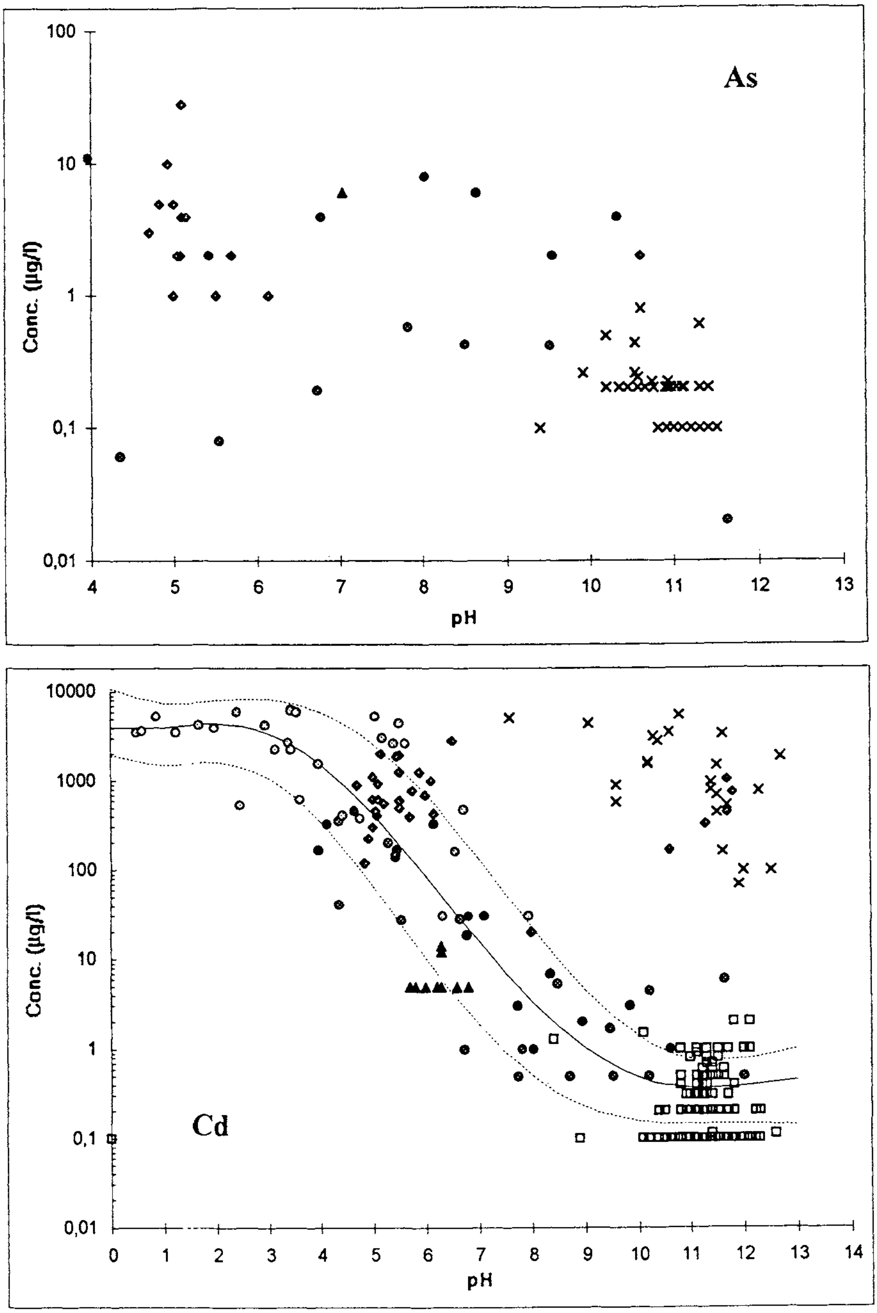
Conc. (mg/l) = $a0 + a1(pH) + a2(pH)^2 + a3(pH)^3 + a4(pH)^4 + a5(pH)^5 + a6(pH)^6$

The derived "unified pH solubility curves" can be used as a basis for evaluating consistency with, or deviation from, typical leaching behaviour. Thus, these curves are used as a benchmark for the interpretation of regulatory leach test results from different jurisdictions, comparison of the effects of different incinerator facility variables (e.g., design, country, operating parameters, etc.), and in modelling the chemical speciation of bottom ash to define the solubility controlling phases. The use of the unified pH solubility curves also may be beneficial for the operators of incinerators as a quality control tool for ash residues, as well as to regulators for defining acceptable and unacceptable behaviour of residues. Control tests can be derived with maximum sensitivity to the parameters chosen for verification of residue quality.

Results are presented in Figure 16.3 for a selection of major elements, Ca, Si, Al, Mg, Fe, Mn, and sulphate, and the trace contaminants As, Cd, Cr, Cu, Ni, Mo, Pb and Zn. Solubility of Na, K and Cl have not been presented because the solubility of these elements is independent of pH.

Arsenic (Figure 16.3a)
The potential leachability of As from bottom ash is relatively small (around 0.1 mg/kg). No clear distinction of its leaching behaviour as a function of pH can be identified as

Figure 16.3ab Composition of Worldwide Leaching Data (n=460) of Unified pH-Solubility Curves for MSWI Bottom Ash Selected Metals



(a)

(b)

observed for coal ash (De Groot et al., 1987), in which a maximum leachability is observed at neutral pH. Arsenic is not regarded as an element of concern in bottom ash due to the small percentage of the already low concentrations in the ash (40 mg/kg). Hydrated iron oxide phases, which are present in abundance, are probably responsible for this retention (Van der Hoek, et al., 1993).

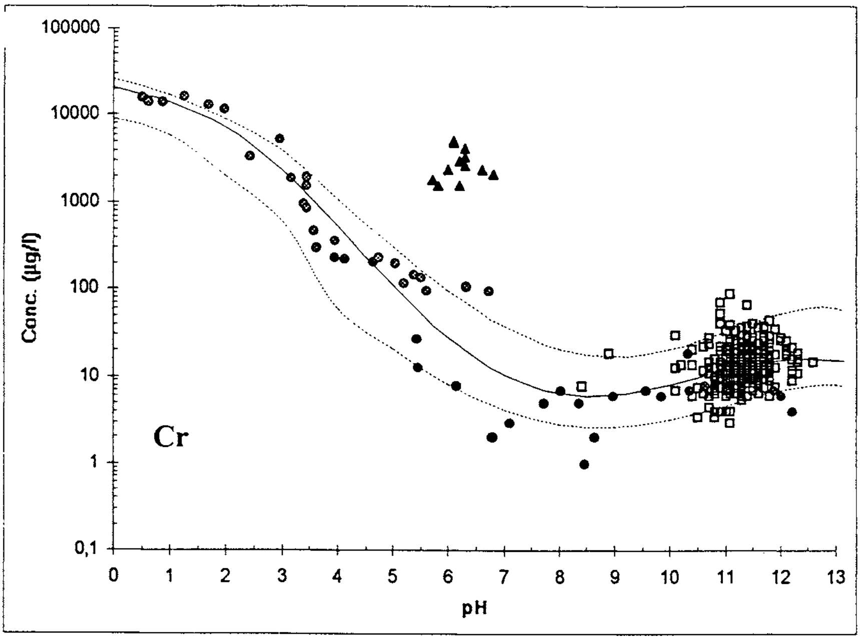
Cadmium (Figure 16.3b)
The solubility of Cd ranges over more than 4 orders of magnitude in the pH range from 4 to 9 with very consistent behaviour. A possible cause for the wide scatter of data around pH 6 may be the result of complexation of Cd with Cl in the ash. Release in the pH range from 0 to 4 reflects the availability of Cd in the bottom ash which is almost the total content. A significant difference in total Cd content may exist between different countries as well as between installations depending on the feed stock of MSW and the combustion efficiency of the incineration (see Chapter 9).

Chromium (Figure 16.3c)
Although the data set is still limited, the results are very consistent. At present, a validated explanation for the observed behaviour is lacking. In view of the fact that Cr III is less leachable than Cr VI at neutral pH, it may be that the shape of the curve reflects the presence of both species. Cr III would be leachable only at relatively low pH values (pH < 4), while a minor portion of the total Cr present is in the hexavalent state which is leachable (similar to other oxy-anionic species such as Mo). This speciation also would explain the depletion of a soluble Cr species as observed in column experiments (Section 16.2.4).

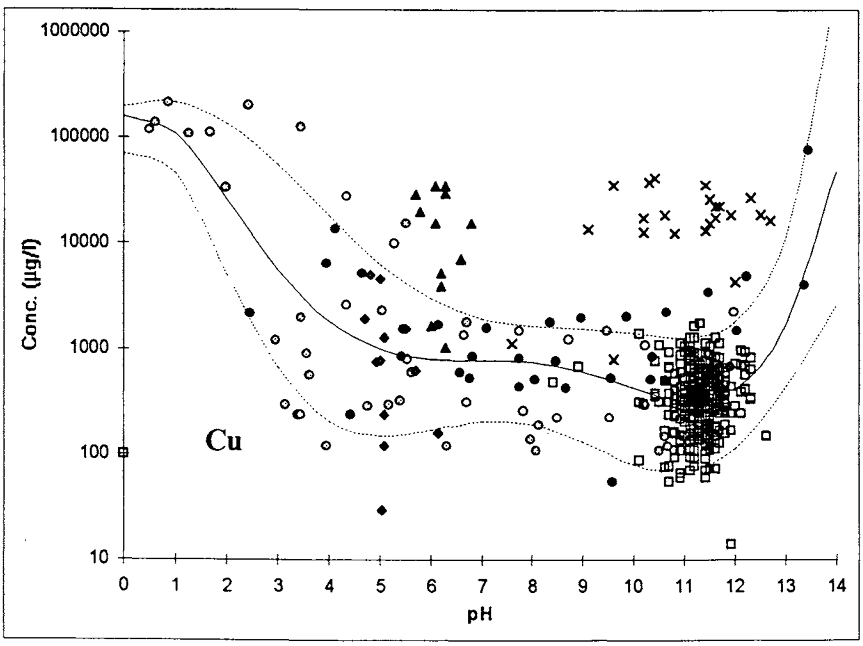
Copper (Figure 16.3.d)
The leachability of copper covers a relatively wide range. Cu leaching data obtained from the acid neutralisation capacity test (Kosson et al., 1993), in particular, showed wide variability. The pH static data are more consistent (Comans et al., 1993; Eighmy, 1993). The behaviour of copper has been studied in detail (van der Sloot et al., 1992; Comans et al., 1993) and various options for explaining the leaching behaviour have been presented. A relation between Cu solubility and the presence of organic matter exists. This aspect will be addressed in more detail in section 16.2.3 on chemical speciation of Cu.

Molybdenum (Figure 16.3e)
The leaching behaviour of Mo is characterised by fairly constant release in the pH range 7 to 13 and a decrease toward pH 4. This is consistent with the leaching behaviour of Mo from coal fly ash (van der Sloot et al., 1989) and may be indicative of a leachability controlling mechanism. Based on the relationship to column test results, it appears that Mo is an element which can be associated to a specific industrial input.

Figure 16.3cd

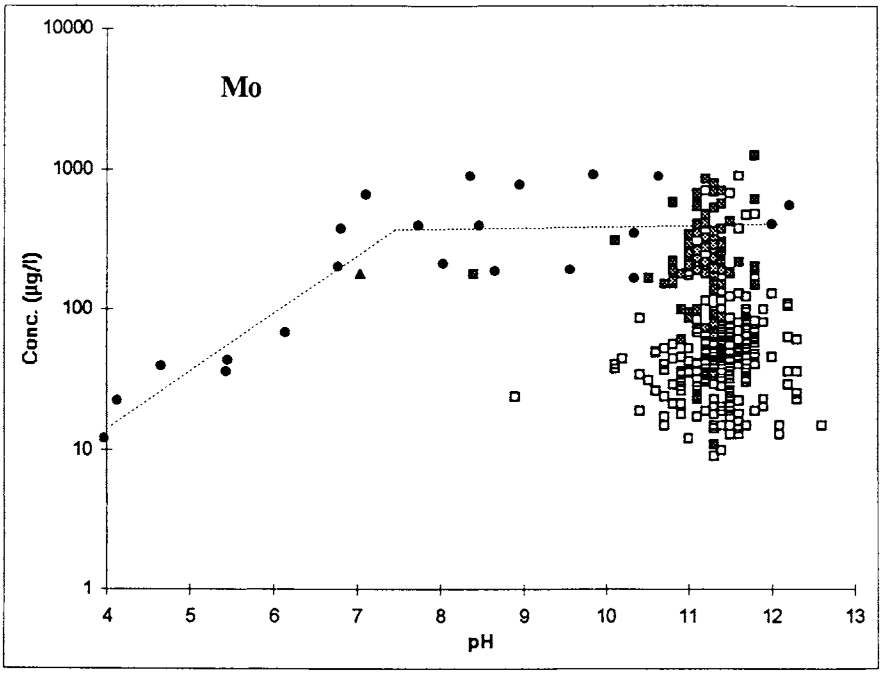


(c)

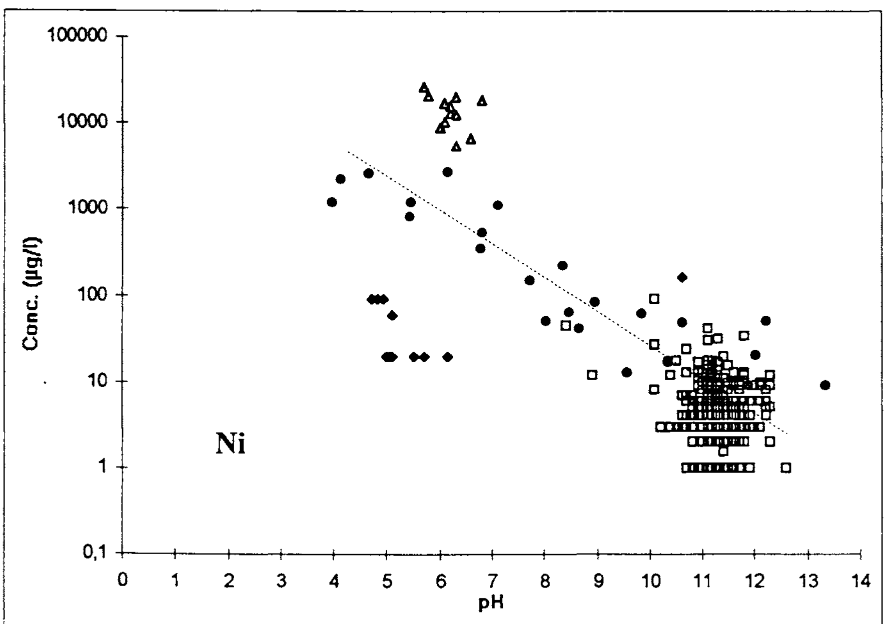


(d)

Figure 16.3ef



(e)



(f)

Relatively high Mo levels occur in only a few specific urban locations, whereas most suburban communities produce waste with relatively low Mo levels. The element is crucial in the evaluation of utilisation in some jurisdictions because of its high mobility. The pH data presented could erroneously lead to a conclusion that leachability decreases at high pH. The leachability appears to be independent of pH in the range 7 to 13.

Nickel (Figure 16.3f)
The leaching behaviour of Ni is consistent based on the limited data available. The behaviour of Ni shows increasing solubility with decreasing pH, reaching a maximum solubility at pH less than 7.

Lead (Figure 16.3g)
The leaching behaviour of lead is surprisingly consistent in spite of the documented heterogeneity of Pb in of bottom ash. The amphoteric nature of Pb compounds is clearly evident, which results in increased solubility by several orders of magnitude at pH >11. Several test methods used for regulatory purposes are consistent with the general pH dependent leaching curve indicating the solubility control for Pb is very significant.

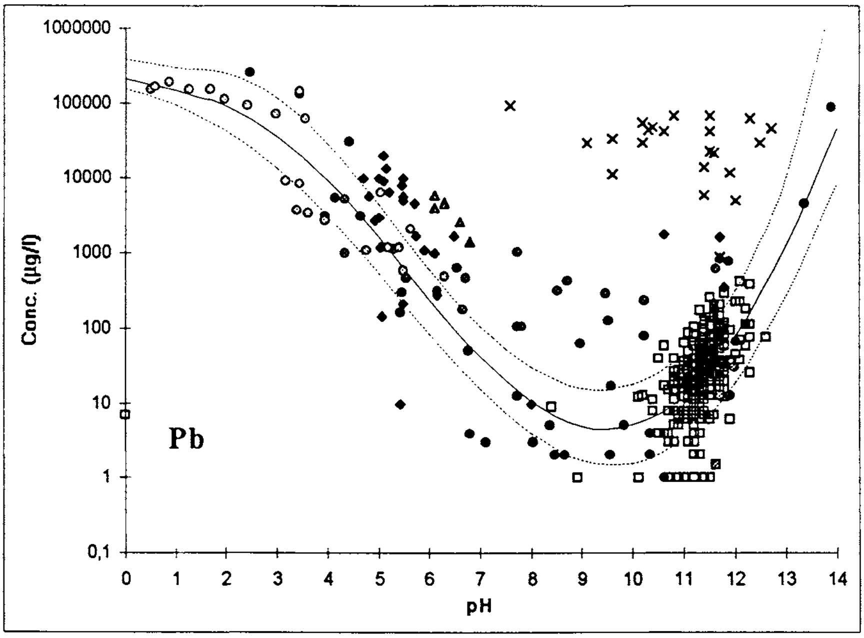
Zinc (Figure 16.3h)
The leaching behaviour of Zn as a function of pH is more consistent than any of the other elements, indicating of a high degree of solubility control. In the pH range below 6, the leachability reflects the amount of Zn available for leaching with the maximum leachability reached between pH 4 and 5. As in the case of Pb, the Zn leaching is characterised by a sharp increase in leachability at high pH due to formation of anionic hydroxide complexes.

16.3.2 APC Residues

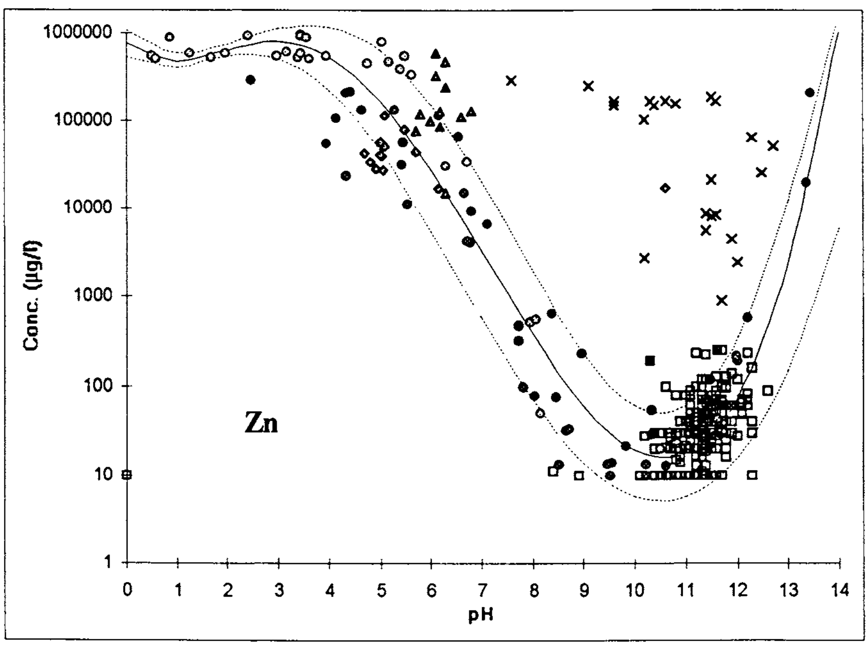
The release of constituents from APC residues as a function of pH is crucial for the understanding of the chemistry behind the observed release from APC residues. Figure 16.4 presents the solubility of B, Ba, Cd, Cr, Cu, Hg, Mo, Pb and Zn from APC residues as a function of pH. The data were obtained from (Eighmy, 1993; van der Sloot et al, 1992; Kosson et al., 1993; Environment Canada, 1993, Hjelmar, 1993). Characteristic solubility controlled release is indicated although insufficient data was available to develop unified leaching curves.

Boron
The leachability of boron from filter ash (without scrubber residue) is consistent with that of bottom ash (Eighmy et al, 1993). At pH greater than 10 the solubility decreases.

Figure 16.3gh



(g)



(h)

Figure 16.4 Comparison of pH Dependent Concentration Data for Selected Metals from APC Residue

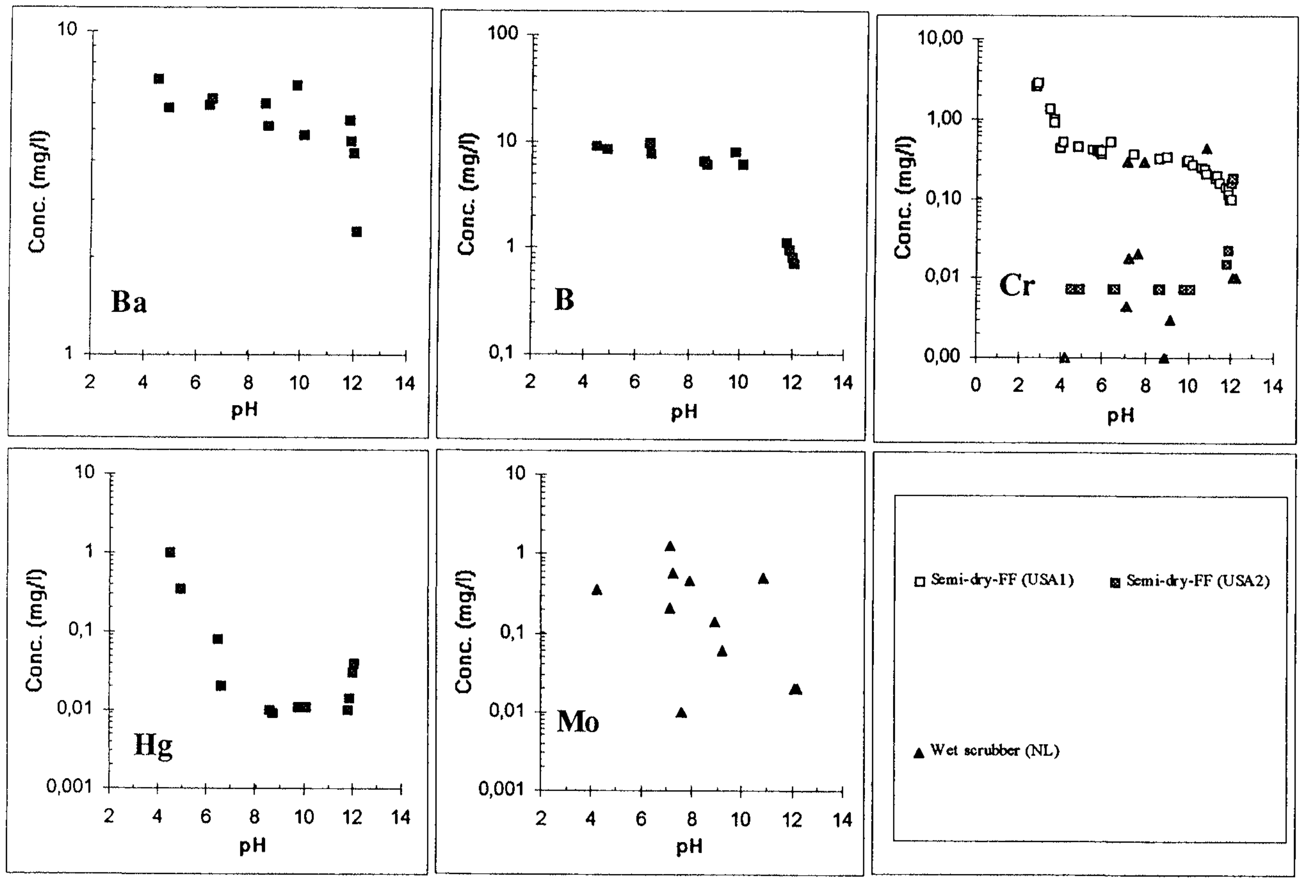
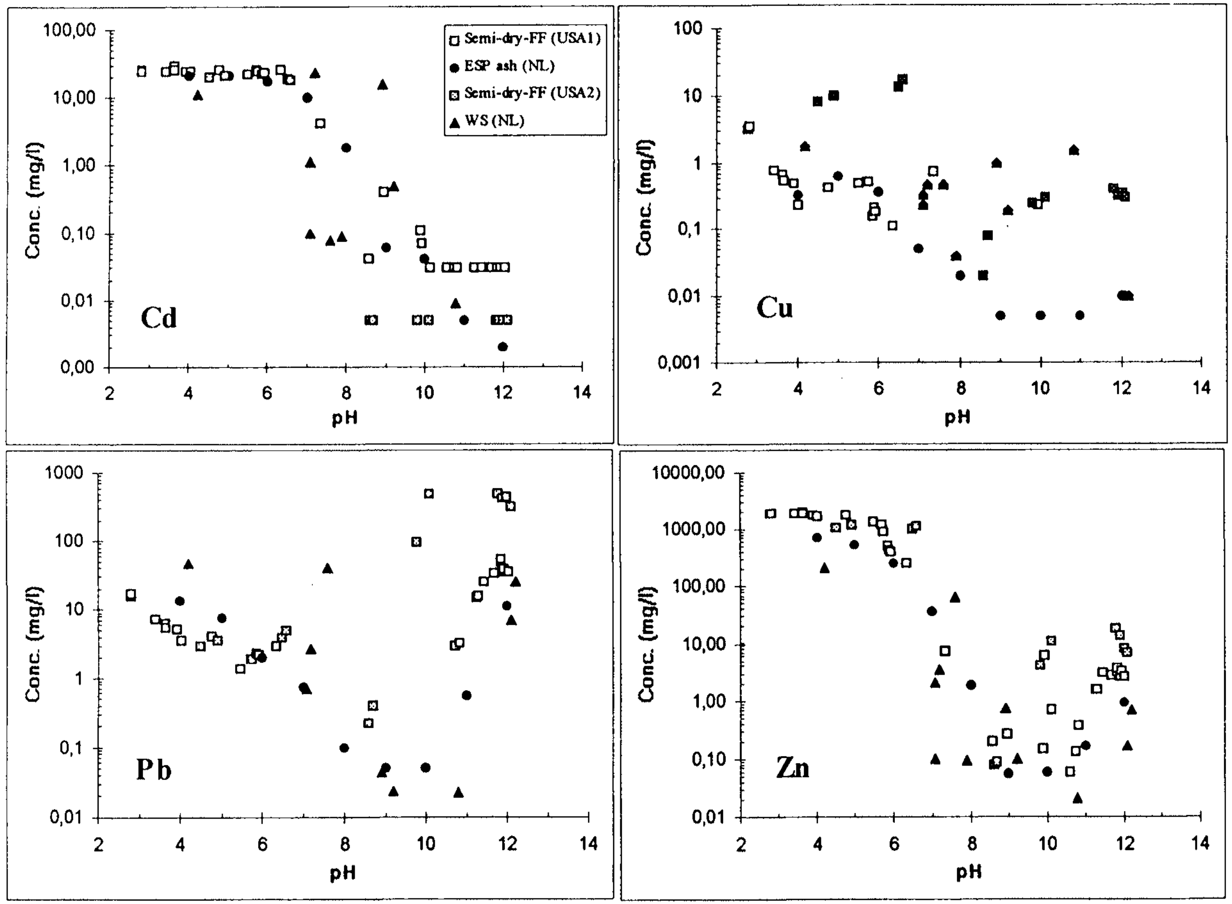


Figure 16.4 Continued



Barium
The leachability of Ba does not show any significant dependence on pH except a slight decrease around pH = 12.

