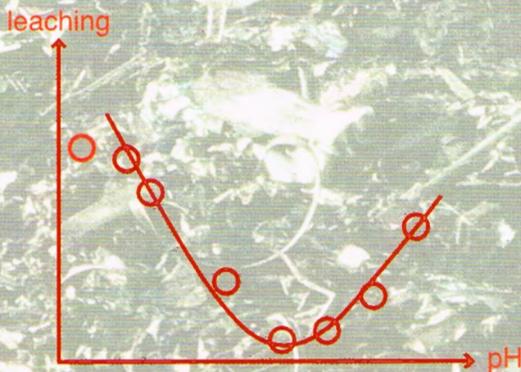


# GEOCHEMICAL MODELLING AND IDENTIFICATION OF LEACHING PROCESSES IN MSWI BOTTOM ASH

Implications for the short-term and long-term release of contaminants

JEANNET A. MEIMA



**GEOCHEMICAL MODELLING AND IDENTIFICATION  
OF LEACHING PROCESSES IN MSWI BOTTOM ASH;**

**IMPLICATIONS FOR THE SHORT-TERM AND LONG-TERM  
RELEASE OF CONTAMINANTS.**

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OF LEACHING PROCESSES IN MSWI BOTTOM ASH;**

**Implications for the short-term and long-term  
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**GEOCHEMISCHE MODELLERING EN IDENTIFICATIE VAN  
UITLOOGPROCESSEN IN BODEMAS;**

Implicaties voor de uitloging van contaminanten  
op de korte en de lange termijn

(met een samenvatting in het Nederlands)

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door

Jeannette Annemarie Meima  
geboren op 29 augustus 1968 te Wezep

Promotor: Prof. Dr. R.D. Schuiling

Universiteit Utrecht

Co-promotor: Dr. R.N.J. Comans

Energieonderzoek Centrum Nederland (ECN)

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# **Chapter 1**

## **Introduction and Overview**

## INTRODUCTION AND OVERVIEW\*

### INTRODUCTION

Municipal Solid Waste Incinerator (MSWI) bottom ash is the major residue that remains after the incineration of Municipal Solid Waste. This slag-like material is produced world-wide in very large and ever-increasing quantities. In the Netherlands, for example, 800 kton a year is produced (BORN AND VEELENTURF, 1997). The incineration of Municipal Solid Waste is economically attractive because the original volume of the waste is strongly reduced (by 90%), energy is recovered, and the resulting bottom ash may be used as a construction material (CHANDLER *et al.*, 1997; BORN AND VEELENTURF, 1997). However, incineration also concentrates the mineral components of the original waste, resulting in solid residues that are enriched in potentially harmful elements relative to soils and sediments (KIRBY AND RIMSTIDT, 1993). To ensure an environmentally safe utilisation or disposal of MSWI bottom ash it is, therefore, necessary to investigate its leaching properties. It is in particular necessary to identify the mechanisms that control leaching, because only then reliable predictions can be made for the long-term leaching of the elements of environmental concern. A very important aspect in long-term leaching is weathering, because the pH of fresh MSWI bottom ash is alkaline and the material consists primarily of meta-stable minerals that decompose during weathering (ZEVENBERGEN AND COMANS, 1994; ZEVENBERGEN *et al.*, 1994b,1996).

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\* Partly Published as: Meima J.A. and Comans R.N.J. (1997) Overview of geochemical processes controlling leaching characteristics of MSWI bottom ash. In: Proceedings of the WASCON conference, Houthem St Gerlach, The Netherlands.

## Chapter 1

This thesis focuses on the geochemical processes that control the short-term and long-term leaching of major and minor elements from MSWI bottom ash. Major elements control important variables such as pH,  $E_H$ , ionic strength, and the availability of sorptive substrates, and therefore, need to be studied before the leaching of minor elements can be understood. The results presented in the **Chapters 2-6** are based on carefully controlled laboratory leaching experiments on MSWI bottom ash at different stages of weathering, spectroscopic analyses of bottom ash samples, and geochemical modelling of aqueous complexation, precipitation/dissolution, and sorption processes. The effects of weathering on the leaching of major and minor elements from MSWI bottom ash are investigated in the **Chapters 2-4**. **Chapter 5 and 6** further investigate the role of two potentially very important processes: the sorption of contaminants to neoformed minerals in weathered bottom ash (**Chapter 5**), and the complexation of Cu with dissolved organic carbon in leachates from fresh and weathered bottom ash (**Chapter 6**). In the final Chapter, **Chapter 7**, samples were taken from a 20-year old disposal of MSWI residues and it was investigated whether the partitioning of elements between pore water and solid phase can be described by similar processes as identified in the previous Chapters on the basis of carefully controlled laboratory leaching experiments.

The present **Chapter** gives an overview of proposed geochemical processes controlling element leaching from MSWI bottom ash at different stages of weathering, including the findings of this thesis. Although we focus on MSWI bottom ash only, the geochemical processes discussed will contribute to a more general understanding of the behaviour of combustion residues or alkaline materials in the environment.

### **MSWI BOTTOM ASH**

Municipal Solid Waste Incinerators usually operate at temperatures averaging from 850-1000°C, depending on furnace-design and on the caloric value of the waste (THEIS AND GARDNER, 1990). The residence time of the waste in the incinerator varies from 45 to 90 minutes.

The heavier ash residue that is collected from the combustion chamber is called bottom ash. Other waste streams are electrostatic precipitator (ESP) ash (also called fly ash), air pollution control (APC) residues, and grate siftings. The hot bottom ash is quenched in a water tank immediately after incineration. The grate siftings are usually mixed with the bottom ash, whereas in some incinerators ESP ash is also mixed with the bottom ash.

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**TABLE 1. Element concentrations generally found in MSWI bottom ash world-wide<sup>a</sup>**

concentration (ppm)	elements
<500000	Ca, Fe, O, Si
<100000	Al, C, Mg, Na
<20000	K, Pb, S
<10000	Cu, P, Ti, Zn
<5000	Ba, Cl, Cr, Ni
<2500	F, Mn, N, Sr
<500	As, B, Br, Co, Mo, Sb, Sn, V
<100	Ag, Au, Cd, Cs, Ga, Hg, I, La, Rb, Sc, Se, Y

<sup>a</sup> after CHANDLER *et al.*, 1997

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Given the variation in waste composition, furnace configuration, combustion temperature, retention time, and quenching process, the elemental composition of MSWI bottom ash from different origin is remarkably similar: bulk chemical analyses of ashes from different facilities usually fall within an order of magnitude (KIRBY AND RIMSTIDT, 1993). Table 1 gives the order of various element concentrations found in MSWI bottom ash world-wide (CHANDLER *et al.*, 1997).

MSWI bottom ash is a highly reactive material because it consists predominantly (>70%) of X-ray amorphous, glassy constituents (KIRBY AND RIMSTIDT, 1993; EIGHMY *et al.*, 1994; ZEVENBERGEN *et al.*, 1994a) and because it has a relatively high surface area due to internal porosity

## Chapter 1

(THEIS AND GARDNER, 1990, 1992; CHANDLER *et al.*, 1997). The high glass-content results from the rapid cooling (quenching) of the hot, partly molten material. Petrographic analysis has led to the following classification scheme of intact bottom ash particles (EIGHMY *et al.*, 1994; EUSDEN *et al.*, 1994):

1. non-combusted materials (15-45%)
  - e.g. waste glass, soil minerals (pyroxenes, quartz, and feldspars), metals, metal alloys, and organics
2. melt products (55-85%)
  - glasses (isotropic silicate glass, schlieren, and opaque metallic glass)
  - crystalline complex silicate minerals  
e.g. melilite group minerals which are rich in Fe and Ca and depleted in Al, and scapolite-like minerals which are rich in Ca and Na and depleted in Fe
  - crystalline complex oxide minerals  
e.g. lime, iron oxides, and spinel-group minerals

The sequence of reactions during incineration has been compared to a melt of melilite-bearing igneous rock which can be described by a CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-Na<sub>2</sub>O-FeO system (EIGHMY *et al.*, 1994). Equilibrium, however, is not obtained, which is illustrated by residual organics in the bottom ash (Table 1) and by the occurrence of thermodynamically incompatible phases in the bottom ash (e.g. quartz and melilite (EIGHMY *et al.*, 1994; EUSDEN *et al.*, 1994)). A detailed overview of minerals and species identified in MSWI bottom ash is given in Table 2.

Constituents of environmental concern in MSWI bottom ash are heavy metals (e.g. copper), oxyanions (e.g. molybdenum and antimony), and soluble salts (e.g. sulphate and chloride) (see Table 1).

## **WEATHERING**

As shown above, MSWI bottom ash consists primarily of meta-stable solids. Upon weathering these solids transform into naturally occurring secondary minerals. Weathering has been shown to strongly affect the leaching of major and minor elements from MSWI bottom ash (ZEVENBERGEN AND COMANS, 1994; **Chapters 2,3,4,7**). In general, weathering reactions in MSWI bottom ash have been shown to be similar to those observed in alkaline soils and volcanic ashes (JANSSEN-JURKOVICOVA AND SCHUILING, 1991; KIRBY, 1993; ZEVENBERGEN AND COMANS, 1994) and basalts (Kirby, 1993).

In **Chapter 2** it is shown that three major stages in weathering can be identified, each stage having a characteristic pH that is controlled largely by Ca minerals and  $p\text{CO}_2$ . Important characteristics of the three weathering stages are discussed below.

### *(A) Unweathered bottom ash, with pH >12*

Stage-A represents the initial alteration processes which take place when the dry bottom ash first contacts water, which is in the quench tank. Reactions include the hydrolysis of the oxides of Ca, Al, Na, and K, and the dissolution/reprecipitation of hydroxides and salts of these main cations (BELEVI *et al.*, 1992; COMANS AND MEIMA, 1994; **Chapter 2**). The resulting bottom ash pH is strongly alkaline (12.4) and controlled by the solubility of portlandite ( $\text{Ca}(\text{OH})_2$ ) (**Chapter 2**).

### *(B) Quenched/non-carbonated bottom ash, with pH10-11.5*

In stage B bottom ash pH may decrease to 10-10.5 by the precipitation of ettringite ( $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$ ), gibbsite ( $\text{Al}(\text{OH})_3$ ), and gypsum ( $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ ) (COMANS AND MEIMA, 1994; **Chapter 2**). When the three minerals coexist, no degrees of freedom are left and pH is fixed at pH 10. Due to continuing hydrolysis secondary minerals such as amorphous Fe/Al-(hydr)oxides, hydrous aluminosilicates, and possibly zeolites begin to precipitate (KIRBY, 1993; ZEVENBERGEN AND COMANS, 1994; **Chapter 2**). If the precipitation of these hydrous aluminosilicates results in a lower Al-leaching as compared to equilibrium with gibbsite, the equilibrium pH of the bottom

ash may increase to 10.5-11.5 (**Chapter 7**). Soluble salts will be leached rapidly with percolating water (e.g. BELEVI *et al.*, 1992; THEIS AND GARDNER, 1992; KIRBY, 1993; ZEVENBERGEN AND COMANS, 1994; **Chapter 2,7**). Biodegradation of residual organic matter and dissolution of reduced mineral phases may create a reducing environment (HJELMAR, 1989; ZEVENBERGEN AND COMANS, 1994; CHANDLER *et al.*, 1997; **Chapter 2,7**).

*(C) Carbonated bottom ash, with pH8-8.5*

In stage C bottom ash pH has further decreased to equilibrium values of 8-8.5 by absorption of CO<sub>2</sub> and subsequent precipitation of calcite (CaCO<sub>3</sub>) (e.g. ZEVENBERGEN AND COMANS, 1994; **Chapter 2,4,7**). The CO<sub>2</sub> required for this carbonation may infiltrate from the atmosphere or come from biodegradation of organic residues (BELEVI *et al.*, 1992; ZEVENBERGEN AND COMANS, 1994; JOHNSON *et al.*, 1995). The neoformation of Fe/Al-(hydr)oxides and hydrous aluminosilicates continues. Similar to the weathering of volcanic ashes, these hydrous aluminosilicates are an intermediate reaction product in the transformation of glasses to clay-minerals (ZEVENBERGEN *et al.*, 1996). The 2:1 clay mineral illite has been found to be a final product of glass weathering in MSWI bottom ash (ZEVENBERGEN *et al.*, 1996).

Weathering has been shown to have a significant effect on the leaching of minor elements from MSWI bottom ash (**Chapter 3,4,7**). The leaching of Cd, Pb, Cu, Zn, and Mo from C-type bottom ash, for example, is generally significantly lower than from more fresh bottom ash (**Chapter 3,4**). A potentially important mechanism is the sorption of minor elements to neoformed (amorphous) Fe/Al-minerals (ZEVENBERGEN *et al.*, 1994b; **Chapter 3,4,5,7**). Furthermore, the neutralisation of bottom ash pH from >10 to 8-8.5 and the formation of less soluble secondary minerals of minor elements will also contribute to reduce leaching (**Chapter 3**). Lower leaching of heavy metals and oxyanions from weathered bottom ash is not necessarily the primary result of a prior release of these elements from the residues during storage (STEGEMANN *et al.*, 1995; **Chapter 3,7**).

## LEACHING

The rate at which an element is leached from the bottom ash is dependent on its abundance in the bottom ash, its availability to the solution, the dissolution kinetics of the primary solids containing the element, whether or not the element will reprecipitate as a secondary solid or will sorb to solid substrates, and the kinetics of these precipitation/sorption reactions (KIRBY AND RIMSTIDT, 1994). KIRBY AND RIMSTIDT (1994) have identified 3 basic types of solution behaviour during batch leaching of MSWI bottom ash:

### *1. Availability*

Availability means that there is a lack of concentration-change due to exhaustion of a phase. This type of behaviour is usually observed for soluble salts, such as Na, K, and Cl (KIRBY AND RIMSTIDT, 1994; ZEVENBERGEN AND COMANS, 1994; **Chapter 2**; CHANDLER *et al.*, 1997). Furthermore, molybdenum may show this type of behaviour at strongly alkaline pH (**Chapter 2**; CHANDLER *et al.*, 1997). In general, the higher the Liquid to Solid (*L/S*) ratio, the more elements will show this type of behaviour.

### *2. Kinetic*

Kinetic means that the rate of mass transfer from the solid to the liquid phase or v.v. is the concentration-limiting step. The contact time between the solid and the liquid phase usually determines whether kinetics are important or not. In general, two steps can be observed in element leaching from bottom ash: a fast release of the element, which is generally completed within 24 h, followed by a slow release or re-binding which may continue for more than 1 week (COMANS *et al.*, 1993a) KIRBY AND RIMSTIDT, 1994; ZEVENBERGEN AND COMANS, 1994; **Chapter 4**). The leaching of silicon, for example, is strongly influenced by slow dissolution/precipitation kinetics of silicate-minerals (KIRBY AND RIMSTIDT, 1994; ZEVENBERGEN AND COMANS, 1994; **Chapter 4**). Furthermore, the slow transformation of the primary high-temperature solids into stable secondary solids has been shown to affect the leaching of several other elements as well (**Chapter 2**; **Chapter 3**). Little is

**TABLE 2. Overview of geochemical processes that have been reported to control the leaching of major and minor elements from MSWI bottom ash at different stages of weathering, and minerals/species identified in the matrix by spectroscopic techniques.**

<b>Unweathered (A-type) bottom ash, pH &gt; 12</b>		
<b>element</b>	<b>controlling mechanism</b>	<b>identified species</b>
<b>Ca, SO<sub>4</sub>, CO<sub>3</sub></b>	solubility-control by portlandite <sup>P</sup> and gypsum <sup>P</sup>	anhydrite <sup>l, P</sup> , calcite <sup>l, P</sup> , portlandite <sup>l</sup> , complex-(Ca)silicate <sup>l</sup>
<b>Al</b>	solubility-control by amorphous Al-silicate <sup>P</sup>	complex-silicates <sup>l</sup>
<b>Fe</b>		magnetite <sup>l, P</sup> , hematite <sup>P</sup> , pseudobrookite <sup>l</sup>
<b>Mg</b>	solubility-control by brucite <sup>P</sup>	complex-silicates <sup>l</sup>
<b>Si</b>	solubility-control by amorphous Al-silicate <sup>P</sup>	quartz <sup>l, P</sup> , glasses <sup>l</sup> , complex-silicates <sup>l, P</sup>
<b>Na, K, Cl</b>		complex-(Na/K)silicates <sup>l</sup>
<b>Mo</b>	solubility-control by powellite <sup>t</sup>	
<b>Cu</b>		metallic/alloy <sup>t</sup>
<b>Pb</b>		metallic/alloy <sup>t</sup>
<b>Zn</b>	solubility-control by zincite <sup>t</sup>	metallic/alloy <sup>t</sup>
<b>Cd</b>	solubility-control by otavite <sup>t</sup> or Cd(OH) <sub>2</sub> <sup>t</sup>	
<b>other</b>		

TABLE 2 (continued-1)

Quenched/non-carbonated (B-type) bottom ash, pH 10-11.5		
element	controlling mechanism	identified species
Ca, SO <sub>4</sub> , CO <sub>3</sub>	solubility-control by ettringite <sup>c, i, p, x</sup> and gypsum <sup>a, c, e, h, i, p, x</sup> / anhydrite <sup>f</sup> ; solubility-control by calcite <sup>a</sup>	ettringite <sup>i, j, p</sup> , anhydrite <sup>d, f, l, p</sup> , gypsum <sup>d, f, i, j, l</sup> , calcite <sup>d, f, i, j, l, p, x</sup> , CaO <sup>f, g</sup> , whitlockite <sup>f</sup> , CaHPO <sub>4</sub> <sup>f</sup> , complex-(Ca)silicates <sup>f, l</sup>
Al	solubility-control by gibbsite <sup>c, e, f, p, u</sup> , amorphous Al(OH) <sub>3</sub> <sup>h, p, u</sup> , or amorphous Al-silicate <sup>x</sup>	gibbsite <sup>f</sup> , corundum <sup>f, l</sup> , AlO <sup>f</sup> , elemental/alloy <sup>f, l</sup> , complex-silicates <sup>f, l</sup> , hercynite <sup>f</sup> , MgAl <sub>2</sub> O <sub>4</sub> <sup>f</sup> , amorphous Al-silicate <sup>i, o, x</sup>
Fe	solubility-control by ferrihydrite <sup>c, f, h, p</sup>	hematite <sup>d, f, j, l, p</sup> , wustite <sup>d, f, l</sup> , maghemite <sup>l</sup> , goethite <sup>l, x</sup> , pyrite <sup>f, l</sup> , pseudobrookite <sup>l</sup> , magnetite <sup>f, g, i, j, l, p, x</sup> , ulvospinel <sup>f, l</sup> , hercynite <sup>f</sup> , jacobsite <sup>l</sup> , chromite <sup>f, l</sup>
Mg	solubility-control by brucite <sup>c, p, x</sup> or magnesite <sup>f</sup>	magnesite <sup>f</sup> , dolomite <sup>f</sup> , MgSO <sub>4</sub> ·2H <sub>2</sub> O <sup>f</sup> , sepiolite <sup>l</sup> , complex-silicates <sup>l</sup> , MgAl <sub>2</sub> O <sub>4</sub> <sup>f</sup>
Si	solubility-control by wairakite <sup>c</sup> , amorphous SiO <sub>2</sub> <sup>p</sup> , or amorphous Al-silicate <sup>x</sup>	quartz & complex silicates <sup>d, f, i, j, l, p, x</sup> , amorphous Al-silicate <sup>l, o, x</sup> , glasses <sup>d, f, g, i</sup>
Na, K, Cl		halite <sup>d</sup> , sylvite <sup>d</sup> , complex-(Na/K)silicates <sup>f, l</sup>
Mo	solubility-control by powellite <sup>c, m, t</sup>	CaMoO <sub>4</sub> <sup>l</sup>
Cu	organic complexation <sup>b, c, m, r, t, w, x</sup> and solubility-control by tenorite <sup>c, m, t, w</sup> / Cu(OH) <sub>2</sub> <sup>f</sup> or sorption-control by amorphous Al-minerals <sup>x</sup>	metallic/alloy <sup>f, l, t</sup> , CuCl <sup>f</sup> , NaCuPO <sub>4</sub> <sup>f</sup> , complex-silicate <sup>f</sup> , CuS <sup>x</sup>
Pb	solubility-control by cerussite <sup>a, m, t</sup> or Pb(OH) <sub>2</sub> <sup>a, c, x</sup> or sorption-control <sup>m</sup> , organic complexation <sup>x</sup>	complex-silicate <sup>f, h, t</sup> , PbO <sup>f</sup> , PbS <sup>x</sup>
Zn	solubility-control by zincite <sup>c, t</sup> , Zn(OH) <sub>2</sub> <sup>a</sup> , or ZnSiO <sub>3</sub> <sup>a, c, f</sup> ; sorption-control by amorphous Al-minerals <sup>x</sup>	zincite <sup>f</sup> , ZnSO <sub>4</sub> <sup>f</sup> , ZnCl <sub>2</sub> <sup>f</sup> , elemental Zn <sup>f</sup> , franklinite <sup>f</sup> , ZnS <sup>x</sup> , incorporated in amorphous Al-silicates <sup>x</sup>
Cd	solubility-control by otavite <sup>c, f, m, n, t</sup> ; sorption-control by calcite <sup>c, n</sup> or amorphous Al-silicates <sup>x</sup>	
other	possible solubility-controlling minerals for Mn, Ba, and V: MnO(OH) <sup>g</sup> ; barite <sup>f</sup> ; Pb <sub>2</sub> V <sub>2</sub> O <sub>7</sub> <sup>f</sup>	rutile <sup>d, f</sup> , barite <sup>f, t</sup> , graphitic carbon <sup>f</sup> , taenite <sup>l</sup> , (species containing Sr, Ni, Cr <sup>f</sup> , Cr-oxides <sup>l</sup> )

TABLE 2 (continued-2)

## Carbonated (C-type) bottom ash, pH 8-8.5

element	controlling mechanism	identified species
Ca, SO <sub>4</sub> , CO <sub>3</sub>	solubility-control by calcite <sup>i, p</sup> and gypsum <sup>p, x</sup>	anhydrite <sup>p</sup> , gypsum <sup>i</sup> , calcite <sup>i, p, u, x</sup>
Al	solubility-control by gibbsite <sup>p, x</sup> or amorphous Al(OH) <sub>3</sub> <sup>u, x</sup>	amorphous Al-silicate <sup>i, k, o, x</sup> , amorphous Al(OH) <sub>3</sub> <sup>u</sup>
Fe	solubility-control by ferrihydrite <sup>p</sup>	magnetite <sup>i, p, x</sup> , hematite <sup>i, p</sup> , wustite <sup>t</sup> , maghemite <sup>t</sup> , iron oxide <sup>t</sup> , goethite <sup>x</sup> , lepidocrocite <sup>x</sup>
Mg	solubility-control by Mg-calcite <sup>p, x</sup> , sepiolite <sup>p</sup> , or dolomite <sup>i</sup>	
Si	solubility-control by illite <sup>p</sup> or amorphous SiO <sub>2</sub> <sup>p</sup>	amorphous Al-silicate <sup>i, k, o, x</sup> , illite <sup>o</sup> , quartz & complex-silicate <sup>i, p, x</sup>
Na, K, Cl		
Mo	sorption-control by ferrihydrite <sup>v</sup> or amorphous Al-minerals <sup>x</sup>	CaMoO <sub>4</sub> <sup>k</sup> , Pb/Mo-rich particle <sup>k</sup>
Cu	organic complexation <sup>w, x</sup> and sorption-control by amorphous Al-minerals <sup>u, v, w, x</sup>	Cu/O-phases (e.g. cuprite, tenorite) <sup>t, x</sup> , metallic/alloy <sup>t</sup> , complex-silicate <sup>t</sup> , Cu/Ca/O-, Cu/Fe/O-, Cu/Al/O-, Cu/Al/O/S/Ca-, Cu/S-phases <sup>t</sup> ; sorbed to neoformed clays <sup>k, x</sup>
Pb	sorption-control <sup>t, v</sup> or solubility-control by chloropyromorphite <sup>t</sup> or cerussite <sup>x</sup>	metallic/alloy <sup>t</sup> , complex-silicate <sup>t</sup> , Pb/O-, Pb/Ca/O-, Pb/Fe/O-, and Pb/Al/O- phases <sup>t</sup> ; sorbed to neoformed clays <sup>k, x</sup>
Zn	solubility-control by zincite <sup>t</sup> ; sorption-control by amorphous Al-minerals <sup>x</sup> ; surface precipitation with Fe(OH) <sub>3</sub> <sup>v</sup>	Zn/O-phases (e.g. zincite <sup>t</sup> ), metallic/alloy <sup>t</sup> , complex-silicate <sup>t</sup> , Zn/Ca/O-, Zn/Fe/O-, Zn/Al/O-, Zn/Al/O/S-phases <sup>t</sup> , sorbed to neoformed clays <sup>k</sup> , incorporated in amorphous Al-silicates <sup>t</sup>
Cd	sorption-control <sup>t, v</sup> ; sorption-control by amorphous Al-minerals <sup>x</sup>	
other	sorption-control of Sb by amorphous Al-minerals <sup>s, x</sup>	Ni sorbed to neoformed clays <sup>k</sup>

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**TABLE 2 (continued-3)**

**list of references**

(a) THEIS AND GARDNER, 1992; (b) VAN DER SLOOT *et al.*, 1992; (c) COMANS *et al.*, 1993b; (d) KIRBY AND RIMSTIDT, 1993; (e) COMANS AND MEIMA, 1994; (f) EIGHMY *et al.*, 1994; (g) EUSDEN *et al.*, 1994; (h) KIRBY AND RIMSTIDT, 1994; (i) ZEVENBERGEN AND COMANS, 1994; (j) ZEVENBERGEN *et al.*, 1994a; (k) ZEVENBERGEN *et al.*, 1994b; (l) PFRANG-STOTZ AND SCHNEIDER, 1995; (m) JOHNSON *et al.*, 1996; (n) VAN DER SLOOT *et al.*, 1996; (o) ZEVENBERGEN *et al.*, 1996; (p) **Chapter 2**; (q) CHANDLER *et al.*, 1997; (r) PAVASARS *et al.*, 1997; (s) MEIMA AND COMANS, 1997; (t) **Chapter 3**; (u) **Chapter 4**; (v) **Chapter 5**; (w) **Chapter 6**; (x) **Chapter 7**.

**list of mineral formulas:**

anhydrite,  $\text{CaSO}_4$ ; barite,  $\text{BaSO}_4$ ; brucite,  $\text{Mg}(\text{OH})_2$ ; calcite,  $\text{CaCO}_3$ ; cerussite,  $\text{PbCO}_3$ ; chloropyromorphite,  $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$ ; chromite,  $\text{FeCr}_2\text{O}_4$ ; corundum,  $\text{Al}_2\text{O}_3$ ; cuprite,  $\text{Cu}_2\text{O}$ ; dolomite,  $\text{CaMg}(\text{CO}_3)_2$ ; ettringite,  $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$ ; ferrihydrite,  $\text{Fe}(\text{OH})_3$ ; franklinite,  $\text{ZnFe}_2\text{O}_4$ ; gibbsite,  $\text{Al}(\text{OH})_3$ ; goethite,  $\text{FeOOH}$ ; gypsum,  $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ ; halite,  $\text{NaCl}$ ; hematite,  $\text{Fe}_2\text{O}_3$ ; hercynite,  $\text{FeAl}_2\text{O}_4$ ; illite,  $\text{K}_{0.6}\text{Mg}_{0.25}\text{Al}_{2.3}\text{Si}_{3.5}\text{O}_{10}(\text{OH})_2$ ; iron oxide,  $\text{Fe}_2\text{O}_3$ ; jacobsonite,  $\text{MnFe}_2\text{O}_4$ ; lepidochrocite,  $\text{FeOOH}$ ; maghemite,  $\text{Fe}_2\text{O}_3$ ; magnesite,  $\text{MgCO}_3$ ; magnetite,  $\text{Fe}_3\text{O}_4$ ; otavite,  $\text{CdCO}_3$ ; portlandite,  $\text{Ca}(\text{OH})_2$ ; powellite,  $\text{CaMoO}_4$ ; pseudobrookite,  $\text{Fe}_2\text{TiO}_5$ ; pyrite,  $\text{FeS}$ ; quartz,  $\text{SiO}_2$ ; rutile,  $\text{TiO}_2$ ; sepiolite,  $\text{Mg}_2\text{Si}_3\text{O}_6(\text{OH})_4\cdot 1.5\text{H}_2\text{O}$ ; sylvite,  $\text{KCl}$ ; taenite,  $\text{Fe,Ni}$ ; tenorite,  $\text{CuO}$ ; ulvospinel,  $\text{Fe}_2\text{TiO}_4$ ; wairakite,  $\text{CaAl}_2\text{Si}_4\text{O}_{12}\cdot 2\text{H}_2\text{O}$ ; whitlockite,  $\text{Ca}_3(\text{PO}_4)_2$ ; wustite,  $\text{FeO}$ ; zincite,  $\text{ZnO}$ .