Cadmium
The solubility of Cd from APC residues follows a similar pattern to Cd in bottom ash, except that the solubility slope is shifted to higher pH caused by complexation with the high chloride content in these residues.

Chromium
Cr solubility measured with the ANC procedure (Kosson et al., 1993) shows a consistent pattern which would reflect Cr III leachability at pH < 4 and a chromate leachability plateau from pH 4 to 10. At pH greater than 10, the concentration of chromate also decreases.

Copper
The leachability data for Cu show a large amount of scatter. The pH stat data for ESP ash are fairly consistent indicating very low solubility of Cu corresponding to tenorite solubility. The irregular behaviour of Cu in APC residues is not well explained.

Mercury
The leachability of Hg indicates a pattern similar to many other metals but only limited data are available.

Molybdenum
The leachability of Mo is scattered. No distinctive trend in its behaviour has been observed.

Lead
The pH dependent leaching behaviour of Pb is consistent with only a few outliers. It is striking to note that the leachability of Pb at pH around 12 exceeds the leachability of Pb at pH = 4. This can result in significant release because the pH of many APC residues is greater than 11. Pb is considered one of the elements of concern in APC residues because results from regulatory testing exceed many current regulatory limits.

Zinc
The leachability of Zn is quite consistent considering the widely different origin of the

residues included in the figure. This may point at the presence of one important solubility controlling phase.

16.4 GEOCHEMICAL MODELLING OF LEACHING EQUILIBRIA

In Chapter 15, several studies on modelling of leaching behaviour from incinerator residues have been discussed (Di Pietro et al., 1987; van der Sloot et al., 1987; Eighmy et al., 1993, Kirby and Rimstedt, 1993; Comans et al., 1993). Two complementary approaches have been used:

- Identifying and quantifying the solid phases in ash and running MINTEQA2 through a solid phase approach (Eighmy et al., 1993); and,
- Using aquatic chemistry to identify the solubility controlling phases using MINTEQA2 based on the measured leachate composition (Comans et al., 1993)

Different sophisticated analytical techniques (see Chapter 7.2.7) are needed for the first approach to carry out species identification and quantification. Eighmy at al (1993) indicated fairly good agreement between test data and modelling results following this approach (See Table 15.5 and 15.6). The leaching test used for the comparison was carried out at controlled pH=4 using a high L/S value. The modelling results for Al and Si are significantly below the measured concentration levels because according to the model quartz (SiO_2), diaspore ($AlO(OH)$) and alunite ($KAl_3(SO_4)_2(OH)_6$) precipitated out.

The second approach presented covers a wider range of pH conditions. Elemental concentrations have been predicted by assuming equilibrium between the leachates (at L/S=5) and potential solubility-controlling minerals in bottom ash. These minerals were selected on the basis of their saturation indexes in prior MINTEQA2 runs and their likeliness to be present or formed under the experimental conditions (Chapter 9). The thermodynamic data from the standard MINTEQA2 (version 3.11, Allison et al., 1991) database were used, unless indicated otherwise. As molybdenum was not present in the database, it was added as the component MoO_4^{2-} together with equilibrium constants for aqueous species and solids reviewed by Rai and Zachara (1984). The model predictions are presented as total element concentrations, rather than free ion activities, in the leachate solutions at each pH. This enables presentation of model results together with the analytical leaching data in a graph of log-concentration as a function of pH, which maintains the characteristic shape and concentration levels of the unified pH leaching curves.

16.4.1 Bottom Ash

Figure 16.5 presents the total dissolved concentrations of major and trace elements in leachates as a function of pH, as well as MINTEQA2 predictions assuming equilibrium with different mineral phases. In the following paragraphs, leaching curves and possible solubility controlling processes are discussed for each element.

Calcium and Sulphate

Ca and SO_4 are the major dissolved components leached from the bottom ash samples, generally reaching concentrations of 3 g/L or greater. Since the solubility of Ca in fossil fuel combustion residues may be controlled by calcite ($CaCO_3$), portlandite ($Ca(OH)_2$) or gypsum ($CaSO_4$*$2H_2O$) (Rai, 1987), the same mineral phases have been considered for MSW incinerator bottom ash. MINTEQA2 calculations indicate that the leachates are not in equilibrium with atmospheric CO_2 (350 ppm) and that measured concentrations of Ca and CO_3 are not in equilibrium with calcite. The steepness of the portlandite solubility curve indicates that the leachates are not in equilibrium with this mineral either. The Ca and SO_4 concentrations between pH 4 and 10 do not depend very strongly on pH and follow the solubility curve for gypsum. This relationship is confirmed by plotting the data in a log Ca^{2+}-activity versus log SO_4^{2-}-activity diagram. Gypsum is a soluble mineral and does allow high concentrations of both Ca and SO_4 to be leached from bottom ash. However, provided enough time, carbonation of the alkaline ash and the formation of calcite will further limit Ca leaching in the near-neutral pH range. Calcium concentrations at pH greater than 10 start decreasing at a lower pH and less sharply than predicted by portlandite solubility. The mineral phase controlling Ca solubility at strongly alkaline pH remains as yet unknown. Ettringite, which has been observed in field applications of compacted bottom ash, may play a role in the solubility of Ca at high pH. Stability data for ettringite is needed to be able to verify this possibility.

Magnesium

Mg concentrations are essentially independent of pH between pH 4 and 7. Normally magnesium also is largely controlled by carbonate minerals. The system is not in equilibrium with atmospheric CO_2 as indicated for Ca already. At higher pH values, concentrations decrease sharply. MINTEQA2 calculations indicate this decrease to be consistent with the solubility line of brucite ($Mg(OH)_2$), a mineral which has often been shown to control magnesium solubility. The data point at pH > 13 deviates due to the very high ionic strength of this particular sample.

Silicon

Dissolved silicon decreases between pH 4 and 10 and increases again at strongly alkaline pH. This leaching pattern is not in agreement with either amorphous or crystalline (quartz) SiO_2, as calculated with MINTEQA2. Fruchter et al. (1990) have

Figure 16.5 Dissolved Metals in Bottom Ash Leachates as a Function of pH Compared with MINTEQA2 Predictions Assuming Equilibrium with Different Mineral Phases

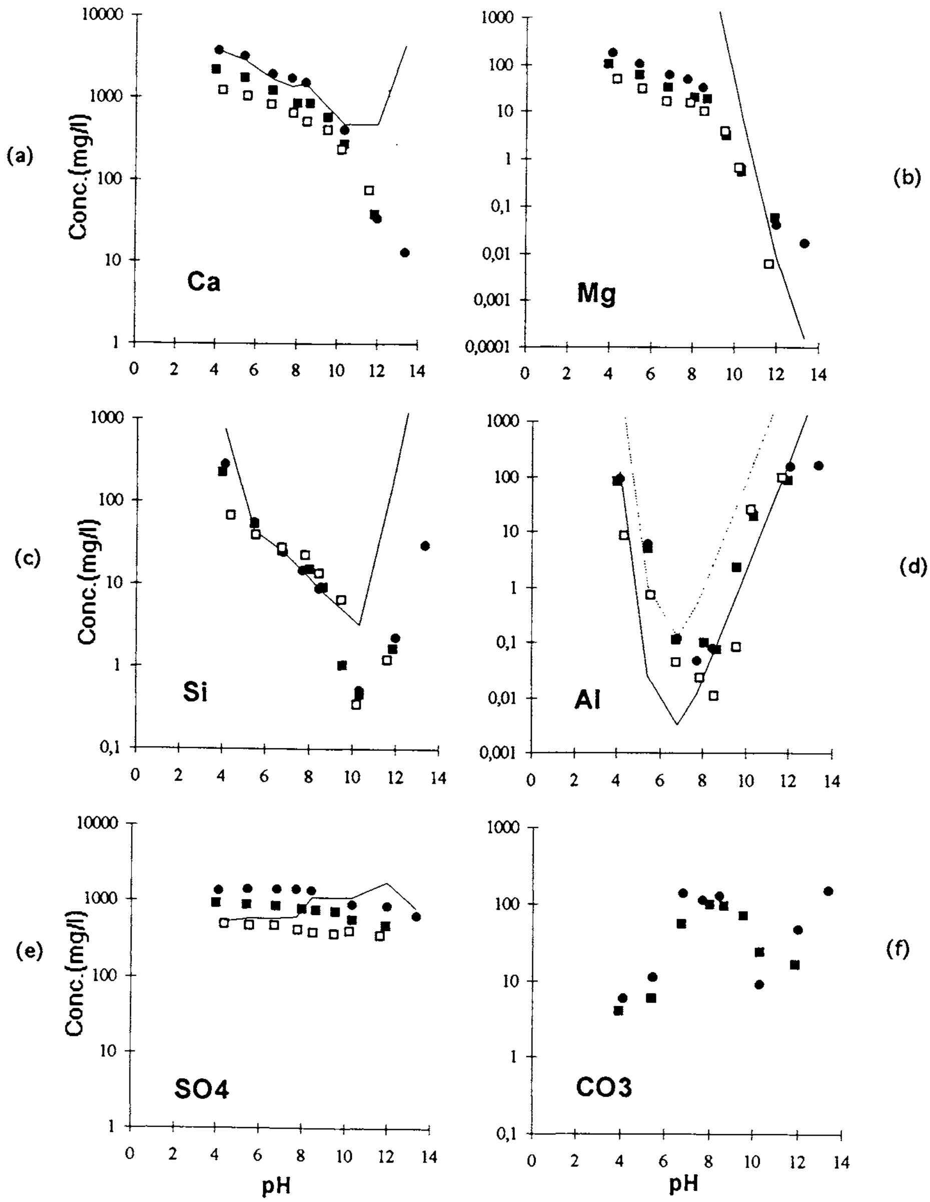
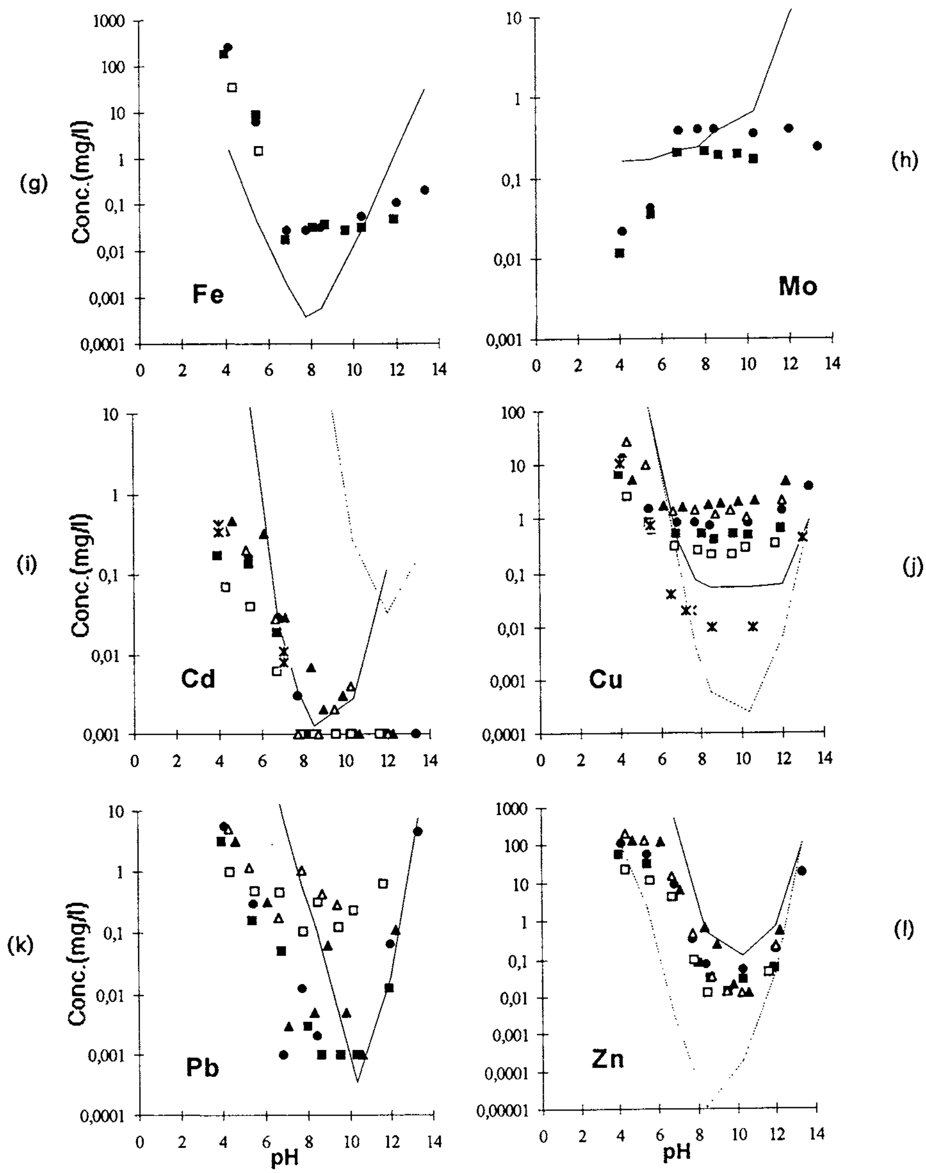


Figure 16.5 Continued



suggested wairakite ($CaAl_2Si_4O_{12}{\bullet}2H_2O$) as the solubility controlling mineral for Si in coal fly ash leachates. Si data from the bottom ash leachates between pH 4 and 10 agree remarkably well with the solubility pattern of wairakite and strongly suggest this mineral phase controls silicon leaching. The data at higher pH deviate from wairakite solubility and suggest that another mineral controls dissolved Si under strongly alkaline conditions. The agreement between measured and calculated data appears to be better than the solid phase approach for this matrix component.

Aluminum

Al leaching from bottom ash is strongly pH-dependent and results in the characteristic V-shaped log-concentration/pH curve which is typical for Al-(hydr)oxide solubility. Model calculations indicate that the leaching data closely follow the solubility curves of gibbsite (crystalline $Al(OH)_3$) and amorphous $Al(OH)_3$. The data below pH 7 are more similar to those calculated in equilibrium with amorphous $Al(OH)_3$, whereas gibbsite seems to be the solubility controlling mineral at higher pH. Similar observations have been reported for coal fly ash (Fruchter et al., 1990). The formation of aluminosilicates may control the solubility of Al in the high pH ranges. Ettringite has been observed in field application of compacted bottom ash (INTRON, 1991)(see also Chapter 9) and may also play a role in Al solubility control at high pH. Kirby and Rimstedt (1993) also suggest amorphous aluminum hydroxide as the most likely solubility controlling phase.

Iron

Fe is leached at relatively high concentrations at low pH, decreases strongly toward neutral pH values and remains essentially pH-independent at neutral to alkaline pH. Amorphous iron hydroxide, or ferrihydrite ($Fe(OH)_3$), is the most obvious solubility controlling mineral for dissolved iron. The measured data at acid to neutral pH follow the calculated solubility line for ferrihydrite, but are up to two orders of magnitude higher in concentration. Similar observations have been attributed to the presence of colloidal iron or inaccuracy of published solubility data for ferrihydrite (Fruchter et al., 1990). The pH-independence at neutral to alkaline pH is not consistent with the calculated ferrihydrite solubility. A second mineral may be controlling Fe leaching in this pH range.

Manganese

Dissolved Mn also decreases strongly with pH, and reaches minimum values at approximately pH 10. A slight increase in concentration occurs at higher pH values. Although the solutions are not in equilibrium with pyrocroite ($Mn(OH)_2$), the shape of the curves may suggest another less soluble Mn-(hydr)oxide to control Mn leaching. Recent work suggests manganite ($MnO(OH)$) as the solubility controlling phase. In view of the difference in concentration at the different LS values studied, Mn is probably not solubility controlled at pH below 8. Mn(hyrdr)oxide appears to control the solubility at pH >12.

Sodium, Potassium, Bromide and Chloride

The alkali metals Na and K, as well as Br and Cl, are very soluble and are leached in high concentrations from the bottom ash in a pH-independent manner. No solubility controlling solids were found for these elements.

Cadmium

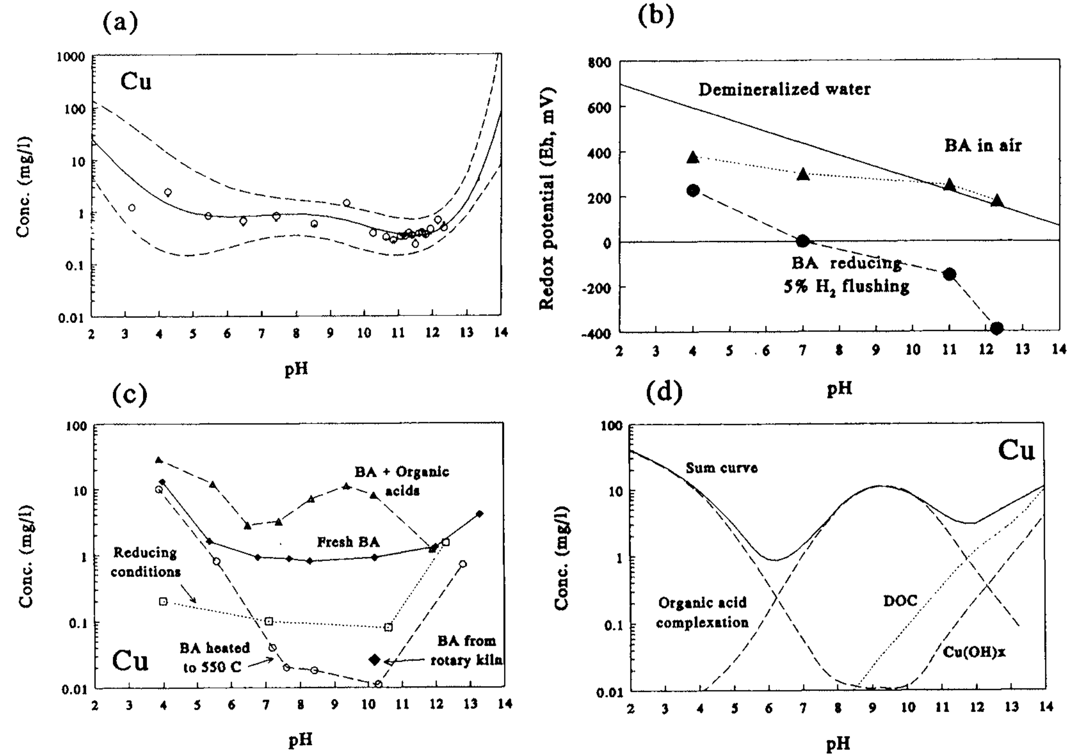
Cd is leached in high concentrations at low pH and decreases strongly toward pH values of 8-9. At higher pH, Cd concentrations are near the ICP detection limit of 1 µg/L shows the stability lines for ottavite ($CdCO_3$) and amorphous-$Cd(OH)_2$. Ottavite stability was calculated using independent measurement of total carbonate (as was mentioned above, the leachates were not in equilibrium with atmospheric CO_2). Cadmium concentrations in the leachates between pH 6 and 9-10 are close to values predicted on the basis of equilibrium with ottavite. Cadmium is also known to have a very high affinity for the surface of calcium carbonate (Comans and Middelburg, 1987). Although there is no evidence from solubility calculations that dissolved Ca and CO_3 were in equilibrium with calcite, some calcite might nevertheless have been formed considering the high Ca concentrations, pH, and contact with the atmosphere. Co-precipitation or solid-solution formation with calcite may limit Cd concentrations to lower levels than would be predicted by the solubility of ottavite (Comans and Middelburg, 1990). It is uncertain at present what role this sorption process plays in controlling Cd solubility during bottom ash leaching and whether it may explain some of the cadmium concentrations below the solubility of ottavite. All leachates were at least two orders of magnitude under saturated with respect to amorphous $Cd(OH)_2$, which rules out the relevance of this mineral in systems containing sufficient carbonate. The role of carbonation and calcite formation during aging of bottom ash appears to be a significant factor for the retention of Cd in the ash matrix. Previous removal of chlorides, thus avoiding the formation of soluble Cd-complexes, will enhance this process. Accelerated carbonation may prove a means to improve ash characteristics.

Copper

Leaching of fresh bottom ash generally leads to high initial concentrations of copper (Figure 16.6). Cu concentrations decrease from pH 4 to 6 but remain constant at higher pH at levels (approx. 1 mg/L), depending on the L/S ratio. Tenorite (CuO) has been suggested as the controlling phase for Cu leaching from coal fly ash (Fruchter et al., 1990) and may also be relevant for bottom ash. However, the leachates are systematically over saturated with respect to this mineral, except at low pH where concentrations are lower than predicted by tenorite solubility.

Substantial amounts of dissolved organic matter can often be released from the uncombusted fraction in the bottom ash. It is speculated that dissolved organic material may increase copper solubility because of the high affinity of this metal for organic species. The relevance of this process was investigated by giving an ash sample an 8-hour heat treatment at 550 °C prior to the leaching experiments. This

Figure 16.6 Leachability of Copper from Bottom Ash



a - Unified pH curve

b - Redox potential in batch experiments under air exposure and in a close container purged with 5% hydrogen

c - Cu leaching from fresh bottom ash, same BA after addition of a mixture of organic acids, same BA after heating to 550°C to remove organic matter, and Cu leaching data point for a rotary kiln facility

d - proposed factors and their pH dependence for leaching pf Cu from bottom ash under ambient conditions procedure was assumed to destroy organo-copper complexes by removing any organic material left in the ash sample. As Figure 16.6c indicates, the leaching of Cu is reduced by the temperature treatment, especially between pH 6 and 11. At low pH, copper complexation by organic species is reduced by protonation of the acid functional groups on the organic material, whereas at high pH the formation of stable hydroxo-copper complexes may out compete Cu complexation by organic species. The treated samples followed the tenorite solubility pattern, but are under saturated with respect to this mineral.

The copper solubility as predicted by MINTEQA2 calculations is, however, strongly affected by the stability of the aqueous Cu(OH) complex. Log K for the reaction $Cu^{2+} + 2H_2O$ _ $Cu(OH) + 2H^+$ equals to -13.7 in the MINTEQA2 database and is more than two orders of magnitude higher than the value of -16.2 which has been reported by others (Rai and Zachara, 1984) as also been shown to be consistent with biological uptake of dissolved copper (Blust et al., 1991). If the value of -16.2 is used, the solubility of tenorite is calculated to be much lower, with leachates below pH 7 being under saturated, and above pH 7 over saturated with respect to this mineral. In summary, the solubility of Cu during bottom ash leaching is complicated by organic complexation and disagreement as to the stability of the aqueous Cu(OH) complex. In view of the above, the deviation of the heat treated ash sample, within an order of magnitude, from the Cu concentrations calculated in equilibrium with tenorite does not rule out this mineral as a possible solubility-controlling solid.

Another approach that was taken was to extract the same bottom ash sample with a mixture of dissolved organic compounds. In Figure 16.6b, the results of the experiment are given indicating an increase in the release by about one order of magnitude after leaching with a mixture of acetic acid, propionic acid, butyric acid and valeric acid, which are present in leachates from domestic waste disposal. It appears that the addition of organic complexants increases the leachability of Cu, particularly in the pH range 9 - 10.5. It is interesting to note that a similar, but less pronounced, peak is observed in the unified pH plot for Cu at this same pH interval (Figure 16.6a).

In Figure 16.6d, the role of different factors - inorganic copper (tenorite), organic acids, DOC controlling Cu leachability is schematically presented.

The influence of reducing conditions on Cu leachability was addressed by using a recently developed redox stat (Comans, 1993) based on equilibration with H_2 gas. The relation between Eh and pH under normal atmospheric conditions and forced reducing conditions is given in Figure 16.6b, whereas the consequences for the Cu leachability are presented in Figure 16.6c. A greater than one order of magnitude difference in leachability in the neutral to moderately alkaline pH range is observed. These results indicate that both changes in redox and removal of organic matter can result in decreased Cu release.

Molybdenum

Mo is known to form very mobile oxy-anions, and is mainly present as MoO4^{2-} above pH 5. This element was measured only in the leachates from one installation (urban), with concentrations increasing strongly with pH between 4 and 7, and remaining virtually constant at higher pH. Of the Mo solids reviewed by Rai and Zachara (1984), which were added to the MINTEQA2 database for the purpose of this study, $PbMoO_4$ and $CaMoO_4$ are the most likely phases to control Mo solubility in the leachates. MINTEQA2 calculations showed the leachates not to be in equilibrium with $PbMoO_4$. The Mo concentrations predicted from solubility control by $CaMoO_4$ are shown in Figure 16.5h and could explain the leaching data between pH 7 and 10. The relationship is confirmed by plotting the data in a log Ca^{2+}-activity versus log MoO_4^{2-}-activity diagram. $CaMoO_4$ may, therefore, control Mo leaching in this pH range. This mineral has also been suggested to control Mo concentrations in high-Ca waters (Hem, 1985), but was calculated not to control Mo leaching from coal fly ash (Fruchter et al., 1991).