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known, however, about the kinetics of these weathering reactions. Alternatively, a slow release may also be the result of diffusion processes, which are believed to become important when the residues are monolithic in form (e.g. incorporated into asphalt pavement), when they are compacted to low permeability, or when they are overlain by an impermeable barrier (KOSSON *et al.*, 1996; CHANDLER *et al.*, 1997).

### 3. Equilibrium

Equilibrium means that the concentration of an element is controlled by a dissolution/precipitation equilibrium or by a sorption equilibrium. Various elements experience retention in the bottom ash matrix by these processes. Table 2 gives an overview of the proposed controlling-mechanisms for MSWI bottom ash at different stages of weathering. Below, we review underlying geochemical processes, such as aqueous complexation, dissolution/precipitation, sorption and redox reactions, which control element leaching from MSWI bottom ash.

## GEOCHEMICAL PROCESSES CONTROLLING LEACHING

### *Complexation processes*

Hydrolysis and complexation with carbonate are the dominant inorganic complexation reactions in bottom ash leachates. These reactions cause, for example, the solubility-curves of amphoteric elements such as Fe, Al, Zn, Cu, and Pb to follow V-shaped patterns as a function of pH (STUMM AND MORGAN, 1981). As a result, pH is a dominant controlling parameter in element leaching from (waste) materials, which is in correspondence with experimental data (e.g. VAN DER SLOOT *et al.*, 1989; DIPIETRO *et al.*, 1989; BELEVI *et al.*, 1992; COMANS *et al.*, 1993b; VAN DER SLOOT *et al.*, 1996; **Chapter 2,3**). Other potentially important inorganic complexes include Cd-Cl complexes, which may become significant in leachates from fresh MSWI bottom ash (VAN DER SLOOT *et al.*, 1996).

MSWI bottom ash releases substantial amounts of dissolved organic carbon (DOC) originating from incomplete combustion of the original waste and/or subsequent biodegradation processes (Belevi *et al.*,

1992; **Chapter 2**; PAVASARS *et al.*, 1997). Copper, which is known to have a very high affinity for organic material (BUFFLE, 1988; BENEDETTI *et al.*, 1996), has been shown to be bound for 95-100% to DOC in leachates of both fresh and 1.5-year old MSWI bottom ash (**Chapter 6**). The conditional stability constants of these Cu-DOC complexes have been determined using a competitive ligand exchange / solvent extraction technique (**Chapter 6**).

#### *Precipitation/dissolution processes*

Precipitation/dissolution processes control bottom ash pH (see above) and the leaching of in particular major elements from MSWI bottom ash (Table 2). In the case of major elements, solubility-controlling minerals indicated by geochemical modelling generally correspond to minerals detected by spectroscopic analyses of the bottom ash (Table 2). Precipitation/dissolution processes may also control the leaching of minor elements from A- and B-type bottom ash. Proposed controlling processes for minor element leaching, however, are often indicated by geochemical modelling only (Table 2) because low bulk concentrations hamper the detection of minor/trace element species by means of spectroscopic techniques (KIRBY AND RIMSTIDT, 1993; **Chapter 3**). A step-wise approach for the geochemical modelling of element-concentrations in equilibrium with potential solubility-controlling minerals is given in **Chapter 2**.

#### *Sorption processes*

Sorption is a general term which refers to all processes, except the precipitation/dissolution of pure mineral phases, which remove a chemical species from the aqueous solution to a solid phase. Sorption processes are expected to be important when suspensions at equilibrium are undersaturated with respect to known solubility-controlling minerals. Potential sorbent minerals in MSWI bottom ash are amorphous or crystalline Fe- and Al-(hydr)oxides, hydrous aluminosilicates, and calcite (ZEVENBERGEN *et al.*, 1994b; **Chapter 4,5,7**).

Recent studies have shown that surface complexation reactions can successfully describe the leaching of minor elements from combustion residues, such as MSWI bottom ash and coal fly ash (THEIS AND

RICHTER, 1979; DZOMBAK AND MOREL, 1992; KERSTEN *et al.*, 1995; VAN DER HOEK AND COMANS, 1996; **Chapter 5,6,7**). In particular amorphous Al-minerals are believed to be very important in the retention of minor elements (ZEVENBERGEN *et al.*, 1994b; **Chapter 5,7**). In a 20-year old disposal of MSWI residues, for example, neoformed amorphous aluminosilicates were found to be significantly enriched in Zn (**Chapter 7**), and in a 12-year old disposal of MSWI bottom ash traces of Zn, Cu, Pb, and Ni were found to be incorporated in amorphous aluminosilicates.

A step-wise approach for the modelling of surface complexation or surface precipitation processes in heterogeneous systems such as MSWI bottom ash is described in **Chapter 5**. This approach is based on (1) the database of surface complexation and surface precipitation reactions and associated equilibrium constants for sorption of ions on Hydrous Ferric Oxide (DZOMBAK AND MOREL, 1990), (2) 'selective' chemical extractions to obtain the available sorbent mineral concentrations, and (3) leaching of the bottom ash at pH-values unfavourable for sorption to obtain the available concentrations of minor elements.

The identification and modelling of sorption processes in heterogeneous solid systems such as MSWI bottom ash is, however, at its beginning. Because of the potential importance of sorption, these processes deserve considerably more attention in future research.

### *Redox processes*

In fresh MSWI bottom ash the prevailing redox conditions are oxidising (THEIS AND GARDNER, 1992; **Chapter 2**). During disposal or utilisation of the bottom ash, however, the redox potential may decrease strongly by biodegradation of residual organic matter and/or by the presence of reduced mineral phases (ZEVENBERGEN AND COMANS, 1994; CHANDLER *et al.*, 1997). Relatively low redox potentials were recorded, for example, in percolate and pore waters from landfilled combined MSWI bottom and fly ash (HJELMAR, 1989; **Chapter 7**) and in a 6-week old storage of fresh MSWI bottom ash (**Chapter 2**). Variations in bottom ash  $E_H$  may affect metal mobilities by:

- directly changing the oxidation states of redox sensitive elements to more soluble/insoluble species. The leaching of Cu (DIPIETRO *et al.*, 1989; FÄLLMAN AND HARTLÉN, 1994; VAN DER SLOOT *et al.*, 1994;

CHANDLER *et al.*, 1997), Cr (FÄLLMAN and HARTLÉN, 1994; CHANDLER *et al.*, 1997), and As and V (FÄLLMAN AND HARTLÉN, 1994), for example, has been shown to increase toward more oxidising conditions, whereas the leaching of Fe was decreased (DiPietro *et al.*, 1989; FÄLLMAN AND HARTLÉN, 1994; **Chapter 2**).

- changing the amount of redox sensitive metal surfaces (Fe/Mn-(hydr)oxides) available for sorption (DiPIETRO *et al.*, 1989); formation of an iron pan at the interface between oxidising and reducing conditions (ZEVENBERGEN *et al.*, 1994b; **Chapter 7**).
- changing the degree of (co)-precipitation or complexation with other redox sensitive cations and anions, e.g. precipitation of heavy metal sulphides (DiPIETRO *et al.*, 1989; HJELMAR, 1989; FÄLLMAN AND HARTLÉN, 1994; CHANDLER *et al.*, 1997; **Chapter 7**).

The cited studies show that the influence of  $E_H$  on metal solubilities in MSWI bottom can be significant and that further research on this topic is required.

## **CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH**

In the past few years important progress has been made in our understanding of the geochemical processes that control the leaching of major and minor elements from MSWI bottom ash. In general, precipitation/dissolution processes were found to control the leaching of the major elements. The leaching of minor elements from relatively *unweathered* residues is thought to be controlled by the precipitation/dissolution of relatively soluble minerals, and in case of more *weathered* residues by sorption processes. Furthermore, it has been shown that organic complexation may strongly enhance the leaching of in particular Cu from fresh and weathered MSWI bottom ash.

Weathering has been shown to strongly affect the leaching of major and minor elements from the bottom ash. The pH of fresh MSWI bottom ash is alkaline and the material consists primarily of meta-stable minerals that decompose during weathering. The most important weathering processes include: (1) Carbonation, which involves the

neutralisation of the alkaline bottom ash. The pH has been shown to be a very important controlling parameter in element leaching because it affects, for example, the speciation of dissolved components and the surface speciation of mineral particles; (2) Formation of more stable minerals, resulting in lower leaching and a higher sorptive capacity of the material; (3) Sorption of minor elements to neoformed minerals. In particular the amorphous Al-minerals are believed to be potentially very important in the retention of heavy metals and oxyanions.

The results imply that the concentrations of salts, heavy metals, and oxyanions in leachates are likely to be greatest in the earliest stages of disposal: the most soluble phases dissolve rapidly, while the capacity of secondary minerals to bind heavy metals and oxyanions may not be large enough. In addition, the presence of dissolved organic carbon may significantly enhance the leaching of Cu. For heavy metals and oxyanions these problems may be overcome by neutralising the pH of the bottom ash and by adding sorbent minerals to the bottom ash (COMANS *et al.*, 1997). On the long term, the leaching of heavy metals and oxyanions from well-burned bottom ash is likely to be reduced in a natural way by the neutralisation of bottom ash pH, by sorption to neoformed minerals, and by biodegradation of organic ligands.

Because of the potential importance of sorption processes and organic complexation processes, the identification/modelling of these processes in particular deserve more attention in future research. Important subjects of research also include the kinetics of weathering/sorption reactions, i.e. the period of time that is required to obtain sufficient reduction in leaching, and the fate of DOC during weathering. Furthermore, there is a great challenge in combining knowledge of geochemical (speciation) processes with knowledge of physical (transport) processes.

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## **Chapter 2**

### **Geochemical modelling of weathering reactions in MSWI bottom ash.**

# GEOCHEMICAL MODELLING OF WEATHERING REACTIONS IN MUNICIPAL SOLID WASTE INCINERATOR BOTTOM ASH\*

Jeannet A. Meima and Rob N.J. Comans

Netherlands Energy Research Foundation (ECN)  
Westerduinweg 3 1755 LE Petten, The Netherlands

## ABSTRACT

The leaching of Municipal Solid Waste Incinerator (MSWI) bottom ash has been studied at different stages of natural weathering. Bottom ash samples, originating from a single incinerator, included grate siftings, unquenched, quenched, 6-week old, 1.5-year old and 12-year old bottom ash. Leaching experiments were performed at various pH levels and liquid/solid ratios. The speciation code MINTEQA2 was used to evaluate whether the leachates are in equilibrium with minerals that are expected to form in MSWI bottom ash environments. Three major stages in weathering are identified, each stage having a characteristic pH which is controlled largely by Ca-minerals and  $p\text{CO}_2$ , but also by soluble Al and  $\text{SO}_4$ : (1) unweathered bottom ash, with  $\text{pH} > 12$  (grate siftings and unquenched samples); (2) quenched/non-carbonated bottom ash, with  $\text{pH} 10\text{-}10.5$  (freshly quenched and 6-week old samples); and (3) carbonated bottom ash with  $\text{pH} 8\text{-}8.5$  (1.5- and 12-year old samples). A comparison of the leaching mechanisms identified for these stages of weathering reveals major differences for Ca, Al, Fe, Si, and  $\text{SO}_4$ ; for Na, K, and Cl, on the other hand, leaching mechanisms appear largely similar. The effect of weathering on the leaching of Pb, Zn, Cu, and Mo is discussed.

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## INTRODUCTION

Recently considerable progress has been made in understanding the behaviour of various waste materials in the environment. By considering waste materials as mineral assemblages, similar to rocks and soils, researchers have been able to use geochemical knowledge to characterise the waste. Recent research has shown that dissolution/precipitation reactions do indeed control the leaching of in particular major elements from waste materials such as Municipal Solid Waste Incineration (MSWI) bottom ash (DIPIETRO *et al.*, 1989; COMANS *et al.*, 1993; COMANS AND MEIMA, 1994; EIGHMY *et al.*, 1994; KIRBY AND RIMSTIDT, 1994; ZEVENBERGEN AND COMANS, 1994; CHANDLER *et al.*, 1997), MSWI ESP ash (EIGHMY *et al.*, 1995), coal fly ash (RAI *et al.*, 1987; FRUCHTER *et al.*, 1990; MATTIGOD *et al.*, 1990), and oil shale solid wastes (ESSINGTON, 1991).

Major elements control important variables such as pH,  $E_H$ , and ionic strength, and form sorptive solid substrates. Ca-minerals in MSWI bottom ash, for example, mainly control leachate pH (COMANS AND MEIMA, 1994; JOHNSON *et al.*, 1995), which in turn has been identified as a major parameter controlling the leaching of many elements. Therefore, we need to study major elements before we can understand the leaching of minor elements.

This research focuses on Dutch MSWI bottom ash, which contains relatively high concentrations of potentially toxic elements and is produced in very large quantities (BORN, 1994). MSWI bottom ash is unstable under atmospheric conditions because it is formed at high temperatures and thereafter cooled fairly rapidly. Weathering, therefore, will change the mineralogical characteristics of the material. Major alteration processes that have been reported are the hydrolysis of oxides of Ca, Al, Na, and K (BELEVI *et al.*, 1992), dissolution/precipitation of hydroxides and salts of these main cations (BELEVI *et al.*, 1992), carbonation (COMANS AND MEIMA, 1994; ZEVENBERGEN AND COMANS, 1994; CHANDLER *et al.*, 1997) and neoformation of clay-like minerals from glasses (ZEVENBERGEN *et al.*, 1996). Carbonation involves the absorption of atmospheric  $CO_2$  by the initially alkaline bottom ash, which causes pH to decrease and calcite to precipitate until the waste is in

equilibrium with atmospheric CO<sub>2</sub>. Changes in mineralogy and pH are likely to affect leaching of major and trace elements. Therefore, the understanding of weathering processes and their effect on element leaching is necessary for a proper assessment of the environmental impact of utilisation and disposal.

A number of recent studies have concentrated on *fresh* MSWI bottom ash, using a mineralogical approach (KIRBY AND RIMSTIDT, 1993; EIGHMY *et al.*, 1994; ZEVENBERGEN AND COMANS, 1994; ZEVENBERGEN *et al.*, 1994a; PFRANG-STOTZ AND SCHNEIDER, 1995) or a geochemical modelling approach (DIPIETRO *et al.*, 1989; COMANS *et al.*, 1993; COMANS AND MEIMA, 1994; EIGHMY *et al.*, 1994; KIRBY AND RIMSTIDT, 1994; ZEVENBERGEN AND COMANS, 1994). However, considerably less attention has been paid to the leaching mechanisms of (naturally) weathered MSWI bottom ash (ZEVENBERGEN AND COMANS, 1994). The effect of quenching on MSWI bottom ash mineralogy has not been discussed much either (BELEVI *et al.*, 1992; JOHNSON *et al.*, 1995). In short, there is a lack of systematic geochemical research on MSWI bottom ash at different stages of weathering.

This paper studies weathering mechanisms of MSWI bottom ash. We compare the leaching behaviour of bottom ash from a single incinerator at different stages of weathering: grate siftings, unquenched, freshly quenched, 6-week old, 1.5-year old, and 12-year old bottom ash. Leaching experiments are performed as a function of pH because of the important role of this parameter in controlling element solubility. In addition, geochemical modelling, mineralogical (XRD) analysis, and experiments at different liquid to solid ratios are used to identify solubility controlling processes.

## **MATERIALS AND METHODS**

### *Bottom ash description*

All bottom ash samples were derived from the same Dutch Municipal Solid Waste incinerator. The incinerator operates at temperatures between 850 and 1000°C; the residence time of the waste in the incinerator is 30-40 minutes. Immediately after incineration the hot

bottom ash is quenched in a water tank together with the grate siftings. Follow-up treatment includes the removal of large pieces of unburned material, the removal of magnetic particles and size reduction by crushing. No fly ash is mixed with the bottom ash.

In February 1994 samples were taken from the following: grate siftings at two locations in the incinerator (GS2 and GS5), unquenched bottom ash (UNQ), freshly quenched bottom ash (QUE1), 6-week old bottom ash (6WK), and 1.5-year old bottom ash (1.5YR). The grate siftings had had furnace residence times of 10-15 minutes (sample GS2) or 25-38 minutes (sample GS5), and were sampled unquenched. The unquenched bottom ash (UNQ) was sampled just before being transferred to the quench tank. No grate siftings are present in this sample. Samples GS2, GS5, and UNQ, unlike the other samples, were not subjected to the incinerator's follow-up treatment described above. Sample QUE1, which represents 'normal' fresh bottom ash, was sampled just before being transferred to the storage piles. The sample 6WK was taken from a storage pile where the temperature was about 40°C; the high temperature was probably due to exothermic (bio)chemical reactions. The 1.5YR sample was taken from the outer layer of a heap that was in open storage in the grounds of the incinerator. Sample volumes were about 5 kg for samples GS2, GS5, and UNQ; and 45 kg for samples QUE1, 6WK, and 1.5YR. The samples were kept under nitrogen until required. Additionally, we investigated two more samples, 12YR and QUE2, which had been sampled and pre-treated earlier as part of other studies (COMANS *et al.*, 1993; ZEVENBERGEN AND COMANS, 1994; ZEVENBERGEN *et al.*, 1994b; ZEVENBERGEN, 1994). Sample 12YR was taken from a 12-year old disposal site used for MSWI bottom ash from the same incinerator. Weathering characteristics of this sample are described elsewhere (ZEVENBERGEN AND COMANS, 1994; ZEVENBERGEN *et al.*, 1994b; ZEVENBERGEN, 1994). Sample QUE2 is a typical quenched bottom ash sample which was taken from the same incinerator over a 2-week period in April 1992. The leaching results obtained with this sample have been presented previously (COMANS *et al.*, 1993).

Samples were pre-treated in the laboratory within one month (UNQ, QUE1, and 1.5YR) or three months (GS2, GS5, and 6WK) after sampling. Sample treatment depended largely on bottom ash pH and

redox potential ( $E_H$ ), which are given in Table 1. Wet samples were dried; samples QUE1 and 1.5YR were air-dried, sample 6WK was dried under  $N_2$  to preserve its relatively low redox potential. Other treatment procedures, however, had been used in the earlier studies: sample QUE2 was dried at 70°C, and sample 12YR was kept undried (residual water 8.5%). Subsequently, the samples GS2, GS5, UNQ, QUE1, and QUE2 were ground in a jaw crusher until all material, except for < 0.5 kg metal scrap, passed through a 2 mm sieve. The samples 6WK, 1.5YR, and 12YR were not ground, but only sieved in order to prevent the breaking-up of weathered grains and the creation of fresh surfaces. After treatment, each sample was thoroughly mixed and, except for the samples taken from the earlier studies, was again stored under nitrogen.

#### *Leaching experiments*

Leaching experiments at various pH levels were performed on the complete set of samples. Each sample was leached at 8 different pH-values in the range 4 to 12 in a pH-stat system at a relatively low L/S-ratio (5 L/kg) to minimise complete dissolution of solubility-controlling minerals. 30 g of bottom ash was suspended in 150 g of nanopure demineralised water in 300 ml Teflon (PFA) reaction vessels, under continuous stirring at 20°C. Nitrogen gas saturated with water was bubbled continuously through the suspensions of GS2, GS5, UNQ, and 6WK to preserve their relatively low redox potentials (Table 1). Suspensions of QUE1, QUE2, 1.5YR, and 12YR, which have a much higher redox potential (Table 1), were kept in contact with the atmosphere. The pH was adjusted with analytical-grade  $HNO_3$  or  $NaOH$ . Experiments were run for 24 hours, because kinetic experiments have shown that in general two steps can be observed in element leaching from bottom ash: a fast process, which is generally completed within 24 hours, followed by a slow process which continues for more than one week (COMANS *et al.*, 1993). Consequently, in this paper we focus on the initial fast reactions between bottom ash and water. After the 24 hours of equilibration, the final pH was recorded, and the redox potential was measured using an  $Ag/AgCl$ -reference electrode. The suspensions were filtered through 0.2  $\mu m$  membrane filters, and the clear filtrates were divided into two samples. One sample was acidified with concentrated

HNO<sub>3</sub> and was used for the analysis of Na, K, Ca, Mg, Al, Si, Fe, Cd, Pb, Zn, Cu, Mo, and P, by ICP-AES; in addition, GF-AAS was used in case element concentrations were below the detection limit of ICP-AES. The other sample was left untreated and was subjected to ion chromatography to measure Cl and SO<sub>4</sub>, whereas a carbon analyser was used to measure total inorganic carbon and dissolved organic carbon (DOC).

Leaching experiments as a function of L/S-ratio were performed on samples UNQ, QUE1, and 1.5YR. Various amounts of bottom ash and nanopure demineralised water were mixed in polyethylene vessels to achieve suspensions with L/S-ratios of 0.5, 2, 5, 10, 20, 50, and 100 L/kg. Vessels were continuously tumbled at 20°C for 24 hours, where upon the final pH was measured. The suspensions were filtered and analysed as described above.

### *Geochemical modelling*

The speciation code MINTEQA2 version 3.11 (ALLISON *et al.*, 1991) was used for geochemical modelling. The stability constants for ettringite ( $\log K_{sp} = -56.7$ ; ATKINS *et al.*, 1991) and illite ( $\log K_{sp} = -12.22$ ; KRUPKA *et al.*, 1988) were added to the standard MINTEQA2 (version 3.11) databases. In addition, we changed the gypsum stability constant ( $\log K_{sp} = +4.62$ ; MOREL AND HERING, 1993) because the original value in the MINTEQA2 databases deviates significantly from other sources (STUMM AND MORGAN, 1981; MOREL AND HERING, 1993). The modelling approach consisted of the following steps:

**STEP 1** MINTEQA2 was used to calculate the activities of the component species using the Davies equation. Input files were composed of (1) total concentrations of inorganic elements measured in the leachates, which are the components of the system, and (2) the pH, which was fixed at the measured value. All solids precipitation was suppressed.

**STEP 2** Potential solubility-controlling minerals were selected on the basis of (1) the likeliness of their presence or formation under the experimental conditions, and/or (2) saturation indices that approach zero ( $-1 < SI < +1$ ), and/or (3) model-predicted curve shapes that follow the measured data in concentration vs. pH graphs.

*STEP 3* The leachate composition in equilibrium with the selected minerals was calculated. This calculation allows us to present the model predictions together with the analytical data in a graph of log-concentration versus pH, which maintains the characteristic shape and concentration levels of general leaching curves. The input files defined previously were modified (1) by adding one of the selected minerals as infinite solids, and (2) by fixing the activities of important ligands at the values obtained from the preliminary calculations in STEP 1. For example, with calcite as the infinite solid, activities of both  $\text{CO}_3^{2-}$  and  $\text{SO}_4^{2-}$  were fixed. To enhance the readability of the graphs, we present the results obtained with this 'infinite solid approach' for a selected number of samples only. For the leachates in this study, model curves based on equilibrium with (hydr)oxide minerals overlap in log-concentration vs. pH graphs and are, therefore, presented for sample QUE1 only. Model curves that do not overlap are shown for three samples (GS5, QUE1, and 1.5YR) which we assume are representative for the three categories of bottom ash that are defined below.

*STEP 4* Finally, we investigate the processes that control bottom ash pH. Bottom ash pH may be controlled by the solubility of one mineral phase, or by the coexistence of several mineral phases. Therefore, we introduced either single or multiple solubility-controlling minerals into the model to calculate the equilibrium pH.

#### *X-Ray Diffraction (XRD) analysis*

An X-ray diffractometer was used to investigate the mineralogical composition of samples UNQ, GS2, GS5, QUE1, 6WK, and 1.5YR. The material used was the fraction <250 $\mu\text{m}$ .

## RESULTS AND DISCUSSION

Differences in the bulk chemical composition of the various samples of bottom ash turned out to be remarkably small (Table 1). The most obvious differences are observed for sample 12YR, which has a relatively high Ca, Si, and Mo content but low Fe content, compared to the other samples. Bulk chemical composition of sample 12YR in relation to weathering is discussed in greater detail elsewhere (ZEVENBERGEN *et al.*, 1994b).

Figure 1 shows the X-ray diffractograms of the various bottom ash samples before leaching. The principal minerals identified are quartz ( $\text{SiO}_2$ ), calcite ( $\text{CaCO}_3$ ), anhydrite ( $\text{CaSO}_4$ ), plagioclase feldspar, magnetite ( $\text{Fe}_3\text{O}_4$ ), and/or hematite ( $\text{Fe}_2\text{O}_3$ ). Additionally, ettringite ( $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$ ) was identified in samples QUE1 and 6WK. Sample UNQ contains much less calcite than the other samples. The diffractogram of sample 1.5YR reveals a higher intensity of peaks from calcite, and a lower intensity of peaks from anhydrite as compared to the other samples; similar results have been obtained for sample 12YR (ZEVENBERGEN AND COMANS, 1994).

Differences in bottom ash pH are large (Table 1). On the basis of bottom ash pH three categories can be distinguished, each category representing a different stage in bottom ash weathering: (A) samples GS2, GS5, and UNQ with  $\text{pH} > 12$ , (B) samples QUE1, QUE2, and 6WK with  $\text{pH} 10\text{-}10.5$ ; and (C) samples 1.5YR and 12YR with  $\text{pH} 8\text{-}8.5$ . This subdivision is also shown in Table 2 and we will use it throughout this paper. Obviously, each category of bottom ash has its own pH-controlling mechanism, imposed by the major element chemistry. Therefore, the mechanisms that control major element leaching are investigated first, using the pH-stat leaching data shown in Figure 2, the data as a function of L/S-ratio shown in Table 3, and the X-ray diffractograms shown in Figure 1.

**TABLE 1. Bulk chemical composition of bottom ash samples used for this study, and pH and  $E_H$  of L/S=5 bottom ash suspensions after a 24-hour equilibration period. Concentrations are expressed in g/kg bottom ash.**

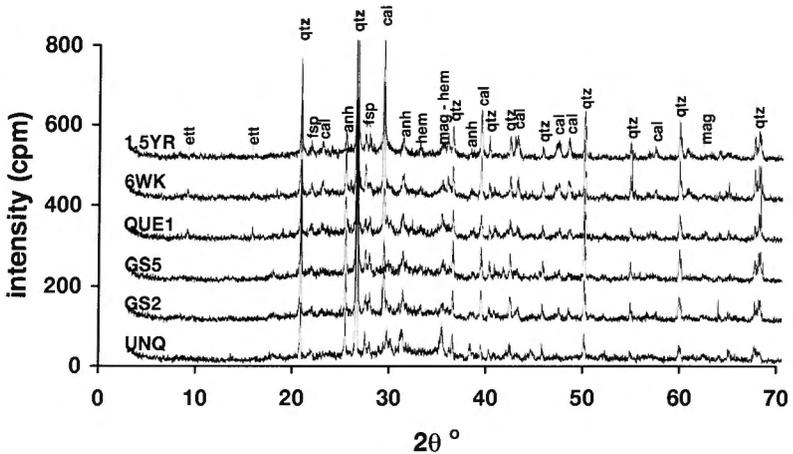
	GS2 <sup>b</sup>	GS5 <sup>b</sup>	UNQ <sup>b</sup>	QUE1 <sup>b</sup>	QUE2 <sup>b</sup>	6WK <sup>b</sup>	1.5YR <sup>b</sup>	12YR <sup>c</sup>
pH	12.23	12.48	12.33	10.31	10.29	10.50	8.53	8.47
$E_H^a$ (mV)	51	-58	97	254	262	189	301	404
Si	244.93	262.18	220.62	222.01	221.54	223.22	232.55	304.55
Fe	83.23	70.46	119.73	106.34	56.68	84.84	86.67	38.67
Ca	80.17	77.13	88.19	73.80	94.63	81.17	71.71	104.92
Al	33.51	33.84	40.42	37.18	39.81	37.34	38.03	40.48
Na	20.21	20.51	19.61	20.00	19.42	12.10	12.99	11.35
Mg	16.53	17.36	12.34	12.31	12.77	12.21	11.65	9.04
K	8.95	8.73	7.86	8.50	10.11	8.19	8.67	12.04
S	7.26	6.54	6.39	5.75	11.08	6.74	3.70	n.a.
P	3.10	3.30	4.08	2.99	2.18	4.02	3.49	n.a.
Cl	7.51	6.45	1.42	3.06	5.17	1.63	1.56	n.a.
Mn	0.92	0.77	1.44	1.65	0.87	1.28	0.90	0.77
Zn	3.18	2.75	4.25	5.62	3.76	3.79	3.55	3.70
Pb	3.12	3.32	1.37	1.57	1.41	1.62	1.95	1.40
Cu	2.87	5.75	7.35	2.30	1.56	2.25	2.19	1.70
Mo	0.029	0.039	0.051	0.031	0.025	0.026	0.024	0.120
Cd	0.005	0.005	0.001	0.009	0.010	0.008	0.007	0.014

n.a. indicates not analysed

<sup>a</sup> relative to  $H_2$ .