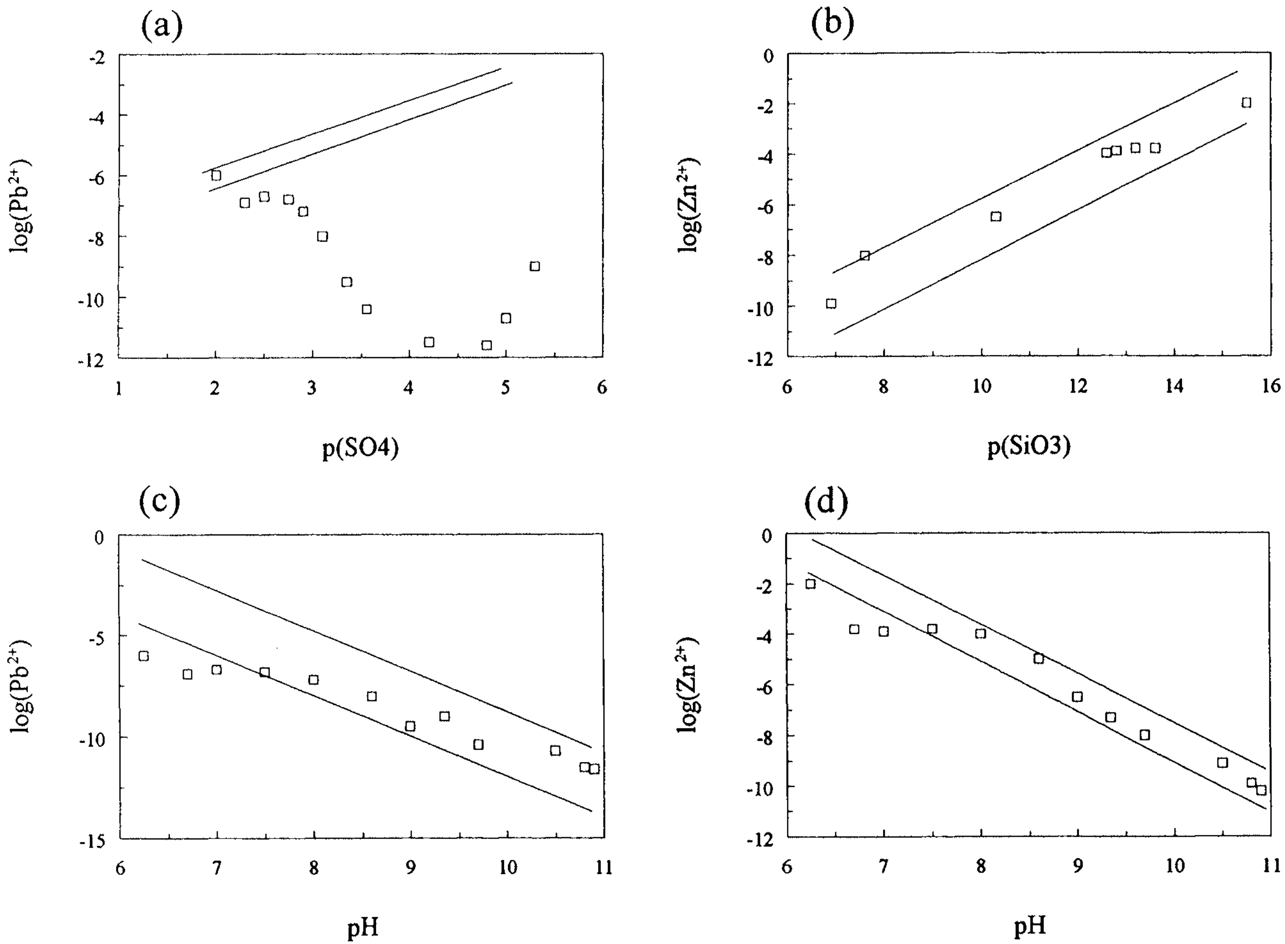
Lead

The Pb leaching patterns for the two bottom ash samples are clearly different from each other. While one bottom ash sample (urban) shows a strong pH dependency, with concentrations decreasing over three orders of magnitude from pH 4 to 10, dissolved Pb leached from the second sample (rural) remains high and is relatively pH-independent (Figure 16.7c). Equilibrium with $Pb(OH)_2$ could explain the first ash sample data above pH 9 or 10, but the mechanisms behind the high Pb leaching from the second ash sample are unclear. Most dissolved Pb data from the first ash sample leachates between pH 7 and 10 are close to the ICP detection limit and do not allow conclusions as to the solubility controlling solid. Modelling studies on fly ash by Gardner (1991) indicate solubility control by $PbSO_4$ in the lower pH ranges and $Pb(OH)_2$ solubility above pH=7. Whether Pb solubility in bottom ash is partly controlled by sulphate remains to be proven.

Zinc

Similar to the other heavy metals discussed above, Zn is leached in high concentrations at low pH and decreases strongly (four orders of magnitude) with pH values up to 10 (Figure 16.7d). Complexation with hydroxide in solution increases dissolved Zn at strongly alkaline pH. The leaching pattern follows the solubility line for zincite (ZnO), with concentrations remaining down to 1 order of magnitude lower. A second possible solubility controlling solid is $ZnSiO_3$. The solubility of $ZnSiO_3$ in Figure 16.7b shows a pH-dependency similar to the leaching data and limits, except at very high pH, dissolved Zn to 1-3 orders of magnitude lower concentrations. Both zincite (at intermediate pH) and $ZnSiO_3$ (pH 4-6 and pH > 12) may contribute in controlling Zn leaching from bottom ash. Gardner (1991) calculates Zn leaching from fly ash to be limited by the solubilities of $Zn(OH)_2$ and $ZnSiO_3$. Zincite is, however, less soluble than $Zn(OH)_2$ and gives a better prediction of the data. It appears that the solubility control in bottom ash and fly ash is not significantly different for Zn.

Figure 16.7 Thermodynamic Activities from Column Experiments on MSWI Fly Ash



16.4.2 Modelling of APC Residue Leachability

The modelling of APC residue leachability requires the application of corrections for the activity coefficient using Pitzer equations (Pitzer et al., 1973 & 1974) because the Davies equation and the Debye-Hückel equation are not valid at the ionic strengths present in leachates from APC residues. However, the general trend as observed for bottom ash is valid for APC residues.

Extending the modelling efforts from bottom ash to APC residues opens a new area of research. The work of Gardner (1991) of modelling fly ash leaching from small columns and batch extractions is very much in accord with observations on bottom ash as described in the previous section. Figure 16.7 presents the solubility control of Pb and Zn from fly ash as a plot of element concentration against counter ion. This type of plot illustrates the boundaries of solubility control by specific mineral phases. It is clear that in different pH ranges, different minerals may control the leachability. It is, however, unlikely that many phases will control leachability at the same time and to the same extent. This implies that with the identification of the most relevant mineral phases (usually 2 or 3), the leachate composition should be adequately predicted. The task is now to sort out the most relevant phases in the relevant pH regions.

16.4.3 Application of Geochemical Modelling Results

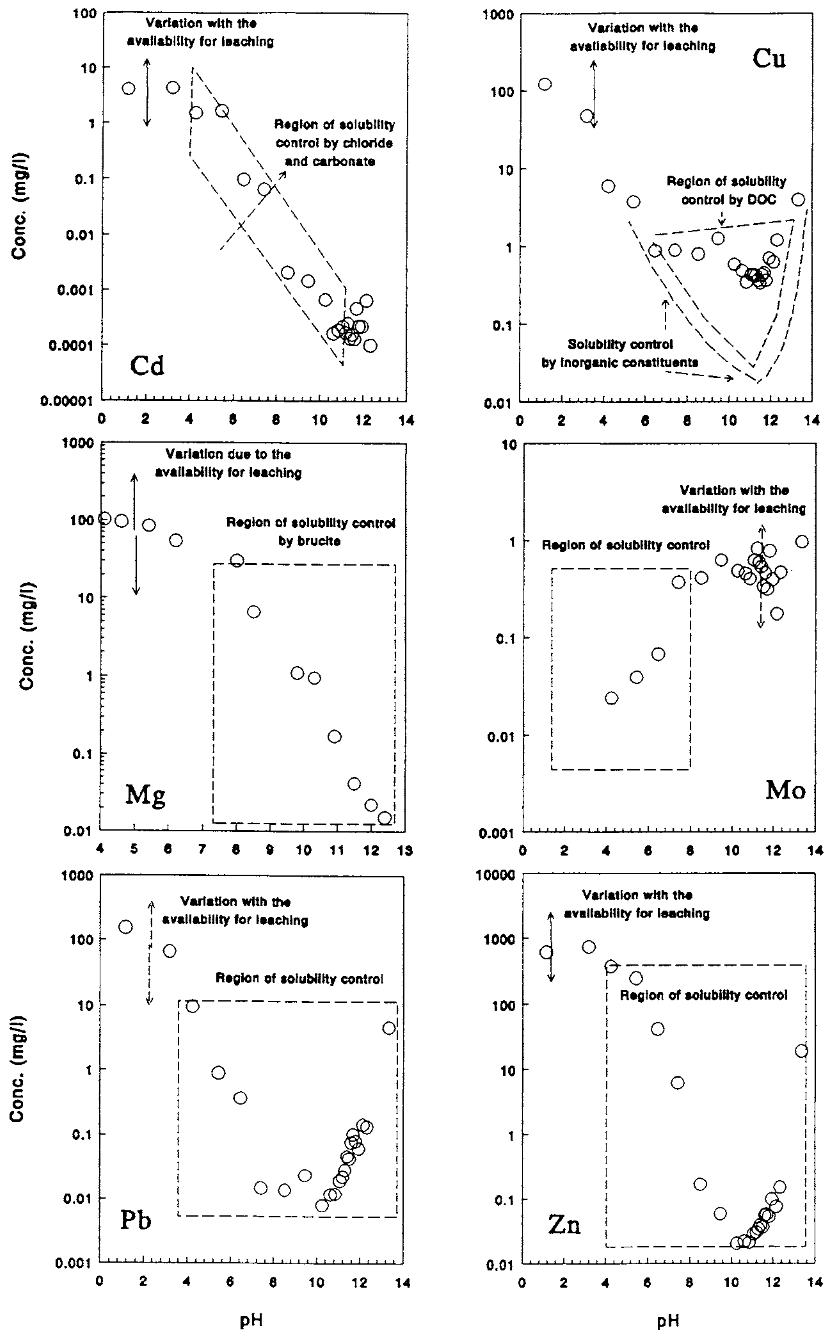
In combination with XRD and other surface techniques as discussed in Chapter 7, specific mineral phases can be identified. The modelling of the solution properties does not provide direct evidence for the existence of specific minerals in the bottom ash matrix, but the results of such studies support the hypothesis that geochemical reactions control the leaching of both major and trace elements from incinerator residues. A number of possible solubility controlling minerals and complexation processes in solution have been suggested that can to a large extent explain the observed leaching behaviour as a function of pH. Knowledge of these processes can be used to:

- Predict the long-term behaviour of incinerator residues in the environment
- Improve the interpretation and further development of regulatory leaching tests, and
- Chemically modify the ash and/or its environment in utilisation or disposal, to minimise contaminant leaching

Further work is needed to clarify the behaviour of some of the elements discussed above. In a number of cases, the degree of agreement between model predictions and actual measurements is very promising.

General leaching behaviour and the impact of waste feed on incinerator operating conditions can be identified based on modelling efforts. In Figure 16.8 some of these

Figure 16.8 Identification of pH Domains with Solubility Control and Availability Control for Cd, Cu, Mo, Mg, Pb and Zn in Bottom Ash



trends are presented, which indicate regions where leachate concentrations are controlled by availability and regions controlled by solubility as defined by geochemical reactions. Such general trends appear to be relevant for other types of residues as well.

16.5 RELEASE RATES OF ELEMENTS

The observed release of a specific element over a time interval is a result of the element's availability, solubility and rate of mass transfer from the solid to the liquid phase. The rate of mass transfer between phases is most frequently controlled by diffusion through the porous solid phase, geometric dimensions of the solid phase, and the mode of liquid solid contact. In general, the following cases can be used to describe the release of elements and inorganic species from incinerator residues:

1. Localised equilibrium is attained between the solid phase and the contacting leachate, resulting in a leachate which is saturated with respect to the element of interest, i.e., solubility is controlling release. This case typically occurs for inorganic species, except alkali metals and halogens (e.g., Na, K, Cl), with percolation of infiltration through residues in the field and during column leaching tests or sequential batch extractions of small particles in the laboratory. For this case, cumulative release with respect to time reflects the product of the liquid to solid ratio (LS) with the elemental solubility at the specified conditions (e.g., pH and Eh).

2. Equilibrium is locally attained between the solid phase and the contacting leachate, but the resulting leachate is not saturated with respect to the element of interest because of limited availability or flow channelling. This case typically occurs for alkali metals and halogens with percolation of infiltration through residues in the field and during column leaching tests or sequential batch extractions of small particles in the laboratory. For this case, greater than 50% of the availability is released at an LS = 1.

3. Release is controlled by diffusion through the solid phase and the contacting leachate is not in equilibrium with the solid. This case typically occurs for most elements and species when flow is around either a monolithic material (e.g., solidified/stabilised residues) or a granular material compacted to low permeability such that is behaves as a monolith (e.g., residues used as a road base and overlain by an asphalt layer). For this case, cumulative release is a function of effective diffusivity, availability and release time interval.

The following sections present observed release rates for elements as a function of L/S to address Cases 1 and 2, above, and diffusion controlled release to address Case 3.

16.5.1 Release As a Function of Liquid to Solid Ratio

The leaching of granular residues is in many cases dictated by percolation, which can be represented by column experiments. This is valid both for utilisation and for disposal, unless measures have been taken to minimise infiltration drastically. In that case infiltration may be reduced to such an extent that diffusion becomes the rate controlling transport mechanism. It also is important to establish the relationship between column and batch testing results because while column tests more closely reflect field scenarios, batch tests are more efficient to carry out in the laboratory. A comparison of leaching data from both column and batch tests has been carried out for a wide variety of waste materials (VVAV, 1988, 1992). The two approaches were agreement except for the cases where the initial release and depletion of one species subsequently resulted in altered release for a second species (van der Sloot et al., 1993). In addition, some long term processes, such as those caused by biological activity can be observed in column tests carried out at low flow rates over extended time periods, but cannot be addressed in short batch tests.

Test results generally are expressed in mg/kg to allow a direct indication of release. Presentation of column leaching results in the form of cumulative release as a function of L/S may be used to discern between different types of release behaviour (Figure 16.9):

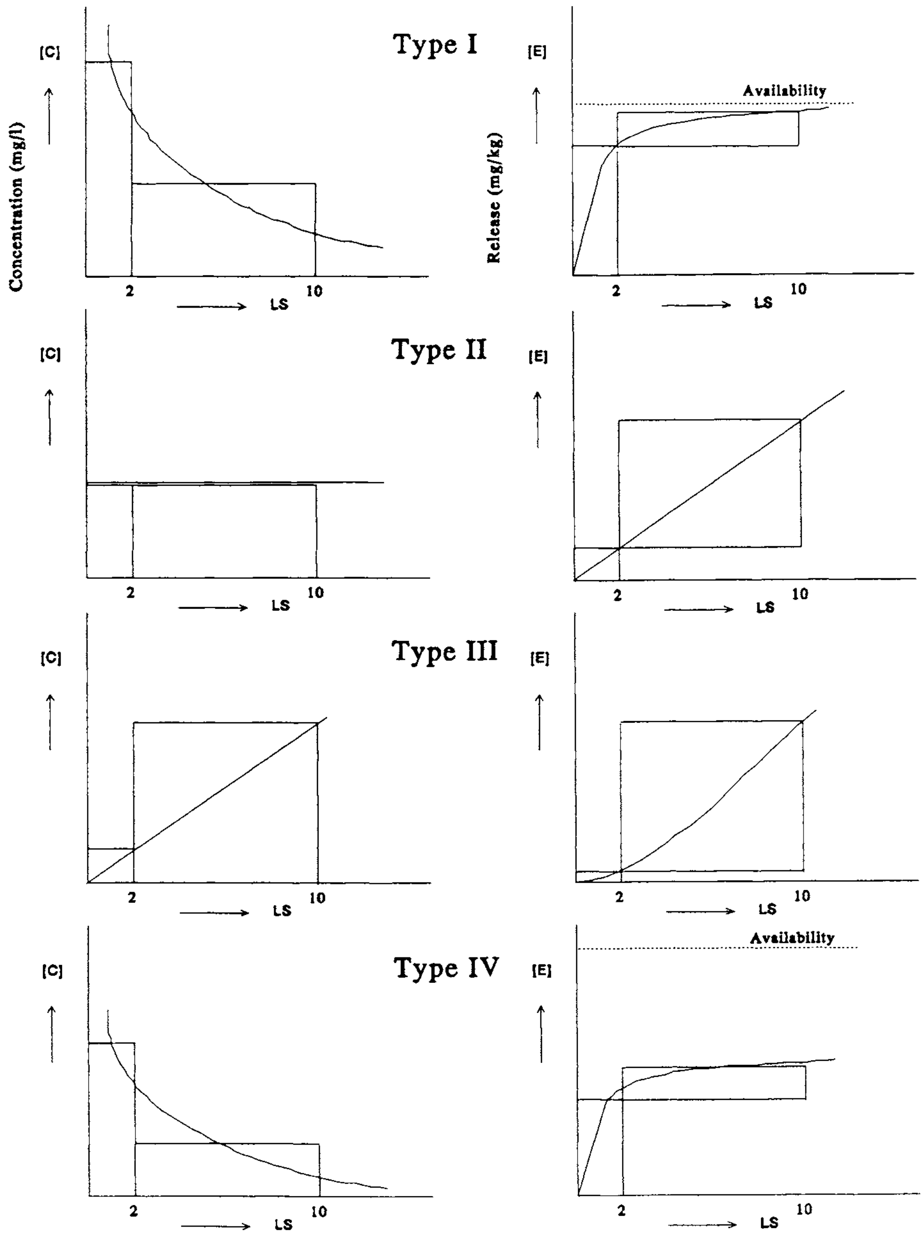
Type I- Rapid release of highly soluble species due to under saturation of the constituents in the leachate even at low L/S. This results in rapid wash out of these species in a percolation dominated system with release of the available quantity within L/S less than 1 or 2. The slope of the cumulative release as a function of L/S typically is greater than or equal to 1 at L/S less 1 followed by a slope of approximately 0, indicating depletion. Elements that exhibit this type of behaviour include alkaline metals and halogens.

Type II- Release controlled by solubility in the aqueous phase which most often is a strong function of pH. Cumulative release as a function of L/S is approximately linear with the slope dictated by the elements solubility. Elements which exhibit this type of behaviour include Pb and Zn.

Type III- Delayed release due to retention in the matrix by a second species controlling solubility which is depleted after a limited time interval. This behaviour is characterised by a transition from linear release at a lesser slope to a greater slope. An example of this behaviour is the release of sulphate which initially may be limited by barium until depletion of that element occurs.

Type IV- Enhanced initial release due to the presence of a complexing agent which increases the solubility of the element of interest. This behaviour

Figure 16.9 Types of Release Identified from Column Tests or Sequential Batch Tests



is characterised by a transition from linear release at a greater slope to a lesser slope. Unlike for Type I release, depletion does not occur. Examples of this behaviour are the initially increased release of copper in the presence of organic acids, and the initially increased release of cadmium from APC residues in the presence of high chloride concentrations.

Bottom Ash

In several studies (Versluijs et al., 1990; Hjelmar, 1992; Fällman, 1992; Eighmy, 1992, van der Sloot et al., 1991) column leaching experiments have been carried out using bottom ash. The results of these studies, presented in Figure 16.10, can be used to compare release from ash generated in Canada, Denmark, Germany, The Netherlands, Sweden, and the United States. The release of the various constituents has been presented as a function of L/S with ranges for total content and availability indicated for comparison.

Results for bottom ash from batch extraction tests with distilled water at L/S=20 are provided along with the column results in Figure 16.10. Cumulative release of Cd, Cl, Cu, Mo, Na, Ni and sulphate observed for column tests at L/S=10 and release observed in batch tests at L/S=20 were similar, indicating that the leachable fraction of these elements was released at L/S less than 10. Solubility controlled release was observed for Ba, Ca and Pb between L/S=10 and 20 based on a linear increase in cumulative release from the column to the batch data.

Antimony

The release of antimony from bottom ash ranged from 0.0005 to 0.5 mg/kg. In contrast, the availability of Sb is approximately 5 to 10 mg/kg, which implies that Sb is largely retained in the ash matrix. Release patterns were very consistent and indicate slow dissolution with increasing L/S. The wide range in Sb release most likely was related to variability in the waste feed composition.

Cadmium

The release pattern for Cd indicated a small initial release of a highly mobile species followed by a slow increase with increasing L/S. The release patterns generally had a slope of 0 after L/S=1, which indicated that the soluble Cd-species was depleted. Possible species responsible for this release behaviour are anionic Cd chloride complexes or organically complexed Cd. The cumulative release at L/S=10 ranged from 0.005 to 0.05 mg/kg compared to availability which was between 0.5 and 5 mg/kg, indicating that Cd release was limited and significant retention in the matrix occurred.

Figure 16.10 Release (mg/kg dry ash) of Selected Metals as a Function of the Liquid to Solid Ratio

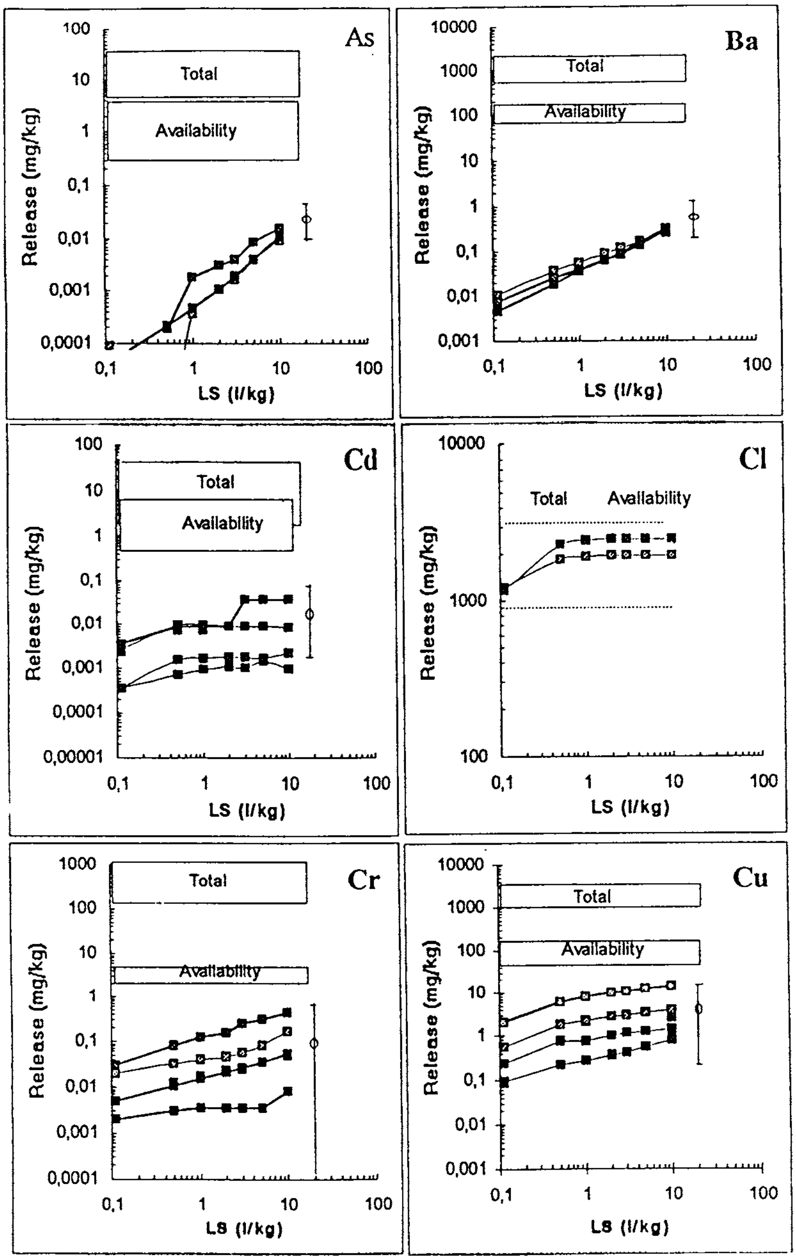
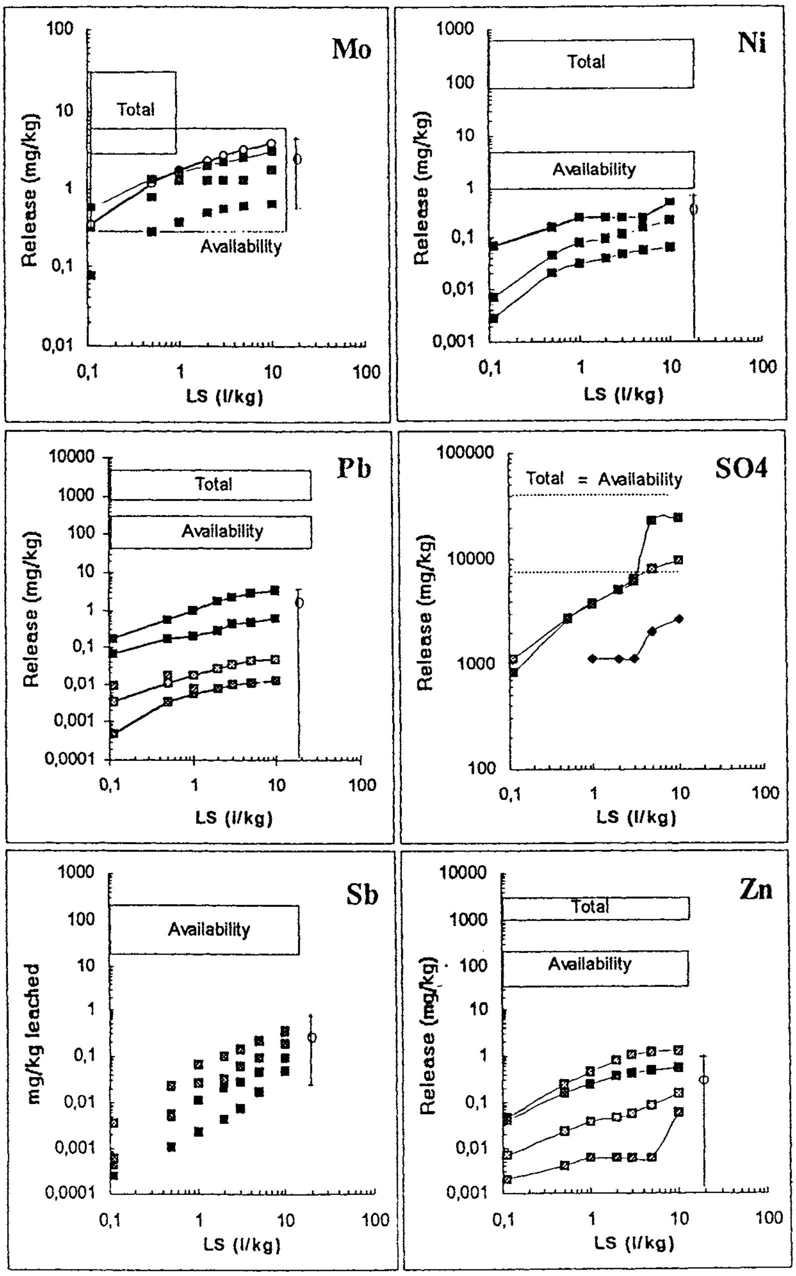


Figure 16.10 Continued



Chromium

The release pattern for Cr indicated depletion of a soluble species after L/S=1 (slope = 0). The fraction initially released may be a chromate species, reflecting the high mobility of Cr (VI) in comparison with Cr(III). A steady increase in release with increasing L/S (slope = 1), indicating slow dissolution, was noted for only one case. Cumulative release at L/S=10 ranged from 0.005 to 0.5 mg/kg, in contrast to availability between 2 and 10 mg/kg.

Copper

The release of copper was very consistent among different sources of ash, as indicated by the parallel pattern of the release curves. The release of Cu was indicative of a highly soluble fraction that was washed out within L/S=1 (approximately 2 pore volumes). The concurrent release of a dissolved organic species which complex Cu has been postulated as an explanation for this initial release. The cumulative release at L/S=10 from many different sources was within a relatively narrow range of 0.3 to 10 mg/kg, which is a small fraction of the availability which varied between 50 and 200 mg/kg.

Molybdenum

Two distinct data groups can be distinguished for Mo. The lower release curve was related to input from typical domestic sources, while it appears that the relatively high releases of Mo observed for two facilities resulted from industrial contributions of Mo rich waste streams which were included with the incinerator feed. Cumulative release at L/S=10 ranged between 0.2 and 10 mg/kg, which was approximately equal to Mo availability. These results indicate that Mo is quite mobile and almost all leachable Mo can be depleted from bottom ash in a relatively short time span. The relatively high initial concentrations of Mo in leachates may be of concern in some jurisdictions.

Lead

The release pattern for Pb was reasonably consistent for most cases, with increasing cumulative release with increasing L/S (slope = 1) indicating solubility controlled release. In a few cases, however, depletion appeared to have occurred. This type of release behaviour may be explained by a decrease in pH during the leaching process, which resulted in decreased Pb solubility. Cumulative lead release was considerably variable between data sets. At L/S=10, the cumulative release varied between 0.005 and 10 mg/kg. The sensitivity of Pb solubility to pH was the primary reason for the wide range in release observed. However, the cumulative release at L/S=10 was several orders of magnitude less than the availability, which indicated considerable retention of Pb with the ash matrix.