<sup>b</sup> bulk chemical composition measured by total digestion / ICP-AES.

<sup>c</sup> bulk chemical composition measured by X-ray fluorescence spectroscopy (data taken from ZEVENBERGEN *et al.*, 1994b).



**Figure 1.** X-ray diffractograms of samples UNQ, GS2, GS5, QUE1, 6WK, and 1.5YR. Abbreviations: ett, ettringite ( $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$ ); qtz = quartz ( $\text{SiO}_2$ ); fsp = plagioclase feldspar; cal = calcite ( $\text{CaCO}_3$ ); anh = anhydrite ( $\text{CaSO}_4$ ); hem = hematite ( $\text{Fe}_2\text{O}_3$ ); mag = magnetite ( $\text{Fe}_3\text{O}_4$ ). For clarity, GS2 is moved 100 units up, GS5 200 units, QUE1 300 units, 6WK 400 units, and 1.5YR 500 units.

## Ca

In A-type bottom ash leachates, Ca is the dominant cation; Ca-concentrations increase from about 800 mg/L at pH 12 to about 5000 mg/L at pH 4 (Figure 2a). Portlandite ( $\text{Ca}(\text{OH})_2$ ) controls Ca-leaching at pH>12 (Fig. 2a). BELEVI *et al.* (1992) have shown that this mineral forms as a result of the hydrolysis of primary CaO in the bottom ash. At these alkaline pH values, the solutions are also close to equilibrium with gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) (Fig. 2a, 2f). XRD has revealed  $\text{CaSO}_4$  (anhydrite) to be present in the dry starting materials (Fig. 1). Below pH 12, portlandite completely dissolves from the matrix, whereas Ca-

**TABLE 2. Subdivision of MSWI bottom ash on the basis of pH.**

sample	code	pH <sup>a</sup>	category
Grate sifting from roller 2	GS2	12.23	A
Grate sifting from roller 5	GS5	12.48	A
Unquenched bottom ash	UNQ	12.33	A
Freshly quenched bottom ash (1994)	QUE1	10.31	B
Freshly quenched bottom ash (1992)	QUE2	10.29	B
6-Week old bottom ash	6WK	10.50	B
1.5-Year old bottom ash	1.5YR	8.53	C
12-Year old bottom ash	12YR	8.47	C

<sup>a</sup> Measured in L/S=5 suspensions after a 24-hour equilibration period.

concentrations remain in equilibrium with respect to gypsum. Similar trends in Ca-leaching are observed for the sample UNQ when leaching is performed at different L/S-ratios (Tab. 3).

In contrast with the A-type, Ca-leaching from B-type bottom ash has strongly decreased at alkaline pH (Fig. 2a). The formation of ettringite is likely to be responsible for this lower Ca-leaching because (1) the leachates are close to saturation with respect to this mineral at alkaline pH (Fig. 2a, Tab. 3), and (2) ettringite was detected by XRD-analysis in B-type bottom ash only (Fig. 1). At lower pH (pH<9.5) and/or very low L/S-ratios, B-type bottom ash leachates are close to equilibrium with respect to gypsum (Fig. 2a, 2f; Tab. 3). Again, CaSO<sub>4</sub> (anhydrite) was detected by XRD-analysis in the dry starting materials (Fig. 1). Although calcite has been identified in A- and B-type bottom ash as well (Fig. 1), both the leachates are strongly oversaturated with respect to calcite (Fig. 2a, 2g; Tab. 3).

C-type bottom ash shows significantly lower Ca-leaching above pH 6.5 than do the other types (Fig. 2a); Ca-leaching gradually increases from about 10 mg/L at pH 12 to 6000 mg/L at pH 4. This lower Ca-leaching is likely to be caused by calcite precipitation since (1) calcite is formed during carbonation of alkaline waste materials (ESSINGTON, 1991; SCHRAMKE, 1992; ZEVENBERGEN AND COMANS, 1994; CHANDLER *et al.*,

1997); (2) XRD-analysis reveals larger quantities of calcite to be present in C-type bottom ash than in A- or B-type bottom ash (Fig. 1, ZEVENBERGEN AND COMANS, 1994); (3) the pH of weathered MSWI bottom ash appears to be mainly buffered by  $\text{CaCO}_3$  minerals (JOHNSON *et al.*, 1995); (4) Ca-leaching is strongly pH-dependent and the pH-stat leachates are relatively close to equilibrium with respect to calcite. Unexpectedly, at decreasing L/S-ratios leachates become increasingly oversaturated with respect to calcite. At L/S=0.5 leachates of sample 1.5YR are even saturated with respect to gypsum (Tab. 3).  $\text{CaSO}_4$ -minerals have indeed been identified as well in C-type bottom ash by XRD-analysis (Fig. 1, ZEVENBERGEN AND COMANS, 1994). Oversaturation with respect to calcite is a common phenomenon in leachates from waste materials (SCHRAMKE, 1992; KIRBY AND RIMSTIDT, 1994; ZEVENBERGEN AND COMANS, 1994; VAN DER WEIJDEN, 1995), and in natural waters (STUMM AND MORGAN, 1981; REDDY *et al.*, 1990). The reason for this oversaturation is still a matter of debate (REDDY *et al.*, 1990; SCHRAMKE, 1992; VAN DER WEIJDEN, 1995).

#### Al

Al-leaching is generally characterised by V-shaped pH-leaching curves (Fig. 2b). Weathered bottom ash displays an Al-leaching curve characteristic of gibbsite ( $\text{Al}(\text{OH})_3$ ). B-type bottom ash leachates approach equilibrium with gibbsite above pH 7.5, whereas below pH 7.5 Al-concentrations are closer to those predicted by equilibrium with amorphous  $\text{Al}(\text{OH})_3$ ; similar trends in Al-leaching have been observed at lower L/S-ratios (Tab 3).

The curve representing A-type bottom ash is slightly different. At strongly alkaline pH leachates are 2-4 orders of magnitude undersaturated with respect to gibbsite (Fig. 2b, Tab. 3). BELEVI *et al.* (1992) have also found very low Al-concentrations in unquenched MSWI bottom ash leachates, whereas their quenched bottom ash leachates were saturated with respect to  $\text{Al}(\text{OH})_3(\text{s})$ . This low Al-leaching is unlikely to be the result of slow reaction kinetics, because after a one-year equilibration period with the sample UNQ, Al-concentrations were still 2 orders of magnitude too low to be in equilibrium with gibbsite (results not shown). Apparently, at strongly alkaline pH a more stable mineral than gibbsite,

## *effects of weathering on major element leaching*

possibly an (amorphous) aluminosilicate, may control Al-solubility (see discussion for Si).

### *Na, K, Cl, and SO<sub>4</sub>*

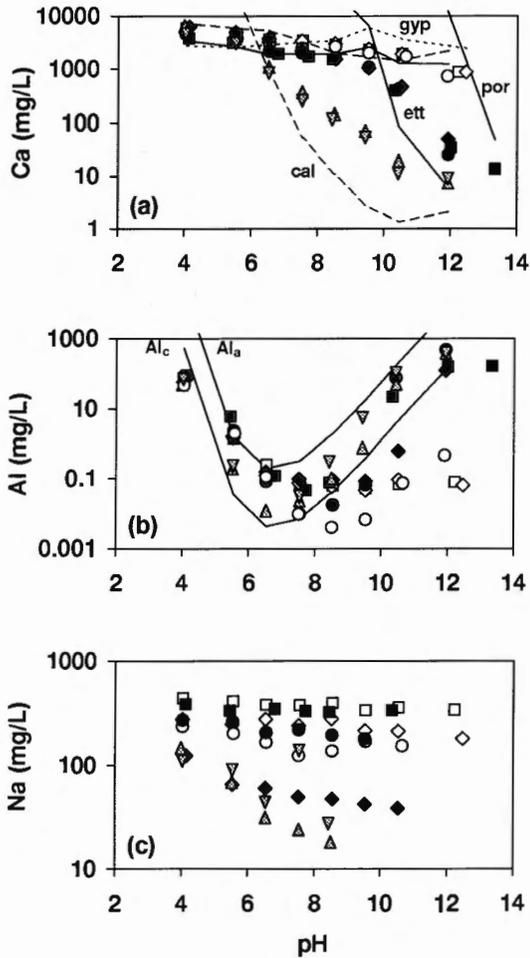
In A-type bottom ash the trends in the leaching curves of Na, K, Cl, and SO<sub>4</sub> are similar: a bottom ash high in Cl-leaching is also high in Na-, K- and SO<sub>4</sub>-leaching (Figures 2c-f). Na, K, Cl, and SO<sub>4</sub> are believed to exist as soluble salts in MSWI bottom ash; these salts dissolve rapidly as soon as the bottom ash contacts water (BELEVI *et al.*, 1992; KIRBY AND RIMSTIDT, 1994). The leaching of Na, K, and Cl increases almost proportionally with decreasing L/S-ratios (Tab. 3), suggesting that solubility-controlling salts have completely dissolved from the matrix. Sulphate, however, is controlled largely by gypsum and in B-type bottom ash by ettringite as well (see above).

Samples 6WK, 1.5YR, and 12YR show relatively low leaching of Na, K, and Cl, indicating that after only 6 weeks in an open storage a large fraction of the available Na, K, and Cl had already been leached from the bottom ash. The increased leaching of Na and K towards low pH possibly results from cation exchange processes or dissolution of aluminosilicate minerals. Sulphate, however, is retained over longer time scales, which is the result of its incorporation in secondary minerals such as ettringite and gypsum (see above).

### *CO<sub>3</sub> and DOC*

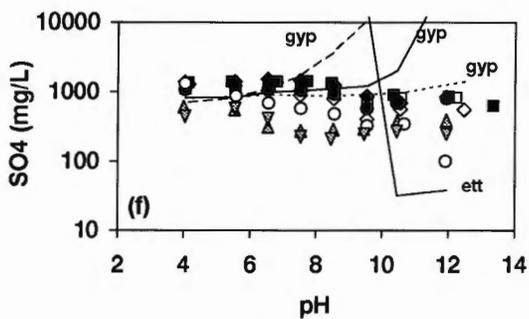
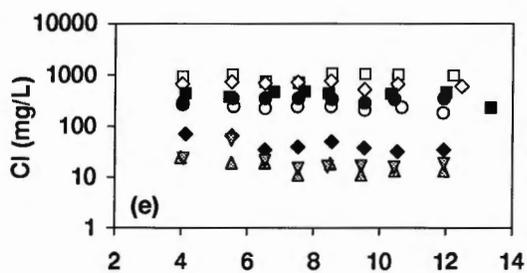
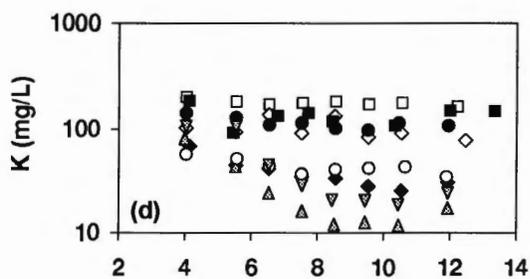
CO<sub>3</sub>-leaching as a function of pH is shown in Figure 2g. Most leachates show a slight increase in CO<sub>3</sub>-leaching as pH decreases from 12 to 8.5 (Fig. 2g), and a strong increase when the L/S-ratio is decreased (Tab. 3); this is probably due to the dissolution of carbonate minerals. The leachates, however, are 1-2 orders of magnitude oversaturated with respect to calcite, as shown for Ca above. The bubbling of N<sub>2</sub> through suspensions of samples UNQ, GS2, GS5, and 6WK may have decreased the leaching of CO<sub>3</sub> relative to the other samples.

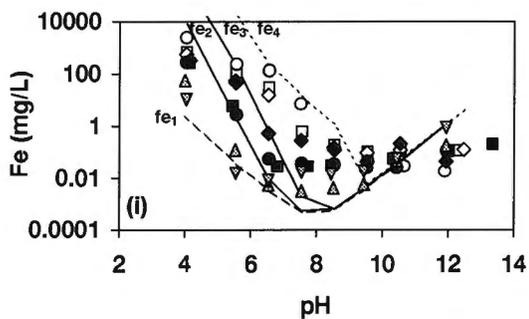
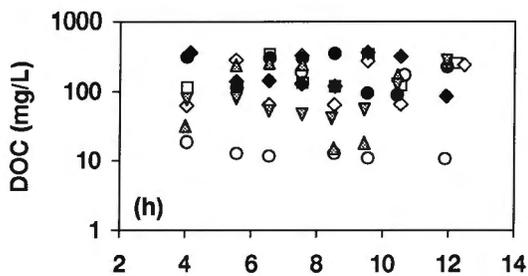
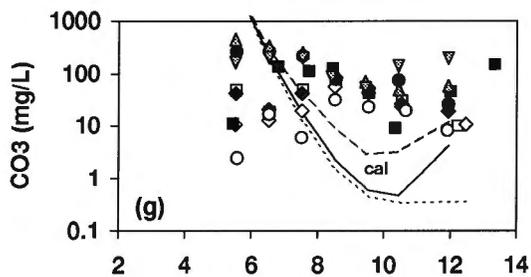
DOC-concentrations leached from the various types of bottom ash as a function of pH are plotted in Figure 2h. DOC-concentrations increase strongly when the L/S-ratio is decreased (Tab. 3), indicating that DOC-leaching is likely to be controlled by the amount of soluble organic

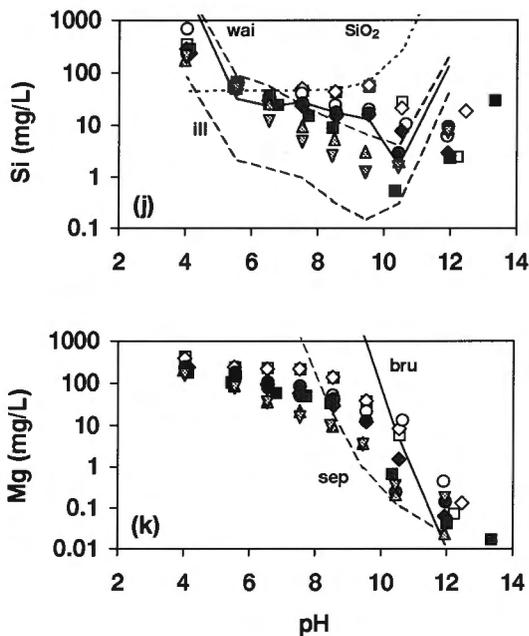


**Figure 2.** Total dissolved Ca (a), Al (b), Na (c), K (d), Cl (e), SO<sub>4</sub> (f), CO<sub>3</sub> (g), DOC (h), Fe (i), Si (j), and Mg (k) in bottom ash leachates at LIS = 5 as a function of pH, and MINTeQA2 predictions assuming equilibrium with different mineral phases. Symbols: □ GS2; ◇ GS5; ○ UNQ; ● QUE1; ■ QUE2; ◆ 6WK; ▲ 1.5YR; ▼ 12YR. Abbreviations: por = portlandite; gyp = gypsum; ett = ettringite; cal = calcite; Al<sub>a</sub> = amorphous Al(OH)<sub>3</sub>; Al<sub>c</sub> = gibbsite; The style of these lines indicates the category of bottom ash on which MINTeQA2 modelling was performed: (----) A-type; (—) B-type; (---) C-type bottom ash. Unless indicated otherwise, samples GS5, QUE1, and 1.5YR were taken as representative for the three categories of bottom ash.

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**Figure 2.** (Continued)

(Symbols:  $\square$  GS2;  $\diamond$  GS5;  $\circ$  UNQ;  $\bullet$  QUE1;  $\blacksquare$  QUE2;  $\blacklozenge$  6WK;  $\blacktriangle$  1.5YR;  $\blacktriangledown$  12YR. Abbreviations: cal = calcite;  $Fe_1$  = ferrihydrite;  $Fe_2$  = ferrihydrite (GS5 with fixed  $E_H$ );  $Fe_3$  = ferrihydrite (6WK with fixed  $E_H$ );  $Fe_4$  = ferrihydrite (QUE1 with fixed  $E_H$ );  $\text{SiO}_2$  = am-SiO<sub>2</sub>; wai = wairakite; ill = illite (12YR); bru = brucite; sep = sepiolite. Lines: (---) A-type; (—) B-type; (- -) C-type bottom ash.

**TABLE 3. Leachate composition of samples UNQ, QUE1, and 1.5YR suspended at L/S-ratios of 5, 2, and 0.5, and Saturation Indices of possible solubility-controlling minerals.**

L/S-ratio pH	sample UNQ			sample QUE1			sample 1.5RY		
	5	2	0.5	5	2	0.5	5	2	0.5
	12.21	12.29	12.38	10.32	10.29	10.28	8.62	8.43	8.29
<b>Leachate composition (in mg/L)</b>									
Ca	566	722	1475	336	491	948	92	189	506
SO <sub>4</sub>	340	433	1235	671	1034	1726	219	493	1475
Cl	167	449	2421	337	808	3124	7	19	74
Na	87	224	1058	182	435	1553	22	51	143
DOC	24	33	68	92	208	683	41	65	197
K	24	59	292	89	206	669	9	16	33
CO <sub>3</sub>	1.44	3.90	12.98	1.87	3.40	10.61	0.35	0.95	2.59
PO <sub>4</sub>	1.28	2.46	10.61	0.72	1.31	3.33	0.39	0.62	1.46
Si	1.10	1.69	2.57	6.66	16.25	51.11	7.64	12.25	27.88
Al	0.04	0.02	0.12	54.06	44.83	5.65	0.12	0.08	0.05
Mg	0.04	0.04	0.10	0.16	0.30	1.12	6.89	17.26	55.73
Fe	0.004	0.002	0.004	0.010	0.013	0.034	0.003	0.000	0.009
<b>Saturation Indices</b>									
portlandite	-0.56	-0.35	0.00	-4.12	-4.49	-4.34	-8.33	-8.49	-8.51
gypsum	-0.63	-0.53	-0.06	-0.46	-0.26	-0.03	-1.17	-0.70	-0.10
ettringite	3.72	3.62	7.58	3.13	2.90	2.15	-13.10	-12.12	-10.70
calcite	0.83	1.85	0.83	1.18	1.01	2.00	0.90	1.14	1.32
am-Al(OH) <sub>3</sub>	-5.46	-5.97	-5.22	-0.68	-0.54	-1.46	-1.40	-1.39	-1.55
gibbsite	-3.85	-4.36	-3.61	0.94	1.07	0.15	0.21	0.23	0.06
ferrhydrite	-2.79	-3.19	-2.95	-0.65	-0.30	0.09	0.66	-0.08	1.34
am-SiO <sub>2</sub>	-4.90	-4.90	-5.00	-1.71	-1.13	-0.65	-0.88	-0.66	-0.30
wairakite	-17.34	-18.16	-16.72	1.43	3.62	3.85	-0.92	-0.20	0.93
illite	-17.72	-18.59	-16.67	3.19	5.50	5.46	2.18	2.98	3.99
brucite	1.06	1.16	1.61	-1.35	-1.60	-1.16	-3.35	-3.42	-3.35
sepiolite	-3.03	-2.84	-2.24	1.72	2.94	5.26	0.22	0.71	1.95

material present. The type of organic compounds that occur in these leachates, as well as their complexing properties, are subjects of current research.

### *Fe*

Fe leaching curves generally approach a V-shape. The concentration-increase towards alkaline pH is, however, less pronounced or absent for A- and B-type bottom ash. Type C bottom ash leachates are close to equilibrium with ferrihydrite ( $\text{Fe}(\text{OH})_3$ ) (Fig. 2i, Tab. 3). Because of the relatively low  $E_H$  of A- and B-type bottom ash samples (Table 1), the model calculations for these samples include the redox couple Fe(II)/Fe(III) and suggest that dissolved Fe-concentrations are likely to be controlled by ferrihydrite at  $\text{pH} < 8$ . The calculations do not explain the apparent absence of an iron hydrolysis effect (i.e. increasing concentrations towards alkaline pH) at  $\text{pH} > 8$ . The leaching data for Fe as a function of L/S-ratio give no additional indication as to the solubility-controlling process in A- and B-type bottom ash at  $\text{pH} > 8$ .

### *Si*

As shown in Fig. 2j, Si-leaching tends to decrease as weathering proceeds. The highest Si-leaching is observed for the grate siftings, with almost pH-independent leaching between pH 5.5 and 9.5 and leachates close to equilibrium with respect to amorphous- $\text{SiO}_2$ . The lowest Si-leaching is observed for the 12YR sample, with a V-shaped leaching curve that is strongly pH-dependent and with a minimum at pH 9-10. The sample UNQ shows a trend similar to the one described for the grate siftings. Samples QUE1, QUE2, and 1.5YR resemble the 12YR-curve. Unexpectedly, sample 6WK shows a trend similar to the one described for the grate siftings.

Sample UNQ shows only a small increase in Si-leaching when the L/S-ratio is decreased from 5 to 0.5, although the leachates are strongly undersaturated with respect to am- $\text{SiO}_2$  at the high pH-values (Tab. 3). This relatively low Si-leaching is unlikely to be due to kinetic constraints on dissolution, because silicon dissolution rates usually increase above  $\text{pH} \sim 8$ ; this has been shown to be typical for compounds such as  $\text{SiO}_2$ , aluminosilicates and basalt glass (SCHOTT, 1990; STUMM, 1992).

Therefore, Si-leaching from sample UNQ at strongly alkaline pH is likely to be controlled by an Si mineral that is less soluble than amorphous SiO<sub>2</sub>. Sample QUE1 shows an almost proportional increase in Si-leaching when the L/S-ratio is decreased (Tab. 3). Geochemical modelling shows that the leachates approach equilibrium with am-SiO<sub>2</sub> at L/S=0.5. This result suggests that Si-leaching from sample QUE1 may not be solubility-controlled, except at very low L/S-ratios. However, at a larger range in pH-values, Si-leaching from sample QUE2 has been shown to be largely independent of L/S-ratio, suggesting solubility-control (COMANS *et al.*, 1993).

KIRBY AND RIMSTIDT (1994) have suggested that silicon dissolution kinetics of MSWI bottom ash are slowed down by the precipitation of a secondary silicate phase at alkaline pH. This phase may be allophane-like (ZEVENBERGEN AND COMANS, 1994; ZEVENBERGEN *et al.*, 1996) or zeolite-like (KIRBY, 1993; ZEVENBERGEN AND COMANS, 1994). Allophane-like precipitates of amorphous aluminosilicates have been observed in alkaline MSWI bottom ash suspensions (ZEVENBERGEN AND COMANS, 1994; ZEVENBERGEN *et al.*, 1996), but an allophane solubility constant is not known to us. Zeolites have not been observed in the MSWI bottom ash matrix. However, quite good modelling results have been obtained by using the zeolite wairakite (CaAl<sub>2</sub>Si<sub>4</sub>O<sub>12</sub>·2H<sub>2</sub>O) to model Si-leaching from freshly quenched MSWI bottom ash (COMANS *et al.*, 1993) and from alkaline coal fly ash (FRUCHTER *et al.*, 1990). B-type bottom ash leachates are indeed calculated to be in equilibrium with wairakite over a large pH-range (Fig. 2j). However, this mineral is still too soluble to explain the low Si-leaching at strongly alkaline pH from A-type bottom ash (Tab. 3). Further research is needed to investigate the role of these minerals in controlling Si-leaching from alkaline MSWI bottom ash.

The increase in Si-leaching from sample 1.5YR as a function of L/S-ratio is relatively small (Tab. 3). Similar to sample QUE1, the leachates approach equilibrium with am-SiO<sub>2</sub> at L/S=0.5. However, if the only source of soluble Si were amorphous-SiO<sub>2</sub>, the leaching curves would not be as strongly pH-dependent as Fig. 2j shows. Therefore, the decrease in Si-leaching as weathering proceeds suggests a transition from initially unstable minerals to more stable (crystalline) minerals. A

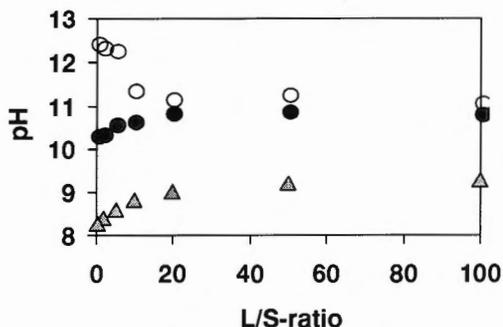
widespread neoformation of the clay mineral illite ( $K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2$ ) has been observed in sample 12YR (ZEVENBERGEN *et al.*, 1994b,1996). Geochemical modelling shows that Si-concentrations in equilibrium with illite produce V-shaped curves similar to those observed for C-type bottom ash (Fig 1j). Therefore, illite may perhaps control Si-leaching from weathered MSWI bottom ash in the long-term.

### *Mg*

Mg-leaching from A-, B-, and C-type bottom ash is almost pH-independent at  $pH < 8.5$ , but decreases strongly at alkaline pH (Fig. 2k). This behaviour suggests solubility control at alkaline pH, whereas at  $pH < 8.5$  the solubility-controlling mineral may have dissolved completely from the matrix.

Various authors have suggested that brucite ( $Mg(OH)_2$ ) controls Mg-leaching from MSWI bottom ash (COMANS *et al.*, 1993; JOHNSON *et al.*, 1995) and coal fly ash (TALBOT *et al.*, 1978; WARREN AND DUDAS, 1984; SCHRAMKE, 1992). According to Fig. 2k and Tab. 3, all leachates of A, B, and C-type bottom ash are close to equilibrium with brucite at strongly alkaline pH.

In weathered MSWI bottom ash the secondary mineral sepiolite ( $Mg_2Si_3O_6(OH)_4 \cdot 1.5H_2O$ ) may control Mg-leaching. Sepiolite formation has been predicted for alkaline coal fly ash (RAI *et al.*, 1987). Because the mineral can only precipitate and persist if the pH is high ( $> 8-10$ ), Mg-activities and Si-activities are high, and soluble Al is low to non-existent (ZELAZNY AND CALHOUN, 1977), sepiolite is not expected in fresh MSWI bottom ash, but it may form in the carbonated ash. Indeed, the 1.5YR and 12YR samples do approach equilibrium with respect to sepiolite between pH 8.5 and pH 12, although at  $L/S=0.5$  leachates become 2 orders of magnitude oversaturated with respect to the mineral (Fig. 2k, Tab. 3). In addition, since Mg can also be incorporated in other minerals such as calcite (Mg-calcite; SCHRAMKE, 1992) and illite (see discussion for Si), these solids may exert control on Mg-leaching from weathered bottom ash as well. The similarity in the leaching curves of Mg and Ca for the carbonated (type C) bottom ash samples supports the possible role of calcite in controlling Mg-leaching.



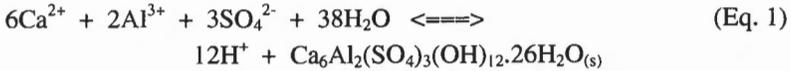
**Figure 3.** Bottom ash pH as a function of L/S-ratio for the samples UNQ (○), QUE1 (●), and 1.5YR (△).

#### *Mechanisms controlling bottom ash pH*

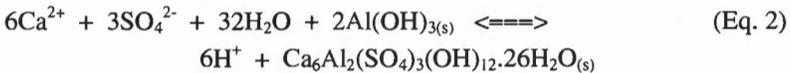
Figure 3 shows bottom ash pH as a function of L/S-ratio for samples UNQ, QUE1, and 1.5YR. A-Type bottom ash leachates (L/S=5) are characterised by a highly alkaline pH (pH>12), equilibrium with respect to portlandite, and a strong undersaturation (factor 100-1000) with respect to gibbsite (Fig. 2a, 2b, Tab. 3). The pH of the sample UNQ approaches a maximum at low L/S (pH 12.4) as shown in Fig. 3. At low L/S-ratios there is equilibrium with respect to both portlandite and gypsum (Tab. 3). The pH calculated by MINTEQA2 for a saturated portlandite solution is 12.4, suggesting that this mineral controls bottom ash pH. When suspensions are diluted, pH quickly decreases to 11.2 at L/S=20, where it stabilises. This behaviour is consistent with the hydrolysis and dissolution of limited amounts of CaO, resulting in leachates that become increasingly undersaturated with respect to portlandite.