Nickel

The release of Ni was similar to that of Cu. Both Cu and Ni have been demonstrated to form strong complexes with dissolved organic matter, which is hypothesised to have been responsible for initial release of both elements. The cumulative release at L/S=10 varied between 0.02 and 0.5 mg/kg, with only two cases having significantly less release. Ni availability was several orders greater than the observed cumulative release, indicating significant retention in the ash matrix.

Sulphate

The release of sulphate approaches the maximum leachability at L/S=100, which indicates that sulphate can be depleted from the bottom ash matrix. The quantity of soluble sulphate present in the ash is such that it becomes a constituent of major concern in relation to potential effects on local ground water quality.

Zinc

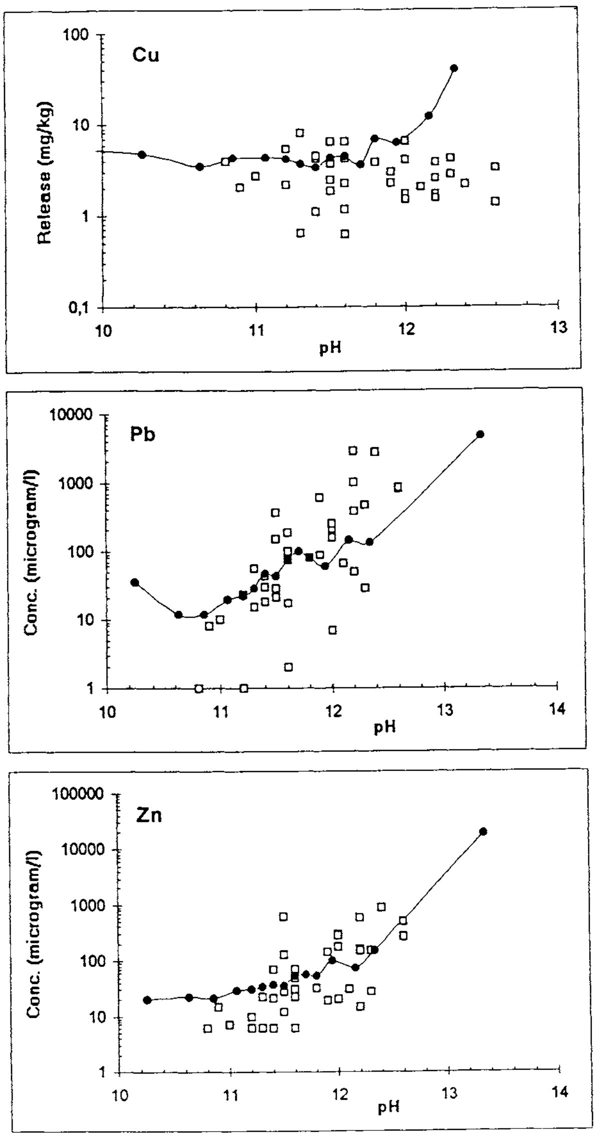
The release patterns for Zn were fairly consistent for a given data set, indicating very slow dissolution from slightly soluble phases. However, considerable variability existed between data sets. Cumulative release of Zn at L/S=10 varied from 0.01 to 3 mg/kg. The primary reason for the variability has been attributed to variable pH, because of the sensitivity of Zn solubility to small changes in pH. This was similar to the behaviour observed for Pb. However, the cumulative release at L/S=10 was a small fraction of the availability, which ranged from 50 to 500 mg/kg.

Alkali Metals and Halogens (e.g. Na, K, Cl, Br)

Alkali metals and halogens, such as Na, K, Cl and Br, were completely leached from the bottom ash at L/S≈1-2. There was no retention of these elements in the matrix, which implies that most equilibrium batch extraction tests can be used to assess the potential release. The quantity of these elements present coupled with their rapid release should be carefully considered during the development of management practices for bottom ash.

The column leaching test results discussed above demonstrate consistent release patterns reflecting depletion, dissolution or in some cases a delayed release due to changes in chemical conditions with time of leaching. For a specific element such as Pb or Zn, cumulative release may vary over several orders of magnitude depending on the origin of the particular bottom ash sample evaluated. This observed variation in cumulative release results primarily from variation in ash alkalinity which controls leachate pH and solubility of elements. This effect is substantiated through the presentation of measured concentrations of elements in leachates from column tests as a function of pH in Figure 16.11. The unified pH-solubility curves also are presented for reference. In general, the pH of leachate from column tests with bottom ash does

Figure 16.11 Release (mg/kg dry ash) of Cu, Pb and Zn as a Function of pH to Indicate Solubility Controlled Release in Column Leaching Test (□) as Compared to the Unified pH Curves (●)



not vary over a wide range. Pb and Zn data from the column experiments are consistent with the unified pH curve, which illustrates the solubility controlled release as a function of pH for bottom ash. Measured concentrations and trends as a function of pH from column and batch tests are consistent.

APC Residues

Column leaching experiments have been carried out using APC residues in several studies. The release from ESP ash has been reported in two studies carried out in The Netherlands (Versluijs et al., 1990; Born, 1993). Additional studies have examined release from dry and semi-dry scrubber systems in Denmark (Hjelmar, 1991) and the United States (Theis and Gardner, 1991).

The results of these studies, presented in Figure 16.12, can be used to compare release from the different types of APC residues. The release of the various constituents has been presented as a function of L/S with ranges for total content and availability indicated. Results for ESP ash from batch extraction tests with distilled water at L/S=20 also are provided along with the column results for comparison.

A typical feature of results from column leaching of APC residues is an initially moderately alkali pH at very low L/S ratios, followed by increasing pH with increasing L/S ratios. It is hypothesised that this behaviour results from the formation of a shell of acid gas reaction products surrounding a carbonate shell, which in turn surrounds a hydroxide interior of the APC residue particle. The carbonate shell subsequently dissolves during leaching with increasing L/S. This effect is greater for dry and semi-dry scrubber residues because of the injection of lime into the flue gas. The resulting changes in leachate pH also effect the release of elements for which solubility is a strong function of pH.

From the leaching curves as a function of L/S it is clear that the cumulative release is constant or increases only slightly after an L/S=1 (As and Cr from two installations are the primary exceptions). This implies that the release within one L/S constitutes the amount available for leaching at the pH controlled by the residue and represents soluble chemical species that are washed out of the system with minimal retention. This mode of release is prominent for many constituents in ESP ash as evidenced by the release-L/S profiles. The variability in leachability of ESP residues within and between installations is substantial. It appears to be related more to the input to the incinerator and facility operation than in the case of bottom ash.

Initial leachate concentrations and release of individual elements from APC residues during column tests typically are in agreement with the solubility as a function of pH derived from batch testing.

Initial solubilities may increase relative to those observed for bottom ash because of the high ionic strength and chloride concentration of the solution. However for APC

Figure 16.12 pH and Release (mg/kg dry ash) of Selected Metals as a Function of the Liquid to Solid Ratio

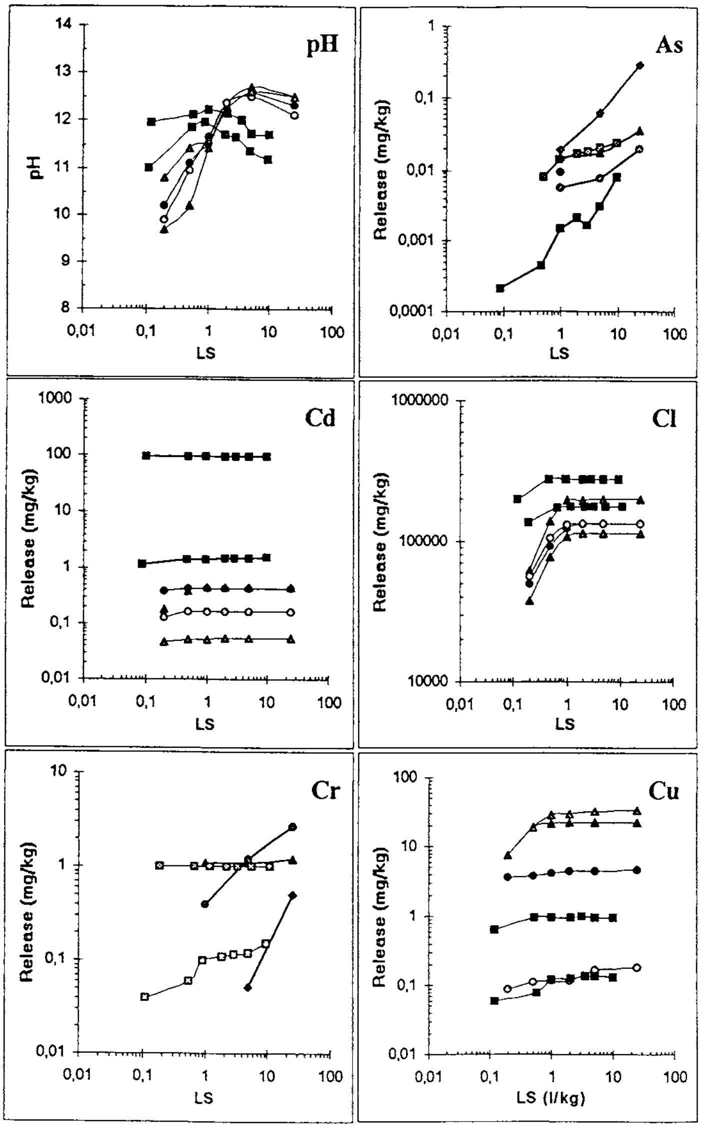
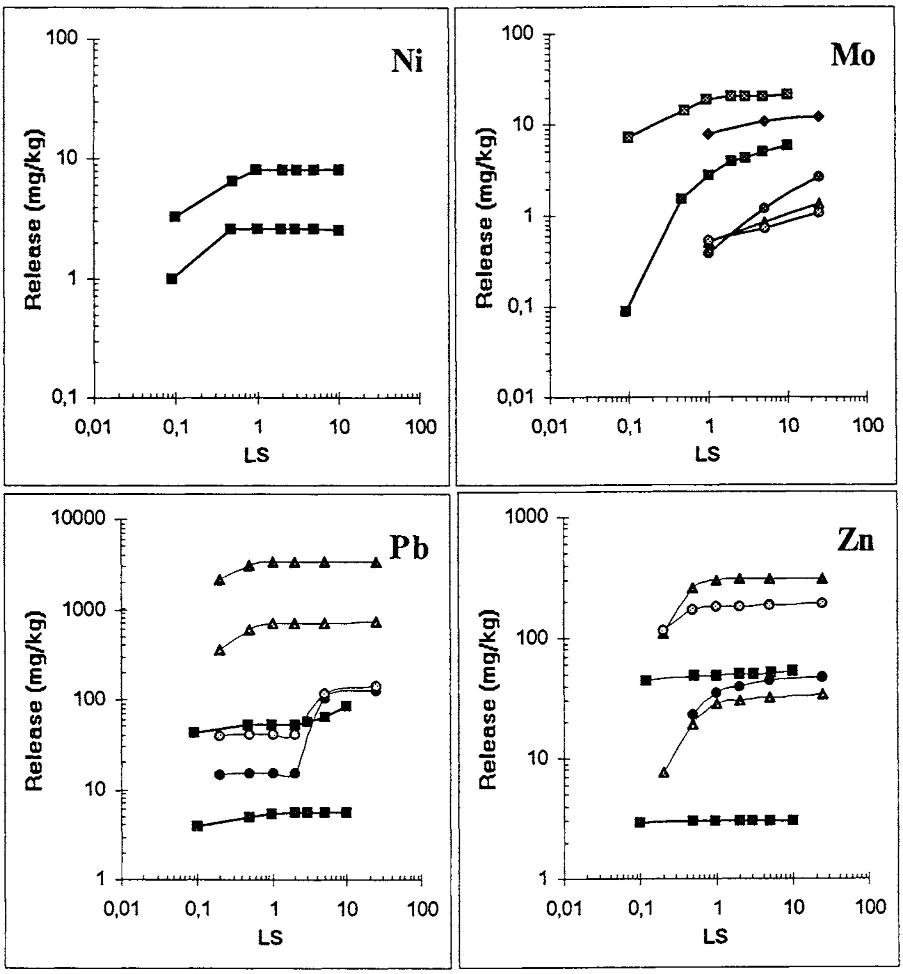


Figure 16.12 Continued



residues, availability is an important parameter controlling the release level with depletion occurring for many elements at L/S less than 1. As a consequence of these observations, column tests are not very functional for the evaluation of APC residue leachability. Availability and pH dependent solubility are much more a practical tools to assess APC properties.

16.5.2 Diffusion Controlled Release

Assessment of constituent release most frequently assumes that the predominant mode of leaching will be by percolation of water through the porous solid matrix. However, in several circumstances the release may not reflect percolation and solid-liquid equilibrium, but rather be controlled by diffusion through the porous solid. This situation may occur when a fine-grained material is placed in a surrounding matrix with a higher permeability, thus creating a preferential flow around, instead of through, the material (Environment Canada, 1990). A similar situation will be encountered when the material is compacted during placement to form a less permeable matrix, or when infiltration of water is minimised through use of low permeability barriers such as compacted clay covers. Evaluation of release under these circumstances requires measurement of diffusion controlled release fluxes.

Measurement of diffusion controlled release fluxes for monolithic solids is achieved by refreshing the leachant in contact with a well-defined surface geometry at regular intervals. An analogous test for compacted granular material has been developed which maintains an undisturbed surface through use of a thin layer of glass beads placed on top of compacted granular material in an inert mold. This test was first applied in the framework of a USEPA study on stabilisation/solidification of incinerator residues (Kosson et al., 1993). After an initial delay in the release caused by the layer of glass beads, the release profile generated permits the calculation of tortuosity and chemical retention within the matrix (refer to Chapter 21). The intrinsic leaching properties obtained from this type of measurement allows prediction of release at longer time scales than the actual testing period. In addition, it provides an estimate of diffusive contribution to transport in a low flow column experiment.

Table 16.5 presents the measured values of tortuosity and pD for several elements in untreated bottom ash, APC residue and combined ash (Kosson et al., 1993). Estimation of the pD values are based on using the availability of each element in the specific matrix as the driving force for diffusion. This approach results in a more accurate estimate of the release parameters than use of the total concentration as the driving force.

Compaction of bottom ash and combined ash resulted in a reduction in permeability, which was reflected in the pD values for mobile species, such as Na, K, and Cl. The difference in physical retention between bottom ash and combined ash compared to APC residue was substantial. The latter behaved as a loose powder without physical

Table 16.5
Diffusivities (-log(m2/s)) Measured using the Compacted Granular Leach Test for Residues

Element	Bottom ash		Combined Ash		APC Residue	
	pD	Std. dev.	pD	Std. dev.	pD	Std. dev.
Tortuosity	24		25			
As				13.6	0.2	
Al	14.06	0.09	13.63	0.19		
Ba	12.3	0.08	12.04	0.08		
Br	10.05	0.17	9.91	0.12		
Cd	>15		>15		15.2	0.6
Ca	12.68	0.06	12.75	0.09	10.3	0.15
Cl	10.5	0.16	10.52	0.21	9.3	0.1
Cr	11.73	*	10.35	*	11.6	0.15
Cu	>14.8		14.57	0.17	14.2	0.2
Fe	14.2	0.19	15.2	0.21	11.2	0.2
Pb	16.17	0.09	16.3	0.37	14.2; 11.8; 12.9	
Li	11.93	*	11.69	*		
Mg	14.66	0.72	15.1	1.06		
Ni	>13		11.02	*	11.2	0.2
NO_3	11.37	0.36	10.36	0.60		
K	10.12	0.07	10.18	0.08	9.0	0.1
Si	14.49	0.12	13.48	0.06		
Na	10.24	0.08	10.26	0.09	9.0	0.1
Sr	11.5	0.07	11.45	0.09		
SO_4	15.62	*	15.27	0.17	13.6	0.4
Zn	15.71	0.18	16.01	0.35	15.9	0.3

* single data.
Kosson et al., 1993

restriction; only chemical retention was due to the chemical environment (high pH). The mobility data for combined ash and bottom ash are very similar, which is largely related to the fact that the pore water conditions (e.g. pH) are very similar. The low retention values for K, Cl, Br, nitrate and Li are in agreement with the high release of these constituents observed in column experiments. The high retention values for several other elements also are in agreement with release observed from column and batch tests. The difference between APC residue and bottom ash is significant for Ca, Fe, Pb and minor for sulphate and Zn. In the case of Pb the difference is largely attributed to the higher pH in the APC residue versus the bottom ash. The large variability in Pb leachability from APC residue reflects the sensitivity to minor changes in pH. The further development and application of this procedure needs to be explored for predicting release from incinerator residues.

16.6 RESIDUE LEACHING IN THE CONTEXT OF REGULATORY LEACHING TESTS AND WASTE FROM OTHER SOURCES

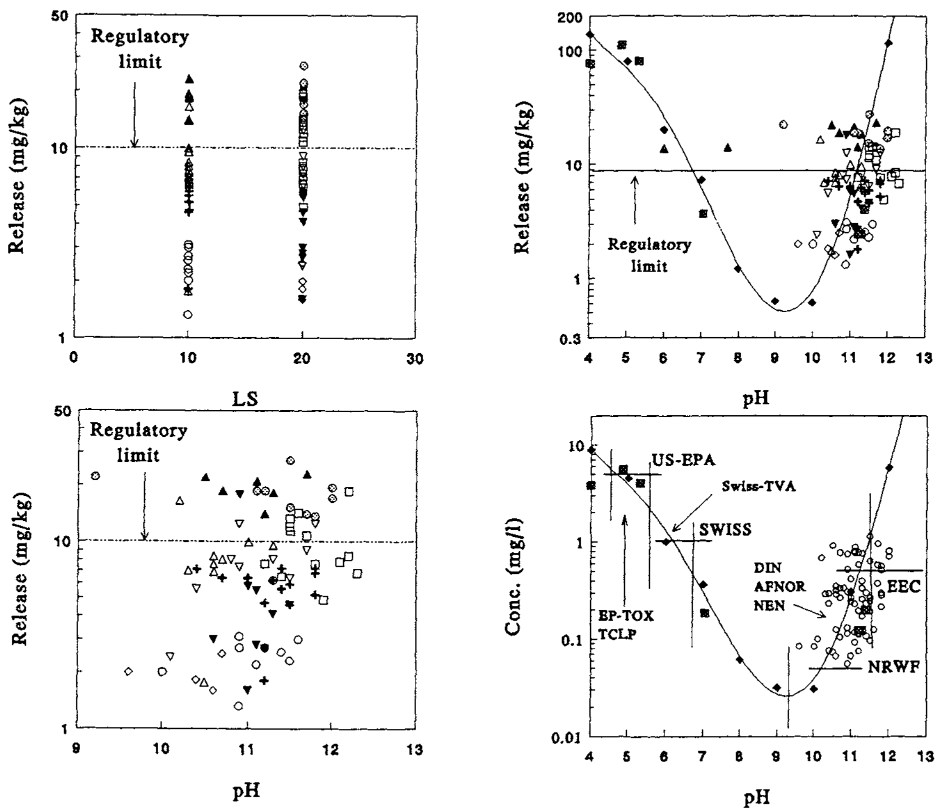
16.6.1 Regulatory Tests and pH Dependent Leaching

Regulatory leaching tests in most jurisdictions are batch tests which control the leaching conditions through definition of the leachant composition, L/S ratio, sample preparation (e.g., particle size reduction) and equilibration period. The final pH of the leachate is controlled to a large extent by the acid neutralisation capacity of the waste being tested. Measured leachate concentrations of elements and species are then compared to fixed regulatory thresholds. Figure 16.13 illustrates the impact of alternative presentations on the interpretation of results. Clearly, pH is the most important independent variable. However, most regulatory data that is obtained is focused on a narrow pH range dictated by the waste being tested, which limits the utility of results for defining characteristic release behaviour. This pH range may not reflect actual disposal or utilisation conditions, and may be in a range for specific elements where small changes in end point pH cause large changes in observed leachate concentration. Thus, the result is often a testing scenario that differentiates between the alkalinity of a waste, not the potential for release of specific elements and environmental impact. Figure 16.13 clarifies this effect through schematic presentation of the results of several regulatory leaching tests for Pb. The unified pH-solubility curve and the concentration range and threshold values for each test are presented. Deviations from a general leachability pattern can be related to changes in solubility controlling properties either imposed by the test, such as the Swiss TVA or the California WET test, or by changes in ash characteristics due to changes in input or operation conditions of the incinerator facility. None of the regulatory tests consider quantity of total soluble salts present in the material being evaluated.

German DIN 38414 (1984) and French AFNOR X-31-210 (1988)

These tests are similar in that they are based on the conditions dictated by the material to be tested. The final leachate pH can vary widely depending on the acidic or alkaline properties of the material being tested. The pH range commonly observed for incinerator residues extends from 9 to 12. In this region, the solubility of some elements changes rapidly with minor changes in pH, especially metals which exhibit amphoteric behaviour. Consideration of this phenomenon should be given when interpreting test results, thus ensuring that the associated test conditions are relevant to actual management practices. For example, leachate pH from bottom ash disposed

Figure 16.13 A Comparison of Different Methods of Presentation of Regulatory Leaching Test Results for Lead



in landfills is rarely greater than 10 and test conditions manipulated higher than pH 10 will require different interpretation.

Japanese Leaching Test

The Japanese Leaching Test is based on extraction with water for 6 hours at L/S=20, however, the short duration of the test may not allow sufficient time for several elements to reach equilibrium. Testing results should resemble those obtained by the DIN and AFNOR procedures, although there is currently a paucity of leaching data on incinerator residues.

Swiss TVA (1988)

The Swiss test method generally produces results which are consistent with the pH dependent leaching curves discussed previously. The acceleration of carbonation provided by bubbling pure carbon dioxide through the leachant produces some side effects that are not representative of field conditions. This test is very sensitive to minor changes in pH because testing is carried out in the pH region where solubility changes quickly with pH. The test has also been shown to produce an exceptionally high release of oxy-anions. This is attributed to diminished retention capacity of the ash by the conversion of lime and basic calcium silicate phases to calcite, via additional carbon dioxide. The rate of retention of oxy-anions in other mineral phases is not as fast as the rate of release resulting from carbon dioxide injection, since these re-mineralisation reactions can be relatively slow. Slow sorption of oxy-anionic species, such as arsenate, selenite and molybdate, on hydrated ferric hydroxide phases is likely to occur in the field, but is too slow to be of significance during the laboratory leach test. This aspect needs to be considered for the relevance of the TVA test for oxy-anions.

USA, California WET Test

The California WET test is a modification of the TCLP test which uses dilute citric acid as the leachant instead of acetic acid. This modification results in much greater complexation of metals than in TCLP. Results of the WET test indicate availability when evaluated on a release basis. Insufficient data is available to assess the comparability of WET test data for anionic species.

US EP Toxicity Test (1980), the Toxicity Characteristic Leaching Procedure (TCLP) (1990) and the Regulation 309 (now 347) Leach Procedure

The intended final pH of 5 of the EP Toxicity and TCLP tests is in a pH region where major changes in metal solubility can result with minor variations in pH. The final pH of the leachate from both tests is highly dependent on the acid neutralisation capacity of the waste, and incinerator residues typically require much more than the maximum 2 meq of acid per gram of ash addition to bring the pH down to 5. However, variation in buffering capacity leads to inherent variability in the test results.

Alternative Approach
Since many of these tests expose ash to conditions which typically would not prevail in most disposal scenarios, an alternative approach is suggested for the regulatory evaluation of incinerator residues. The leaching properties of these materials are now well characterised. Testing of the materials should be focused on evaluating whether or not the sample being tested exhibits the same characteristic leaching behaviour for elements or species of concern. This would allow for implementation of management strategies which are most effective for the general material class and rejection of materials with characteristics beyond acceptable variability limits. An example of this approach would be to specify acceptable ranges of alkalinity and leachability in relevant pH domains, in particular at neutral pH. This would be valid for disposal and for utilisation. However, the criteria for acceptance would be different.

16.6.2 Systematic Leaching Behaviour Among Different Incinerator Residues Streams and Other Wastes

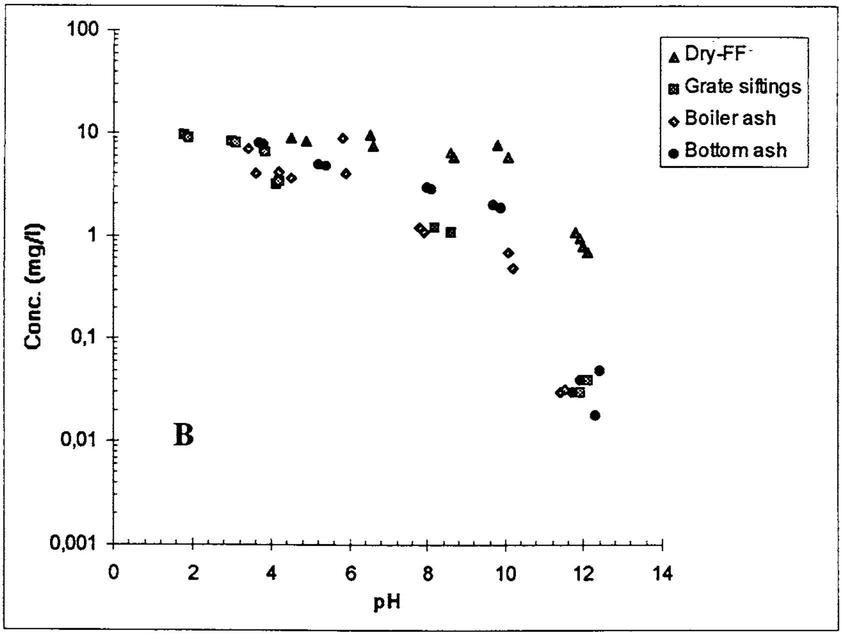
Figure 16.14 presents a comparison of the release (mg/kg) of several constituents from different residue streams. It is striking to note that the curves show many similarities in spite the substantial differences in composition and origin. The solubility control in the pH region 6 to 11 is very pronounced for the metals. The primary difference observed between the residues is the total availability, which is generally higher for the combined ash than for bottom ash. For the APC residues, the availability can be one to two orders of magnitude greater than for bottom ash. The grate siftings typically indicate approximately an order of magnitude greater availability for Cu and Pb compared to bottom ash.

The behaviour of Ba is very consistent for all incinerator residues. The solubility of Ba was independent of pH for most residues except from boiler ash, which decreases with increasing pH. The key to this behaviour is the influence of sulphate, which was not reported, because $BaSO_4$ is the solubility controlling phase in most cases.

The most significant difference between incinerator residues was noted for Cd, where the greater chloride concentrations in the APC residues results in increased Cd leachability at alkaline pH. For Cu, low content of organic matter in certain residues (e.g., ESP ash, boiler ash) tends to lead to low leachability of Cu. However, LOI is not a proper measure for the possible increased Cu leachability, because char alone does not affect Cu leachability (see section 16.2.3.1). Cr is more soluble in the boiler ash and SD-FF residue than the grate siftings and the D-FF residue. The reason for this is unclear but may be related to Cr speciation (e.g., Cr^{+6} is more soluble at neutral and alkaline pH than Cr^{+3}). The leachability of Zn is the most consistent for all residues. Even the availability does not differ more than a factor of three to five.

Table 16.6 provides a comparison of the total content, availability, and leachable fraction of several elements in the different residue streams. The availability is

Figure 16.14 Comparison of the Leaching of Selected Metals as a Function of pH from Bottom Ash, Combined Ash, ESP Filter Ash, Fabric Filter Ash, Grate Siftings and Boiler Ash



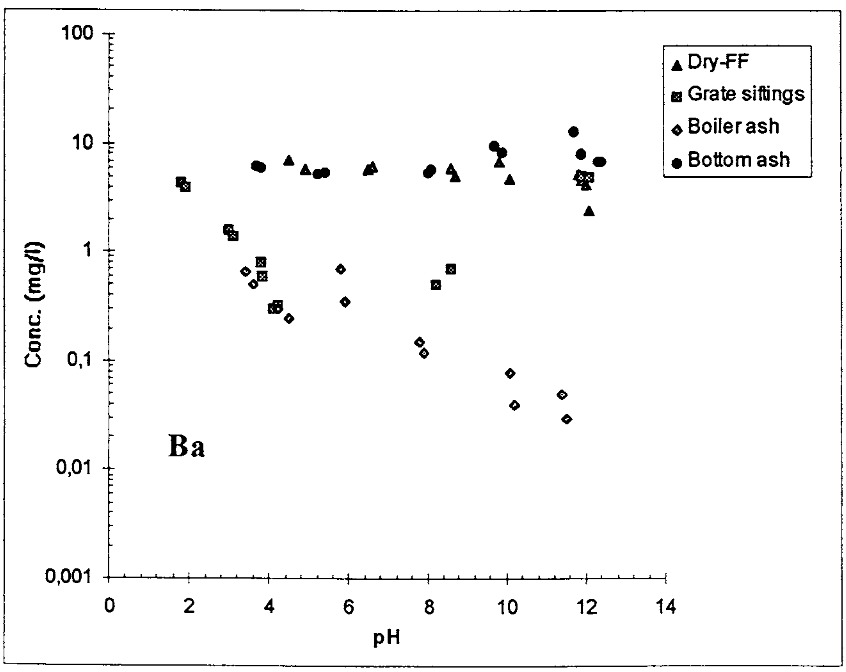
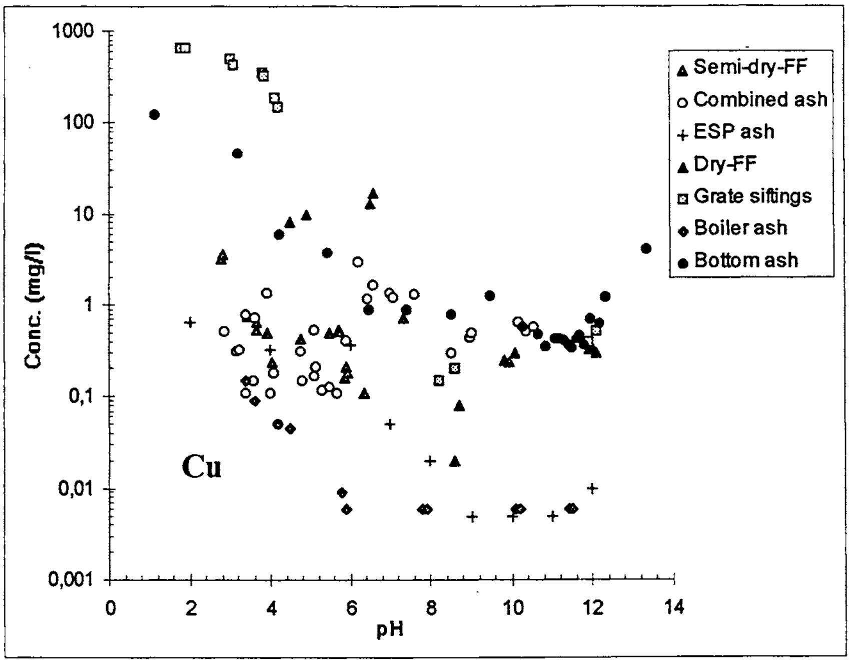


Figure 16.14 Continued



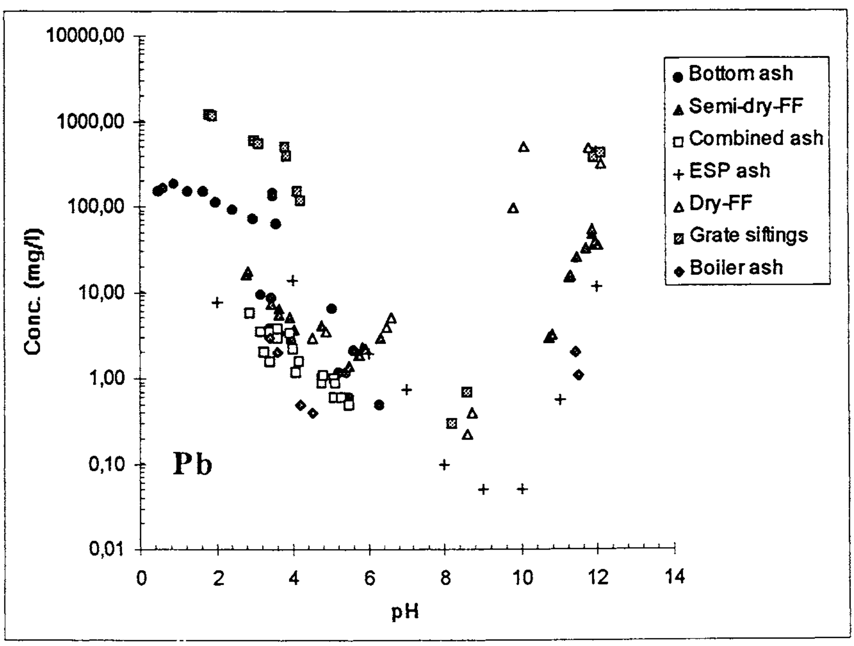
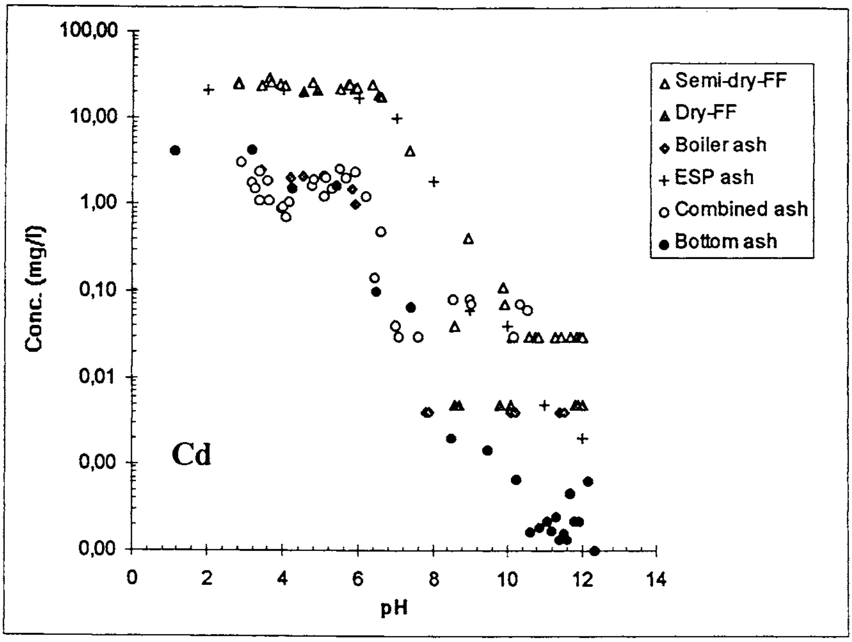


Figure 16.14 Continued



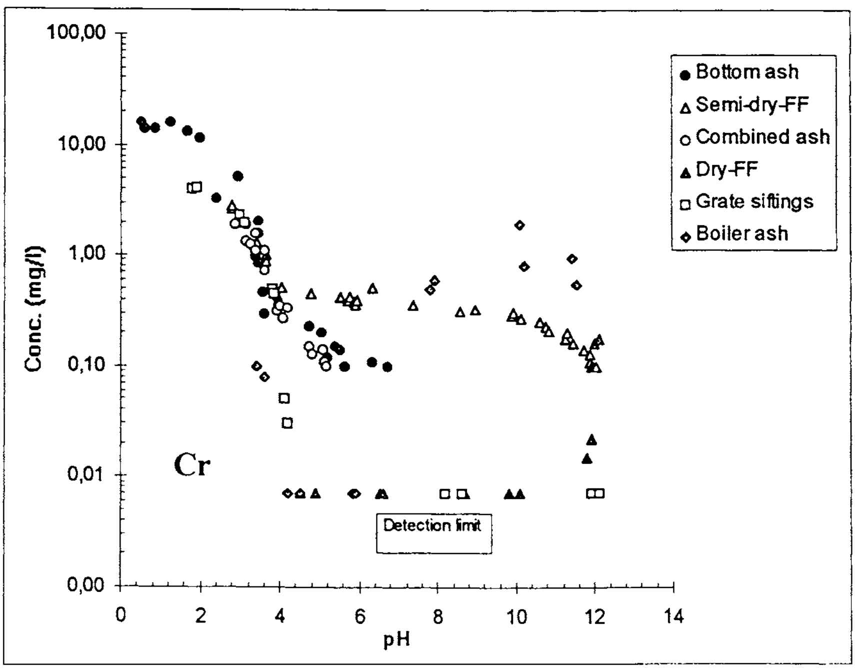


Figure 16.14 Continued

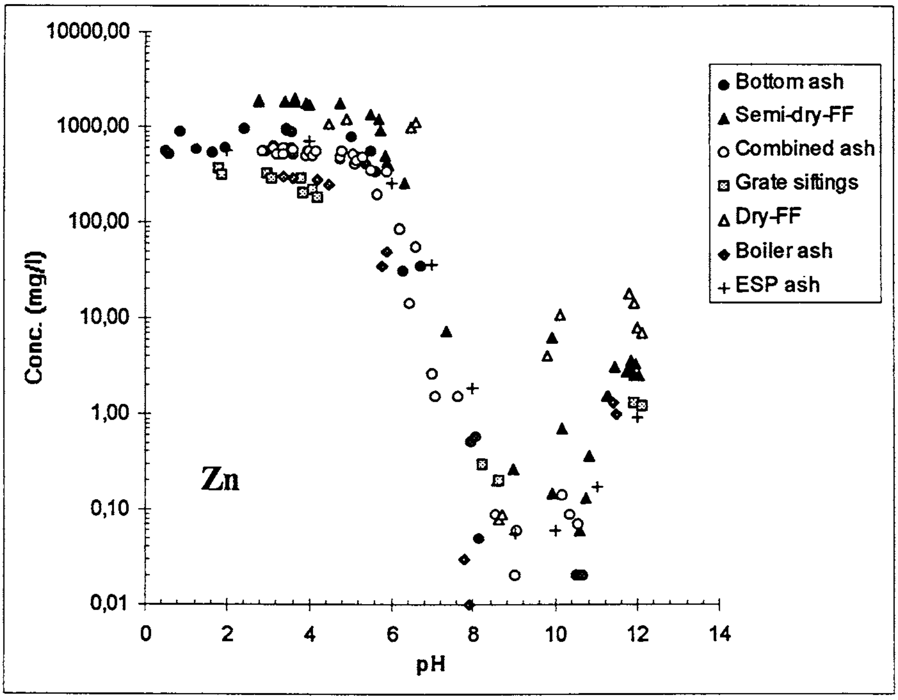


Table 16.6
Total Content and Availability of Several Elements for Each MSWI Residue Stream

Availability is presented on the basis of release per mass of ash, release per mass of MSWI incinerated, and fraction of total content

Stream	As		B		Ba		Ca		Cd	
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
Availability (mg/Mg MSW)										
Bottom ash	0.09	1.5	15	60	15	60	6000	21000	0.15	1.5
Grate siftings			0.75	3			450	1050	<0.01	<0.01
Boiler ash			0.2	0.4			250	500	0.02	0.05
Filter ash	0.02	0.04			0.6	1.6	1000	2000	2	6
APC resiaue			0.6	1.8			600	720	1.2	3.6
Total available mass per element	0.11	1.54	16.55	65.2	15.6	61.6	8300	25270	3.38	11
Availability (mg/kg ash)										
Bottom ash	0.3	5	50	200	50	200	20000	70000	0.5	5
Grate siftings			50	200			30000	70000	0.1	0.1
Boiler ash			40	80			50000	100000	5	10
Filter ash	1	2			30	80	50000	100000	100	300
APC residue			50	150			50000	60000	100	300
Total content (mg/kg ash)										
Bottom ash	5	40	80	200	500	1800	50000	90000	2	25
Grate siftings									0.5	1
Boiler ash			30	80					100	500
Filter ash	30	100	30	80	1500	3000	50000	200000	100	500
APC residue	50	100			100	800	50000	200000	300	900
Fraction Available (-)										
Bottom ash	0.06	0.13	0.63	1.00	0.10	0.11	0.40	0.78	0.25	0.20
Grate siftings									0.20	0.10
Boiler ash			1.33	1.00					0.05	0.02
Filter ash	0.03	0.02	0.00	0.00	0.02	0.03	1.00	0.50	1.00	0.60
APC residue							1.00	0.30		

Total mass of individual streams (mg/Mg MSW):
Bottom ash, 300; Grate siftings, 15; Boiler ash, 5; Filter ash, 20; APC residue, 12.

Table 16.6 Continued

Stream	Cl		Cr		Cu		Hg		K	
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
Availability (mg/Mg MSW)										
Bottom ash	300	1800	0.6	3	15	60	<0.01	0.03	300	900
Grate siftings	3	6	0.03	0.15	30	90				
Boiler ash	15	35	0.005	0.05	0.01	0.15			10	20
Filter ash	600	1000	0.2	2	0.1	0.4	0.02	0.06	200	500
APC residue	360	720	0.06	0.24	0.01	1.2	0.05	0.12	120	360
Total available mass per element	1278	3561	0.90	5.44	45	151	0.07	0.21	630	1780
Availability (mg/kg ash)										
Bottom ash	1000	6000	2	10	50	200	0.01	0.1	1000	3000
Grate siftings	200	400	2	10	2000	6000				
Boiler ash	3000	7000	1	10	1	30			2000	4000
Filter ash	30000	50000	10	100	5	20	1	3	10000	25000
APC residue	30000	60000	5	20	1	100	4	10	10000	30000
Total content (mg/kg ash)										
Bottom ash	1000	3000	200	1000	1200	2500	0.5	1	7000	20000
Grate siftings										
Boiler ash	8000	30000	300	800	750	2000				
Filter ash	30000	60000	400	800	300	1000	1	20	20000	40000
APC residue			100	500	800	2000			20000	40000
Fraction Available (-)										
Bottom ash	1.00	2.00	0.01	0.01	0.04	0.08	0.02	0.10	0.14	0.15
Grate siftings										
Boiler ash	0.38	0.23	0.00	0.01	0.00	0.02				
Filter ash	1.00	0.83	0.03	0.13	0.02	0.02	1.00	0.15	0.50	0.63
APC residue									0.50	0.75

Total mass of individual streams (mg/Mg MSW):
Bottom ash, 300; Grate siftings, 15; Boiler ash, 5; Filter ash, 20; APC residue, 12.

Table 16.6 Continued

Stream	Mg		Mo		Pb		Sb		SO_4		Zn	
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
Availability (mg/Mg MSW)												
Bottom ash	300	900	0.3	1.2	15	90	0.3	0.6	2400	5400	15	150
Grate siftings					75	135			45	75	30	75
Boiler ash					0.1	0.5			150	400	15	35
Filter ash	80	300	0.02	0.08	2	6	0.01	0.02	600	1600	100	160
APC residue					1.2	60			360	1200	120	240
Total available mass per element	380	1200	0.32	1.28	93.3	292	0.31	0.62	3555	8675	280	660
Availability (mg/kg ash)												
Bottom ash	1000	3000	1	4	50	300	1	2	8000	18000	50	500
Grate siftings					5000	9000			3000	5000	2000	5000
Boiler ash					20	100			30000	80000	3000	7000
Filter ash	4000	15000	1	4	100	300	0.5	1	30000	80000	5000	8000
APC residue					100	5000			30000	100000	10000	20000
Total content (mg/kg ash)												
Bottom ash	10000	30000	5	30	1500	3000	30	200	12000	30000	2000	4000
Grate siftings												
Boiler ash					2000	10000					10000	20000
Filter ash	10000	30000	20	60	4000	8000	150	500	30000	90000	10000	20000
APC residue			5	25	5000	20000	50	950			5000	40000
Fraction Available (-)												
Bottom ash	0.10	0.10	0.20	0.13	0.03	0.10	0.03	0.01	0.67	0.60	0.03	0.13
Grate siftings												
Boiler ash					0.01	0.01					0.30	0.35
Filter ash	0.40	0.50	0.05	0.07	0.03	0.04	0.00	0.00	1.00	0.89	0.50	0.40
APC residue												

Total mass of individual streams (mg/Mg MSW):
Bottom ash, 300; Grate siftings, 15; Boiler ash, 5; Filter ash, 20; APC residue, 12.

presented both on the basis of the content within the individual residue stream (mg/kg residue) and on the basis of the original MSW feed (mg/Mg MSW). Calculation of availability on the basis of the original feed permits comparison of the relative contribution of the availability from a specific residue stream to the overall release potential from all waste streams. Thus, the relative mass of each residue stream is considered. Using this approach, the following observations can be made.

The total amount of Cd available for all residues is approximately 6 g/Mg MSW, of which 0.8 g/Mg is present in the bottom ash, 5 g/Mg is present in the APC residues, less than 0.001 g/Mg is present in the grate siftings and 0.03 kg/Mg is present in the boiler ash. Similarly, the total amount of Cl available for all residues is approximately 1400 g/Mg MSW, of which 450 g/Mg is present in the bottom ash, 800 g/Mg is present in the APC residues, 3 g/Mg is present in the grate siftings and 20 g/Mg is present in the boiler ash. The total amount of Zn available for all residues is approximately 350 g/Mg MSW, of which 80 g/Mg is present in the bottom ash, 200 g/Mg is present in the APC residues, 40 g/Mg is present in the grate siftings and 20 g/Mg is present in the boiler ash. Consequently, separating the APC residue from the other streams would make sense, since the majority of the available elemental inventory is in the APC residue

Conversely, the total amount of Cr available for all residues is approximately 3 g/Mg MSW, of which 2 g/Mg is present in the bottom ash, 1 g/Mg is present in the APC residues, 0.01 g/Mg is present in the grate siftings and 0.03 g/Mg is present in the boiler ash. The total amount of Cu available for all residues is approximately 80 g/Mg MSW, of which 30 g/Mg is present in the bottom ash, 0.8 g/Mg is present in the APC residues, 45 g/Mg is present in the grate siftings and 0.1 g/Mg is present in the boiler ash. The total amount of Pb available for all residues is approximately 150 g/Mg MSW, of which 45 g/Mg is present in the bottom ash, 30 g/Mg is present in the APC residues, 70 g/Mg is present in the grate siftings and 0.3 g/Mg is present in the boiler ash. Since the greatest inventory of these metals resides in the bottom ash or grate siftings, separation of these streams from other streams would not make much difference. However, segregating the grate siftings would be advantageous for reducing Pb and Cu loadings in bottom ash destined for utilisation.

Figure 16.15 provides a comparison of release as a function of pH for Cd, Cu, Pb and Zn in six different waste materials of widely different origin (van der Sloot, 1994). The wastes compared include ash from a refuse derived fuel incinerator (RDF ash), bottom ash from mass burn systems, ESP ash (fly ash), waste from car shredders (Shredder waste), soil amended with sewage treatment sludge (Sewage amended soil), coal fly ash and a natural soil (Terra rossa). Although the general trends in release as a function of pH are very similar, the absolute release for each varies by several orders of magnitude in the pH regime where availability is controlled. It is clear that the major elements, dictating the leachate composition for the most part, also control the leachability of trace contaminants to a large extent. The differences between the behaviour of individual elements in different wastes can be attributed to specific factors,

Figure 16.15 Release of Cd, Cu, Pb and Zn as a Function of pH from Different Waste Materials in Comparison with MSWI Residues