B-Type bottom ash leachates (L/S=5) show lower pH-values (pH 10.5) than the A-type bottom ash and show equilibrium with respect to the secondary minerals gibbsite and ettringite (Fig. 2a, 2b, Tab. 3). Leachates are undersaturated with respect to portlandite (Fig. 2a, Tab. 3). A-type bottom ash has not been in contact with water before, and,

therefore, has remained relatively unweathered. When this dry bottom ash contacts water, e.g. in the quench tank, weathering reactions start. Minerals hydrolyse and oxidise by reacting with water and oxygen, causing Al to dissolve and gibbsite to precipitate. Precipitation of the mineral ettringite from the oversaturated A-type bottom ash leachates (Fig. 2a) can account for the decrease in pH, as demonstrated in Eq. 1.



The pH of the QUE1 sample is lowest at low L/S-ratios (pH10.3), with leachates close to equilibrium with respect to gypsum, ettringite and gibbsite (Tab. 3). This pH is slightly higher than the equilibrium pH of 10.0 predicted by the coexistence of ettringite, gypsum, and gibbsite. When the three minerals coexist, no degrees of freedom are left and pH is fixed (COMANS AND MEIMA, 1994). At higher L/S, however, pH increases and stabilises at pH11 for L/S>20. This increase in pH results from the exhaustion of gypsum at higher L/S-ratios (Tab. 3). When only ettringite and gibbsite coexist, there is one degree of freedom left, and pH may vary as illustrated in Eq. 2, which is obtained from Eq. 1 by subtracting the reaction for the formation of gibbsite.



According to Eq. 2, the larger the undersaturation with respect to gypsum, i.e. the lower the  $\text{Ca}^{2+}$  and the  $\text{SO}_4^{2-}$ -activity, the higher the equilibrium pH. The maximum pH is dependent on the alkalinity of the bottom ash.

C-Type bottom ash leachates (L/S=5) approach equilibrium with respect to atmospheric  $\text{CO}_2$  and calcite, and consequently, bottom ash pH is about 8.5. Ettringite has dissolved during carbonation. Equilibrium with respect to gypsum is only reached at L/S=0.5 (Tab. 3). MINTEQA2 modelling shows that the pH of calcite in equilibrium with atmospheric  $\text{CO}_2$  is 7.75 in the presence of, and 8.29 in the absence of gypsum, which results from the higher Ca-activity in case gypsum is present. According

to our measurements, however, the pH of the sample 1.5YR increases from 8.3 to 9.3 between L/S=0.5 and L/S=100 (Fig. 3); these relatively-high pH-values result from the slight oversaturation with respect to calcite (Tab. 3).

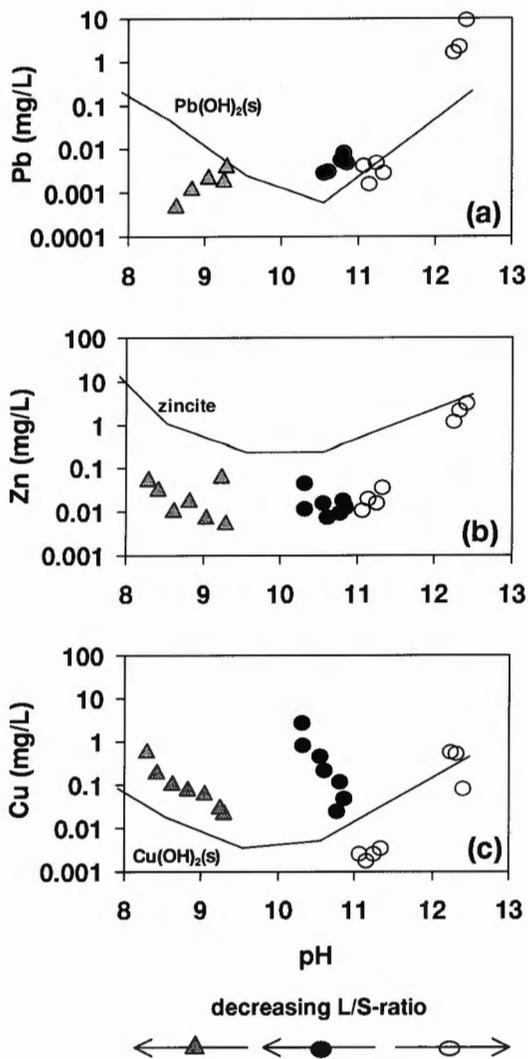
*Pb, Zn, Cu, and Mo*

Figure 4 shows the leaching of Pb, Zn, Cu, and Mo from samples UNQ, QUE1, and 1.5YR at different L/S-ratios, at the "natural" pH of the bottom ash. Since the "natural" pH of bottom ash is a function of the L/S-ratio (Fig. 3), concentrations are plotted vs. pH. Figure 4 shows two important aspects of trace element leaching: (1) whether or not trace element leaching is solubility-controlled, and (2) the effect of weathering.

Leaching is likely to be solubility-controlled if leachate concentrations are relatively independent of L/S-ratio. Since concentrations increase also as a result of hydrolysis (STUMM AND MORGAN, 1981), we compare the shape of the leaching curves to the solubility curves of pure  $Me(OH)_2(s)$  phases. This comparison suggests that the leaching of Pb, Cu, and Zn from sample UNQ, the leaching of Pb and Zn from sample QUE1, and the leaching of Pb, Cu, and Mo from sample 1.5YR may be solubility-controlled (Fig. 4). No concentration-limiting mechanism, however, seems to exist for the leaching of Cu from sample QUE1, and the leaching of Mo from samples UNQ and QUE1: leachate concentrations increase almost proportionally to the L/S-ratio (Fig. 4).

Weathering clearly leads to lower Pb-leaching, possibly as a result of sorption processes and/or formation of more stable mineral phases. Weathering effects on the leaching of Zn closely follow the changes in bottom ash pH; lowest concentrations are observed between pH 9 and 10 (Fig. 4; COMANS *et al.*, 1993). The effect of weathering on the leaching of Cu is more difficult to establish. It has been suggested that dissolved Cu in MSWI bottom ash leachates is largely bound to DOC (COMANS *et al.*, 1993; CHANDLER *et al.*, 1997). Mo-leaching seems to decrease as weathering proceeds. Although Mo may have become incorporated into secondary minerals during weathering, this mobile element may also have been released from the bottom ash during ageing/storage.

effects of weathering on major element leaching



**Figure 4.** Total dissolved Pb (a), Cu (b), Zn (c), and Mo (d) in bottom ash leachates at L/S-ratios of 100, 50, 20, 10, 5, 2, and 0.5, and MINTEQA2 predictions assuming equilibrium with  $Pb(OH)_2(s)$ ,  $Cu(OH)_2(s)$ , and zincite ( $ZnO$ ). Symbols: ○ UNQ; ● QUE1; ▲ 1.5YR.

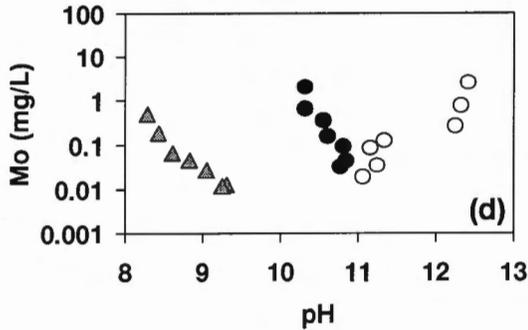


Figure 4. (continued)

(Symbols: ○ UNQ; ● QUE1; ▲ 1.5YR)

In summary, weathering has a significant effect on trace element leaching from MSWI bottom ash. Changes in leached concentrations are related to the pH differences between A, B, and C-type bottom ash. The solubility-controlling mechanisms cannot be identified from the above data, but recent findings suggest that surface complexation with metal oxides in the bottom ash matrix may be important (Meima and Comans, 1997a).

## GENERAL DISCUSSION

The subdivision of bottom ashes on the basis of pH has shown itself to be very useful in that within each category, different bottom ashes show largely similar leaching, whereas between categories leaching mechanisms are different for several elements. Table 4 summarises the minerals that are likely to control major element leaching from MSWI bottom ash.

The pH-controlling mechanisms outlined above for MSWI bottom ash may also operate in other alkaline (waste) materials. The carbonation process is known to occur in for example alkaline coal fly ash (TALBOT *et al.*, 1978; ROY *et al.*, 1984; SCHRAMKE, 1992) and oil shale solid wastes (REDDY *et al.*, 1986; ESSINGTON, 1991). Buffering of alkaline waste at pH

10, which we believe is caused by the coexistence of ettringite, gibbsite, and gypsum, has also been observed in several studies on artificial weathering of alkaline coal fly ash (TALBOT *et al.*, 1978; WARREN AND DUDAS, 1984; SCHRAMKE, 1992). In addition, during artificial weathering of oil shale solid waste, ettringite was detected by XRD-analysis only in early weathering stages; when weathering continued, ettringite disappeared and both gypsum and calcite precipitated (ESSINGTON, 1991).

**TABLE 4. Summary of inferred solubility-controlling minerals for major elements.**

element	bottom ash		
	A-type	B-type	C-type
pH	> 12	10-10.5	8-8.5
Ca	portlandite	ettringite <sup>a,b</sup>	CaCO <sub>3</sub> <sup>a,b</sup>
SO <sub>4</sub>	gypsum	gypsum <sup>b-d</sup>	gypsum <sup>b</sup>
Al		gibbsite <sup>d</sup>	gibbsite
Fe			ferrihydrite
Si			
Mg	brucite	brucite	

<sup>a</sup> minerals detected by XRD as part of this research; minerals detected by ZEVENBERGEN AND COMANS, 1994<sup>b</sup>; KIRBY AND RIMSTDT, 1994<sup>c</sup>, and EIGHMY *et al.*, 1994<sup>d</sup>.

Weathering has a significant effect on the leaching of trace elements from MSWI bottom ash. In general, weathering results in lower leaching of Pb, Zn, and Mo. This reduction in leaching can be explained by (a) the neutralisation of bottom ash pH and/or (b) sorption processes or formation of more stable mineral species as weathering proceeds. The leaching of Cu seems to be related to the leaching of DOC: Cu may be associated, to a significant degree, with dissolved organic carbon. We investigate the mechanisms controlling trace element leaching in more detail in separate papers (MEIMA AND COMANS, 1997a,b; MEIMA *et al.*, 1997).

## Chapter 2

For the development and interpretation of standardised leaching-tests, this study may imply that materials should be tested at pH 10 and/or pH 8.3, depending on the conditions of usage or disposal. If materials have limited contact with air and water, a pH of 10 is expected on shorter and longer time scales, and a leaching-test at pH 10 is sufficient. For example, an average pH of 10.15 was measured over a 10-year period in the percolate from a 60000 m<sup>3</sup> co-disposal site, containing MSWI residues such as bottom ash, fly ash, scrap metal, poorly burned ash, and Mg-treated seed corn (HJELMAR, 1989). When materials are used in contact with air, a leaching-test at pH 10 simulates relatively short time periods, and a leaching-test at pH 8.3 is required to predict leaching over longer periods of time as pH decreases due to carbonation.

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## **Chapter 3**

**The leaching of trace elements  
from MSWI bottom ash  
at different stages  
of weathering.**

# THE LEACHING OF TRACE ELEMENTS FROM MUNICIPAL SOLID WASTE INCINERATOR BOTTOM ASH AT DIFFERENT STAGES OF WEATHERING\*

Jeannet A. Meima and Rob N.J. Comans

Netherlands Energy Research Foundation (ECN)  
Westerduinweg 3 1755 LE Petten

## ABSTRACT

For a proper assessment of the environmental impact of the utilisation and disposal of Municipal Solid Waste Incinerator (MSWI) bottom ash it is necessary to understand weathering processes and their effects on (trace) element leaching. We have investigated the processes that control the leaching of Cd, Pb, Zn, Cu, and Mo from three categories of bottom ash: (A) unweathered bottom ash (grate siftings and unquenched samples), (B) quenched/non-carbonated bottom ash (freshly quenched and 6-week old samples), and (C) weathered bottom ash (1.5- and 12-year old samples). Leaching experiments were performed in a pH-stat at a large range of pH values. The speciation code MINTQA2 was used for subsequent modelling of precipitation/dissolution processes. The speciation of trace elements in weathered bottom ash was also investigated by microanalytical techniques. In A- and B-type bottom ash the general controlling processes are thought to be precipitation/dissolution of relatively soluble minerals or, in the case of Cu in particular, extensive complexation with dissolved organic carbon. At the "natural" pH of the samples, the leaching of Cd, Pb, Cu, Zn, and Mo is generally significantly lower from C-type bottom ash than from less weathered types of bottom ash. This reduction in leaching is due to the neutralisation of bottom ash pH and the formation of less soluble species of these elements as weathering continues. In the more weathered (C-

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type) bottom ash trace element leaching does not seem to be solubility-controlled; in those samples the controlling mechanism is probably sorption to neoformed minerals.

## INTRODUCTION

Municipal Solid Waste Incinerator (MSWI) bottom ash contains relatively high concentrations of potentially hazardous elements and is produced in very large quantities (BORN, 1994). Since MSWI bottom ash is incinerated at high temperatures and thereafter cooled fairly rapidly, the material is unstable under atmospheric conditions. Weathering, therefore, will change the mineralogical characteristics of the material. Three major stages in weathering have been identified (MEIMA AND COMANS, 1997a), each stage having a characteristic pH: (A) unweathered bottom ash, with pH > 12 (grate siftings and unquenched samples); (B) quenched/non-carbonated bottom ash, with pH 10-10.5 (freshly quenched and 6-week old samples); and (C) carbonated bottom ash, with pH 8-8.5 (1.5- and 12-year old samples). Bottom ash pH is controlled largely by Ca minerals and pCO<sub>2</sub>, but soluble aluminium and sulphates also play a role (COMANS AND MEIMA, 1994; MEIMA AND COMANS, 1997a). Major alteration processes include the hydrolysis of oxides of Ca, Al, Na, and K (BELEVI *et al.*, 1992), dissolution/precipitation of hydroxides and salts of these main cations (BELEVI *et al.*, 1992; MEIMA AND COMANS, 1997a), carbonation, which involves the absorption of atmospheric CO<sub>2</sub> by the initially alkaline material (SCHRAMKE, 1992; COMANS AND MEIMA, 1994; ZEVENBERGEN AND COMANS, 1994; CHANDLER *et al.*, 1997; MEIMA AND COMANS, 1997a), and neoformation of clay-like minerals from glasses (ZEVENBERGEN *et al.*, 1996).

The effect of weathering on trace element leaching is likely to be significant, because pH is a dominant parameter in metal solubility and complexation (STUMM AND MORGAN, 1981) and pH has also been recognised experimentally to be a very significant parameter in trace element leaching from waste materials and contaminated soils (DIPIETRO *et al.*, 1989; COMANS *et al.*, 1993a; CHANDLER *et al.*, 1997; VAN DER SLOOT *et al.*, 1996). Furthermore, mineral neoformation may lead to the

formation of reactive sorptive solid substrates which can bind trace elements. For a proper assessment of the environmental impact of ash utilisation and disposal it is, therefore, necessary to understand weathering processes and their effects on (trace) element leaching.

Currently, our knowledge of trace element speciation and trace element leaching is limited mainly to *fresh* MSWI bottom ash (DIPIETRO *et al.*, 1989; COMANS *et al.*, 1993a; EIGHMY *et al.*, 1994; VAN DER SLOOT *et al.*, 1996). We know of only one study which discusses some mineralogical aspects of trace element speciation in weathered MSWI bottom ash (ZEVENBERGEN *et al.*, 1994). In that study Cu, Pb, Zn, and Ni were found to be incorporated in neoformed clay-like minerals, and Mo was detected as powellite ( $\text{CaMoO}_4$ ) and as an Mo/Pb-rich particle. EIGHMY *et al.* (1994) investigated the mineralogy of fresh MSWI bottom ash using various microanalytical techniques. They identified the following species: metallic Pb, Cu, and Zn, oxides of Pb and Zn, salts of Cu and Zn, and franklinite ( $\text{ZnFe}_2\text{O}_4$ ). Pb was found incorporated largely in complex silicate melt structures (EIGHMY *et al.*, 1994). Furthermore, sequential chemical extraction showed that significant amounts of Cd and Pb are associated with acid-soluble (carbonate) phases in combined MSWI bottom and fly ash (KIRBY AND RIMSTIDT, 1993).

It has been suggested that the leaching of Cd, Pb, Zn, Cu, and Mo from *fresh* MSWI bottom ash is solubility-controlled (COMANS *et al.*, 1993a; EIGHMY *et al.*, 1994; VAN DER SLOOT *et al.*, 1996). Leaching experiments at different liquid to solid (L/S) ratios also indicated that the leaching of Pb, Zn, and Cu from unquenched bottom ash, the leaching of Pb and Zn from freshly quenched bottom ash, and the leaching of Pb, Zn, Cu, and Mo from 1.5-year old MSWI bottom ash is probably solubility-controlled (MEIMA AND COMANS, 1997a). However, the leaching of Cu and Mo from fresh MSWI bottom ash did not seem to occur via a concentration-limiting mechanism, because the concentration of these metals in the leachates were found to increase almost in proportion to the L/S ratio (MEIMA AND COMANS, 1997a). The following minerals have been proposed as potential solubility-controlling minerals in fresh MSWI bottom ash: otavite,  $\text{CdCO}_3$  (COMANS *et al.*, 1993a; EIGHMY *et al.*, 1994; VAN DER SLOOT *et al.*, 1996);  $\text{Pb(OH)}_2$  (COMANS *et al.*, 1993a); anglesite,  $\text{PbSO}_4$  (EIGHMY *et al.*, 1994); zincite,  $\text{ZnO}$  (COMANS *et al.*, 1993a;

EIGHMY *et al.*, 1994; VAN DER SLOOT *et al.*, 1996);  $\text{ZnSiO}_3$  (COMANS *et al.*, 1993a); tenorite,  $\text{CuO}$  (COMANS *et al.*, 1993a);  $\text{Cu(OH)}_2$  (EIGHMY *et al.*, 1994); and powellite,  $\text{CaMoO}_4$  (COMANS *et al.*, 1993a). Similar types of minerals are believed to control the leaching of these elements from alkaline coal fly ash (RAI *et al.*, 1987; EARY *et al.*, 1990; FRUCHTER *et al.*, 1990) and from MSWI fly and ESP ash (EIGHMY *et al.*, 1995).

This paper studies the effects of weathering on the leaching of Cd, Pb, Zn, Cu, and Mo from MSWI bottom ash. The samples were taken from a single incinerator and represent different stages of natural weathering: (A) unweathered (grate siftings and unquenched bottom ash), (B) quenched/non-carbonated (freshly quenched and 6-week old bottom ash), and (C) carbonated (1.5- and 12-year old bottom ash). The speciation code MINTEQA2 is used to calculate the composition of the leachates in equilibrium with potential solubility-controlling minerals. Furthermore, trace element associations in weathered (1.5-year old) bottom ash are investigated by microanalytical techniques. Major weathering reactions of the above-mentioned samples are described in MEIMA AND COMANS (1997a).

## MATERIALS AND METHODS

### *Used MSWI bottom ash*

All MSWI bottom ash samples came from the same Dutch MSW incinerator. The types of bottom ash used, their sample code, pH and  $E_H$  of suspensions with a liquid/solid (L/S) ratio of 5 L/kg, and bulk chemical compositions are summarised in Table 1. The different samples of bottom ash were subdivided into three categories on the basis of differences in pH and major element leaching (MEIMA AND COMANS, 1997a). Each category of bottom ash represents a different stage of weathering:

- A Unweathered bottom ash (grate siftings and unquenched samples)
- B Quenched/non-carbonated bottom ash (freshly quenched and 6-week old samples)
- C Carbonated bottom ash (1.5-year old and 12-year old samples)

*effects of weathering on minor element leaching*

Unlike A-type bottom ash, B- and C-type bottom ash were quenched in a water tank immediately after incineration. Grate siftings form part of all samples, except the unquenched sample. The 6-week and 1.5-year old samples were taken from open storage piles in the grounds of the incinerator. The 12-year old sample was taken from a disposal site.

**TABLE 1. Bulk chemical composition of the bottom ash samples used for this study, their sample code, and pH and  $E_H$  of L/S=5 suspensions after a 24-hour equilibration period<sup>a</sup>.**

used bottom ash	Grate sifting (roller 2)	Grate sifting (roller 5)	Unquenched	Freshly quenched	6-Week old	1.5-Year old	12-Year old
code	GS2	GS5	UNQ	QUE1	6WK	1.5YR	12YR
category	A	A	A	B	B	C	C
pH	12.23	12.48	12.33	10.31	10.50	8.53	8.47
$E_H$ (mV) <sup>b</sup>	51	-58	97	254	189	301	404
Si	244.93	262.18	220.62	222.01	223.22	232.55	304.55
Fe	83.23	70.46	119.73	106.34	84.84	86.67	38.67
Ca	80.17	77.13	88.19	73.80	81.17	71.71	104.92
Al	33.51	33.84	40.42	37.18	37.34	38.03	40.48
Na	20.21	20.51	19.61	20.00	12.10	12.99	11.35
Mg	16.53	17.36	12.34	12.31	12.21	11.65	9.04
K	8.95	8.73	7.86	8.50	8.19	8.67	12.04
S	7.26	6.54	6.39	5.75	6.74	3.70	n.a.
P	3.10	3.30	4.08	2.99	4.02	3.49	n.a.
Cl	7.51	6.45	1.42	3.06	1.63	1.56	n.a.
Mn	0.92	0.77	1.44	1.65	1.28	0.90	0.77
Zn	3.18	2.75	4.25	5.62	3.79	3.55	3.70
Pb	3.12	3.32	1.37	1.57	1.62	1.95	1.40
Cu	2.87	5.75	7.35	2.30	2.25	2.19	1.70
Mo	0.029	0.039	0.051	0.031	0.026	0.024	0.120
Cd	0.005	0.005	0.001	0.009	0.008	0.007	0.014

n.a. indicates not analysed.

<sup>a</sup> data taken from MEIMA AND COMANS (1997a); Concentrations are expressed in g/kg.

<sup>b</sup> relative to  $H_2$ .

*Mineralogical and electron microscopic analysis*

Scanning electron microscopy (SEM) was performed on bulk <2mm fractions of samples GS5, UNQ, and QUE1. Transmission electron microscopy (TEM) was performed on ultramicrotomed thin-sections of bulk <2mm fractions of sample 1.5YR. In these SEM/TEM analyses the backscattered electron image was used to locate particles of interest, i.e. particles containing heavy metals and/or molybdenum. A semi-quantitative estimate of the composition of specific particles was made by energy-dispersive X-ray spectroscopy (EDS).

In addition, a density-based separation technique was used in an attempt to separate the particles containing Cd, Pb, Cu, Zn, and Mo from the bulk bottom ash of sample 1.5YR. First, the 50-125 $\mu$ m particle-size fraction, from which magnetite had been removed with a hand magnet, was placed in a 500 ml separating funnel containing acetylene tetrabromide (specific gravity 2.96 g/ml at 25°C). The particles with a specific gravity higher than 2.96 g/ml were separated, washed with ethanol, and dried. A portion of the collected material was dissolved in concentrated HCl/H<sub>2</sub>SO<sub>4</sub> to determine the total concentrations of Cd, Pb, Cu, Zn, and Mo by ICP-AES. A second portion was used for the analysis of crystalline mineral phases by means of XRD. A third portion was subjected to SEM-EDS in order to obtain X-ray spatial images for Cu, Zn, Pb, Fe, Al, Si, Ca, S, P, and O. The spectra of Pb and S largely overlap and associations of Pb and S, therefore, could not be detected. Associations of Pb and S with other elements, however, could be detected because it was possible to differentiate between Pb and S on the basis of the brightness of the backscattered electron image, which increases for elements with increasing atomic number. Particles consisting of BaSO<sub>4</sub>, however, also give bright images and, therefore, an additional X-ray spatial image was obtained for barium to separate between bright Pb-rich and bright S-rich particles. Approximately 250 Zn-rich particles, 90 Cu-rich particles, and 65 Pb-rich particles were analysed. Phase associations were recorded for each of these grains, and were typed as 'metallic', 'alloy', 'silicate', 'complex silicate', and associated mainly with 'O', 'Ca/O', 'Fe/O', 'Al/O', and 'S', respectively. Since carbon could not be analysed for, it was not possible to differentiate between (hydr)oxide phases and carbonate phases.

## *effects of weathering on minor element leaching*

The mineralogical and chemical composition of gel-like precipitates, which had been found in the 1.5-year old bottom ash, was analysed by X-ray diffraction (XRD) and by SEM-EDS.

### *pH-stat leaching experiments*

Sample treatment and pH-stat leaching experiments are described in detail in MEIMA AND COMANS (1997a). Experiments consisted of batch leaching for 24-hours at an L/S-ratio of 5 L/kg and at various pH values between 4 and 12 using a pH-stat system. The pH was adjusted with analytical-grade HNO<sub>3</sub> or NaOH. Suspensions were stirred continuously by a magnetic stirrer. Experiments were run for 24 h, because kinetic experiments have shown that in general two steps can be observed in element leaching from bottom ash: a fast process, which is generally completed within 24 h, followed by a slow process that continues for more than 1 week (COMANS *et al.*, 1993b). Consequently, in this paper we focus on the initial fast reactions between bottom ash and water. Equilibrated suspensions were filtered through 0.2µm membrane filters, and the clear filtrates were analysed for Na, K, Ca, Mg, Al, Si, Fe, Cd, Pb, Zn, Cu, Mo, and P by ICP-AES or GF-AAS in case element concentrations were below the detection limit of ICP-AES. Furthermore, chlorides and sulphates were analysed by ion chromatography, and inorganic carbonates and dissolved organic carbon by a carbon analyser.

### *Geochemical modelling*

For geochemical modelling purposes the computer code MINTQA2 version 3.11 (ALLISON *et al.*, 1991) was used. Additions and modifications made to the standard MINTQA2 databases are given in Table 2. A step-wise modelling approach was used to calculate the composition of the leachates in equilibrium with potential solubility-controlling minerals, as described in detail in MEIMA AND COMANS (1997a). Potential solubility-controlling minerals were selected on the basis of (a) the likelihood of their presence or formation under the experimental conditions, and/or (b) saturation indices that approach zero ( $-1 < SI < +1$ ), and/or (c) model-predicted curve shapes that follow the measured data in concentration vs pH graphs. This approach allowed us to present model predictions together with the analytical data in a graph

**TABLE 2. Additional or modified thermodynamic data used in the MINTEQA2 calculations.**

<b>aqueous species</b>	<b>log K</b>	<b>source</b>
$\text{Cu}(\text{OH})_2^0$	-16.20	MOREL AND HERING, 1993
$\text{HMoO}_4^-$	4.24	RAI AND ZACHARA, 1984
$\text{H}_2\text{MoO}_4^0$	8.24	RAI AND ZACHARA, 1984
$\text{CaMoO}_4^0$	2.57	ESSINGTON, 1992
$\text{MgMoO}_4^0$	3.03	ESSINGTON, 1992
<b>minerals</b>		
$\text{CdCO}_3$ (c) (otavite)	12.10	STIPP <i>et al.</i> , 1993
$\text{ZnFe}_2\text{O}_4$ (c) (franklinite)	-9.85	LINDSAY, 1979
$\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ (hydrozincite)	-9.65	SCHINDLER <i>et al.</i> , 1969
$\text{Cu}_4(\text{OH})_6\text{SO}_4 \cdot 1.3\text{H}_2\text{O}$ (c)	-17.27	LINDSAY, 1979
$\text{CuOH}$ (c)	0.70	LINDSAY, 1979
$\text{PbSO}_4 \cdot \text{PbO}$ (c)	0.19	LINDSAY, 1979
$\text{Pb}_4\text{O}(\text{PO}_4)_2$ (c)	36.86	LINDSAY, 1979
$\text{Pb}(\text{H}_2\text{PO}_4)_2$ (c)	48.95	LINDSAY, 1979
$\text{H}_2\text{MoO}_4$ (c)	13.37	RAI AND ZACHARA, 1984
$\text{MoO}_3$ (c) (molybdate)	12.10	RAI AND ZACHARA, 1984
$\text{MoO}_2$ (c)	30.02	RAI AND ZACHARA, 1984
Mo (c)	19.73	RAI AND ZACHARA, 1984
$\text{CaMoO}_4$ (c) (powellite)	7.94	RAI AND ZACHARA, 1984
$\text{CuMoO}_4$ (c)	6.48	LINDSAY, 1979
$\text{Fe}_2(\text{MoO}_4)_3$ (c)	35.29	RAI <i>et al.</i> , 1987
$\text{FeMoO}_4$ (c)	7.70	RAI AND ZACHARA, 1984
$\text{MgMoO}_4$ (c)	0.62	RAI AND ZACHARA, 1984
$\text{MnMoO}_4$ (c)	4.13	RAI AND ZACHARA, 1984
$\text{PbMoO}_4$ (c) (wulfenite)	15.80	RAI AND ZACHARA, 1984
$\text{ZnMoO}_4$ (c)	4.40	RAI AND ZACHARA, 1984
Ba $\text{MoO}_4$ (c)	8.26	RAI AND ZACHARA, 1984
$\text{SrMoO}_4$ (c)	7.89	RAI AND ZACHARA, 1984

of log-concentration versus pH. To enhance the readability of the graphs, we present the modelling results for a selected number of samples only. For the leachates in this study, model curves based on equilibrium with (hydr)oxide minerals overlap in graphs depicting log-concentration vs pH and are, therefore, presented for sample QUE1 only. Model curves that do not overlap are shown for samples GS5, QUE1, and 1.5YR only, which we assume are representative for the three categories of bottom ash.

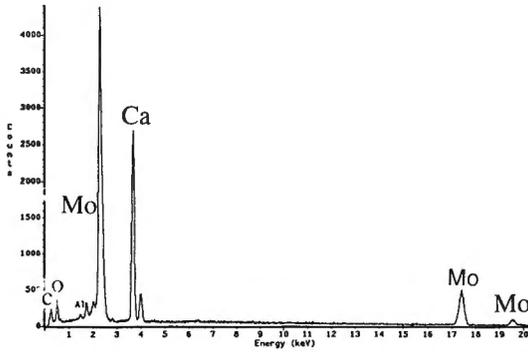
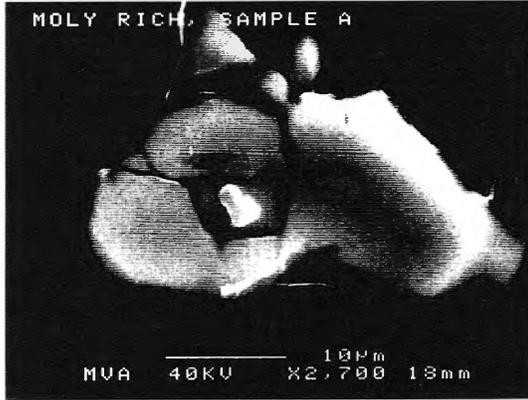
## **RESULTS AND DISCUSSION**

### *Composition and microscopic analysis of bulk bottom ash*

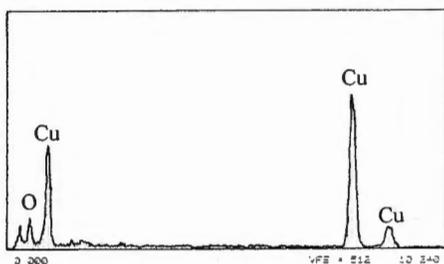
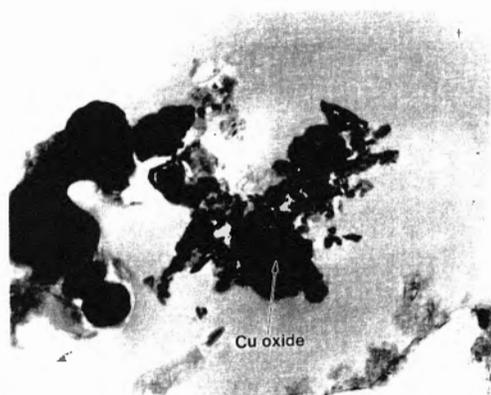
Table 1 gives total concentrations of Cd, Pb, Cu, Zn, and Mo in the various samples of bottom ash. For unknown reasons the Mo-concentration in sample 12YR is much higher than in the other samples of bottom ash.

The SEM-EDS analyses that were performed on bulk samples GS5, UNQ, and QUE1 revealed the presence of discrete particles of various size consisting of metallic Zn, Cu, and Pb, and of Pb silicates. Similar species have been observed earlier in fresh MSWI bottom ash (EIGHMY *et al.*, 1994). Furthermore, a  $\text{CaMoO}_4$ -particle was identified in sample QUE1 (see Figure 1). It has been observed several times before in MSWI bottom ash that Mo is present in the form of  $\text{CaMoO}_4$ -particles (ZEVENBERGEN *et al.*, 1994 and ZEVENBERGEN, unpublished results). The TEM/EDS analyses of bulk 1.5-year old bottom ash revealed  $\text{CuO}$  particles, probably tenorite, with an open structure (Fig. 2), suggesting that the mineral formed as a secondary precipitate.

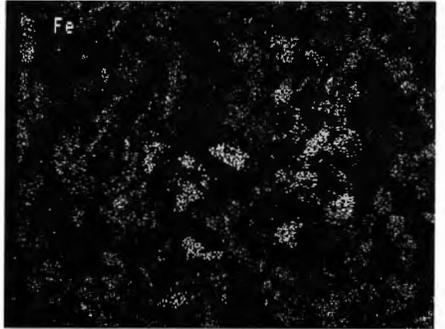
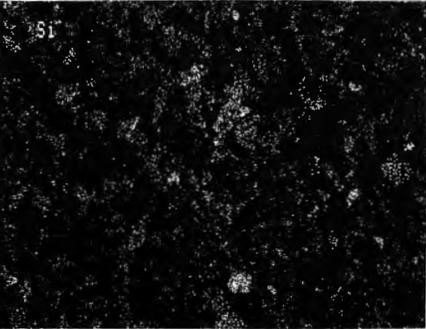
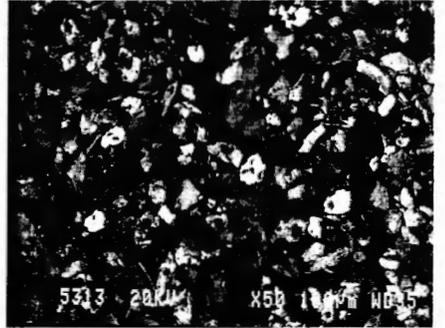
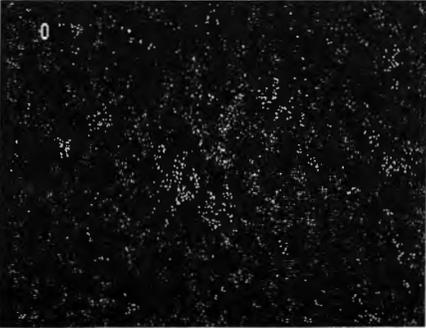
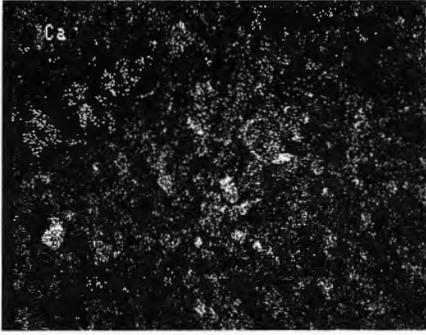
The gel-like precipitates that had been found in sample 1.5YR appeared to be X-ray amorphous. SEM-EDS analysis revealed that in one precipitate Zn was associated with Al, O, and S, whereas in another precipitate both Cu and Zn were found in a matrix consisting mainly of Al and O, and of smaller amounts of Ca and S. These observations indicate that Cu and Zn may coprecipitate with amorphous Al-minerals during weathering.

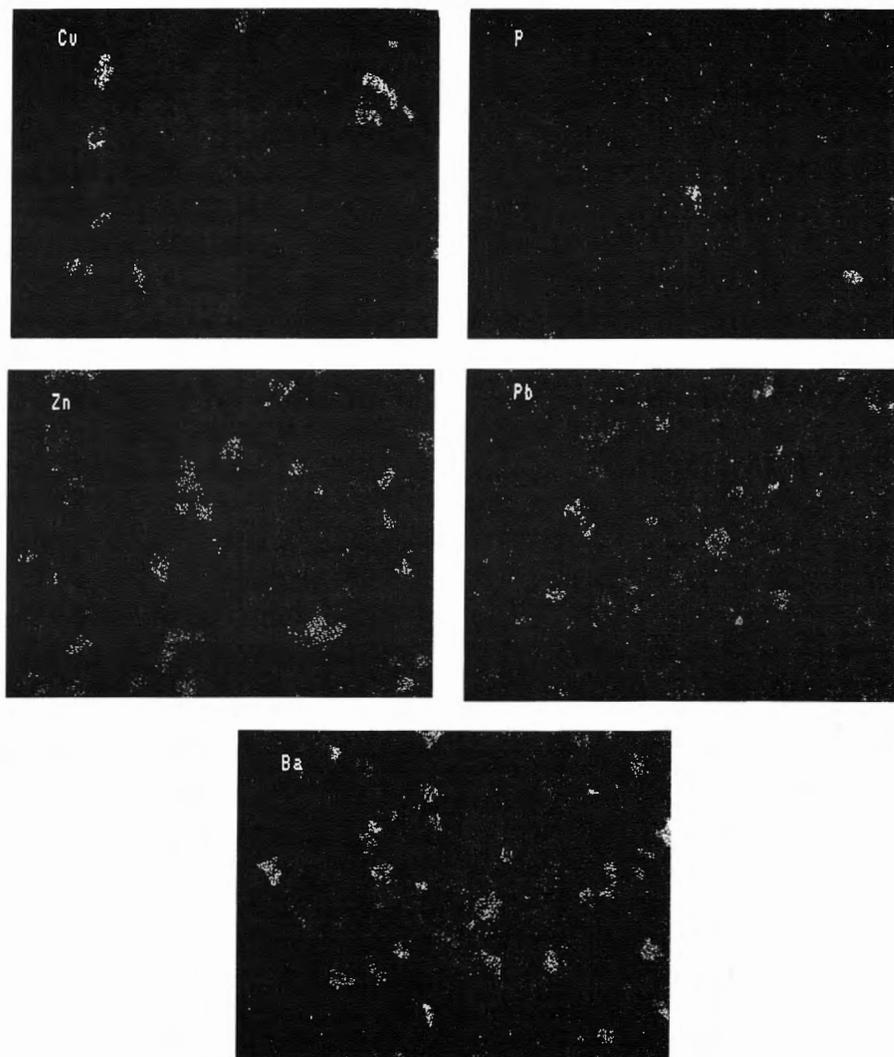


**Figure 1.** Scanning electron micrograph and corresponding EDS spectrum of a  $\text{CaMoO}_4$ -particle in sample QUE1.



**Figure 2.** *Transmission electron micrograph and corresponding EDS-analysis of a thin section of sample 1.5YR. The particles probably consist of tenorite.*





**Figure 3.** Scanning electron micrograph of the high-density fraction of 1.5-year old MSWI bottom ash and corresponding X-ray maps showing the distribution of Ca, Zn, Fe, O, Al, P, Cu, Si, Ba, and Pb/S over the various particles.

*Mineralogical and microscopic analysis of the high-density fraction of sample 1.5YR*

The dense fraction separated from sample 1.5YR represented 1.1 percent of the original mass. Trace element concentrations in this fraction had increased to 5.9 % Zn, 1.9 % Cu, 0.9 % Pb, 73 ppm Mo, and 38 ppm Cd. The XRD analysis revealed the presence of hematite ( $\text{Fe}_2\text{O}_3$ ), wustite ( $\text{Fe}_{0.95}\text{O}$ ), maghemite ( $\text{Fe}_2\text{O}_3$ ), zincite ( $\text{ZnO}$ ), and possibly tenorite ( $\text{CuO}$ ) and cuprite ( $\text{Cu}_2\text{O}$ ). Element associations identified with SEM-EDS are summarised in Table 3, whereas corresponding X-ray spatial images are given in Figure 3 for one electron micrograph. Dominant phase associations of Zn, Cu, and Pb are 'Me/O', 'metallic', 'alloy', and '(complex) silicate'. Furthermore, Pb in particular was found to be also associated with iron oxides, and Cu and Zn with Ca/O compounds. No associations of Cu, Zn, or Pb with P were detected. Identified associations with S are Cu/S and Zn/Al/S/O.

**TABLE 3. Identified trace element associations in weathered MSWI bottom ash.**

identified associations <sup>a</sup>	particles analysed		
	Zn	Cu	Pb
metallic	67	16	23
alloy	21	11	4
simple silicate	22	9	11
complex silicate	15	12	12
associated with O <sup>b</sup>	95	31	10
associated with Ca/O	16	5	1
associated with Fe/O	5	2	4
associated with Al/O <sup>c</sup>	8	1	1
other: Cu/S	-	2	-

<sup>a</sup>The various categories of element associations indicated in this Table are based on SEM-EDS analyses of 250 Zn-rich particles, 90 Cu-rich particles, and 65 Pb-rich particles which were concentrated in the high-density fraction of sample 1.5YR. Particles enriched in Cd or Mo could not be detected.

<sup>b</sup>In addition, XRD-analysis of the high-density fraction of sample 1.5YR indicated that zincite ( $\text{ZnO}$ ), and possibly tenorite ( $\text{CuO}$ ) and cuprite ( $\text{Cu}_2\text{O}$ ) are present in the sample.

<sup>c</sup>In addition, SEM-EDS analysis of gel-like precipitates found in sample 1.5YR indicated the presence of Zn in a matrix consisting of Al, O, and S, and the presence of both Cu and Zn in a matrix consisting of Al and O, and of smaller amounts of S and Ca.

## *effects of weathering on minor element leaching*

In summary, the 1.5-year old bottom ash contains substantial amounts of mineral phases of Pb, Cu, and Zn which are stable at atmospheric conditions and may have formed secondarily, but unweathered 'metallic' and 'silicate phases' of these elements were also detected. Unfortunately, we were not able to investigate the speciation of Cd and Mo because their bulk concentrations were too low, even when the density-based separation technique was used. The observed element associations are very useful to help evaluate potential precipitation/dissolution processes identified by geochemical modelling (see below).

### *Trace element leaching*

#### *Cd*

Figure 4a shows pH-stat leaching data for Cd together with model-predicted concentrations. Two characteristic leaching curves are distinguished. The first shows almost pH-independent leaching over a large range of pH values; this is typical for samples of A- and B-type bottom ash. The second shows more pH-dependent leaching with the lowest concentrations at pH 8.5-9.5, which was found to be typical for C-type bottom ash.

The relatively strong Cd-leaching observed for the grate siftings and for samples of B-type bottom ash is consistent with solubility-control by otavite and amorphous  $\text{Cd}(\text{OH})_2$  at intermediate and alkaline pH, respectively. Since otavite readily precipitates from oversaturated solutions (MIDDELBURG AND COMANS, 1991) and carbonates are probably important Cd-phases in combined MSWI bottom ash and fly ash (KIRBY AND RIMSTIDT, 1993), it is very likely that otavite controls Cd-leaching from A- and B-type bottom ash. Cd-leaching from sample UNQ is too low to be in equilibrium with any known Cd-mineral, and the almost constant leaching as a function of pH indicates that the Cd in the solid phase is not readily available for leaching.

The V-shaped leaching curves for C-type bottom ash are characterised by a strong undersaturation with respect to any known Cd-mineral, whereas the acid-soluble amount of Cd is comparable or even higher than observed for A- and B-type bottom ash. Since weathering has

been shown to result in the formation of large amounts of reactive sorbent minerals such as Fe/Al-(hydr)oxides, amorphous aluminosilicates, and calcite (ZEVENBERGEN AND COMANS, 1994; ZEVENBERGEN *et al.*, 1994; MEIMA AND COMANS, 1997a; MEIMA *et al.*, 1997a), Cd-leaching at relatively low concentrations is probably controlled by sorption processes. In considering the processes that control the partitioning of ions between the solid and liquid phase, we use the general term "sorption" to refer to processes other than precipitation/dissolution of pure mineral phases, i.e. adsorption and coprecipitation processes. Sorption processes are expected to be important when suspensions are undersaturated with respect to known solubility-controlling minerals (see also general discussion below).

### *Pb*

Figure 4b shows leaching data and model curves for Pb. The curves for A- and B-type bottom ash show relatively pH-independent leaching over a large range of pH values. The leaching of Pb from C-type bottom ash, however, appears to be more dependent on the pH and the concentrations at intermediate pH are considerably lower than found for A- and B-type bottom ash.

In general, all leachates remain undersaturated with respect to the mineral anglesite ( $\text{PbSO}_4$ ). The mineral  $\text{Pb}(\text{OH})_2$  does not seem to control Pb-leaching either, since leachates are strongly oversaturated with respect to  $\text{Pb}(\text{OH})_2$  at alkaline pH. Consistent with this result is the finding by MARANI *et al.* (1995a) that  $\text{Pb}(\text{OH})_2$  did not precipitate from aqueous solutions of Pb,  $\text{SO}_4$ , and  $\text{CO}_3$  which were equilibrated for 10 months at room temperature and were oversaturated with respect to  $\text{Pb}(\text{OH})_2$ ; anglesite, hydrocerrusite ( $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ ) or cerrusite ( $\text{PbCO}_3$ ) precipitated instead. Our leachates were generally undersaturated with respect to cerrusite, which is the most stable Pb-carbonate mineral. KIRBY AND RIMSTIDT (1994) observed Pb-concentrations to decrease slowly with time in leachates from fresh MSWI (mixed) bottom & fly ash. Possibly, Pb is solubilised initially from very soluble compounds which transform slowly into more stable phases. Soluble Pb-compounds may include carbonate phases, since it has been suggested that carbonates are

important Pb-phases in combined MSWI bottom ash and fly ash (KIRBY AND RIMSTIDT, 1993).

The curves of C-type bottom ash resemble the curve for  $\text{Pb}(\text{OH})_2$  above pH 9.5. Below pH 9.5, Pb-concentrations are too low to be in equilibrium with any Pb-mineral in the database except Pb phosphates. Fig. 4b shows that Pb-concentrations approach the curve for chloropyromorphite ( $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$ ) over a very large range in pH. However, no associations of Pb and P were detected in any of the 65 Pb-rich particles analysed in sample 1.5YR by SEM-EDS; this decreases the probability that Pb-leaching from C-type bottom ash is solubility-controlled. Below we discuss the probability of sorption-control.

### *Zn*

The leaching of Zn is strongly dependent on the pH for all types of bottom ash. The lowest concentrations are generally observed at pH 9.5. Given these similarities, there may be one single mechanism which controls Zn-leaching irrespective of the degree of weathering.

MINTEQA2 modelling indicates that almost all Zn-minerals in the database are too soluble to control Zn-leaching. Exceptions are franklinite ( $\text{ZnFe}_2\text{O}_4$ ),  $\text{ZnSiO}_3$ , and willemite ( $\text{Zn}_2\text{SiO}_4$ ). All leachates are strongly oversaturated with respect to both franklinite and  $\text{ZnSiO}_3$ , which suggests that there are kinetic constraints on the precipitation of these two minerals. Best modelling results have been obtained for willemite (Fig. 4c), but although the mineral has been found as a secondary mineral in the oxidised zone of zinc deposits (KLEIN AND HURLBUT, 1985), it was not detected by workers who synthesised Zn-silicates from aqueous solutions kept at room temperature and 1 atm. (TILLER AND PICKERING, 1974; LEGGETT, 1978). Furthermore, in an experiment in which  $1.10^{-5}\text{M}$  Zn and  $3.10^{-4}\text{M}$  Si were equilibrated for 24 hours at pH 8.5, 9.5, and 10.5, final Zn-concentrations were one order of magnitude higher than those observed in Figure 4c, although the solutions were strongly oversaturated with respect to willemite (unpublished results). These results indicate that willemite does not readily precipitate from oversaturated solutions and lower the probability that it is a controlling solid in MSWI bottom ash leachates. Zincite, on the other hand, has been detected in both fresh (EIGHMY *et al.*, 1994) and weathered MSWI bottom ash (this study), and

the curve for zinc concentrations in equilibrium with zincite follow the shape of the pH-leaching data. However, except for sample 12YR at  $\text{pH} > 9.5$ , most leachates remain about one order of magnitude undersaturated with respect to zincite. Alternatively, sorption may control Zn-leaching (see below).

### Cu

As shown in Figure 4d, each category of bottom ash is represented by a distinct Cu-leaching curve. For A-type bottom ash Cu-leaching is pH-independent, even at low pH, indicating that the Cu in the solid phase is not readily available for leaching. The leaching of Cu from B-type bottom ash is also largely pH-independent, but concentrations are 2 orders of magnitude higher than for A-type bottom ash and increase below pH 6. The leaching of Cu from C-type bottom ash leads to V-shaped concentration curves; minimum leaching occurs at pH 8.5 at concentrations comparable to those in A-type bottom ash.

MINTEQA2 modelling shows that several secondary Cu-minerals may precipitate from A-, B-, and C-type bottom ash leachates. Among these, malachite ( $\text{Cu}_2(\text{OH})_2\text{CO}_3$ ) and azurite ( $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$ ) have solubility-curves that match the data from C-type bottom ash fairly closely (Fig. 4d). Tenorite, however, is among the least soluble Cu-minerals at  $\text{pH} > 7.5$ . Because tenorite precipitates from alkaline sulphate-rich aqueous solutions at atmospheric pressure and temperature (MARANI *et al.*, 1995b), and because observations by electron microscopy and X-ray diffraction analysis of sample 1.5YR also suggest the mineral to be present (Fig. 2; Table 3), tenorite is the expected solubility-controlling mineral for Cu. However, above pH 8 all leachates appear to be strongly oversaturated with respect to tenorite. From leaching experiments as a function of the L/S-ratio we have concluded earlier that the leaching of Cu from fresh MSWI bottom ash does not seem to occur via a concentration-limiting mechanism (MEIMA AND COMANS, 1997a). Furthermore, recent findings show that the dissolved Cu in leachates from fresh and 1.5-year old MSWI bottom ash is largely bound to dissolved organic carbon (DOC) (MEIMA *et al.*, 1997b), which is likely to explain the observed high Cu-concentrations in Fig. 4d. Currently, we are investigating the conditional stability-constants of Cu-DOC complexes in

MSWI bottom ash leachates, so that these complexation reactions can be incorporated in future modelling (e.g. MEIMA *et al.*, 1997b).

Given the potential importance of Cu-DOC complexes, malachite and azurite may well be too soluble to precipitate from C-type bottom ash leachates. The mechanism that leads to the observed V-shaped leaching curves, therefore, remains unclear. The observed association of Cu with amorphous Al-minerals (Table 3), however, suggests that sorption may also be important (see general discussion).

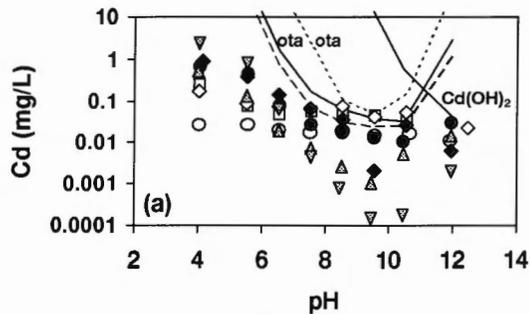
### *Mo*

A-type bottom ash shows relatively strong but almost pH-independent Mo-leaching (Fig 4e). Mo-leaching from B- and C-type bottom ash generally decreases below pH 7.5, and is largely pH-independent above pH 7.5 (B-type bottom ash) or shows a continuous increase (C-type bottom ash). The high Mo-concentration that is leached from sample 12YR at alkaline pH is consistent with the fact that the sample has a higher bulk Mo-content than the other samples (Table 1).

A-type bottom ash leachates are almost saturated with respect to powellite. Since powellite has been shown to precipitate by direct reaction of sodium molybdate with  $\text{CaCl}_2$  at atmospheric pressure and temperature (KINDNESS *et al.*, 1994), and  $\text{CaMoO}_4$  has been detected in sample QUE1 (Figure 1), it is likely that powellite controls Mo-leaching from A-type bottom ash.

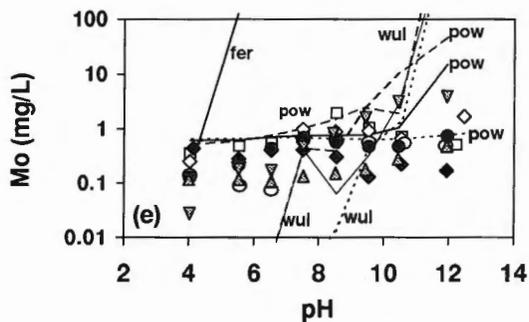
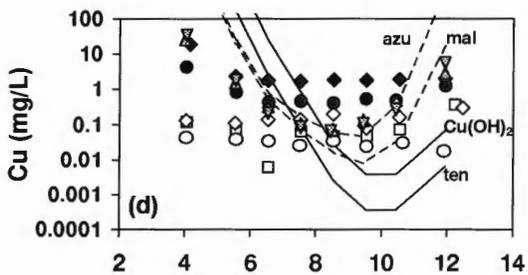
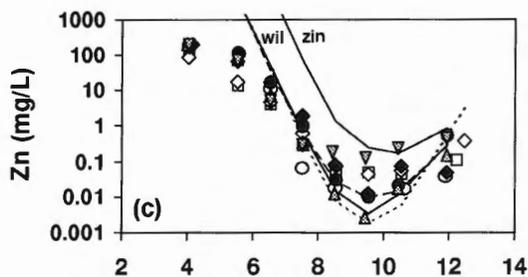
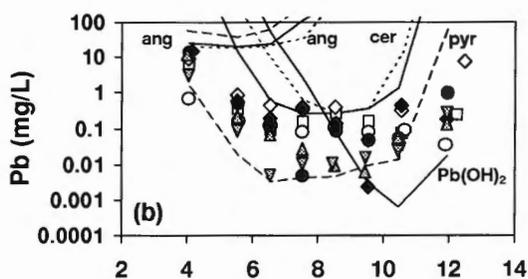
B- and C-type bottom ash leachates, however, are mostly undersaturated with respect to powellite; the main reason for this is the lower concentration of Ca at alkaline pH due to the precipitation of ettringite ( $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$ ) or calcite, respectively (MEIMA AND COMANS, 1997a). At pH 8.5 leachates are close to equilibrium with wulfenite ( $\text{PbMoO}_4$ ), but at lower pH all leachates become strongly oversaturated with respect to this mineral (Fig. 4e). Below pH 4 the mineral  $\text{Fe}_2(\text{MoO}_4)_3(\text{s})$  becomes stable and may control Mo-solubility. Alternatively, above pH 4 Mo-leaching from B- and C-type bottom ash may be controlled by sorption processes rather than by the solubility of a pure Mo-mineral. The decrease in Mo-leaching towards low pH is consistent with the affinity of anions for metal(hydr)oxide surfaces (e.g. DZOMBAK AND MOREL, 1990). The plateau in Mo-leaching for B-type

bottom ash above pH 7.5 may then be caused by a limited availability of Mo. This is consistent with the observation that the amount of Mo released is proportional to the L/S-ratio (COMANS *et al.*, 1993a; MEIMA AND COMANS, 1997a). It is reasonable to assume that weathering has increased the availability of Mo as well as the amount of secondary metal(hydr)oxides in C-type bottom ash. These characteristics would also support sorption-control as an explanation for the continuous increase in Mo-leaching from C-type bottom ash at alkaline pH.



**Figure 4.** Total dissolved Cd (a), Pb (b), Zn (c), Cu (d), and Mo (e) in bottom ash leachates at  $L/S=5$  as a function of pH, and MINTQA2 predictions assuming equilibrium with different mineral phases. Symbols:  $\square$  GS2;  $\diamond$  GS5;  $\circ$  UNQ;  $\bullet$  QUE1;  $\blacklozenge$  6WK;  $\blacktriangle$  1.5YR;  $\blacktriangledown$  12YR. Abbreviations: Cd(OH)<sub>2</sub>, am-Cd(OH)<sub>2</sub>; ota, otavite (CdCO<sub>3</sub>); ang, anglesite (PbSO<sub>4</sub>); cer, cerrusite (PbCO<sub>3</sub>); pyr, chloropyromorphite (Pb<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>Cl); wil, willemite (Zn<sub>2</sub>SiO<sub>4</sub>); zin, zincite (ZnO); azu, azurite (Cu<sub>3</sub>(OH)<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub>); mal, malachite (Cu<sub>2</sub>(OH)<sub>2</sub>CO<sub>3</sub>); ten, tenorite (CuO); pow, powellite (CaMoO<sub>4</sub>); wul, wulfenite (PbMoO<sub>4</sub>); fer, Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>. The style of the lines indicates the category of bottom ash on which MINTQA2 modelling was performed: ----- A-type; (—) B-type; (---) C-type bottom ash. Samples GS5, QUE1, and 1.5YR were taken as representative for the three categories of bottom ash.