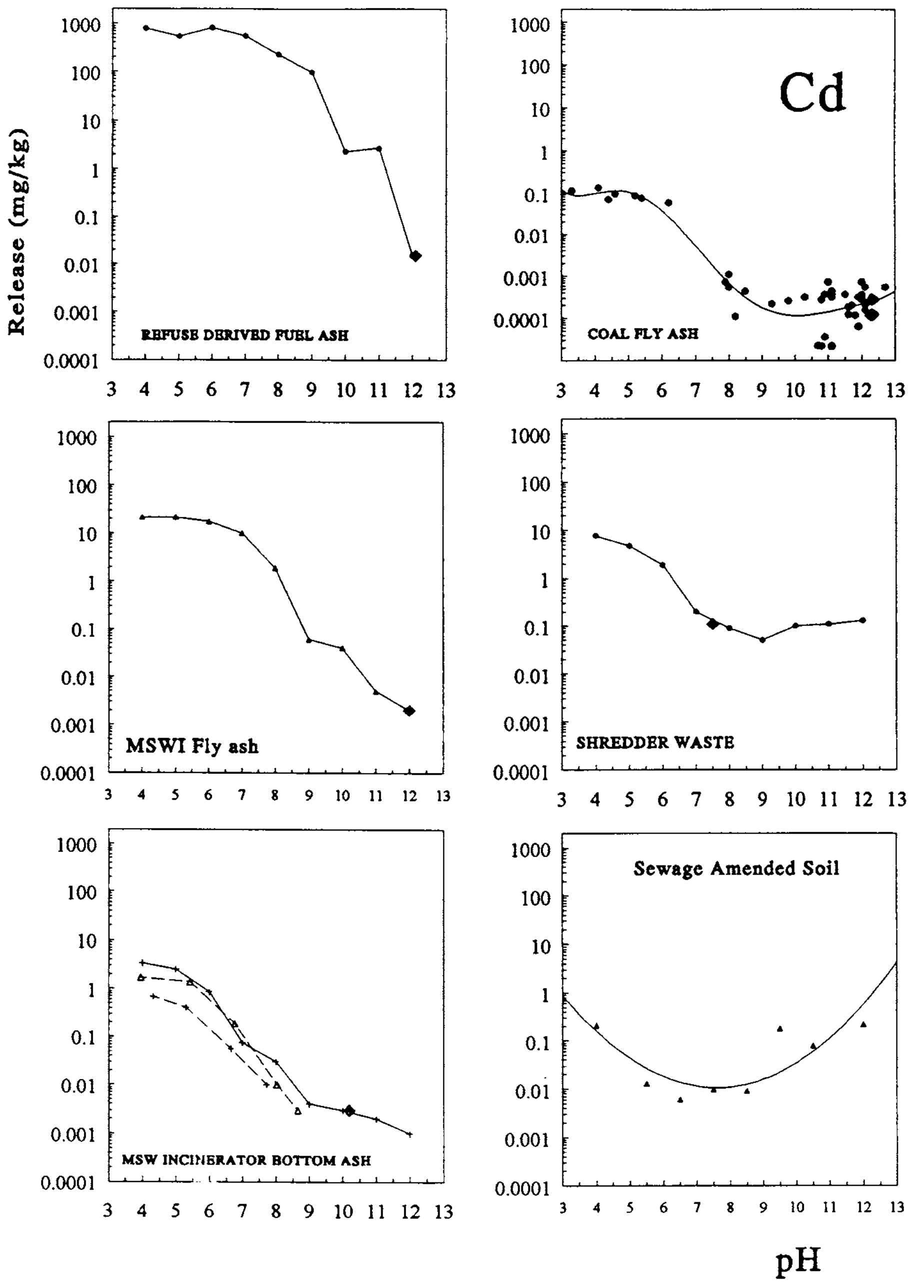


Figure 16.15 Continued

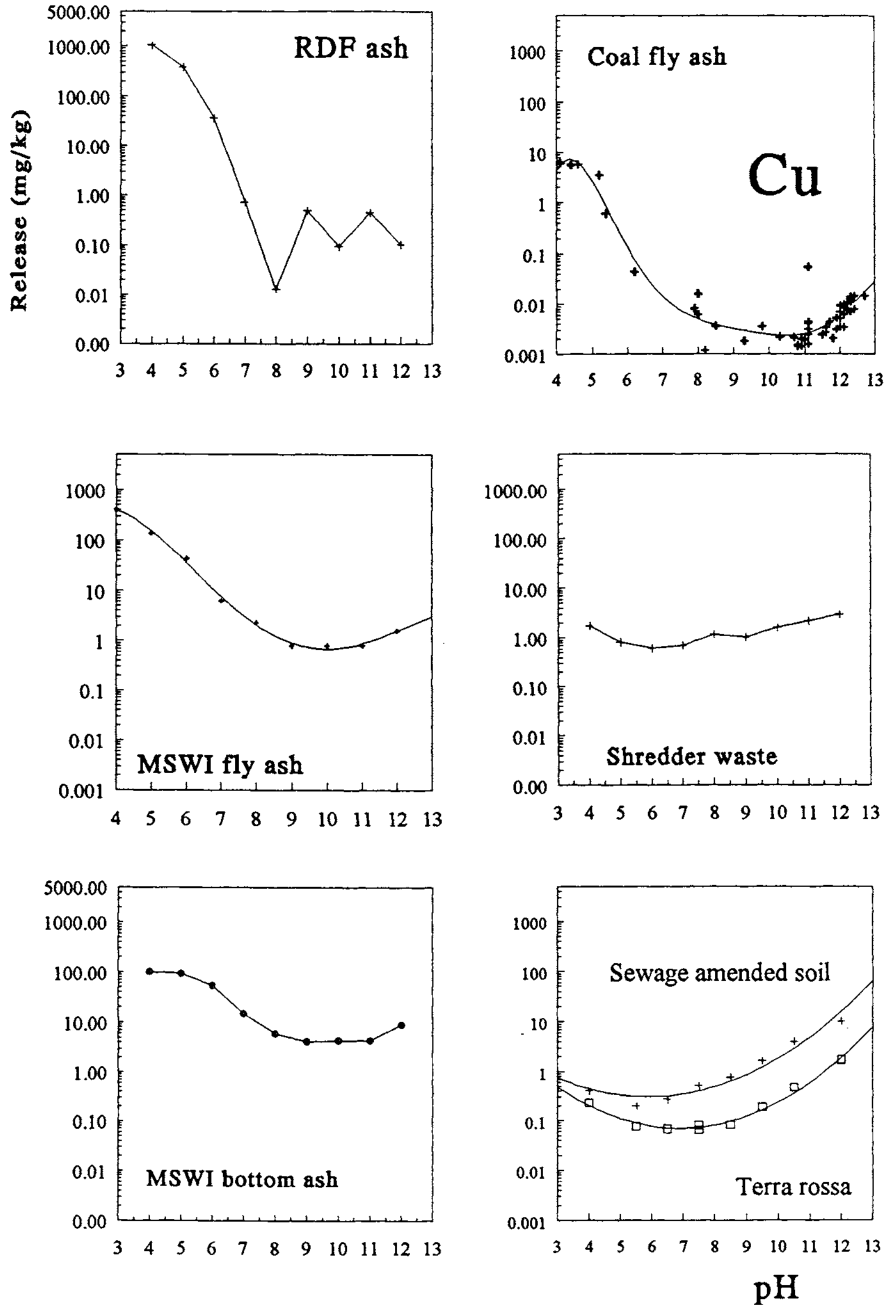


Figure 16.15 Continued

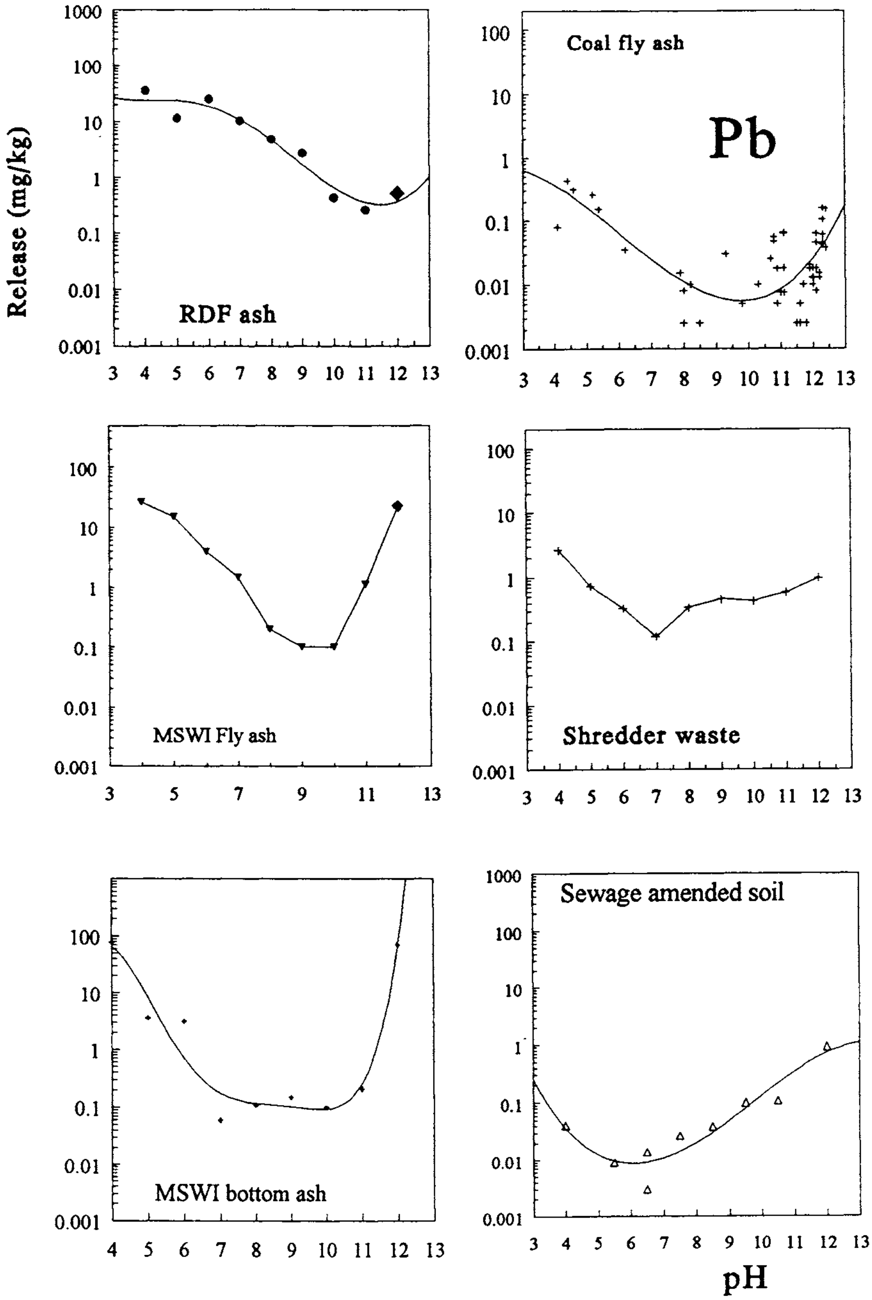
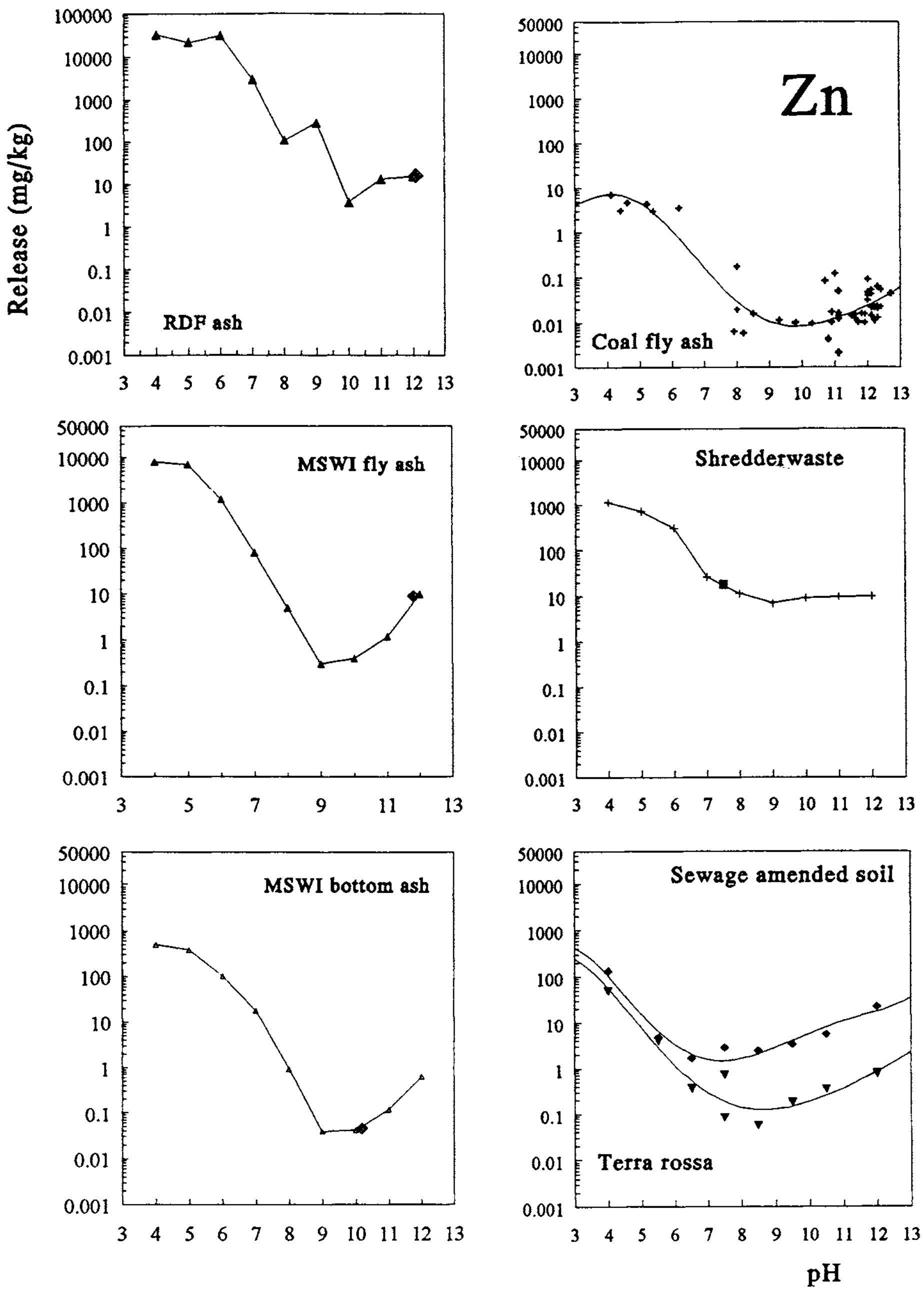


Figure 16.15 Continued



such as the presence of high concentrations of dissolved organic matter (e.g., humic and fulvic substances) in sewage sludge amended soil. In the case of Cu, the higher leachability from bottom ash is related to the presence of dissolved organic matter (DOC) in bottom ash, which is absent in coal fly ash. The high leachability of Cu from shredder waste is directly related to the high amount of dissolved organic matter characteristic for this waste.

Cd is another example of an element which behaves differently in different wastes. For Cd the influence of Cl on release is substantial. The release of Cd from a variety of materials (RDF ash - Bottom ash - Fly ash - Shredder waste - Coal fly ash) with different Cl levels shows the sensitivity to the Cl level. The increase in Cd release at higher pH with increasing Cl concentration in the leachate is very pronounced and can be modeled with geochemical speciation models (Allison et al., 1991). The relationship between bottom ash, fly ash and RDF ash form an interesting sequence in this respect, because of increasing Cl content, respectively.

The Zn leachability curves for different wastes are very consistent. A slight shift in solubility with pH occurs for RDF ash as a result of the high Cl content in this waste. Some mobilisation of Zn through DOC complexation is noted for shredder waste.

16.7 LEACHING OF ORGANIC CONSTITUENTS

The relevance of organic constituents in incinerator residues was discussed in Chapter 8. This Chapter follows that discussion along by describing the potential trace element complexation with organic compounds. Organic constituents in incinerator residues can be classified as:

- Organic contaminants of potential human health concern, such as PCBs, PCDDs, PCDFs, chlorophenols and PAHs
- Low molecular weight organic acids and related soluble organic species (e.g., phenols, sugars, etc.)
- Humic and fulvic type substances resulting from microbial activity in an ash repository

Organic contaminants of potential human health concern can be grouped as polar (chlorophenols and chlorobenzenes) and non-polar compounds (PAHs, PCBs, PCDFs and PCDDs). The leaching behaviour of the relatively polar organic species can be described in a similar manner as inorganic species, where solubility and liquid-solid partitioning controls release. The significance of a leaching test with water is questionable for non-polar compounds with a very low water solubility because the main mechanism of release is not dissolution. Here the role of "facilitated transport" (McCarthy and Zachara, 1989) is important. To assess leachability of non-polar organic species by leaching with water the main focus should be on the potential by-products of degradation of organic matter, which can then facilitate transport of non-polar compounds. A method proposed for assessing the magnitude of this fraction is an extraction using 1 N KOH (van der Sloot, 1992). This releases a fraction of organic matter that may be considered readily available for degradation. It is speculated that the organic contaminants associated with this fraction can be used as a first estimate of potential long term release of non-polar organic contaminants, however, further work is needed to explore this approach.

Organic contaminants of potential human health concern are present in greatest concentrations in the APC residues. The NITEP program included extensive testing for organic contaminants in different APC residues (Environment Canada, 1993). In a system containing consecutively a wet/dry spray reactor, a dry reactor and a fabric filter dust collector, the composition and leachability of PCDD, PCDF, PCB, PAH, chlorobenzenes and chlorophenols were measured. Organic contaminants were not detected in any of the leachates with the exception of chlorophenols, of which less than 10% of the total quantity was solubilised. After leaching, the leached residues were analysed again and the concentrations of organic contaminants were corrected for the loss of soluble solids. This resulted in virtually complete recovery of PCDD, PCDF, PAH, chlorobenzenes and chlorophenols from the solid, indicating that within the analytical limitations, no significant fraction of the organic contaminants were leached from the ashes.

However, some data has indicated that there is another potential mechanism for release of organic compounds, namely colloidal transport. This process may explain some of the findings of water insoluble organic contaminants at distances from a site beyond the expectations from laboratory testing (McCarthy and Zachara,1989). Fortunately, the organic matter content of APC residues is very small, thus minimising the risk of release. Alternatively, bottom ash which can have a significant organic matter content, does not contain appreciable concentrations of the organic contaminants of concern (Sawell et al., 1986), thus the issue of leaching of organic contaminants from incinerator residues is not considered a problem.

The concentration and significance of these organic constituents in the residue streams is different. Low molecular weight organic acids, humic and fulvic acids are most prevalent in bottom ash as a result of their presence either in the ash, the degradation of incompletely combusted organic matter, or through alkali hydrolysis of higher molecular weight organic matter. Leaching of these organic species can have a significant effect on the short-term leachability of specific elements, such as Cu. In addition to the influence of these compounds, the presence of unburned organic matter may also serve to generate reducing conditions within the ash matrix, which can decrease the release of heavy metals.

The dissolution of low molecular weight organic acids and humic and fulvic compounds have been shown to be significantly increased at high pH due to alkali hydrolysis. At pH greater than 12, the extent of dissolution is greatest (Figure 16.6c). At pH values below 9 the leachability of humic substances is probably insignificant, whereas the low molecular weight organic acids and fulvic substances may continue to play a role in the complexation of metals.

16.8 EFFECTS OF INCINERATOR OPERATION ON LEACHING

16.8.1 Combustion Efficiency (Burn out) and Facility Operation

It appears that the variability in the waste stream composition masks most possible differences in leaching behaviour between installations. In a detailed study carried out in the NITEP program (Sawell et al., 1988, 1989, 1991) included investigation of the impact of waste feed rate, furnace temperature, air supply, temperatures in the flue gas system and lime feed rates on residue properties. Given that the leaching of most trace elements is dominated by the major element chemistry, the influence of facility operation within the normal bounds of good combustion on bottom ash leaching is a secondary effect. Overall, poorer burnout tended to reduce the release of most trace metals, either due to dilution from the increased mass of material, or through sorption onto activated carbon in the ash. Significant changes in APC residue pH (Figure 16.16), alkalinity and chloride content (Figure 16.17) were observed as a function of lime feed stoichiometry and operation (Sawell et al., 1988). This can have a significant influence on results observed for regulatory leaching tests because the extraction pH is controlled by the residue alkalinity, which in turn controls measured concentrations for many elements.

16.8.2 Waste Feed Composition

The influence of waste feed composition on leachability is complex for several reasons:

- The speciation of a particular element in the waste feed can significantly effect the partitioning of that element between the bottom ash, grate siftings and APC residues.
- Although the overall inventory of an element may change, the change may only have a limited effect on the overall available fraction of that element across all residue streams, especially if the availability is only a small fraction of the total amount present in the residues. Thus, changes in the speciation of an element present in the feed may be as important as the total quantity in the input.
- Changes in the availability of an element may not effect the solubility controlled release of that element under relevant testing or field conditions. Thus, significant reductions in input of a specific element may have no noticeable effect on regulatory testing results or impact on field leachate quality.

Figure 16.16 Influence of MSW Operation on pH of ESP Ash

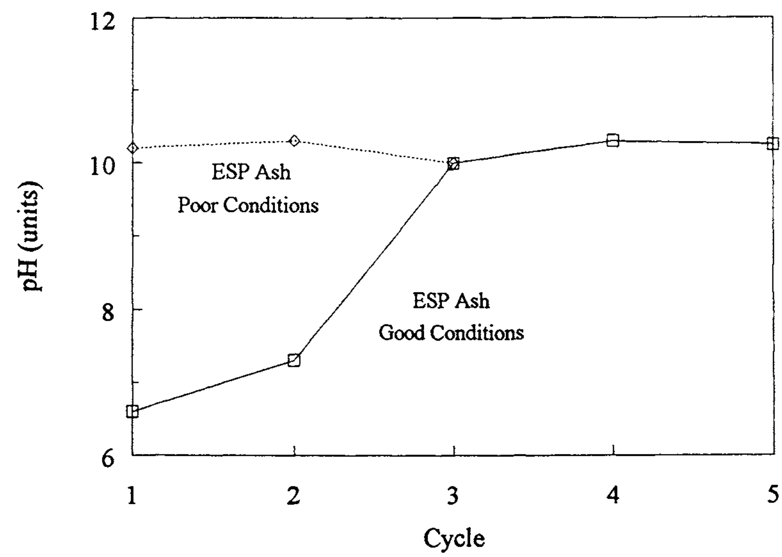
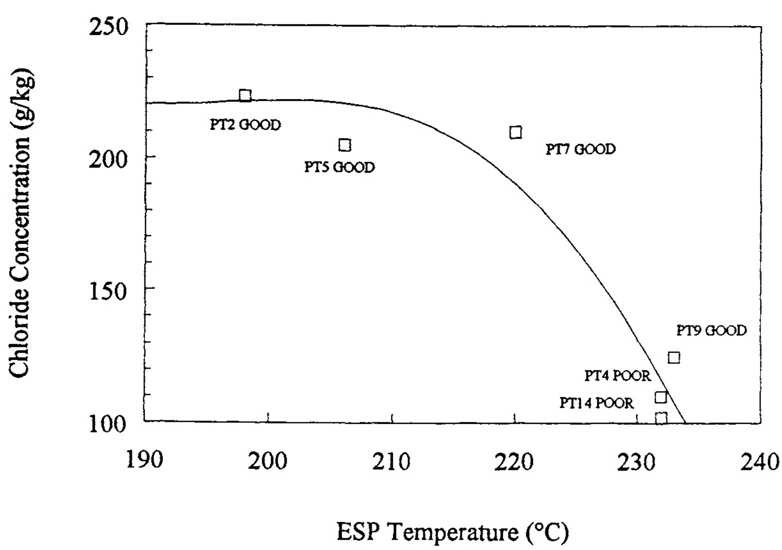


Figure 16.17 Influence of ESP Temperature on the Cl Level in Precipitator Residues



- The most significant changes in leaching of trace elements may be achieved by modification of the major element composition or chemistry of the residues rather than by modification of the input of trace elements of concern. This is because the major elements typically control residue alkalinity, solubility and availability in many cases.

A limited number of studies have been conducted using sorted waste as a feed to an incinerator to evaluate the impact on leachability. In the WASTE Program (1993) experiments were carried out where the waste feed to a mass burn incinerator was spiked with lead-acid batteries, Cd in the form of PVC pellets, Cd as a Cd-benzoate solution, and a combination of all these materials simultaneously. The various residue streams were sampled and subjected to both the Sequential Chemical and Sequential Batch Extraction Procedures. In general, although the total concentrations of these elements increased in certain residue streams due to the spiking, the solubility of the elements did not change appreciably based on results gleaned using the SCE procedure. For example, the increase of concentrations of lead in the grate siftings did not increase the fraction of lead available for leaching, because much of the increase was attributed to elemental lead which melted on and dripped through the grates. Since elemental lead (coated with a PbO layer) is relatively insoluble, the spiked lead did not contribute to the leachable fraction. Furthermore, results from a distilled water leach test indicated that the fraction of leachable Cd and Pb actually decreased in the fly ash residues from the spiked runs (see Figures 16.18 and 16.19). Consequently, the species of an element is the most important consideration when assessing change in the leaching characteristics of a residue.

The impacts of three waste compositions were compared in a study carried out with the Hague incinerator (NOH/RIVM, 1991). The three waste compositions were:

i. MSW as collected from the curbside

ii. MSW with putrescibles, glass, paper and domestic chemical waste removed, resulting in a feed analogous to thorough source separation, and

iii. MSW preprocessed in the same way as (ii) above, but also crushed on-site to create a more homogeneous feed

Each type of waste was incinerated over a three day period and bottom ash samples from each day of operation were leached using an L/S=20 with distilled water. The most significant impact on the leaching test results was a reduction in leachate pH from a range of 7.4-11.8 for Case i to 5.5-8.2 for Case ii. This change could not be attributed to the removal of waste components because the pH range for Case iii was 10.8 - 11.6. No significant impact was observed on the leachate concentrations for Cu, Cr, Pb or Mo. Results for Cu and Pb are presented in Figure 16.20. Cu leaching relative to the unified pH curve may have been reduced due to less soluble organic matter present in the ash, but the results were inconclusive.

Figure 16.18 Fraction of Cadmium Leached During the SBEP - Stabiliser Spike

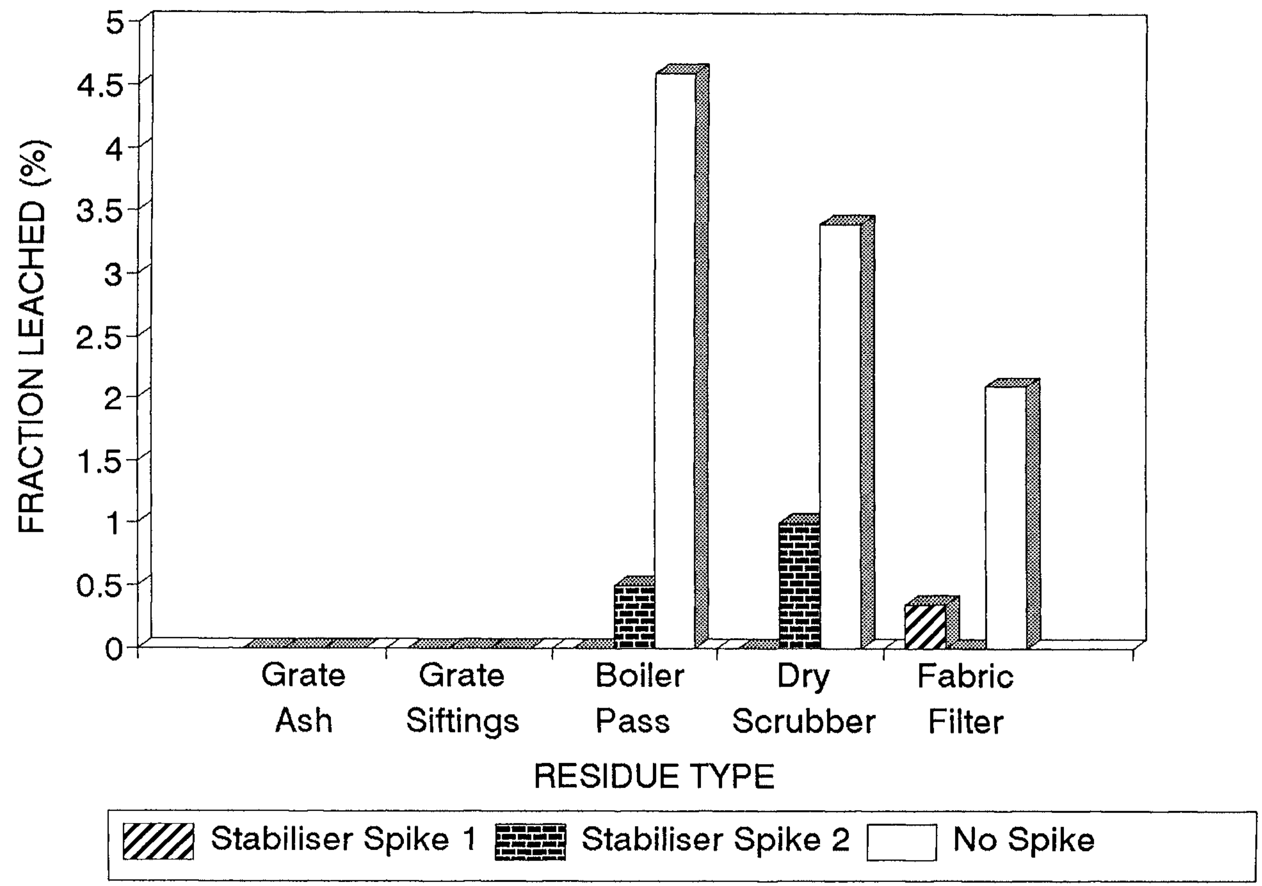
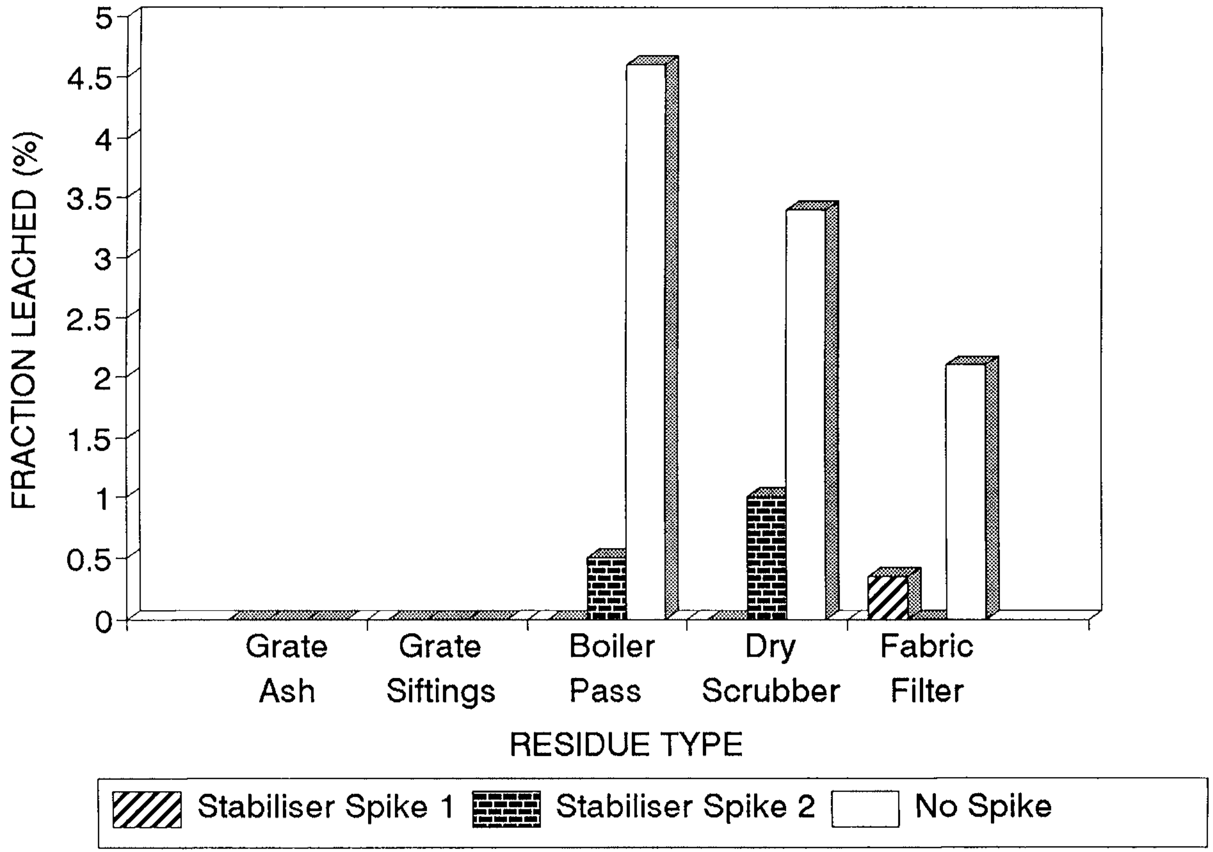
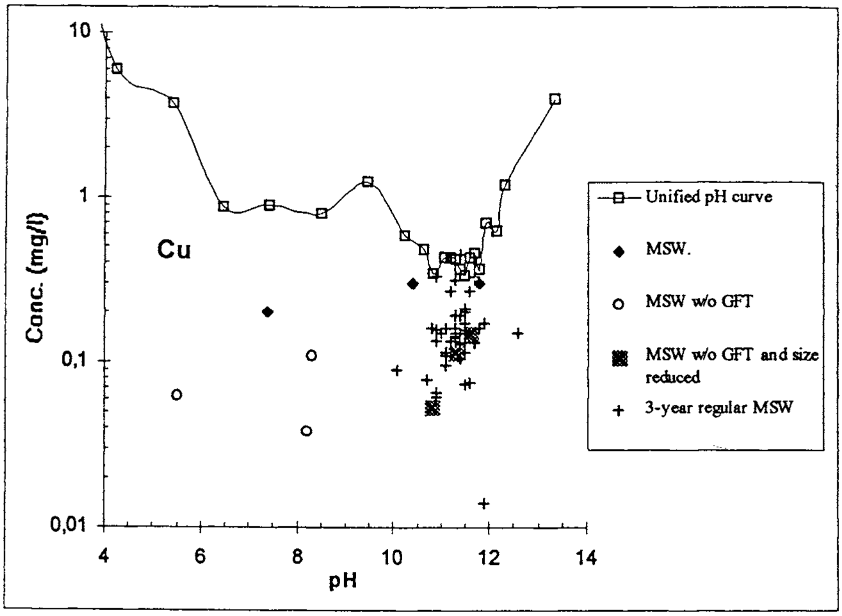


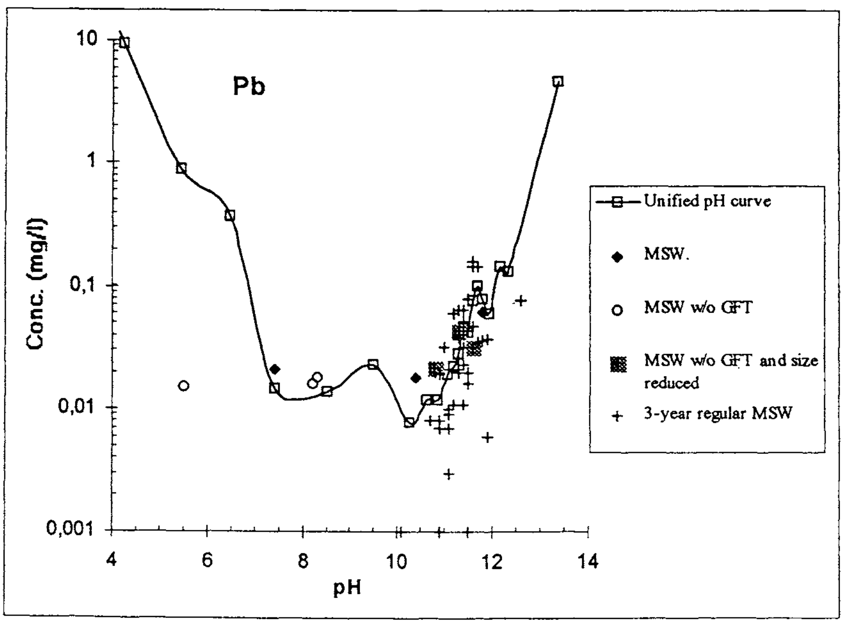
Figure 16.19 Fraction of Cadmium Leached During the SBEP - Pigment Spike



Concentrations expressed in microgram/l in a batch test at LS=20.

Figure 16.20 Effects of Changes in MSW Feed on Leachability of Cu and Pb in Bottom Ash from the Hague Incinerator





These relationships clearly indicate that knowing which factors have the greatest effect on leachability is important to facilitate significant improvements in leachate quality or release of critical contaminants during residue management. This does not imply that source separation of certain materials such as automobile and household batteries or Hg thermometers is a futile activity. Clearly, if a specific waste contributes a large fraction of a trace element to the overall loading, its separation is fully warranted. Moreover, if a specific waste contributes a large fraction of a potentially leachable metal, it should be targeted. However, the justification for source separation should not be focused primarily on reducing ash leachability. Some measures, such as removal of metallic lead (Pb^0) or copper (Cu^0), may reduce the inventory of these elements, but may have no effect on ash leachability.

Overall, the fate of constituents in waste components should be evaluated in more detail to identify their potential impact. The role of changes in bottom ash alkalinity due to changes in waste input also should be examined further because of the potential impact on release of many elements.

16.8.3 Seasonal Variations in Leaching

The leaching data obtained from a 6 year waste characterisation program (VVAV, 1988, 1992, 1993) have been evaluated for differences within installations and for differences over the seasons. Bottom ash samples were leached using a batch extraction method with distilled water at an L/S of 20:1. Differences between installations as a result of MSW input were generally more significant than variability in ash leachability over the seasons. Identification of the causes for differences in the feed to an incinerator, such as commercial waste, may provide clues to the possible reason for differences.

The 6 installations clearly form two groups: those in the municipality of Rotterdam and the others (rural). Figure 16.21 presents the weekly variability in ash leachate pH and Pb concentration from one facility. Increases in Pb concentrations were correlated with decreases in leachate pH. Seasonal factors have been suggested to effect the MSW feed to an incinerator and possibly impact on the leaching of the residues. Results for the seasonal impact on the leaching of 8 elements are presented in Figure 16.22. Slight increases in pH ($\approx$ 0.2 pH units) were observed during the summer in predominantly residential areas. This effect may have resulted from increased quantities of grass clippings and other garden waste, however, no significant seasonal effect was observed for As, Cd, or Cr. The following additional observations were made:

Copper

There appeared to be two clusters of installations, urban-based facilities with relatively higher levels of Cu leachability and those rural facilities with lower levels of Cu leachability. Bottom ash leachates from the 4 urban incinerators did indicate some

Figure 16.21 Variability in pH (▲) and Pb (□) Concentration Using a Serial Batch Extraction with Bottom Ash from One Installation Over a Period of Two Years

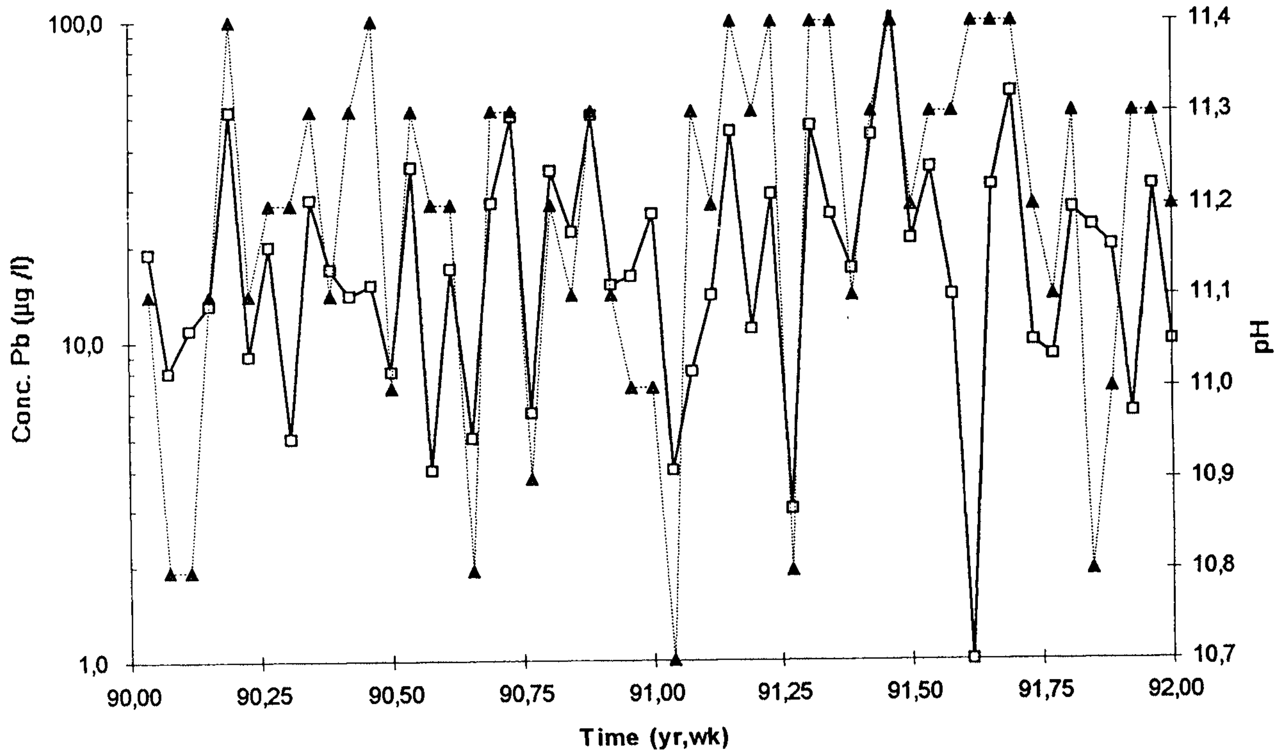
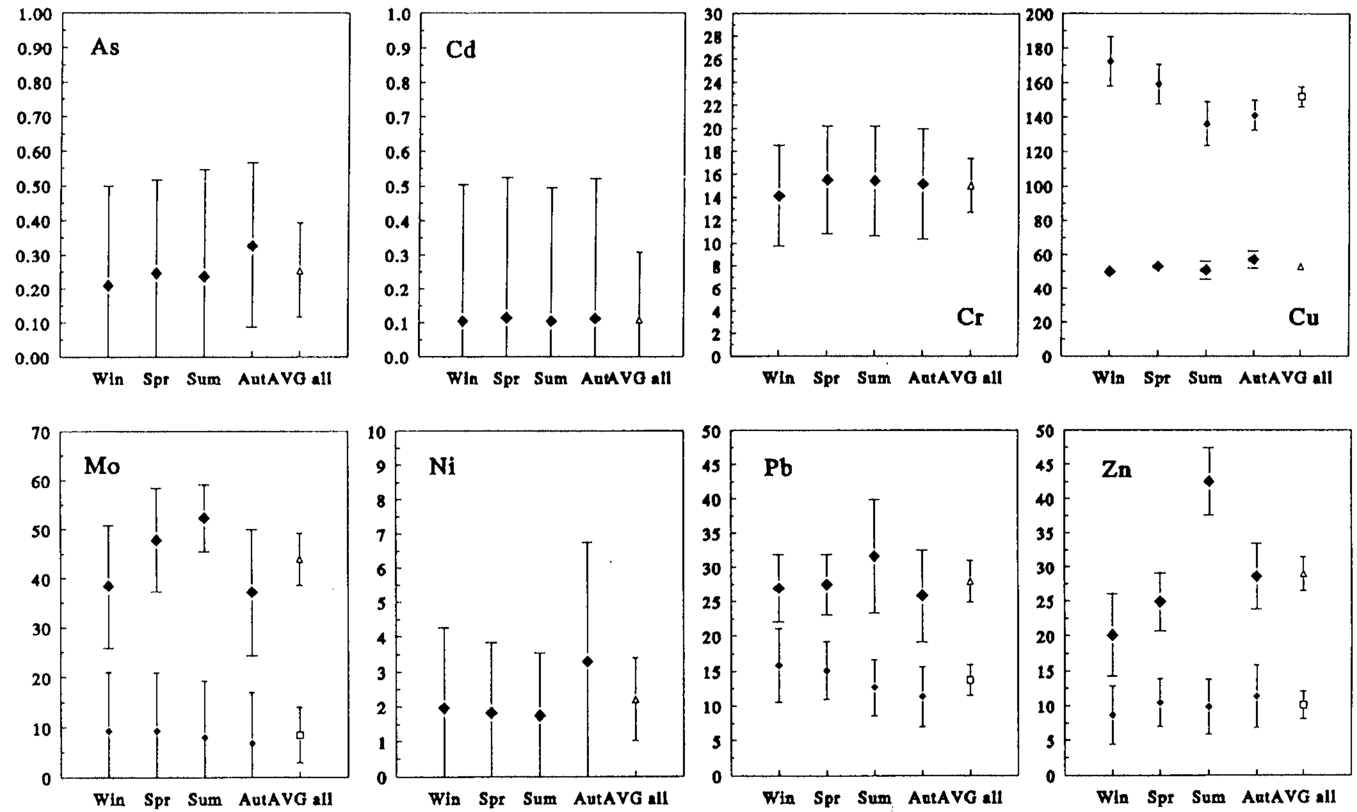


Figure 16.22 Seasonal Variations in Concentrations of Selected Metals in Extracts of Bottom Ash from 6 Installations



concentrations expressed in µg/l in a batch test at LS=20 seasonal effect with maximum Cu solubility observed in the winter months. The main factor here may have been the presence of dissolved organic matter capable of complexing copper to varying degrees.

Molybdenum

Some seasonal variability in the Mo leachability was observed for the urban facilities with a maximum in summer. The relatively high Mo input likely to be from a (small) industrial input to the incinerator. The use of Mo in lubricants has been postulated as a possible source of such inputs.

Nickel

Except for the autumn period the Ni leachability is very consistent between installations and between seasons. In autumn there are two installations with a significantly higher leachability in comparison with the other installations. The reasons for this higher mobility is unknown.

Lead

The Pb leaching data are fairly consistent over the seasons. Two installations show consistently higher Pb leachability than the others. This may be related both to input as well as to small differences in pH.

Zinc

On average the highest levels of zinc leachability were observed in the summer periods for two installations. The difference between the installations is also significantly different based on an annual average. A seasonal trend indicating higher leachability in summer and low leachability in winter appears to exist for three of the installations from an urban origin. The cause of this effect is not clear.

16.8.4 Quench Water Quality

Depending on the quantities of make-up water added, the quality of the quench water should be very similar in composition to the first leachate from a column leaching test on freshly collected ash. Generally, it has been observed that quench water contains high concentrations of salts and relatively high Cu levels. Table 16.7 compares quench water composition column data at low LS and field lysimeter leachate (Reimann, 1990; Chandler, 1993; AVR, 1995). The results indicate strong similarities between the quench water and leachate. A significant deviation is the high Ba content measured in data provided from Canada. The reason for the difference could be that the high carbon content in the ashes from this two-stage combustion system produced strong reducing conditions in the quench tank. As a result, sulphate was probably reduced to sulphide which, in turn, increased the leachability of Ba. The exceptionally low Cd and Pb concentrations measured in this quench water are consistent with this hypothesis. The Cd concentration observed in quench waters also is directly related to the Cl concentration and pH. The relatively high Pb and Zn concentrations in AVR quench water are consistent with the pH dependent leaching behaviour of bottom ash for these elements. For quench water quality, the pH (generally high) and the low LS are crucial factors for the concentration levels observed. Solubility control is already important in quench water, in spite of the limited contact time.

Table 16.7
Comparison of Quench Water Quality, Laboratory Column Leachate and Field Lysimeter Pore Water (mg/l)

Element	Quench water		Column leachate (L/S=0.2)	Lysimeter pore water
	[Reiman, 1990]	[Chandler, 1993]	[Versluijs et al, 1993]	Hjelmar, 1991
As	0.003	< 0.1	0.002	0.006
Ba		9.4	0.1	
Cd	0.15	< 0.050	0.020	0.001
Cl	1540		6000	4500
Cr	0.1		0.01	0.005
Cu	0.26		0.02	0.3
F	1.7		1	
Hg	0.015			
Mo			2	0.9
Ni	0.25		0.4	0.18
Pb	0.8	< 0.200	0.02	0.02
SO_4	1500		5000	1500
Zn			0.1	0.15
pH			9.0	9.3
Eh				150

16.9 EFFECTS OF RESIDUE PROCESSING AND MANAGEMENT ON LEACHING

16.9.1 Size-Reduction And Size Fractionation

Testing of bottom ash in the laboratory will usually require size reduction (see Chapter 7). Size reduction influences the leaching of bottom ash by exposing fresh surfaces which contains hydroxides which have not absorbed carbon dioxide and been converted to carbonates. This results in an observed increase in pH when the ash is extracted.

Size fractionation of bottom ash also may effect leaching behaviour because of varying composition as a function of particle size. The influence of particle size on the leachability of bottom ash has been studied by testing different size fractions (SOSUV, 1989) which were prepared with and without size reduction. Ash samples were separated into the following sieve fractions:

4 - 31.5 mm
1 - 4 mm
0.5 - 1 mm
0.125 - 0.5 mm
<0.125 mm

In addition, an aliquot of both the intact and size reduced (<3 mm) samples were subjected to a batch extraction at L/S=5 with distilled water. Analysis of chemical composition and the availability leach test was also carried out on sample (further size reduction of the respective fractions to <0.125 mm was required). Figure 16.23 presents results of the chemical analysis and leaching tests for Ca, Na, Cu, Mo, Pb and Zn in the different size fractions. Total sodium content increased with increasing particle size. This effect was not as pronounced for the other elements.

Availability varied by a factor of 2 to 5 over a particle size range of more than two orders of magnitude (<0.125 - 31.5 mm), with the exception of Na which was depleted in the coarse fraction. In almost all cases, the leachability was lowest in the coarse fraction and highest in the fraction less than 0.125 mm. The nominal particle size in this fraction was well below 0.125 mm, which indicates that the general relation between particle size and leachability is related to external surface area.

The final pH in the batch extractions varied from 11.5 to 12.5. The release of Pb in the batch extraction reflects the difference in pH as a function of particle size. Batch extraction results are presented as function of pH along with the respective pH-solubility curve for Cu, Mo, Pb and Zn in Figure 16.24. The primary effect of particle size reduction therefore may be a change in pH with its consequent effect on metal solubility.

Laboratory test results on size reduced bottom ash (column dia. 5 cm, h=20 cm) has also been compared with data obtained from large columns (column dia. 65 cm, h=275 cm) containing untreated bottom ash, operated both in up flow and down flow

Figure 16.23 Influence of Size Fractionation and Size Reduction on the Leachability of Ca, Cu, Na, Mg, Mo, Pb and Zn from Bottom Ash

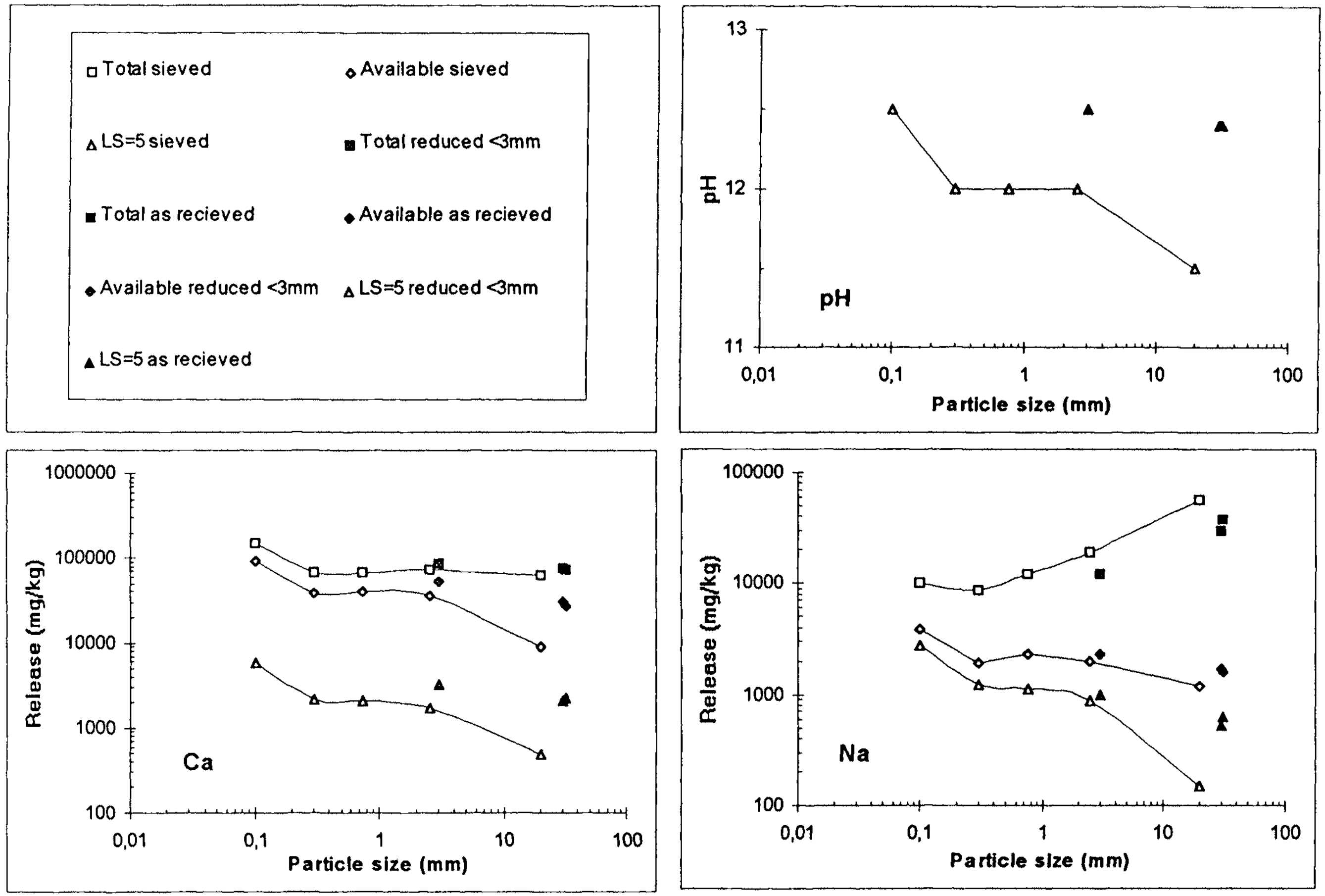


Figure 16.23 Continued

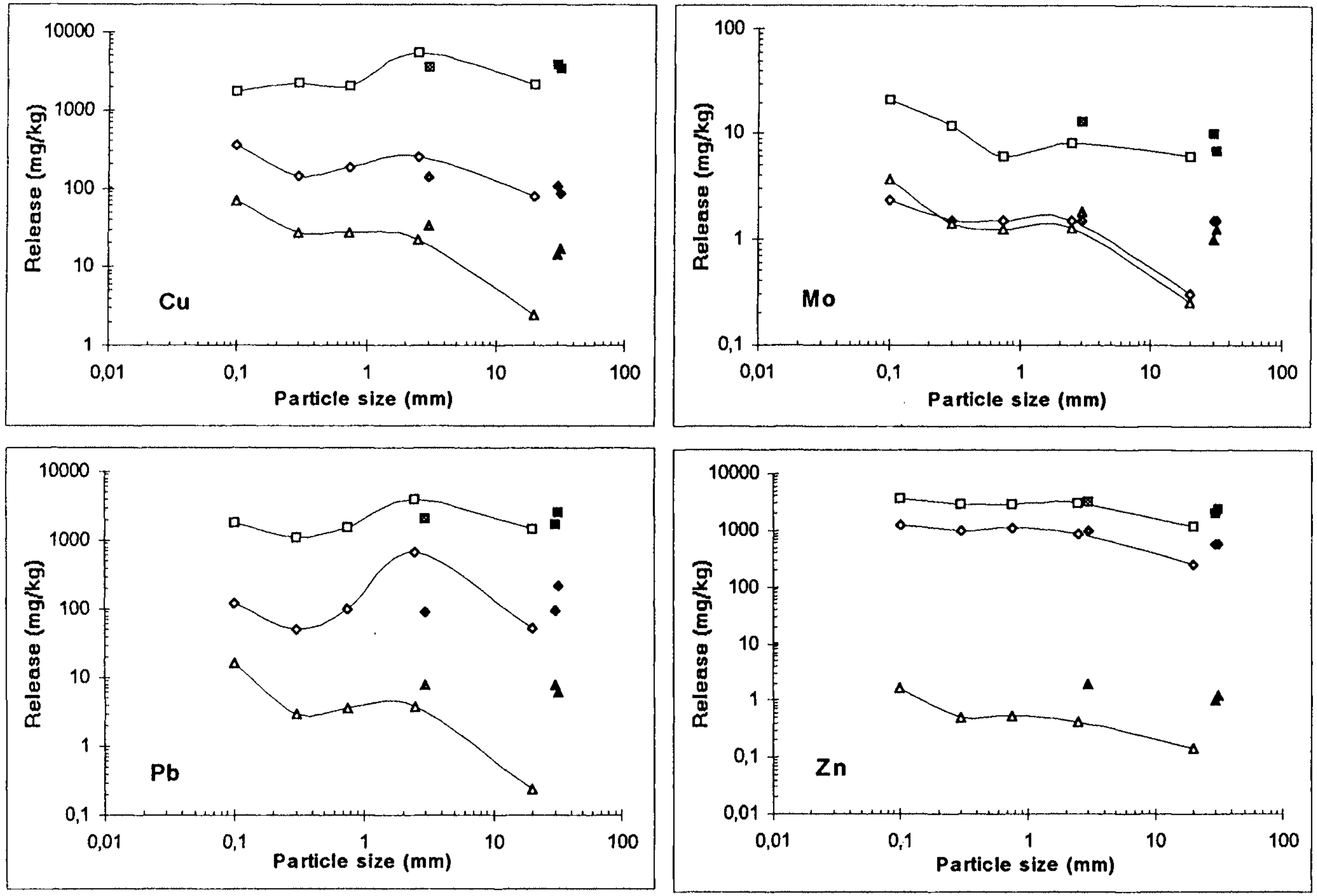
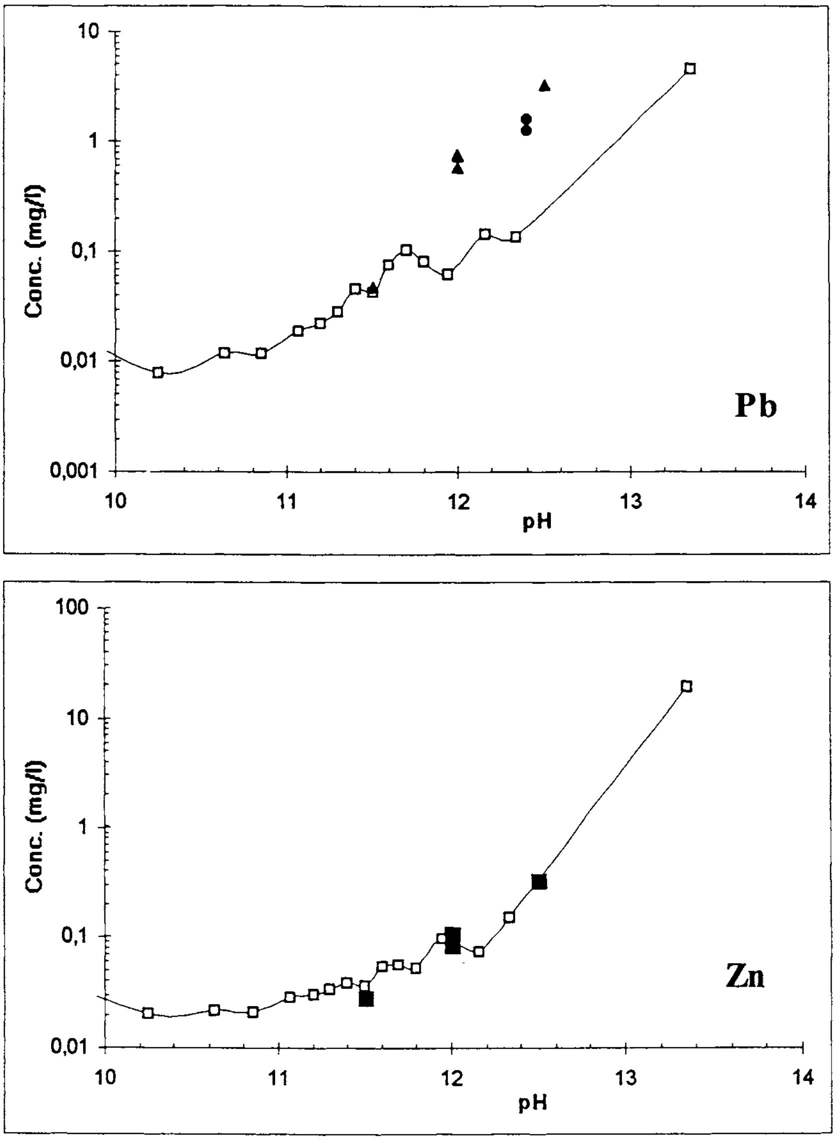


Figure 16.24 Increase in pH as a Consequence of Size Reduction and the Corresponding Change in Concentration of Pb and Zn Compared to the Unified pH Curve



configurations (Versluijs et al., 1990). Cumulative release at L/S=10 for several elements is presented in Table 16.8. An increase in pH of approximately 1.5 units was observed for the leachate from the small columns containing size reduced ash as compared to the leachate from the large columns. This result was similar to the effect observed for batch testing. This difference resulted in a different leachability in accordance with the pH - release relations established previously. The effect of the increased pH was most pronounced for Pb because the resulting initial pH for the small column was approximately 12, which is where the amphoteric Pb compounds become soluble.