*effects of weathering on minor element leaching*



## GENERAL DISCUSSION

If we study MSWI bottom ash leaching at its "natural" pH, the lowest concentrations of Cd, Pb, Zn, Cu, and Mo are generally observed for the more weathered and carbonated (C-type) bottom ash. Appropriate explanations are reviewed below. First, there is a pH-effect: during weathering, bottom ash pH decreases from >12 (A-type), via 10-10.5 (B-type) to 8-8.5 (C-type) (MEIMA AND COMANS, 1997a). Since the "natural" pH of C-type bottom ash almost coincides with the minima of the V-shaped leaching curves (Fig. 4a-d), weathering is expected to result in a reduced leaching of heavy-metals. Secondly, the processes controlling leaching from carbonated bottom ash are likely to be different, since the leaching patterns of C-type bottom ash are generally clearly different from those of A- and B-type bottom ash. In A- and B-type bottom ash the general processes are thought to be precipitation/dissolution of relatively soluble minerals, such as otavite, cerrusite, and powellite, whereas Cu in particular is likely to be solubilised by extensive complexation with DOC. In C-type bottom ash trace element leaching does not seem to be solubility-controlled, and sorption to neoformed minerals may be the controlling-mechanism (see below). Poorer leaching does not seem to be caused primarily by a prior release of Cd, Pb, Zn, Cu, or Mo from the bottom ash during ageing/storage: if this process were significant, leaching curves of C-type bottom ash would lie below those of B-type bottom ash over the whole range of pH values studied. However, according to Fig. 4, leaching curves of C-type bottom ash lie below those of B-type bottom ash at intermediate pH values only, i.e. the potentially available amount for leaching in B- and C-type bottom ash is similar. This conclusion is consistent with the results of a lysimeter washing experiment in which the percolation of contaminants (e.g. Cd, Pb, Zn, Cu) from MSWI bottom ash was studied over a 2-year period (STEGEMANN *et al.*, 1995): suspensions of fresh and washed ash yielded similar concentrations of Cd, Pb, Zn, and Cu after reacting the ash with CO<sub>2</sub> to a final pH of approximately 6.

Sorption is potentially an important mechanism in controlling the leaching of Cd, Zn, Cu, Pb, and Mo from C-type bottom ash, as was suggested above. Reactive sorbent minerals such as Fe/Al-(hydr)oxides

are present in large amounts, particularly in weathered MSWI bottom ash (ZEVENBERGEN AND COMANS, 1994; MEIMA AND COMANS, 1997a; MEIMA *et al.*, 1997a). Each of the elements Cd, Pb, Zn, Cu, and Mo has a high affinity for Fe/Al-hydroxides (KINNIBURGH *et al.*, 1976; DZOMBAK AND MOREL, 1990). Moreover, fresh calcite will precipitate as a result of carbonation, which may also affect the leaching of Cd and Zn because of their high affinity for calcite (JENNE, 1977; COMANS AND MIDDELBURG, 1987). Sorption on these minerals is qualitatively consistent with the observed leaching patterns: the affinity of heavy-metals for these minerals increases with increasing pH, whereas Me-hydrolysis and Me-complexation with carbonate may lead to higher total dissolved concentrations at strongly alkaline pH. The affinity of oxyanions (Mo) increases with decreasing pH. The identification of associations of Pb, Zn, and Cu with Ca/O, Fe/O, and Al/O in weathered bottom ash (Table 3) also supports this hypothesis. In view of the large impact of weathering in reducing trace element leaching in the long-term, we are currently trying to identify and model sorption processes in weathered MSWI bottom ash (e.g. MEIMA AND COMANS, 1997b)

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## **Chapter 4**

### **Carbonation processes in MSWI bottom ash and their effect on the leaching of Cu and Mo.**

# CARBONATION PROCESSES IN MUNICIPAL SOLID WASTE INCINERATOR BOTTOM ASH AND THEIR EFFECT ON THE LEACHING OF COPPER AND MOLYBDENUM\*

Jeannet A. Meima<sup>1</sup>, Renata D. van der Weijden<sup>‡</sup>,  
T.Taylor Eighmy<sup>¶</sup>, Rob N.J. Comans<sup>1</sup>

<sup>1</sup> Netherlands Energy Research Foundation (ECN),  
Westerduinweg 3, 1755 LE Petten, The Netherlands

<sup>‡</sup> Baan Research, P.O. Box 250, 6710 BG Ede, The Netherlands

<sup>¶</sup> Environmental Research Group, University of New  
Hampshire, A115 Kingsbury Hall, Durham, New Hampshire

## ABSTRACT

The interaction of CO<sub>2</sub> with Municipal Solid Waste Incinerator (MSWI) bottom ash was studied in order to investigate the resulting changes in pH and bottom ash mineralogy and the impact that these changes have on the mobility of Cu and Mo. Carefully controlled carbonation experiments were performed on bottom ash suspensions and on filtered bottom ash leachates. Changes in leachate composition were interpreted with the geochemical model MINTEQA2, and neoformed minerals were investigated by means of chemical/spectroscopic analyses. The leaching of Cu and Mo during artificial carbonation is compared to the leachability of Cu and Mo from a sample of naturally carbonated bottom ash from the same incinerator. During carbonation in the laboratory, a precipitate was formed that consisted mainly of Al-rich amorphous material, calcite, and possibly gibbsite. Carbonation to pH  $\approx$  8.3 resulted in a reduction of more than 50% in Cu-leaching, and a reduction of approximately 3% in Mo-leaching. The reduction in Cu leaching is attributed to sorption to the neoformed amorphous Al-minerals. During natural weathering/carbonation of bottom ash, additional sorption sites are formed which further reduce the leaching of Cu and Mo on a time scale of months to years.

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## INTRODUCTION

Municipal Solid Waste Incinerator (MSWI) bottom ash contains potentially toxic elements and is produced in very large quantities. In particular copper and molybdenum have been shown to be leached in relatively large amounts from Dutch MSWI bottom ash (BORN, 1994). Since MSWI bottom ash is formed at high temperatures and subsequently cooled fairly rapidly, the material is unstable under atmospheric conditions. Weathering will, therefore, change the mineralogical characteristics of the material. For a proper assessment of the long-term environmental impact of ash utilisation and disposal, it is necessary to understand these weathering processes and their effect on (trace) element leaching.

Carbonation has been recognised to be an important weathering process affecting alkaline (waste) materials such as MSWI bottom ash (COMANS AND MEIMA, 1994; ZEVENBERGEN AND COMANS, 1994; CHANDLER *et al.*, 1997; MEIMA AND COMANS, 1997a), coal fly ash (e.g. SCHRAMKE, 1992), and oil shale solid wastes (e.g. REDDY *et al.*, 1986; ESSINGTON, 1991). Carbonation involves the absorption of CO<sub>2</sub> by an initially alkaline material; this causes the pH to decrease and calcite (CaCO<sub>3</sub>) to precipitate until the material is in equilibrium with (atmospheric) CO<sub>2</sub>. During the carbonation of MSWI bottom ash Al(OH)<sub>3</sub>(s) and amorphous aluminosilicates have also been found to precipitate (ZEVENBERGEN AND COMANS, 1994). Aluminium minerals are likely to precipitate because the solubility of Al is strongly reduced when the pH decreases from >10 to 8-8.5 (STUMM AND MORGAN, 1981; MEIMA AND COMANS, 1997a). The CO<sub>2</sub> required for carbonation may originate from the atmosphere or from the biodegradation of organic residues (BELEVI *et al.*, 1992).

The effect of carbonation on trace element mobility has been investigated recently for cement-solidified wastes (LANGE *et al.*, 1996), alkaline coal fly ash (REDDY *et al.*, 1994), and oil shale solid wastes (REDDY *et al.*, 1991, 1994). In these experiments a significant reduction in the leaching of Cu was observed and in some cases also in the leaching of Mo. Less is known about the impact of carbonation on the leaching of trace elements from MSWI bottom ash. Recent experiments, however,

have shown that significantly less Cu and Mo are leached from naturally weathered MSWI bottom ash than from fresh ash (MEIMA AND COMANS, 1997a,b). The lower leaching from weathered bottom ash has been attributed to the neutralisation of bottom ash pH and to the sorption of Cu and Mo to neoformed minerals (MEIMA AND COMANS, 1997b,c).

This paper describes a study on mineral neoformation during the carbonation of MSWI bottom ash and investigates the impact that carbonation has on the mobility of Cu and Mo. Experiments consisted of (a) monitoring leachate composition and CO<sub>2</sub>-absorption during the carbonation of bottom ash *suspensions* in water, (b) monitoring leachate composition during the carbonation and acid neutralisation of filtered bottom ash *leachates*, and (c) chemical/spectroscopic analysis of the precipitate that was formed during the carbonation of filtered bottom ash leachates.

## **MATERIALS AND METHODS**

### *Bottom ash description*

Freshly quenched bottom ash was obtained from a Dutch municipal solid waste incinerator in 1994 and in 1996. The 1996-sample was used in the larger-scale carbonation experiment with filtered bottom ash leachate (see below). Both samples were air-dried and subsequently sieved through a 2mm-sieve. The 1994 sample was crushed so that all material, except for some metal-scrap, would pass through the 2mm-sieve. Sample treatment and leaching characteristics of the 1994 sample have been described in more detail elsewhere (MEIMA AND COMANS, 1997a,b).

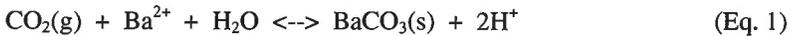
### *Carbonation experiments with suspended MSWI bottom ash*

Carbonation experiments with suspended bottom ash were performed in duplicate in 300 ml Teflon (PFA) reaction vessels at a constant temperature of 20°C. Suspensions of 50 g bottom ash (batch 1994) in 250 ml nanopure demineralised water were allowed to equilibrate for 4 weeks in closed vessels prior to carbonation. Carbonation was initiated by bubbling a constant flow (5.0 ± 0.4 litre/hour) of moistened air through the ash suspensions until its pH

stabilised at 8-8.5; this procedure took 3-4 days. The pH was monitored continuously. Leachate composition and CO<sub>2</sub>-absorption were monitored in separate suspensions as described below.

The sampling procedure was as follows: without interruption of the experiment, 10 ml of suspension was pipetted through a sample port in the reaction vessel. Aliquots were taken before starting carbonation, and 2.5 hours, 1 day, 3 days, and 1 week after starting carbonation. Additional aliquots were taken from a separate suspension during the 4-week equilibration period prior to carbonation. After collection, each aliquot was filtered through a 0.2 µm membrane filter and the clear filtrates were divided in two. One half was acidified with concentrated suprapure HNO<sub>3</sub> and was used for the analysis of Na, K, Ca, S, Al, Si, Fe, Cu, and Mo by ICP-AES. The other half was left untreated and was used to measure total inorganic carbon and total dissolved organic carbon with a carbon analyser. Final leachates (after carbonation) were also subjected to ion chromatography in order to measure Cl.

CO<sub>2</sub>-absorption was monitored continuously in suspensions of 20g bottom ash (batch 1994) and 100 ml nanopure demineralised water. The absorbed CO<sub>2</sub> was measured as the difference between CO<sub>2(in)</sub>, which is the CO<sub>2</sub>-content of the original moistened air, and CO<sub>2(out)</sub>, which is the CO<sub>2</sub>-content of the air that had passed through the bottom ash suspension. To analyse CO<sub>2(in)</sub> and CO<sub>2(out)</sub>, the CO<sub>2</sub> was trapped quantitatively in a 500 ml solution of pH 10.5 containing 100 g/L Ba(ClO<sub>4</sub>)<sub>2</sub>, 10% (v/v) tertiary butanol, and 10% (v/v) glycerine. The acid that is produced by the reaction between CO<sub>2</sub> and barium (see Eq. 1) was back-titrated automatically with NaOH.



#### *Carbonation experiments with filtered bottom ash leachates*

Filtered bottom ash leachate was obtained from a suspension of 200 g MSWI bottom ash (batch 1994) and 1L nanopure demineralised water, which was equilibrated for 24 hours and was subsequently filtered through a 0.2µm membrane filter. The clear filtrate was divided over four 300 ml Teflon (PFA) reactions vessels equipped with magnetic stirrers,

and a small portion was left for chemical analysis. The temperature of the vessels was kept at 20°C.

*Vessel 1.* In vessel 1 carbonation was initiated by bubbling a constant flow of moistened air through the leachate. Samples were withdrawn without interrupting the experiment (see above) at pH 9.5, 9.0, and 8.2, which pH-values were reached after approx. 4, 8, and 24 hours of carbonation, respectively. Samples were filtered through 0.2µm membrane filters and were subjected to chemical analysis as described for the suspensions.

*Vessel 2.* In vessel 2 the concentration of Ca was doubled by the addition of 600 mg/L Ca(OH)<sub>2</sub> for the purpose of investigating increased calcite precipitation on leachate composition. The solution was subsequently equilibrated for 24 hours in a pH-stat system at the pH of the original solution. The pH was adjusted by the addition of analytical grade HNO<sub>3</sub> or NaOH. After equilibration, a subsample was taken for chemical analysis, and carbonation was carried out as described for vessel 1.

*Vessel 3.* In vessel 3 the leachate pH was neutralised by the addition of HNO<sub>3</sub>. HNO<sub>3</sub> was added to prevent the precipitation of calcite and to investigate the effect of pH-neutralisation only. The rate of pH-neutralisation was adjusted to the carbonation rate of vessel 1. Samples were taken as described for vessel 1.

*Vessel 4.* In vessel 4 the concentration of Al was doubled by the addition of 480 mg/L AlCl<sub>3</sub>.6H<sub>2</sub>O. This aluminium salt was added in order to investigate increased Al(OH)<sub>3</sub> precipitation on leachate composition. The solution was subsequently equilibrated for 24 hours at the pH of the original solution as described for vessel 2. Then, a subsample was taken for chemical analysis, and the pH was neutralised as described for vessel 3.

To obtain ≥ 1 g of the minerals that precipitate during carbonation, 1 kg of fresh MSWI bottom ash (batch 1996) was suspended in 5L of nanopure demineralised water. The suspensions were tumbled continuously for 3 days and were subsequently filtered through 0.2 µm membrane filters. The clear filtrate was divided over two 2L-polyethylene vessels. Carbonation was initiated by bubbling a constant

flow of moistened air through the leachates. The leachates were stirred continuously by a magnetic stirrer. Carbonation was continued until the pH stabilised at 8-8.5; this took approx. 1 day. The solutions were filtered through a 0.2  $\mu\text{m}$  membrane filter to collect the precipitate that had formed. Initial and final leachates were analysed by ICP-AES, ion-chromatography, and a carbon analyser as described above for the suspensions. The precipitate was vacuum-dried, and its analytical composition was determined by redissolution and subsequent ICP-AES analysis. The mineralogical composition was investigated by means of X-ray diffraction analysis (XRD), X-ray photo electron spectroscopy (XPS), and scanning electron microscopy in combination with energy-dispersive X-ray spectroscopy (SEM/EDS). The spectroscopic methods are described elsewhere (EIGHMY *et al.*, 1994; ZEVENBERGEN *et al.*, 1994).

#### *Geochemical modelling*

The computer code MINTEQA2 version 3.11 (ALLISON *et al.*, 1991) was used to calculate the composition of the leachates in equilibrium with potential solubility-controlling minerals as described in detail elsewhere (MEIMA AND COMANS, 1997a). The following additions and modifications were made to the standard MINTEQA2 databases:  $\log K [\text{Cu}(\text{OH})_2^{\circ}] = -16.20$  (MOREL AND HERING, 1993);  $\log K [\text{HMoO}_4^-] = 4.24$  and  $\log K [\text{H}_2\text{MoO}_4^{\circ}] = 8.24$  (RAI *et al.*, 1984);  $\log K [\text{CaMoO}_4^{\circ}] = 2.57$  and  $\log K [\text{MgMoO}_4^{\circ}] = 3.03$  (ESSINGTON, 1992a);  $\log K_{\text{sp}} [\text{ettringite, Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}] = -56.70$  (ATKINS *et al.*, 1991);  $\log K_{\text{sp}} [\text{gypsum, CaSO}_4\cdot 2\text{H}_2\text{O}] = 4.62$  (MOREL AND HERING, 1993);  $\log K_{\text{sp}} [\text{powellite, CaMoO}_4 \text{ (c)}] = 7.94$  (RAI *et al.*, 1984).

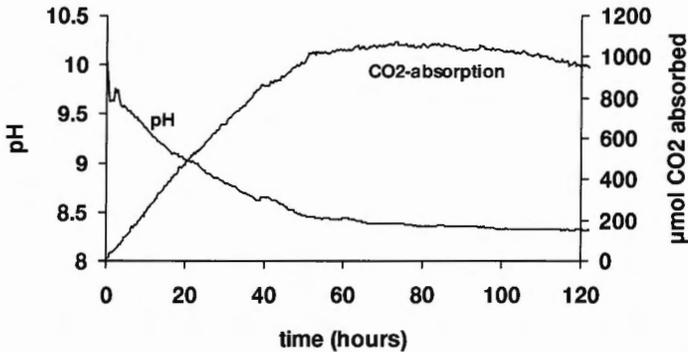
## RESULTS AND DISCUSSION

### *The extent of CO<sub>2</sub>-absorption and resulting changes in bottom ash pH*

Figure 1 shows in detail the observed changes in bottom ash pH and CO<sub>2</sub>-absorption as carbonation proceeds. Initially, the pH of the bottom ash dropped quickly from pH 10.1-10.2 to 9.7-9.6, and then gradually to a pH of 8.3 after approx. 70 hours. MINTEQA2 calculations show that

after 70 hours leachates are in equilibrium with atmospheric  $p\text{CO}_2$ . Altogether, 1 mmol of  $\text{CO}_2$  was absorbed by the 20g of bottom ash (Fig. 1), which equals 0.050 mmol  $\text{CO}_2/\text{g}$  bottom ash or 0.10 mmol  $\text{H}^+/\text{g}$  bottom ash. For comparison, the Acid Neutralising Capacity (ANC) of this bottom ash, measured by titration with  $\text{HNO}_3$  to pH 8.5, is 0.54 mmol/g, whereas values of 0.6-1.0 mmol/g have been reported for other samples of fresh MSWI bottom ash (BELEVI *et al.*, 1992; JOHNSON *et al.*, 1995). Apparently, the neutralisation of MSWI bottom ash with  $\text{CO}_2$  requires significantly less  $\text{H}^+$  than does neutralisation with  $\text{HNO}_3$ . Possibly, carbonation has produced a coating of  $\text{CaCO}_3$  around basic Ca-minerals, which would slow down the dissolution of underlying minerals.

Fig. 1 also shows that the rate of  $\text{CO}_2$ -absorption is highest in the early stages of carbonation, which is consistent with the higher affinity of  $\text{CO}_2$  for more alkaline solutions. The average efficiency of  $\text{CO}_2$ -absorption by these well-stirred suspensions is less than 50%, which was calculated from the fraction of  $\text{CO}_{2(\text{in})}$  that was absorbed by the suspensions. Higher efficiencies, however, may be reached with bottom ash that is only moistened (REDDY *et al.*, 1994).



**Figure 1.** Bottom ash pH and  $\text{CO}_2$ -absorption as a function of carbonation run time in a suspension of 20 g MSWI bottom ash and 100 ml nanopure water.

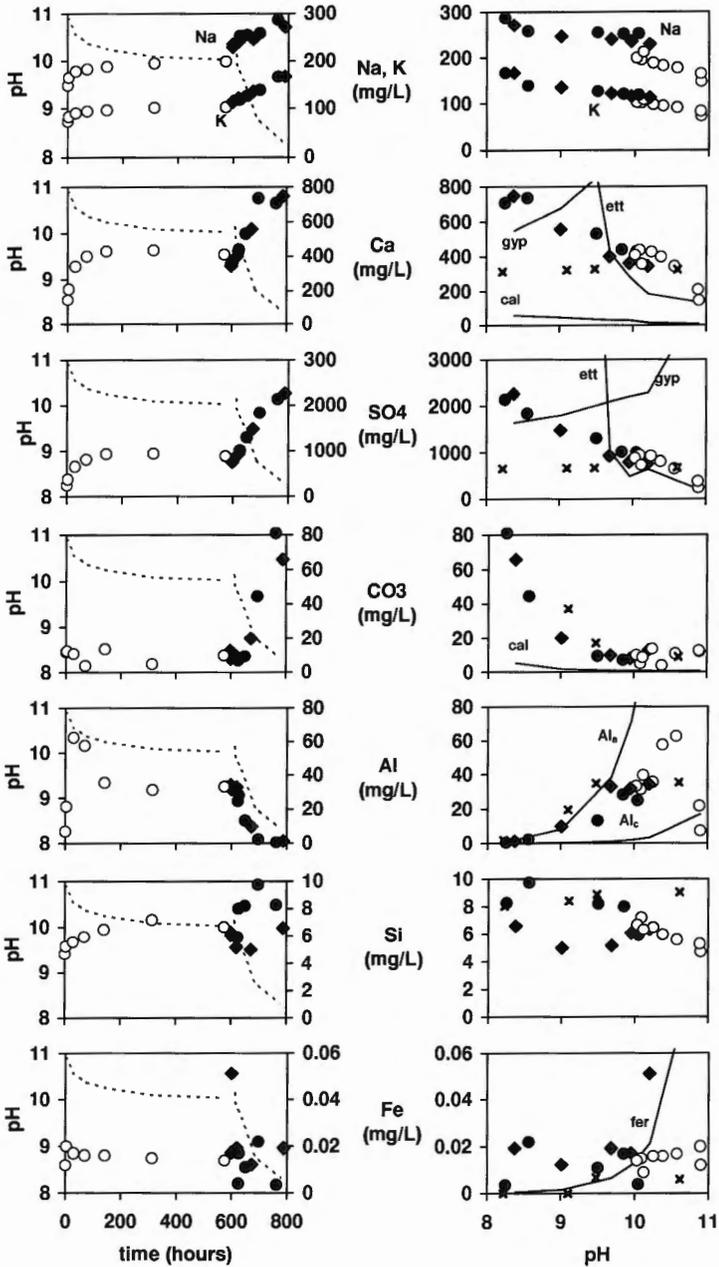
*General leaching trends*

Table 1 shows the bulk chemical composition of the bottom ashes and inferred solubility-controlling minerals as indicated by MEIMA AND COMANS (1997a,b).

Figure 2 shows the leachate concentrations of Na, K, Ca, SO<sub>4</sub>, CO<sub>3</sub>, Al, Si, and Fe as a function of equilibration run time, carbonation run time, and bottom ash pH, and also shows MINTEQA2 modelling results. During the 4-week equilibration period prior to carbonation, the pH and the concentrations of major elements (Na, K, Ca, SO<sub>4</sub>, Al, Fe, Si, CO<sub>3</sub>) reached almost constant values. Bottom ash pH stabilised at 10.1-10.2, which is close to the equilibrium pH of 10.0 predicted by the coexistence of ettringite (Ca<sub>6</sub>Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>(OH)<sub>12</sub>·26H<sub>2</sub>O), gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O), and gibbsite (Al(OH)<sub>3</sub>) (MEIMA AND COMANS, 1997a). MINTEQA2 model-curves show that leachates are close to equilibrium with ettringite and ferrihydrite (Fe(OH)<sub>3</sub>), slightly undersaturated with respect to gypsum, and 1-1.5 orders of magnitude oversaturated with respect to gibbsite and calcite (CaCO<sub>3</sub>). Al-leaching seems to be controlled by amorphous Al(OH)<sub>3</sub> rather than by crystalline Al(OH)<sub>3</sub>. Si-leaching tends to decrease after approx. 2 weeks of equilibration. Since leachates are strongly undersaturated with respect to amorphous SiO<sub>2</sub>, this decrease may result from the precipitation of amorphous aluminosilicates, such as allophane-like or zeolite-like minerals (ZEVENBERGEN AND COMANS, 1994; MEIMA AND COMANS, 1997a).

**Figure 2.** Total dissolved Na, K, Ca, SO<sub>4</sub>, CO<sub>3</sub>, Al, Si, and Fe in bottom ash leachates at LIS = 5 as a function of experimental run time (left), and as a function of bottom ash pH (right). Symbols: ○ element concentrations in the 4-week equilibration period prior to carbonation; ●/◆ element concentrations during carbonation of bottom ash suspensions (in duplicate); ✕ element concentrations during carbonation of filtered bottom ash leachates. Solid lines give MINTEQA2-predictions of elements in equilibrium with different solubility-controlling minerals. Abbreviations: gyp, gypsum; ett, ettringite; cal, calcite; Al<sub>a</sub>, am-Al(OH)<sub>3</sub>; Al<sub>c</sub>, gibbsite; fer, ferrihydrite. Dashed lines give bottom ash pH as a function of experimental run time.

carbonation processes



## Chapter 4

As a result of carbonation, leachate concentrations of Ca, SO<sub>4</sub>, and CO<sub>3</sub> increased, Al-concentrations decreased, and concentrations of Fe and Si remained almost constant (Fig. 2). These trends are consistent with the solubility-controlling mechanisms proposed above: ettringite dissolved during carbonation, the concentration of Al decreased according to the solubility of amorphous Al(OH)<sub>3</sub>, and leachates approached equilibrium with gypsum. Leachates remain oversaturated with respect to calcite. The reason for this generally observed oversaturation of leachates with respect to calcite, however, is the subject of debate (REDDY *et al.*, 1990; SCHRAMKE, 1992; VAN DER WEIJDEN, 1995). Furthermore, Na shows a relatively strong increase with longer carbonation run times (up to a factor of 1.15), probably caused by the evaporation of water from the bottom ash suspensions.

**TABLE 1. Bulk chemical composition of the bottom ash samples used for this study, and solubility-controlling minerals for major elements. Concentrations are expressed in mg/kg bottom ash.**

Element	Batch 1994 <sup>a</sup>	Batch 1996	Solubility-controlling minerals <sup>a</sup>
Si	222012	196428	
Fe	106344	109309	ferrhydrite <sup>a</sup> (Fe(OH) <sub>3</sub> )
Ca	73798	98791	ettringite <sup>a</sup> (Ca <sub>6</sub> Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (OH) <sub>12</sub> ·26H <sub>2</sub> O)
Al	37176	43282	gibbsite <sup>a</sup> (Al(OH) <sub>3</sub> )
Na	19996	16531	
Mg	12306	15164	brucite <sup>a</sup> (Mg(OH) <sub>2</sub> )
K	8496	8082	
S	5750	9220	gypsum <sup>a</sup> (CaSO <sub>4</sub> ·2H <sub>2</sub> O)
P	2994	4210	
Cl	3064	n.a.	
Cu	2296	3475	tenorite(?) <sup>b</sup> (CuO)
Mo	31	33	powellite(?) <sup>b</sup> (CaMoO <sub>4</sub> )

n.a. indicates not analysed.

<sup>a</sup>from MEIMA AND COMANS, 1997a

<sup>b</sup>from MEIMA AND COMANS, 1997b

**TABLE 2. Bulk chemical composition of the precipitate that formed during carbonation of filtered bottom ash leachates. Concentrations are expressed in mg/kg precipitate.**

Al	165710	Fe	335
Ca	110696	Sr	280
SO <sub>4</sub>	37996	Zn	161
Si	10254	Sn	112
Cu	6306	Mo	72
Na	2969	V	62
PO <sub>4</sub>	944	Ni	23
K	442	Co	12

#### *Mineral neoformation during carbonation*

Table 2 gives the analytical composition of the 1.2 g of precipitate that formed as a result of the carbonation of 4.25 litres of filtered leachate. Al and Ca, and to a lesser degree SO<sub>4</sub> and Si, form the bulk of the precipitate. The other elements are too soluble to precipitate (e.g. Na, K), and/or were present in relatively low concentrations in the original alkaline leachate (e.g. Fe, Mg, Mn). On the basis of the previous discussion of leaching mechanisms, we expect aluminium to precipitate mainly as amorphous Al(OH)<sub>3</sub>, calcium mainly as calcite, and silicon mainly as an (amorphous) aluminosilicate. The most abundant Al-mineral is likely to be Al(OH)<sub>3</sub>, because the concentration of Al in the precipitate far outweighs the concentration of Si. Sulphate is not expected to have precipitated as gypsum, because the filtered leachates remain undersaturated with respect to this mineral (Fig. 2). In naturally weathered bottom ash gel-like precipitates were found consisting mainly of Al, O, and S (MEIMA AND COMANS, 1997b); this suggests that sulphate may have precipitated as a basic Al-sulphate. MINTEQA2 modelling indicates that final leachates approach equilibrium with alunite (KAl<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>) and Al<sub>4</sub>(OH)<sub>10</sub>SO<sub>4</sub>. Calculated saturation indices for these minerals are -0.49 and -1.43, respectively.

The analysis of the precipitate with X-ray powder diffraction methods and computer search-match routines of replicate diffractograms revealed that calcite was the dominant crystalline phase. Very low figure of merits and a high degree of match between the sample and standard

pattern were observed. Estimates of the amount of calcite in the precipitate exceed 10%. Gibbsite was also observed, with relatively low figures of merit and less match between the observed and standard pattern. Additionally, the diffractograms showed a large background peak between 6 and 50 degrees of two theta; indicative of significant amounts of amorphous material. A number of elements were detected with XPS analysis of the precipitate. Elements included C, O, Al, Ca, Si, and trace amounts of S and Cu. After energy referencing and component curve fitting, a number of mineral phases were identified in the precipitate. Calcite was identified using the Ca 2p<sub>3/2</sub>, C 1s, and O 1s photoelectrons. Estimated abundance of calcite in the precipitate is about 13%. A number of potential aluminium phases were identified using the Al 2p and/or the O 1s photoelectrons; including gibbsite/bayerite (Al(OH)<sub>3</sub>), boehmite (AlOOH), corundum (Al<sub>2</sub>O<sub>3</sub>), and general aluminium oxides. It is difficult to ascribe the exact aluminium species. However, given the observation of gibbsite with X-ray diffraction, Al(OH)<sub>3</sub> is the most likely phase. The majority of the aluminium species present in the sample, however, may be non-crystalline Al-(hydr)oxides. Figure 3 shows a typical electron micrograph of the precipitate: calcite crystals in a matrix of Al-(hydr)oxide minerals. In summary, the XRD, XPS, and electronmicroscopic analyses give further evidence that the precipitate largely consists of amorphous Al-rich material, calcite, and possibly gibbsite.

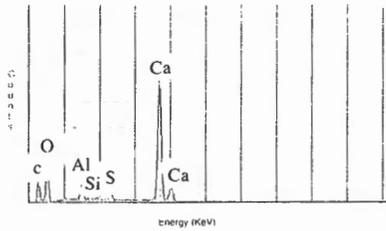
The carbonation experiment with suspended bottom ash, however, led to an approximately 10-fold higher precipitation of calcite than the carbonation experiment with filtered bottom ash leachates. Approximately 4.5 g calcite / kg bottom ash had precipitated from the bottom ash L/S=5 suspension, which amount was calculated from the total amount of CO<sub>2</sub> absorbed (50 ± 5 mmol/kg bottom ash, Fig. 1) minus the increase in dissolved carbonate (5.3 ± 0.8 mmol/kg bottom ash, Fig. 2), on the assumption that all CO<sub>2</sub> had reacted to calcite. Only 0.3 g calcite / kg bottom ash had precipitated from the filtered L/S=5 leachate, which amount was calculated from the data in Table 2 and on the assumption that all Ca had precipitated as calcite. This difference in calcite precipitation is due to the presence of basic Ca-minerals (lime,

portlandite) in the suspended bottom ash; these minerals supply additional Ca for the precipitation of calcite.

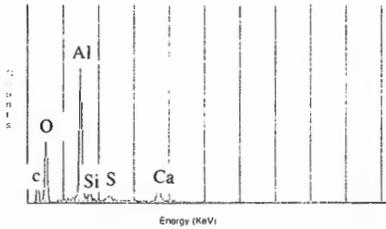
(a)



(b)



(c)



**Figure 3.** Electron micrograph of the precipitate that formed during carbonation of filtered bottom ash leachates (a), and EDS analyses of (b) the  $\text{CaCO}_3$ -crystal and (c) the material surrounding the  $\text{CaCO}_3$ -crystals.

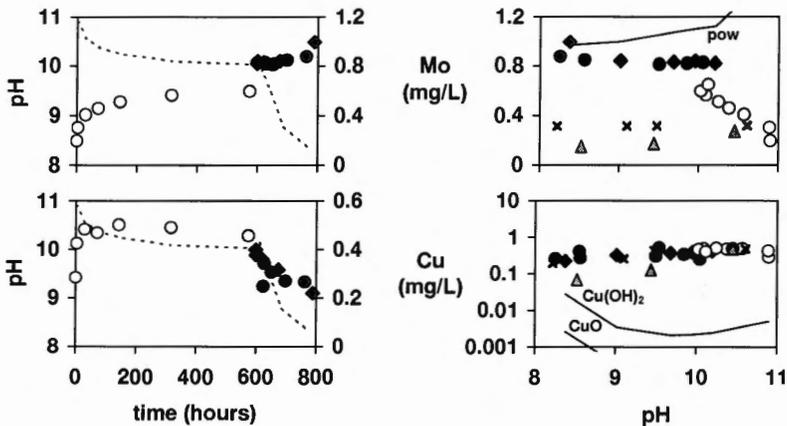
*Copper and Molybdenum*

Figure 4 shows leaching data for Cu and Mo together with MINTEQA2 modelling results. During the 4-week equilibration period leachate concentrations of Cu and Mo reached almost constant values. Concentrations of Mo become close to equilibrium with powellite ( $\text{CaMoO}_4$ ), which is believed to control the leaching of Mo from alkaline waste materials (REDDY *et al.*, 1991; ESSINGTON, 1992b; KINDNESS *et al.*, 1994; MEIMA AND COMANS, 1997b). The observed slight decrease in the leaching of Cu from pH 11 to 10 is consistent with the hydrolysis of the metal. Leachate concentrations of Cu, however, are considerably higher than expected on the basis of the solubility of tenorite ( $\text{CuO}$ ) or  $\text{Cu}(\text{OH})_2(\text{s})$ , which are believed to control the leaching of Cu from MSWI bottom ash (COMANS *et al.*, 1993; EIGHMY *et al.*, 1994; MEIMA AND COMANS, 1997b) and alkaline coal fly ash (FRUCHTER *et al.*, 1990). Because recent findings also show that the dissolved Cu in MSWI bottom ash leachates is bound to DOC to a significant extent (MEIMA *et al.*, 1997), the model-predicted Cu-concentrations shown in Fig. 4 may largely underestimate the Cu-concentrations in equilibrium with tenorite. Currently, we are investigating the conditional stability-constants of Cu-DOC complexes in MSWI bottom ash leachates, so that these complexation reactions can be incorporated in future modelling (MEIMA *et al.*, 1997).

During the carbonation of bottom ash suspensions, Cu-concentrations are reduced by approx. 50%, whereas Mo-concentrations remain almost unaffected. Mo-concentrations remain in equilibrium with powellite. The large reduction in Cu-leaching is unlikely to be due to the precipitation of tenorite because the solubility-curve of tenorite indicates that its solubility strongly increases when the pH drops from 10.5 to 8-8.5 (Fig. 4). Alternatively, sorption to neoformed minerals may explain the observed reduction in Cu-leaching (see also below). The concentration of Cu in the precipitate that had formed during the carbonation of filtered bottom ash leachates (Table 2) turned out to be too low for the detection of crystalline Cu-minerals by means of XRD, XPS, or SEM/EDS analysis.

Table 3 gives the amounts of Cu, Mo and major elements that precipitated during the carbonation and acid neutralisation experiments

with filtered bottom ash leachates. These experiments show a strong reduction in Cu-leaching and also a small reduction in Mo-leaching. The most important finding in this experiment is that the removal of both Cu and Mo is closely related to the precipitation of amorphous Al-minerals. In the case of Mo this reduction is observed in both the carbonation and the acid neutralisation experiments, and is largest in the experiment with elevated Al-concentrations (Table 3). In the case of Cu, the correlation is



**Figure 4.** Total dissolved Mo and Cu in bottom ash leachates at  $L/S = 5$  as a function of experimental run time (left), and as a function of bottom ash pH (right). Symbols: ○ element concentrations during the 4-week equilibration period prior to carbonation; ●◆ element concentrations during carbonation of bottom ash suspensions (in duplicate); × element concentrations during carbonation of filtered bottom ash leachates; ▲ pH-stat leaching data of 1.5-year old MSWI bottom ash (from MEIMA AND COMANS, 1997b);  $L/S$ -ratio = 5, equilibration time = 24 hours. Solid lines give MINTQA2-predictions of Mo and Cu in equilibrium with tenorite ( $\text{CuO}$ ),  $\text{Cu}(\text{OH})_2$ , and powellite (pow). Dashed lines give bottom ash pH as a function of experimental run time.

shown graphically in Figure 5, where the data of the carbonation experiment, the acid neutralisation experiment, and the acid neutralisation experiment with elevated Al-concentrations, are all plotted on a single curve. The data of the carbonation experiment with elevated Ca-concentrations, however, form a second curve in Figure 5 that is similar in shape to the other one, but represents significantly lower Cu-concentrations. Table 3 shows that only a fraction of the available calcium precipitated as calcite. We cannot explain the low Cu-solubility in this experiment with elevated Ca-concentrations. Furthermore, the concentration of DOC has also been shown to decrease along with the precipitation of amorphous Al-minerals (Table 3). Because the dissolved

**TABLE 3. Amounts of Cu, Mo, and major elements that precipitated during carbonation of filtered bottom ash leachates.**

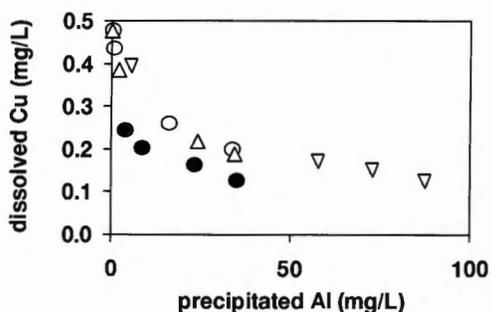
	initial	carbonation				initial	acid neutralisation <sup>1</sup>			
	mg/L	precipitated amount (%)				mg/L	precipitated amount (%)			
<b>pH</b>		<b>10.61</b>	<b>9.48</b>	<b>9.10</b>	<b>8.22</b>		<b>10.61</b>	<b>9.48</b>	<b>9.09</b>	<b>8.20</b>
Al	35.24	0.0	1.1	44.6	94.7	35.24	0.0	5.2	68.5	97.2
Ca	325.66	0.0	0.0	0.9	3.8	325.66	0.0	-0.5	1.6	0.8
S	223.85	0.0	0.6	1.0	2.8	223.85	0.0	0.0	1.8	2.7
Si	9.03	0.0	1.6	6.8	10.9	9.03	0.0	4.2	3.9	1.9
DOC	96.87	0.0	4.2	5.5	8.1	96.87	0.0	-0.2	1.0	3.5
Cu	0.48	0.0	8.7	46.0	59.1	0.48	0.0	19.0	53.8	60.1
Mo	0.32	0.0	0.5	1.0	1.2	0.32	0.0	-0.7	2.5	3.1
<b>pH</b>		<b>10.56</b>	<b>9.45</b>	<b>9.01</b>	<b>8.02</b>		<b>10.56</b>	<b>9.50</b>	<b>9.03</b>	<b>8.08</b>
Al <sup>2</sup>	35.24	10.5	23.6	65.3	98.0	89.24	6.4	66.0	82.8	99.3
Ca <sup>2</sup>	~650	0.6	2.4	3.4	3.8	325.66	0.0	0.0	0.0	4.7
S <sup>2</sup>	223.85	1.2	3.3	3.0	4.0	223.85	0.0	0.4	1.4	7.6
Si	9.03	3.9	3.9	4.9	10.3	9.03	8.6	9.2	4.5	4.6
DOC	96.87	1.2	2.8	5.9	8.3	96.87	2.1	6.6	7.9	11.1
Cu	0.48	49.5	58.4	66.3	73.8	0.48	17.4	63.5	68.1	73.6
Mo	0.32	0.8	4.8	2.3	3.9	0.32	3.5	4.2	6.5	10.8

<sup>1</sup> Precipitated amounts are corrected for dilution by dosed acid. (dilution factor is ~ 1.03)

<sup>2</sup> The addition of Al to equilibrated bottom ash leachates resulted in the precipitation of ettringite before the start of the acid neutralisation experiment. The data for Ca, Al, and S are corrected for this ettringite precipitation. At pH 10.6 we estimate that 0.11 mmol/L ettringite had precipitated, at pH 9.5 0.15 mmol/L, and at pH 9.0 0.14 mmol/L.

Cu is largely bound to DOC (MEIMA *et al.*, 1997), Cu may also be removed from solution by forming ternary complexes with DOC bound to the precipitate.

The existence of a mechanism of Cu-immobilisation by sorption to amorphous Al-minerals is supported by other studies: (a) in naturally weathered bottom ash Cu was detected in gel-like precipitates that consisted mainly of Al and O (MEIMA AND COMANS, 1997b); (b) Cu has a very high affinity for amorphous Al(OH)<sub>3</sub> (KINNIBURGH *et al.*, 1976; MCBRIDE, 1982); and (c) Cu-leaching from weathered bottom ash is well described by surface complexation if the available binding sites of amorphous Al-minerals are included in the modelling (MEIMA AND COMANS, 1997c). The low degree of Mo-sorption is consistent with the low affinity of oxyanions such as Mo for amorphous Fe/Al-hydroxides at alkaline pH-values. However, at pH-values close to 8, which is the pH of carbonated bottom ash, Mo-sorption to amorphous Fe/Al-hydroxides may become significant (REISENAURER *et al.*, 1962; BIBAK AND BORGGGAARD, 1994; MEIMA AND COMANS, 1997c).



**Figure 5.** Total dissolved Cu in filtered bottom ash leachates as a function of the precipitation of aluminium. The symbols represent different types of experiments: ○ carbonation; ● carbonation with elevated Ca-concentrations; △ acid neutralisation; ▽ acid neutralisation with elevated Al-concentrations.

*Comparison with naturally weathered bottom ash*

Figure 4 includes data for the leaching of Cu and Mo from a naturally weathered and carbonated bottom ash from the same incinerator as the fresh bottom ash used for the artificial carbonation experiments (data taken from MEIMA AND COMANS, 1997b). Figure 4 shows that the leaching of Cu and Mo from this naturally weathered and carbonated MSWI bottom ash is considerably lower than from the bottom ash that was carbonated artificially. A prior release of Cu and Mo from this naturally weathered bottom ash is unlikely to explain this difference, because the total concentrations of Cu and Mo that are readily available for leaching were found to be similar or even higher than found for the fresh ash (MEIMA AND COMANS, 1997b). Weathering processes other than carbonation, therefore, also contribute to the observed reduction in trace element leaching. In the long-term, the oxidation of iron particles and the transformation of glasses via allophane-like minerals into clay minerals, for example, will result in the formation of additional sorption sites (ZEVENBERGEN *et al.*, 1994; MEIMA AND COMANS, 1997c), which may bind additional amounts of trace elements. The identification of these sites and the geochemical modelling of sorption processes in weathered bottom ash are the subjects of another paper (MEIMA AND COMANS, 1997c).

## CONCLUSIONS

Two important effects of carbonation have been identified. The most obvious effect is the neutralisation of the pH of the alkaline bottom ash, the second effect is the immobilisation of trace elements by sorption to neoformed minerals. Artificial carbonation experiments have shown that the leaching of Cu is reduced significantly by sorption to amorphous Al-minerals, but that the leaching of Mo remains largely unaffected. The low extent of Mo-sorption is consistent with the low affinity of oxyanions for sorption to (hydr)oxide minerals at alkaline pH. However, during and after natural carbonation in the environment (on a time scale of months to years), the weathering of the bottom ash matrix creates additional sorption sites which further reduce the mobility of contaminants such as

Cu and Mo. Identification of these sorption sites and mechanisms is mandatory to understand and predict the long-term behaviour of alkaline materials such as MSWI bottom ash in the environment.

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## **Chapter 5**

**Application of surface complexation/  
precipitation modelling to  
contaminant leaching from  
weathered MSWI  
bottom ash.**

**APPLICATION OF SURFACE  
COMPLEXATION/PRECIPITATION MODELLING  
TO CONTAMINANT LEACHING FROM WEATHERED  
MUNICIPAL SOLID WASTE INCINERATOR BOTTOM ASH\***

Jeannet A. Meima and Rob N.J. Comans

Netherlands Energy Research Foundation (ECN)  
Westerduinweg 3, 1755 LE Petten

**ABSTRACT**

In this paper we have successfully applied surface complexation/precipitation modelling to describe the leaching of contaminants from weathered Municipal Solid Waste Incinerator (MSWI) bottom ash. A combination of 'selective' chemical extractions and leaching at pH values unfavourable for sorption has been shown to be useful for obtaining sorbent mineral and sorbate concentrations. Model calculations are based on the Diffuse Layer Model and a database of sorption constants for Hydrous Ferric Oxide (HFO), both of which are incorporated in the computer code MINTEQA2. This approach to sorption modelling shows that the leaching of Mo, Pb, and Cu from weathered MSWI bottom ash is well described by surface complexation, whereas the surface precipitation model is needed to describe the leaching data of Zn. The leaching of Cd cannot be explained with these models since the affinity of Cd for HFO is too low. Our results suggest that Mo and Zn are bound mainly to HFO. Additional sorbent minerals, e.g. amorphous Al-(hydr)oxides, are required to describe the leaching of Cu and Pb.

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## INTRODUCTION

Municipal Solid Waste Incinerator (MSWI) bottom ash releases relatively high amounts of potentially hazardous elements. To be able to predict how much of these elements will be leached in the long-term, it is necessary to identify the underlying geochemical processes. Geochemical processes, such as precipitation/dissolution of common minerals, control the leaching of in particular major elements from e.g. MSWI bottom ash (COMANS *et al.*, 1993; KIRBY AND RIMSTIDT, 1994; MEIMA AND COMANS, 1997a), MSWI electrostatic precipitator ash (EIGHMY *et al.*, 1995), and coal fly ash (FRUCHTER *et al.*, 1990; MATTIGOD *et al.*, 1990). Geochemical processes that control the leaching of trace elements are less well understood. Precipitation/dissolution may control trace element leaching from fresh bottom ash, but is unlikely to be important in the weathered ash (MEIMA AND COMANS, 1997b). The leaching of Cu, Mo, Zn, Pb, and Cd from MSWI bottom ash decreases as a result of weathering, and it has been suggested that this may be due to the neutralisation of bottom ash pH and to sorption processes (MEIMA AND COMANS, 1997b). Other observations confirm that sorption processes may control contaminant leaching from combustion residues such as MSWI bottom ash and coal fly ash (e.g. THEIS AND RICHTER, 1979; EARY *et al.*, 1990; FRUCHTER *et al.*, 1990; DZOMBAK AND MOREL, 1992; KERSTEN *et al.*, 1995; VAN DER HOEK AND COMANS, 1996). In particular amorphous Fe- and Al-(hydr)oxides are known to strongly sorb heavy metals and molybdenum (KINNIBURGH *et al.*, 1976; STUMM AND MORGAN, 1981; DZOMBAK AND MOREL, 1990). Since these types of minerals also form in MSWI bottom ash during weathering (MEIMA AND COMANS, 1997a), they may play an important role in the retention of trace elements in this ash. Therefore, in this paper we focus on the role that sorption processes on (amorphous) Fe- and Al-(hydr)oxides play in controlling trace element leaching from weathered MSWI bottom ash.

Laboratory studies on pure metal (hydr)oxides have shown that sorption processes can successfully be described by surface complexation (e.g. DZOMBAK AND MOREL, 1990). The leaching of As and Se from acidic coal fly ash could also be modelled with a (simplified) surface complexation model for sorption of ions on Hydrated Ferric Oxide (HFO)

(VAN DER HOEK AND COMANS, 1996). DZOMBAK AND MOREL (1990) have compiled a database of surface complexation reactions and associated equilibrium constants for sorption of ions on HFO, based on an extensive literature review. HFO, also called amorphous Fe-hydroxide or ferrihydrite, is an almost X-ray amorphous solid phase which forms upon rapid hydrolysis of ferric iron solutions at 20-30°C (DZOMBAK AND MOREL, 1990). There are no such extensive databases available for (amorphous) Al-(hydr)oxide or other natural (hydr)oxides. Therefore, researchers sometimes use HFO as a surrogate sorbent mineral in more complex systems (DZOMBAK AND MOREL, 1992; KERSTEN *et al.*, 1995).

The sorption database for HFO (DZOMBAK AND MOREL, 1990) has been used previously to model the leaching of trace elements from incineration residues (DZOMBAK AND MOREL, 1992; KERSTEN *et al.*, 1995). However, these researchers used the concentration of the sorbent mineral and/or sorbed concentrations as fitting parameters. No attempts have been made to measure these parameters for MSWI bottom ash. The first aim of this study is to obtain these parameters from measurements made on the bottom ash.

Our parameters for the sorption model are evaluated on the basis of (a) leaching experiments at pH values unfavourable for sorption, which give sorbed concentrations, (b) 'selective' chemical extractions, which give the available sorbent mineral concentrations. 'Selective' chemical extractions have often been used to estimate sorbent mineral concentrations in sediments and soils (e.g. HIGASHI AND IKEDA, 1974; PARFITT AND CHILDS, 1988; KOSTKA AND LUTHER, 1994), and recently also in coal fly ash (VAN DER HOEK AND COMANS, 1996). The selectivity of various chemicals for iron minerals has recently been evaluated thoroughly by KOSTKA AND LUTHER (1994). These workers have concluded that HFO is most selectively dissolved by extraction with ascorbate. Less is known about the selectivity of various chemicals for aluminium minerals. The oxalate extraction is usually used to dissolve short-range order aluminosilicates, such as amorphous Al(OH)<sub>3</sub> and allophane-like minerals (e.g. HIGASHI AND IKEDA, 1974; PARFITT AND CHILDS, 1988). Therefore, we will use the ascorbate extraction to estimate the HFO-content of the bottom ash, and we will use the oxalate

extraction to measure the quantity of amorphous Al-(hydr)oxides present in the bottom ash.

In addition to surface complexation, we will consider the possibility of surface precipitation because the relatively high availability of contaminants in MSWI bottom ash may lead to the saturation of available (monolayer) sorption sites. The surface precipitation model, which is an extension of the surface complexation model, may become significant when the dissolved sorbate concentration exceeds one-tenth of its solubility or one half of the total surface site concentration (DZOMBAK AND MOREL, 1990). A scheme with surface complexation/precipitation reactions was first developed by FARLEY *et al.* (1985).

In this paper we evaluate whether surface complexation/precipitation can explain the leaching of Cd, Pb, Zn, Cu, and Mo from weathered MSWI bottom ash. Our calculations are based on the Diffuse Layer Model and database with sorption constants for HFO of DZOMBAK AND MOREL (1990), both of which are incorporated in the computer code MINTEQA2. The necessary parameters, such as the sorbent mineral concentration in the bottom ash and the amount of trace elements available for sorption, were obtained from measurements made on the bottom ash.

## MATERIALS AND METHODS

### *MSWI bottom ash and pH-stat leaching experiments*

Naturally weathered bottom ash was taken from a major Dutch Municipal Solid Waste Incinerator. The bottom ash had been in open storage in the grounds of the incinerator for 1.5 years. Sample treatment and pH-stat leaching experiments have been described in detail elsewhere (MEIMA AND COMANS, 1997a). In short, the bottom ash was subjected for 24 hours to batch leaching at various pH values between 4 and 12 using a pH-stat system and a Liquid to Solid (L/S) ratio of 5 L/kg. Suspensions were kept in contact with the atmosphere. Figure 1 shows the acid/base consumption by the bottom ash suspensions at different pH during the 24-hours of equilibration and indicates that the solids had approached "equilibrium" with respect to pH over this period. The equilibrated

suspensions were filtered over 0.2µm membrane filters, and the clear filtrates were analysed by ICP-AES, GF-AAS, ion chromatography, and a carbon analyser to obtain the total concentrations of Na, K, Ca, Mg, Al, Si, Fe, Zn, Cu, Mo, Cd, Pb, Cl, SO<sub>4</sub>, and CO<sub>3</sub>. Having collected our set of data, we then performed similar pH-stat leaching experiments at pH 1-3 to measure trace metal concentrations at pH values unfavourable for sorption. In the pH-stat experiments, HNO<sub>3</sub> and NaOH were used to adjust the bottom ash pH. Bulk chemical characteristics of this 1.5-year old bottom ash are summarised in Table 1.

**TABLE 1. Bulk chemical characteristics of the 1.5-year old MSWI bottom ash<sup>a</sup>**

**elemental composition**

	(m/m%)		(ppm)
Si	23.3%	P	3486
Fe	8.7%	Cl	1556
Ca	7.2%		
Al	3.8%	Zn	3551
Na	1.3%	Pb	1950
Mg	1.2%	Cu	2194
K	0.9%	Mo	24
S	0.4%	Cd	7

**pH and E<sub>H</sub> (suspension at L/S=5; t = 24 hours)**

pH	8.53
E <sub>H</sub> (mV)	301

**bulk crystalline minerals**

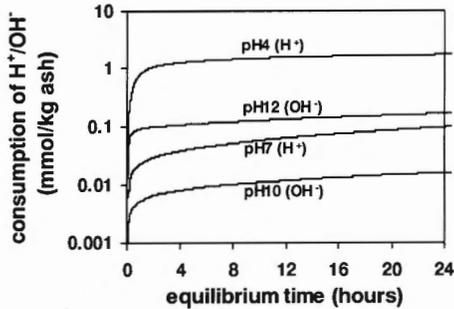
quartz (SiO<sub>2</sub>), calcite (CaCO<sub>3</sub>)<sup>b</sup>, anhydrite (CaSO<sub>4</sub>), feldspar, magnetite (Fe<sub>3</sub>O<sub>4</sub>), and hematite (Fe<sub>2</sub>O<sub>3</sub>)

**solubility controlling minerals**

calcite, gypsum (CaSO<sub>4</sub>.2H<sub>2</sub>O), ferrihydrite (Fe(OH)<sub>3</sub>), gibbsite (Al(OH)<sub>3</sub>).

<sup>a</sup> data taken from MEIMA AND COMANS, 1997a

<sup>b</sup> The calcite content is 7.9 (m/m)% measured by acid addition and subsequent determination of the CO<sub>2</sub> released (this study).

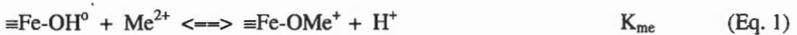


**Figure 1.** Acid/base consumption by the 1.5-year old MSWI bottom ash suspensions at different pH during the 24-hour equilibration period.

#### Surface complexation model (SCM)

The geochemical speciation code MINTEQA2 version 3.11 (ALLISON *et al.*, 1991) was used to model sorption reactions of Cd, Pb, Zn, Cu, and Mo with minerals in the bottom ash matrix. Supplements and improvements to the standard MINTEQA2 databases are given in Tab. 2.

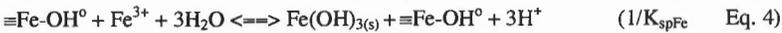
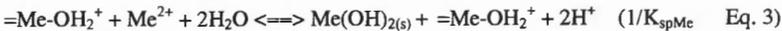
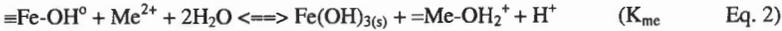
For surface complexation modelling we have used the Diffuse Layer Model, and the database with surface complexation reactions and associated equilibrium constants for the sorption of ions on HFO. Both are included in MINTEQA2 and are based on the work of DZOMBAK AND MOREL (1990). Equation 1 gives the general surface complexation reaction for the sorption of divalent cations on HFO:



The parameters that are required to run the surface complexation model are discussed in a separate section below. The model predictions are presented as total element concentrations in the leachate solutions at each pH. This approach lets us present the results together with the analytical data in a graph of log-concentration versus pH, which maintains the characteristic shape and concentration levels of general leaching curves.

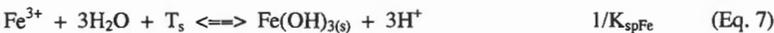
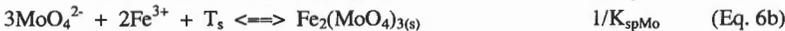
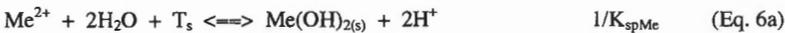
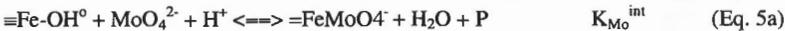
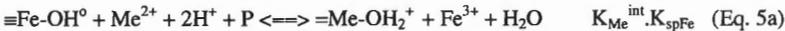
*Surface precipitation model (SPM)*

The surface precipitation model extends the surface complexation model by taking into account the formation of a new surface phase, which is described as an ideal solid solution of  $\text{Me}(\text{OH})_{2(s)}$  and  $\text{Fe}(\text{OH})_{3(s)}$ . This approach results in a continuum between adsorption and bulk solution precipitation of the sorbing ion. For the sorption and subsequent precipitation of a divalent cation on HFO, the following reactions are considered (DZOMBAK AND MOREL, 1990):



The symbols  $\equiv$  and  $=$  denote bonds at the surface;  $\equiv\text{Fe}-\text{OH}^{\circ}$  represents  $[\text{Fe}(\text{OH})_3]_n$ , and  $\equiv\text{Me}-\text{OH}^{\circ}$  represents  $[\text{Me}(\text{OH})_2]_n$ , which means that reaction 2 is balanced with respect to H and O. The assumption of ideal solid-solution behaviour implies (a) that the activities of the solid species can be represented by their mole fractions, and (b) that solubility constants of bulk solution precipitation can be used to describe the solid solution (DZOMBAK AND MOREL, 1990). The precipitation constants used for surface precipitation modelling are given in Table 2.