Table 16.8
Comparison of Cumulative Release (mg/kg) at L/S=10 for Small and Large Scale Laboratory Column Tests

Element	Lab scale	Large scale		Availability
	up flow	down flow	up flow	
As	< 0.4	0.04-0.06	0.02-0.04	1.1
Ba	2.0	0.7	0.4-0.5	84
Cu	5.5	6.2	3.8	11.8
Cr	0.14	0.3-0.4	< 0.5	1.0
Mo	0.7	0.4-0.7	0.5-0.8	< 1
Ni	0.01-0.1	0.08-0.40	0.2-0.5	1.0
Pb	0.4	0.01-0.05	0.01-0.05	24
Ca	5000	2500	3200	41000
K	490	975	950	800
Na	580	990	971	1100
Cl	2040	2490	2560	2800
SO_4	3990	5470	6750	13400
pH	12.1-11.8	10.3-8.7	9.8-8.5	4

The leaching data for size-reduced and size-screened ashes are consistent with the unified pH curves permitting conversion of the extraction data to comply with the pH of the actual ash sample.

A crucial aspect of large column operation is avoidance of column effluent contact with air. Carbon dioxide uptake can result in a decreased pH in leachate samples and precipitation of elements such as Pb. This is especially a concern during collection of leachate from field lysimeters.

16.9.2 Storage and Aging

The impact of ash storage and aging on leaching can be classified as:

- Lowering of pH due to uptake of CO_2 from the air or biological activity
- Establishment of anoxic, reducing conditions including sulphide production resulting from biodegradation of residual organic matter
- Local reducing properties from evolution of hydrogen through the oxidation with water of reduced metals at high pH (e.g. Al, Zn, Pb), and
- Hydration and other changes in mineral phases, including cohesion of particles due to formation of calcite

One of the most significant changes in bottom ash leaching behaviour as a function of aging is the change in pH from moderately alkaline (pH 9.5 - 10.0) to almost neutral as a result of uptake of carbon dioxide from the air and biological activity, as well as neutralisation reactions between acidic and alkaline components in the ash. At the same time the biological activity increases as a result of biodegradation of the residual unburned organic matter. This leads generally to a depletion of oxygen and the subsequent generation of reducing conditions in the ash. Sulphate is abundant to sulphidegenic biodegradation. These reactions can proceed for long periods of time.

The presence native metals (Al, Cu, Zn, Pb) in the ash will lead to the formation of hydrogen, thus contributing to the reducing conditions is ash (Oberste-Padberg and Sweden, 1990). However, biological activity is generally considered to have the most pronounced effect on ash redox conditions.

Recently the formation of clay minerals has been demonstrated in aged ash deposits (Zevenbergen et al., 1993). The resulting increase in cation exchange capacity may have an effect on the retention capabilities of ash. However, it will not affect the release of soluble salts and certain oxy-anions (e.g. Mo, B) and may be of minor importance relative to sulphide precipitation from biological activity. The changes observed in aged ash can for the most part be explained by changes in pH, redox properties of ash or complexation reactions. Re-mineralisation reactions may result in cohesion of ash particles which has been mistaken for pozzolanic reactions similar to those which occur in coal fly ash (Trondheim, 1990). It does provide some reduction in tortuosity as observed in testing compacted bottom ash (Kosson et al., 1993). Further work in this area is needed to be able to relate changes in ash leaching properties over the long term to parameters that can be quantified in through laboratory measurements.

A comparison of release observed from fresh bottom ash and bottom ash which has been aged for 10 years is presented in Table 16.9 (Zevenbergen et al., 1993b). A batch extraction at L/S=10 with distilled water was used to evaluate release. The pH of the ash decreased to neutral over the aging interval. However, significant release did not occurred based on the similarity in the Mo release, which is an element that should be readily depleted. Significant differences are only noted for Cu and Pb, which show an order of magnitude reduction in samples which were in the field for more than 10 years in comparison with fresh bottom ash.

Table 16.9
Comparison of Batch Leaching Test Results (L/S=10 with Distilled Water) on Fresh Bottom Ash and Bottom Ash Aged for 10 Years in the Field (mg/kg)

Element	Fresh bottom	Aged bottom ash (10 yr)
As	0.18	0.032
Cd	0.069	0.001 - 0.006
Cr	0.073	0.040 - 0.059
Cu	4.6	0.50
Mo	3.49	4.56
Ni	0.13	0.15
Pb	0.43	0.006 - 0.054
Sb	0.18	0.28
Zn	0.41	0.35
pH	9.8 - 11	7 - 8

Stability of ash during laboratory storage is also an important consideration for sample analysis and archival. Table 16.10 provides a comparison of release data obtained from an ESP ash sample analysed in 1985 and again in 1992 (Versluijs et al., 1990; van der Sloot et al., 1992). The ash was stored dry, at room temperature in a sealed container. Total content and availability was measured at both times. The only significant change that occurred was a reduction in the availability of Pb. The reason for this effect is not known. The difference observed for Mo has been attributed to a modification of the availability test, which was introduced to optimise the release of oxy-anionic constituents.

The relationship between column test data obtained on the same sample of ESP ash in 1985 and 1992 are presented in Figure 16.25. The difference in initial Cd and Pb leachability is related to the initial pH, which was lower in the first percolate in 1992 (pH 11.7) in comparison with the 1985 data (pH=11.9). This effect is consistent with a decrease in pH of approximately 0.1 unit on the respective pH-solubility curves for Cd and Pb.

Figure 16.25 Bottom Ash Landfill and Lysimeter Leachate Composition for Cd, Cr, Cu, Mo, Ni, Pb and Zn Compared with the Unified pH Curve for Bottom Ash

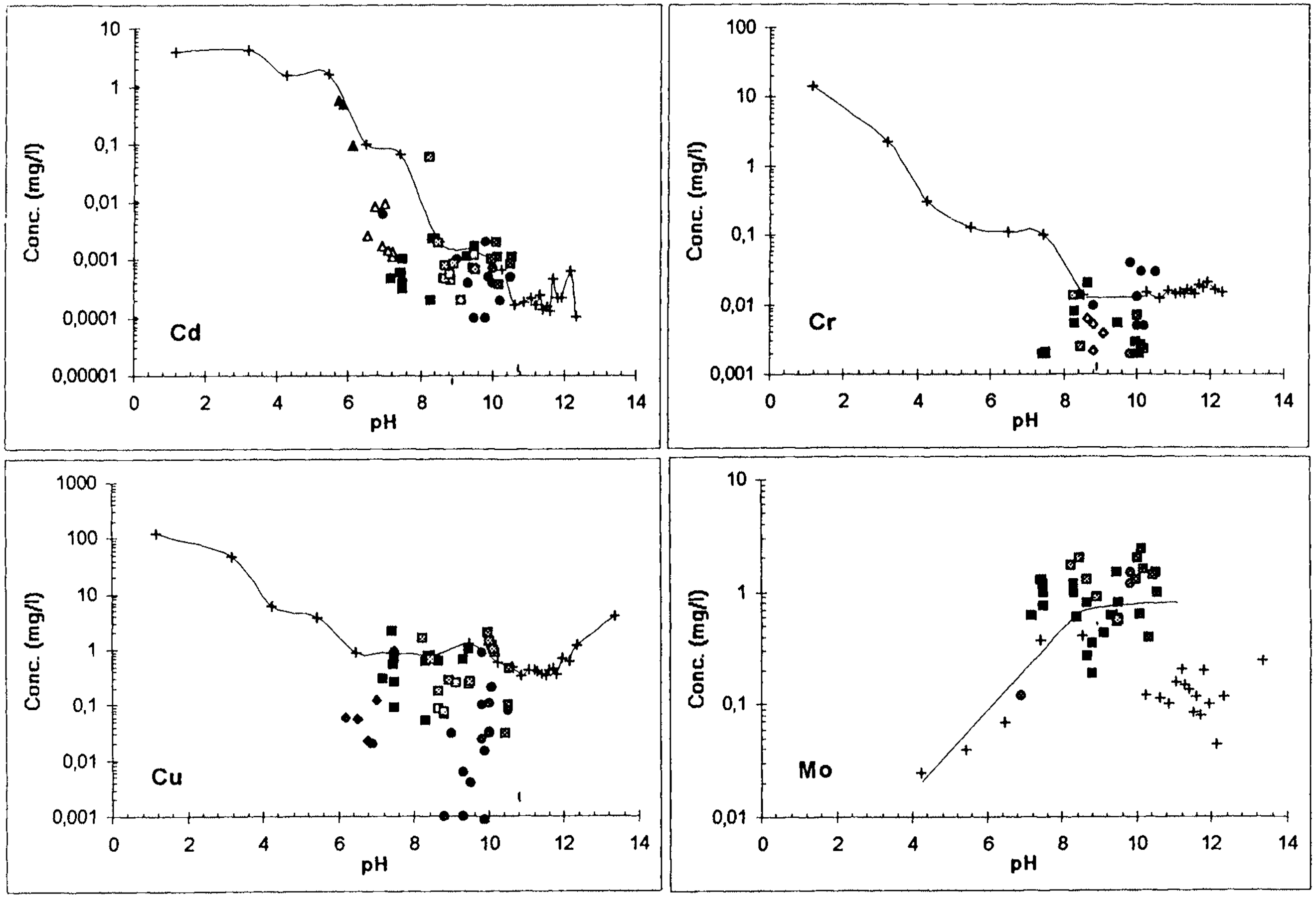


Figure 16.25 Continued

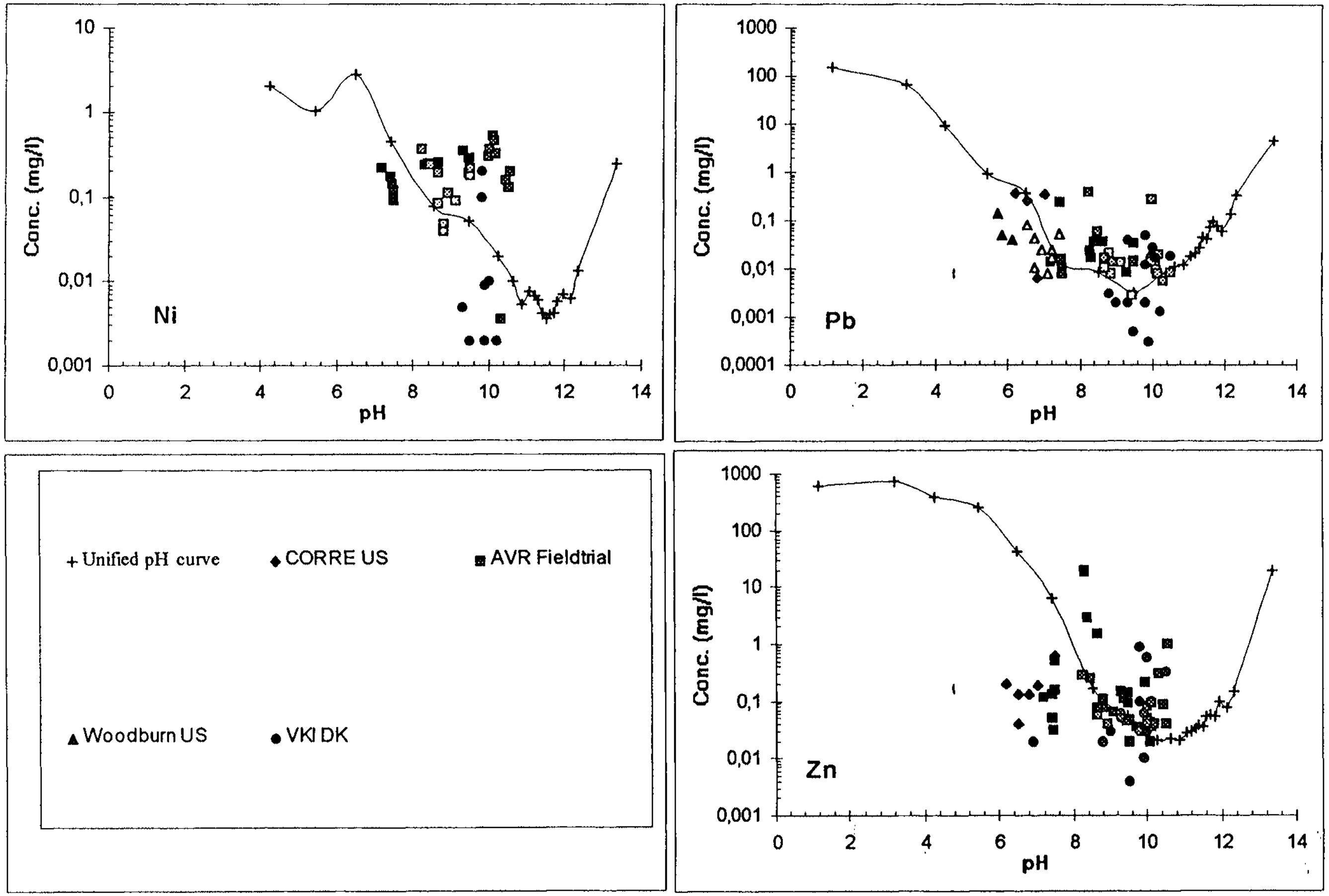


Table 16.10
Fly Ash Total Content and Availability Measured in 1985 and 1992 for the Same Sample (mg/kg)

Element	Total		Available (pH=4) Available (pH=7 and 4)	
	1985	1992	1985	1992
Ca	125353	124409	67350	82015
Cd		304	240	309
Mo	30.5	34	1.0	3.7
Zn	14864	16315	9420	10654
Pb	5936	6477	816	337
Cu	647	713	213	251

The effects of aging on scrubber residues has not been studied. It is anticipated that the major changes with time will be (i) a decrease in pH due to uptake of carbon dioxide from air and (ii) the rapid release of soluble salts. The potential for release of very large quantities of very soluble salts and the attendant potential for impact on soil and water supplies warrants careful consideration during development of APC residue management practices.

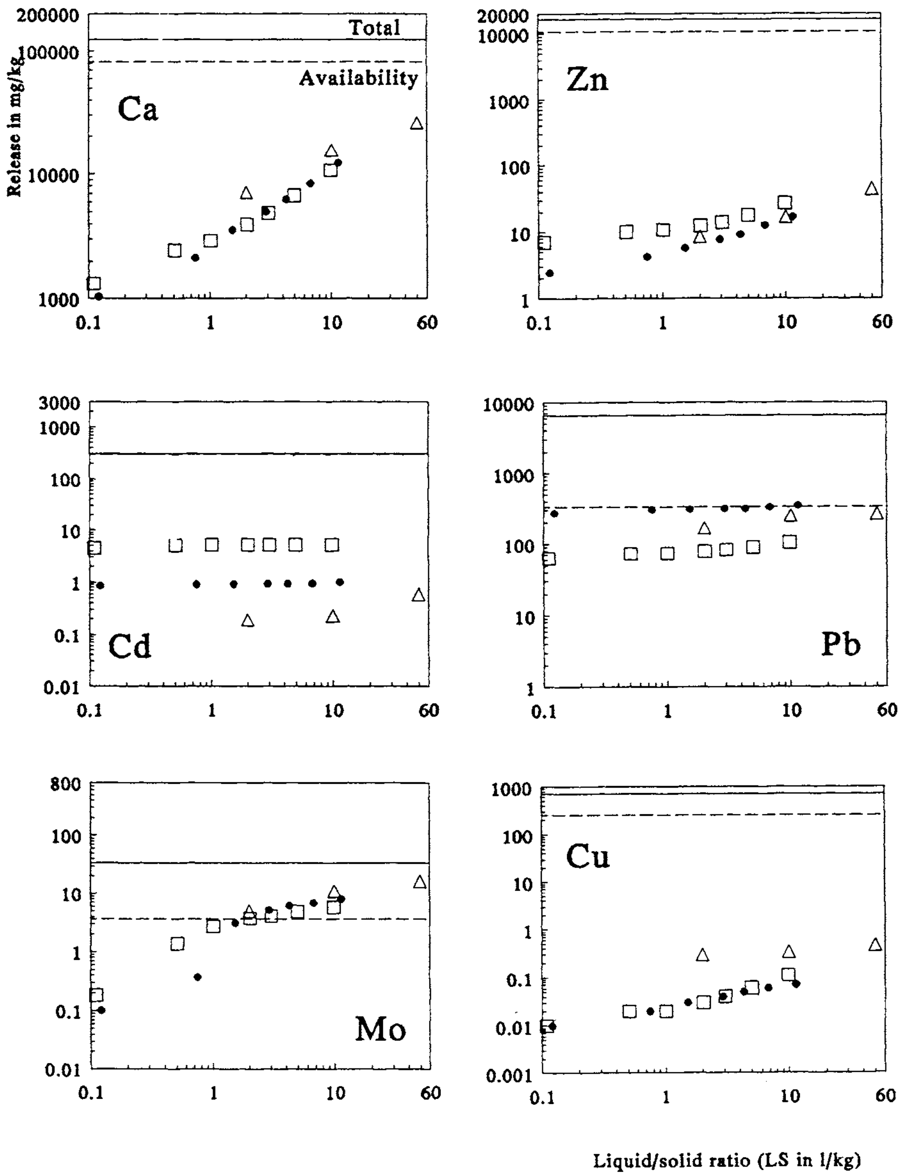
16.9.3 Comparison of Laboratory Data to Field Measurements

In Figure 16.26 a and b, the data obtained in field measurements (Cambotti and Roffman, 1993; Hjelmar, 1991, Hjelmar, 1992, 1993; van der Sloot and Hoede, 1991; Ratsma, 1991; Roffman, 1991; Ash pile project, 1992; RWS-DWW, 1992) are related to the concentrations measured in laboratory leaching tests. Data were gathered from the following studies:

Ash type	Location	Country
Bottom ash	Rotterdam	Netherlands
Bottom ash	Copenhagen	Denmark
Combined ash	Several monofills	USA
Combined ash	Woodburn, OR	USA
Bottom ash		USA
Bottom ash	HW 15	Netherlands

No field studies were available for release from APC residues only.

Figure 16.26 Reproducibility in Testing the Same Fly Ash after 7 Years and the Changes in Release Resulting from Aging



The pH range in field measurements and lysimeter studies were significantly lower (pH=7 - 10) than the pH range found in laboratory tests on fresh ash (pH = 9.5 - 12). This also suggests that translation of laboratory data to actual field conditions requires adjustment based on pH-solubility curves, when it is desired to evaluate the long term behaviour of bottom ash. The pH-solubility curve for the sample to be evaluated can be obtained through use of pH static testing or similar tests. However, pH data generated in both field and lysimeter studies should be regarded with caution, since collection tanks or drainage systems usually are not isolated from contact with air. It is possible that the alkaline pH of collected pore water is neutralised during prolonged contact with air. The concentrations measured in field leachate and lysimeter studies are in equilibrium with the measured (lower) pH, which are not representative of the condition within the ash.

The range of the concentrations measured in the field for most elements is within the range of results obtained in the laboratory. The Cu data from the field range about an order of magnitude below the lab data. This is related to Cu speciation as discussed in section 16.2.3.1 and the occurrence of reducing conditions in the field and in large scale lysimeters. The leachability of Pb deviates in some cases by an order of magnitude from the lab data. This has been attributed to the co-combustion of other waste streams with MSW. The Cr data in the field are up to an order of magnitude lower than the unified pH curve. Reducing conditions in the field may lead to reduction of chromate to trivalent chromium, which is less soluble than chromate in this pH region. With just a few exceptions (e.g. some Zn field data) the field data generally fall below the results obtained in the lab, which makes the laboratory evaluation a conservative approach.

Leachate has been analysed from below Highway 15 in The Netherlands, where bottom ash was used as a road subbase (The Netherlands, RWS-DWW,1992). Results are provided in Table 16.11. The field measurements generally agree with laboratory data. Measured concentrations of Cl were higher than laboratory observations, but was the impact of the lower L/S on very soluble species in the field. The observed release of TDS may be a concern during utilisation of bottom ash in many locations (see Chapter 22).

Field experiments also have been carried out to assess the behaviour of bottom ash in a harbour filling operation in Rotterdam (van der Sloot and Hoede, 1991; Ratsma, 1991). The experiment consisted of setting up a container (2.5 x 2.5 x 15 m) with bottom ash under each of the following conditions:

- Closed on the top to prevent rainwater infiltration
- Closed at the bottom with runoff from rainwater drained by overflow, and
- Drainage through the bottom with percolate collected separately

Table 16.11
Composition of Leachate Collected Under Highway 15 (The Netherlands) where Bottom Ash was Used as Road Base Compared to Laboratory Column Test Data

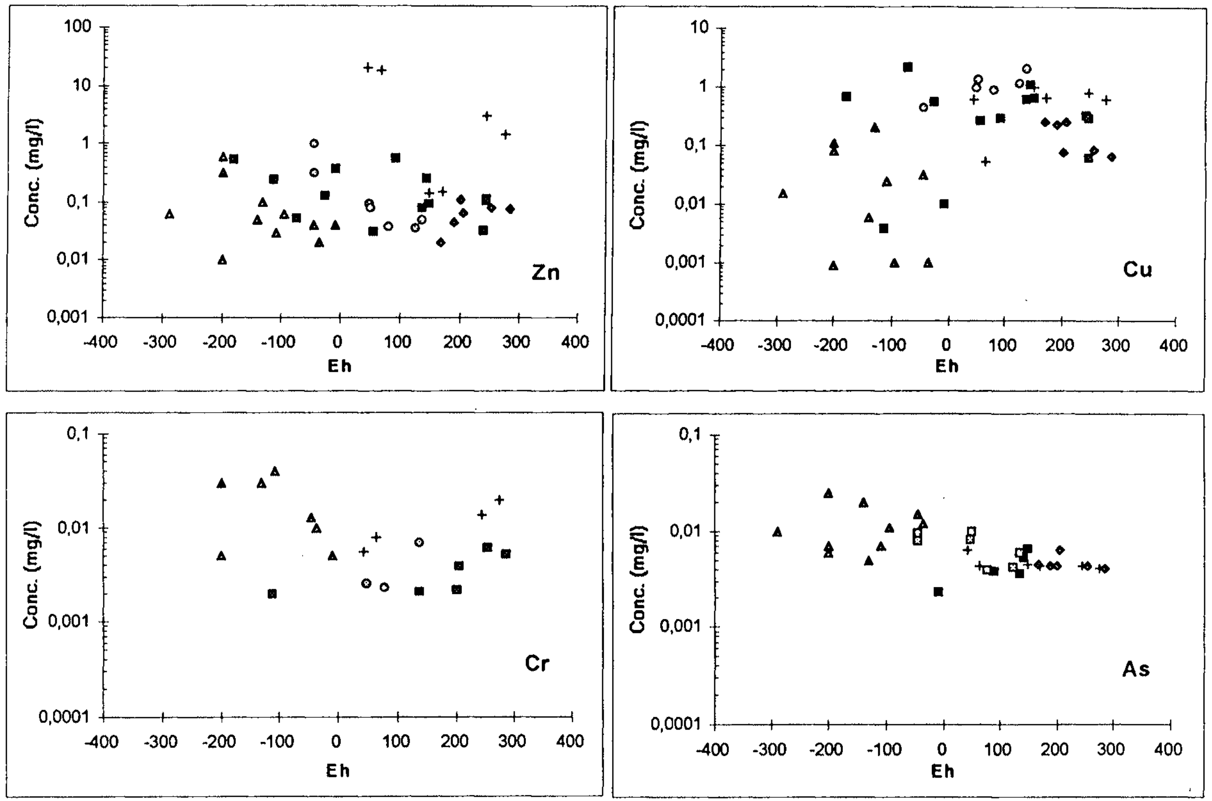
Element	Column test (L/S=0.2)	Field data (L/S ≈ 0.04)
Cl	6000	12000 - 16000
SO_4	5000	3000 - 4000
F	1	0.5 - 1
Cu	< 20	20
Mo	2000	50 - 200
As	2	5
Pb	<20	<20
Cr	<10	10
Cd	5-20	6
Ba	<100	300
Ni	390 - 500	50
Zn	120 - 75	200 - 1000
pH	9 ± 0.2	6.9 ± 0.1*

*Reported pH may have been affected by carbon dioxide uptake from air during collection.

The pore water composition within the ash layer near the top and bottom was measured over a 1.5 year interval. The dissolved species concentrations in the three containers varied only marginally between one another. However, considerable changes were noted over time. Table 16.12 provides the pore water composition for three representative periods. Changes in pore water pH were relatively small in the center of the containers. The pH values measured in collection tanks should be viewed with caution because of contact with air, which results in more neutral observed pH.

Measured Cd concentrations were low due to the high pH. The high dissolved concentrations of Cu and Ni are noteworthy. Figure 16.27 presents the observed concentrations of As, Cu, Cr and Zn as a function of redox potential. Cu was the only element for which a significant difference in concentration was noted in response to changes in the redox potential. The field results for Cu were consistent with laboratory results which indicated a reduction in Cu release when the redox potential decreases to less than -100 mV (Comans, 1993). A significant difference between the top and bottom concentrations was observed for Cl, sulphate, Ni and Mo indicating the washout of soluble components with progressive percolation.

Figure 16.27 Concentration of As, Cu, Cr and Zn as a Function of the Redox Potential in Pore Water Samples from Bottom Ash Field Studies



AVR, Rotterdam

Table 16.12
Pore Water Composition in Bottom Ash as a Function of Time in the Field

Element	Unit	t=0	t=150d	t=300d**	t=400d
As	µg/l	6	8	8	5
SO_4	mg/l	1500	4800	6700	3500
Cd	µg/l	1	2	0.1	0.2
Cl	mg/l	4500	5000 (3800)*	5500 (3500)*	5500 (3400)*
Cr	µg/l	5	<1	<1	<1
Cu	µg/l	300	1000	10	60
Mo	µg/l	900	1800	900	1400
Ni	µg/l	180	240	4	150
Pb	µg/l	20	200	6	3
Sb	µg/l	18	4	<2	<2
Zn	µg/l	150	120	220	70
pH***		9.3	9-10	9-10	9-9.7
Eh	mV	150	120	-100 to -300	-100 to -200

* Container with percolation (Cl wash-out)
** Sharp decrease in redox potential
*** In percolate and over flow water pH=7.2 (carbonate uptake from the air)

The concentrations of specific elements or species of interest in leachate from field sampling and lysimeter studies have been shown to equal to or less than the unified pH curve based on laboratory leaching tests. This indicates that the solubility controlling phases in the field are not significantly different from those in the laboratory. Cumulative release of specific elements under field conditions can be estimated based on knowledge of the unified pH curve, availability, anticipated pH in the field and the anticipated liquid to solid ratio in the field. These estimates can be refined further if the extent and effects of reducing conditions in the field are known.

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