The surface precipitation model is not incorporated in the standard 3.11 version of MINTEQA2. Therefore, we implemented the scheme of reactions worked out by DZOMBAK AND MOREL (1990) by adding to the sorption database reactions for the sorption (Eq. 5a) and subsequent precipitation (Eq. 6a and 7) of Cd, Pb, Zn, and Cu on HFO. The same approach was used for Mo (Equations 5b, 6b, and 7).



The symbol 'P' represents the coulombic term 'exp(-Fψ/RT)', which is used in all surface complexation reactions.  $T_s$  is a 'dummy' component, and represents the total concentration of material in solid solution.  $T_s$  is used to express the activity of solid species, which are represented by their mole fractions in the solid solution:  $\{Me(OH)_{2(s)}\} = [Me(OH)_{2(s)}]/[T_s]$ . Because MINTEQA2 uses the equilibrium activity of  $T_s$  in solution when equilibrating Equations 6 and 7, the *activity* of  $T_s$  specified as input in the model should be fixed to the value of the total *concentration* of solid material in the solid solution.

**TABLE 2 Additional or modified thermodynamic data used in the MINTEQA2 calculations<sup>a</sup>**

aqueous species	log K	source
$Cu(OH)_2^0$	-16.20	MOREL AND HERING, 1993
$HMoO_4^-$	4.24	RAI AND ZACHARA, 1984
$H_2MoO_4^0$	8.24	RAI AND ZACHARA, 1984
$CaMoO_4^0$	2.57	ESSINGTON, 1992
$MgMoO_4^0$	3.03	ESSINGTON, 1992
<b>minerals</b>		
$Fe_2(MoO_4)_3(s)$	35.29	RAI <i>et al.</i> , 1987
<b>sorbed species</b>		
$=X_1MoO_4$	9.50 <sup>b</sup>	DZOMBAK AND MOREL, 1990
$=X_2MoO_4$	9.50 <sup>b</sup>	DZOMBAK AND MOREL, 1990
$Fe(OH)_3(s)$	-2.50	DZOMBAK AND MOREL, 1990
$Zn(OH)_2(s)$	-11.70	DZOMBAK AND MOREL, 1990
$Cu(OH)_2(s)$	-8.64	ALLISON <i>et al.</i> , 1991
$Pb(OH)_2(s)$	-8.15	ALLISON <i>et al.</i> , 1991
$Cd(OH)_2(s)$	-13.73	ALLISON <i>et al.</i> , 1991
$Fe_2(MoO_4)_3(s)$	35.29	RAI <i>et al.</i> , 1987

<sup>a</sup> The components of the reactions are  $H_2O$ ,  $H^+$ ,  $Me^{2+}$ ,  $Fe^{3+}$ ,  $MoO_4^{2-}$ ,  $=X_1OH^0$ ,  $=X_2OH^0$ . All constants refer to formation reactions.

<sup>b</sup> This constant was estimated on the basis of linear free-energy relationships.

*Parameters for the surface complexation/precipitation model*

**1. leachate composition**

The concentrations of Na, K, Ca, Mg, Al, Si, Fe, PO<sub>4</sub>, Cl, SO<sub>4</sub>, CO<sub>3</sub>, and NO<sub>3</sub> measured in the pH-stat leachates served as input for the major components of the system. The pH was fixed at the measured value. The Davies equation was used to calculate activity coefficients ( $I < 0.1$  for pH  $\geq 6.5$ , and  $0.1 < I < 0.5$  for pH 4 - 5.5).

**2. sorbate concentrations, i.e. the concentration of Cd, Pb, Zn, Cu, and Mo in the solution phase plus surface phase**

Low-pH (1-4) extracts were used to estimate heavy metal concentrations available for sorption, and alkaline (pH 10.5-12) extracts to estimate the Mo-concentration available for sorption. The higher the affinity of a heavy metal for HFO (and/or the higher the amount of sorbent mineral), the lower the pH required for complete desorption:  $\text{pH}(\text{Pb}) < \text{pH}(\text{Cu}) < \text{pH}(\text{Zn}) < \text{pH}(\text{Cd})$ , whereas for Mo the reverse holds (DZOMBAK AND MOREL, 1990). To estimate the appropriate sorbate concentrations, we used the surface complexation model to calculate the highest (Cd, Pb, Cu, Zn) or lowest (Mo) pH values at which individual trace elements are completely desorbed. These calculations were performed for the scenario with the highest amount of sorbent minerals, i.e. HFO + amorphous Al-(hydr)oxides (see below). Table 3 gives the obtained total sorbate concentrations, which were used in subsequent modelling. All model calculations were run with all sorbates present at the appropriate concentrations.

**3. sorbent mineral concentration**

The HFO-content of the bottom ash was measured by ascorbate extraction, and is referred to as ASC(Fe). The amorphous Al-(hydr)oxide content of the bottom ash was measured by oxalate extraction, and is referred to as OX(Al).

Prior to the chemical extractions, the bottom ash was mixed with water until  $L/S=2.5$  L/kg. These suspensions were subsequently equilibrated for 24 hours at 4 different pH values in the pH-stat, i.e. at pH 4, pH 6.5, pH 8.5, and pH 10.5. The equilibrated suspensions were filtered over 0.2 $\mu\text{m}$  membrane filters, and the remaining solid material

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was extracted as described below. HFO was extracted from 15 g bottom ash with 300 ml ascorbic acid solution (20 g/L) according to the method of FERDELMAN (1988) described in KOSTKA AND LUTHER (1994). The extractions were performed at pH 8 and took 24 hours at room temperature. Amorphous Al-(hydr)oxide minerals were extracted from 3 g bottom ash with 300 ml 0.2M ammonium oxalate at pH 3 for 4 hours in the dark (BLAKEMORE *et al.*, 1987). All Fe- and Al-extracts were analysed by ICP-AES to obtain the concentrations of Fe and Al. These values were then recalculated to represent the amount of sorbent minerals present at L/S = 5 L/kg.

The model is first used on the assumption that HFO is the primary sorbent mineral in weathered MSWI bottom ash, and secondly, on the assumption that amorphous Al-(hydr)oxides also play an important role in the sorption process. For modelling purposes, HFO was taken as a surrogate sorbent for amorphous Al-(hydr)oxides because of the absence of a complete and systematic database for sorption reactions on amorphous Al-(hydr)oxides. We believe that the use of HFO as a surrogate for amorphous Al-(hydr)oxides is justified for the following reasons: The most reactive Al- and Fe-(hydr)oxides are Fe(OH)<sub>3</sub> (ferrihydrite/HFO) and Al(OH)<sub>3</sub>. Iron(III) and Al(III) are known to substitute for each other in natural metal (hydr)oxides, in which both metals have 6-fold coordination. The most reactive surface groups in these sorbents are singly-coordinated hydroxyl groups. According to bond-valence principles, outlined in HIEMSTRA *et al.* (1989), the reactivity of these groups is determined by the coordination number of the metal (Al(III), Fe(III)), and the number of coordinated metals per surface group (HIEMSTRA *et al.*, 1989). As both the charge and coordination number of Fe(III) and Al(III) in these (hydr)oxides are the same, these principles suggest that Al- and Fe-(hydr)oxides have a similar reactivity (HIEMSTRA *et al.*, 1996). Differences in the reactivity of these oxides are determined by detailed structural differences, which cannot be dealt with in the present generation of surface complexation models.

With respect to the input of sorbent mineral concentrations in MINTEQA2, one mol of Al was assumed to be representative of one mol of Fe. The molecular weight of 89g HFO/mol Fe recommended by

DZOMBAK AND MOREL (1990) was used to calculate the concentration of HFO from the extracted Fe and Al. Accordingly, sorbent mineral concentrations were calculated from ASC(Fe), representing the HFO-content only, and from OX(Al)+ASC(Fe), representing the content of both HFO and amorphous Al-(hydr)oxides present in the bottom ash. Resulting total sorbent mineral concentrations are given in Table 3.

#### **4. the specific surface area of HFO**

We used the general value of  $600 \text{ m}^2/\text{g}$  recommended by DZOMBAK AND MOREL (1990).

#### **5. the concentration of binding sites on HFO**

Sorption sites on HFO are divided into two types, i.e. low-capacity/high-affinity sites and high-capacity/low-affinity sites. We used the concentrations recommended by DZOMBAK AND MOREL (1990), i.e.  $5 \text{ mmol/mol Fe}$  and  $0.2 \text{ mol/mol Fe}$ , respectively.

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**TABLE 3. Summary of sorbent and sorbate concentrations input in the sorption model.**

**sorbent/site concentrations on the basis of ASC(Fe)**

Fe extracted (mol/kg ash)	2.88E-02
[sorbent mineral] (in g/L)	5.12E-01
[site 1] (mol/L)	2.88E-05
[site 2] (mol/L)	1.15E-03

**sorbent/site concentrations on the basis of OX(Al) + ASC(Fe)**

Fe/Al extracted (mol/kg ash)	2.95E-01
[sorbent mineral] (in g/L)	5.24E+00
[site 1] (mol/L)	2.95E-04
[site 2] (mol/L)	1.18E-02

**sorbate concentrations (in mol/L)**

Mo (concentration at pH 10.5)	2.8E-06
Cd (concentration at pH4)	4.6E-06
Pb (concentration at pH2)	4.0E-04
Zn (concentration at pH 4)	3.0E-03
Cu (concentration at pH 2)	2.2E-03

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## RESULTS AND DISCUSSION

### *Leaching and extraction data*

The leaching of Mo, Cd, Pb, Zn, and Cu from weathered MSWI bottom ash is shown in Figure 2 as a function of pH (data at  $\text{pH} \geq 4$  were taken from MEIMA AND COMANS, 1997b). For comparison, the solubilities of pure  $\text{Me}(\text{OH})_{2(s)}$  minerals and  $\text{Fe}_2(\text{MoO}_4)_{3(s)}$  are also shown in Figure 2. In a previous study we have shown that trace-element leaching from this 1.5-year old MSWI bottom ash does not seem to be controlled by the precipitation/dissolution of pure mineral phases (MEIMA AND COMANS, 1997b). Over a large range in pH values, leachates were generally calculated to be undersaturated with respect to common secondary minerals such as (hydr)oxides, carbonates, sulphates, and phosphates. Exceptions were Cu-(hydroxy)carbonates (e.g. azurite,  $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$ ) and Pb-phosphates (e.g. chloropyromorphite:  $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$ ), but further evidence for their possible role in controlling the leaching of Cu and Pb from weathered MSWI bottom ash was not found (MEIMA AND COMANS, 1997b).

Qualitatively, the observed leaching-trends (Fig. 2) are consistent with sorption on (hydr)oxide minerals: the affinity of heavy metals for sorption on (hydr)oxide minerals increases with increasing pH, whereas for oxyanions such as Mo it increases with decreasing pH (e.g. DZOMBAK AND MOREL, 1990). The increased leaching of Pb, Zn, and Cu at strongly alkaline pH is consistent with significant Me-hydrolysis and Me-complexation with carbonate. The observed increase in Cd-leaching above pH 9, however, is not consistent with known inorganic complexation reactions: MINTEQA2 modelling shows significant hydrolysis or inorganic complexation of Cd above pH 12 only. Since we also observed a strong increase in the leaching of dissolved organic carbon (DOC) at  $\text{pH} > 9$  (MEIMA AND COMANS, 1997a), complexation with DOC may have desorbed Cd, and possibly other (trace) elements as well. In particular Cu is known to have a very high affinity for DOC (BENEDETTI *et al.*, 1996). Recently, we have started a specific investigation of the role of DOC in Cu-leaching from MSWI bottom ash.

The pH at which bottom ash was leached prior to the ascorbate or oxalate extractions did not greatly influence the extraction yields.

Therefore, average extraction yields are considered only. Table 3 summarises our parameter estimates for the amounts of sorbates and sorbent minerals present in the system. The estimation of accurate parameters is the most difficult step in applying a surface complexation model to a heterogeneous system such as MSWI bottom ash. We estimated sorbate concentrations from a single approach, i.e. by leaching the bottom ash at pH values unfavourable for sorption, and used chemical extractions to obtain two different total sorbent mineral concentrations:

1. the concentration of HFO, represented by ASC(Fe),
2. the concentration of HFO plus amorphous Al-(hydr)oxides, represented by ASC(Fe)+OX(Al).

Surface precipitation is likely to become significant when the dissolved sorbate concentration exceeds one-tenth of its solubility or one half of the total surface site concentration (DZOMBAK AND MOREL, 1990). Following these criteria, surface precipitation must be considered (see Table 3).

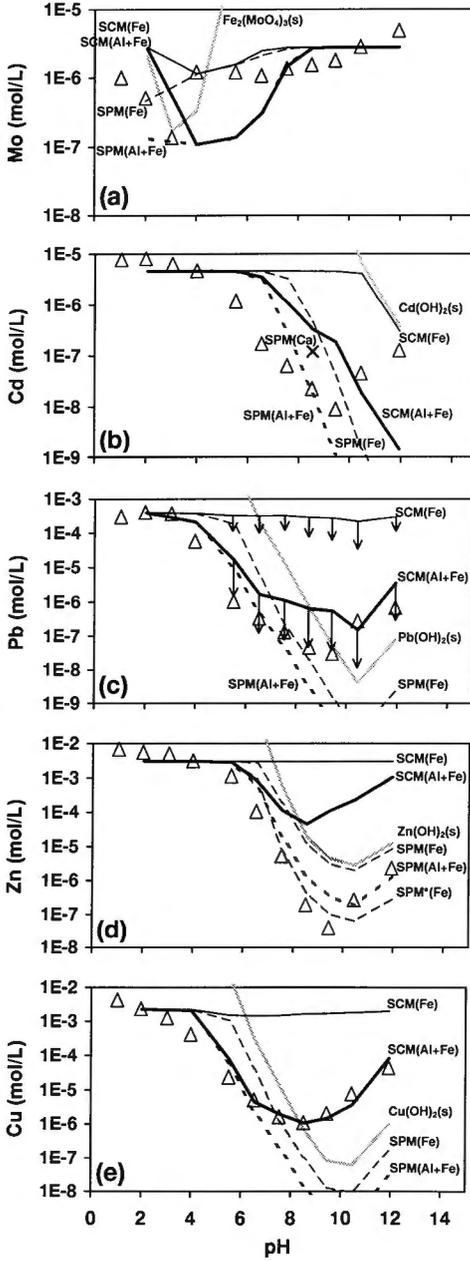
#### *Results of sorption modelling*

The results of this approach to sorption modelling are shown in Figure 2 together with the leaching data.

Mo-leaching (Fig. 2a) is described quite well by surface complexation with HFO over a large range of pH values (pH4-10). If amorphous Al-(hydr)oxides are also included, the leaching of Mo is strongly underestimated at intermediate pH. Surface precipitation becomes significant at pH < 4 only. However, bulk precipitation of pure  $\text{Fe}_2(\text{MoO}_4)_3(\text{s})$  seems more likely to control Mo-leaching at these low pH values.

The modelling results for Cd, however, are inconclusive. Cd-concentrations are too low to be explained by surface complexation with HFO or amorphous Al-(hydr)oxides (Fig. 2b). The model based on HFO shows significant Cd-sorption above pH 10 only, and if amorphous Al-(hydr)oxides are included, predicted Cd-concentrations still remain one order of magnitude higher than the measured concentrations. The use of the surface precipitation model does not significantly improve the match between observed and predicted concentrations. Alternatively, calcite may contribute to Cd-sorption because Cd is known to have a very high affinity for calcite (e.g. DAVIES *et al.*, 1987; COMANS AND MIDDELBURG,

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1987), and the mineral is known to have precipitated in large amounts during carbonation of the fresh alkaline bottom ash (MEIMA *et al.*, 1997). However, a generally applicable model with intrinsic sorption and surface precipitation constants for calcite is not available. Therefore, as a first approximation, we have used the apparent sorption and surface precipitation constants for the sorption of Cd on calcite which were estimated by COMANS AND MIDDELBURG (1987) for  $\text{pH} \approx 8\text{-}8.5$ . Since electrostatic interactions at the calcite surface cannot, at present, be considered explicitly, adsorption and subsequent surface precipitation of Cd on calcite could only be modelled at this pH, using otherwise the same approach as described above for HFO. Site concentrations were estimated from the  $\text{CaCO}_3$ -content of the bottom ash (Table 1) and the general site-densities used by COMANS AND MIDDELBURG (1987). However, this model strongly overpredicts the leaching of Cd at pH 8.5 (see Fig. 2b) and cannot, at this stage, lend support to the potential role of calcite in controlling Cd-leaching.

**Figure 2.** Total dissolved Mo (a), Cd (b), Pb (c), Zn (d), and Cu (e) in L/S=5 L/kg leachates of 1.5-year old MSWI bottom ash vs pH, and MINTEQA2 predictions on the basis of surface complexation/precipitation modelling. The Symbol  $\Delta$  represents the leaching data. Model-predicted concentrations on the basis of surface complexation are represented by solid lines (thin lines for HFO, thick lines for amorphous Fe+Al (hydr)oxides). Model-predicted concentrations on the basis of surface precipitation are represented by dashed lines (thin lines for HFO, thick lines for amorphous Fe+Al (hydr)oxides). Grey lines represent equilibrium with bulk  $\text{Me}(\text{OH})_2(\text{s})$  or  $\text{Fe}_2(\text{MoO}_4)_3(\text{s})$ . The symbol X in (b) represents model-predicted Cd-concentrations on the basis of surface precipitation with calcite. The arrows in the model-predicted Pb-concentrations in (c) indicate the effect of a higher sorption constant for low-affinity sites ( $\log K_2^{\text{int}} = 1.7$  instead of 0.3, see text). The line marked 'SPM\*(Fe)' in (d) has been modelled on the basis of  $\log K_{\text{sp}(\text{Zn})} = 10.2$  (from FARLEY *et al.*, 1985).

Pb-leaching is described reasonably well by surface complexation if the sorbent mineral concentration is estimated by ASC(Fe)+OX(Al) (Fig. 2c). The leaching of Pb is largely overestimated if HFO is considered only, and is underestimated by 3-4 orders of magnitude at alkaline pH if the surface precipitation model is used. The arrows in the model-predicted Pb-concentrations indicate the effect of a higher sorption constant for the *low*-affinity sites. The original constant in the MINTEQA2 (version 3.11) databases was estimated from linear free-energy relationships, and was considered by DZOMBAK AND MOREL (1990) to be probably an underestimate. We used a higher log K value of 1.7 in the calculations to be consistent with the general trend of an approximately 3-log unit difference between the sorption constants for the high and low affinity sites (DZOMBAK AND MOREL, 1990). Figure 2c shows that this modification further improves the match between the surface complexation model on the basis of ASC(Fe)+OX(Al) and the measurements.

Zn-leaching is likely to be controlled by surface precipitation on HFO because (a) Zn may occupy almost 100% of the sites on HFO (Tab. 3), (b) surface complexation largely underestimates Zn-sorption, even if amorphous Al-(hydr)oxides are included (Fig. 2d), and (c) the shape of the surface precipitation curves in Fig. 2d follows the pattern of the leaching data closely. However, measured Zn-concentrations between pH 6 and 10 are up to one order of magnitude lower than the surface precipitation model predicts. This gap cannot be explained unless one assumes the presence of unreasonable amounts of sorbent minerals or sorbed Zn. Possibly, the surface precipitation constant ( $\log K_{spZn} = 11.7$ ) for Zn is too high. If we use the much lower  $K_{sp(Zn)}$  of 10.2 published by FARLEY *et al.* (1985), which these authors obtained by fitting the SPM to sorption data of Zn on HFO, the resulting SPM-curve does indeed closely overlap the leaching data over a large range of pH values (Fig. 2d).

Cu-leaching is described quite well by surface complexation over the whole range of pH values if the model uses ASC(Fe)+OX(Al) as the total sorbent mineral concentration (Fig. 2e). If amorphous Al-(hydr)oxides are not included, the model largely overestimates leachate concentrations of Cu, and if surface precipitation is taken into account, the leaching of Cu is strongly underestimated at alkaline pH. An

association of Cu with amorphous Al-(hydr)oxides is supported by mineralogical observations: Cu was detected in an amorphous gel-like precipitate consisting mainly of Al and O which was found in the bottom ash at the 1.5-year old disposal site (MEIMA AND COMANS, 1997b); during carbonation of filtered MSWI bottom ash leachates a significant amount of Cu coprecipitated with amorphous Al-(hydr)oxides (MEIMA *et al.*, 1997); and in 12-year old MSWI bottom ash Cu has been found to be incorporated in neoformed clays (ZEVENBERGEN *et al.*, 1994). We emphasise that we did not take into account the possible complexation of copper by dissolved organic carbon, whereas this process may be significant in bottom ash leachates (MEIMA *et al.*, in prep.).

In summary, the combination of 'selective' chemical extractions performed on the bottom ash and leaching at pH values unfavourable for sorption has been shown to be useful in obtaining sorbent mineral and sorbate concentrations for the surface complexation and precipitation model. Important results of this approach to sorption modelling are: (a) surface complexation describes the leaching of Mo, Pb, and Cu from weathered MSWI bottom ash satisfactorily and (b) surface precipitation must be taken into account to explain the leaching of Zn. Furthermore, the data suggest that Mo and Zn are bound mainly to HFO, whereas additional sorbent minerals, e.g. amorphous Al-(hydr)oxides, are required to describe the leaching of Cu and Pb. Our results for Cd are inconclusive.

The amount of amorphous Al-(hydr)oxides exceeds the HFO-content of the bottom ash by a factor of 10. Considering the high affinity of trace elements for amorphous  $\text{Al}(\text{OH})_{3(s)}$  (KINNIBURGH *et al.*, 1976), amorphous Al-(hydr)oxides are potentially important for the retention of trace elements in MSWI bottom ash. A more thorough evaluation of the role of this adsorbent, however, requires the development of a database containing sorption constants for amorphous Al-(hydr)oxides which can be applied to heterogeneous systems such as MSWI bottom ash.

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## **Chapter 6**

### **Complexation of Cu with dissolved organic carbon in MSWI bottom ash leachates**

# THE COMPLEXATION OF CU WITH DISSOLVED ORGANIC CARBON IN MUNICIPAL SOLID WASTE INCINERATOR BOTTOM ASH LEACHATES\*

Jeannet A. Meima, André van Zomeren, Rob N.J. Comans

Netherlands Energy Research Foundation (ECN)  
Westerduinweg 3, 1755 LE Petten, The Netherlands

## ABSTRACT

The complexation of Cu with dissolved organic carbon (DOC) in leachates from fresh and 1.5-year old Municipal Solid Waste Incinerator (MSWI) bottom ash was studied using a competitive ligand-exchange solvent extraction procedure. At least two different sites appear to be involved in the complexation of copper with DOC. Conditional stability constants are in the range found for natural waters, but site densities on DOC are much lower. The dissolved Cu appears to be 95-100% organically-bound in leachates from both the fresh and the weathered bottom ash, and geochemical modelling indicates that the leaching of Cu from these ashes is primarily controlled by the availability of the organic ligands in the bottom ash. The mechanism that binds Cu to the solid phase is likely to be tenorite in the fresh bottom ash, and sorption to amorphous Fe/Al-(hydr)oxides in the weathered bottom ash.

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## INTRODUCTION

Municipal Solid Waste is being incinerated in increasing quantities, leaving behind large amounts of bottom ash enriched in potentially harmful elements relative to soils and sediments. For the environmentally safe usage or disposal of these residues, knowledge of the processes controlling the release of potentially harmful elements is required. This paper focuses on the relatively high amounts of copper that are often leached from Municipal Solid Waste Incinerator (MSWI) bottom ash (COMANS *et al.*, 1993; MEIMA AND COMANS, 1997a).

It has been suggested that the leaching of Cu from MSWI bottom ash is significantly enhanced by the complexation of Cu with dissolved organic carbon (SLOOT *et al.*, 1992; COMANS *et al.*, 1993; JOHNSON *et al.*, 1995; CHANDLER *et al.*, 1997; MEIMA AND COMANS, 1997a). Dissolved organic carbon (DOC) has been shown to be a major component of MSWI bottom ash leachates (BELEVI *et al.*, 1992; MEIMA AND COMANS, 1997b), and copper is known to have a very high affinity for organic ligands (e.g. BUFFLE, 1988; BENEDETTI *et al.*, 1996). Bottom ash leachates were calculated to be strongly oversaturated with respect to common secondary copper minerals such as tenorite (CuO(s)) and Cu(OH)<sub>2</sub>(s) in case only inorganic complexation reactions were taken into account (COMANS *et al.*, 1993; MEIMA AND COMANS, 1997a). However, when the residual organic material was removed by heating the bottom ash for 8 hours at 550°C, a strong reduction in the leaching of Cu was obtained (COMANS *et al.*, 1993). Typical values for LOI (loss on ignition) for MSWI bottom ash from mass-burn incinerators range from 2-6%, which represent mainly organic carbon, carbonates, and tightly bound water (CHANDLER *et al.*, 1997). Until recently, no quantitative information is available about the nature and stability of possible Cu-DOC complexes.

In this research a competitive ligand-exchange solvent extraction (CLE-SE) technique is used to determine concentrations and stability constants of Cu-DOC complexes in leachates from freshly-quenched and naturally weathered/carbonated MSWI bottom ash. Subsequently, geochemical processes controlling the leaching of Cu from MSWI

bottom ash are reviewed, while explicitly accounting for the role of organic complexation.

## **MATERIALS AND METHODS**

### *MSWI bottom ash samples*

Freshly-quenched and naturally weathered/carbonated bottom ash were obtained from a Dutch MSW incinerator. The naturally-weathered bottom ash had been in open storage on the grounds of the incinerator for 1.5 years. Sample treatment, bulk chemical composition, and geochemical processes controlling the leaching of major and trace elements are described in detail elsewhere (MEIMA AND COMANS, 1997abc).

### *pH-stat leaching experiments*

Leaching experiments consisted of batch leaching at pH-values of 6.5, 8.5, and 10.5 using a pH-stat system at a Liquid to Solid (L/S) ratio of 5 L/kg. The experiments were performed in 300 ml Teflon (PFA) reaction vessels under continuous stirring at a constant temperature of 20°C. The pH was adjusted with analytical-grade 1M HNO<sub>3</sub> or 1M NaOH. After 24 hours of equilibration, the final pH was recorded, and the suspensions were filtered through 0.2 µm membrane filters. A subsample was subjected to ion chromatography to measure Cl and a carbon analyser was used to measure total inorganic carbon and Dissolved Organic Carbon (DOC). Another subsample was acidified with concentrated suprapure HNO<sub>3</sub> and was used for the analysis of Na, K, Ca, S, Mg, Al, Si, Fe, and Cu by ICP-AES. The remaining volume of the clear filtrate was used for CLE-SE analysis, as described below.

### *CLE-SE analysis*

The CLE-SE technique was used as described in MOFFET AND ZIKA (1987) and MILLER AND BRULAND (1994) for the analysis of organic copper complexes in sea water. Before CLE-SE analysis, sample-solutions were filtered through pre-washed 0.2 µm membrane filters and the pH of the solutions was recorded. The filters were pre-washed with

nanopure water before use to remove residual DOC. Then, acetylacetone (at concentrations specified below), 3.5 ml toluene, and 35 ml of sample-solution were added to a Teflon (FEP) separatory funnel, which was shaken vigorously for at least 1 minute. The acetylacetone (acac) reacts with the Cu mainly to form a neutrally charged  $\text{Cu}(\text{acac})_2^\circ$ -complex, which is distributed between the water phase and the toluene phase. In addition, small amounts of a  $\text{Cu}(\text{acac})^+$ -complex are formed which complex remains in the water phase. Preliminary experiments with leachates from fresh- and 1.5-year old MSWI bottom ash have shown that: (a) the reactions approach equilibrium or steady-state within seconds, and (b) that without acetylacetone present, virtually no Cu (1.4-1.9%) dissolves into the toluene.

In order to measure the concentration of  $\text{Cu}(\text{acac})_2^\circ$  in the toluene phase, the water phase was removed after approx. 15 minutes and the copper in the organic phase was quantitatively dissolved into diluted  $\text{HNO}_3$ . For this purpose, MOFFET AND ZIKA (1987) used 2 ml 1M  $\text{HNO}_3$  in their sea water analysis. These two ml, however, were found to be insufficient to dissolve the considerably larger amounts of Cu that occur in bottom ash leachates as compared to sea water. Therefore, the toluene phase was first extracted with 3 ml of 1M  $\text{HNO}_3$  and then, after phase-separation, with an additional 2 ml of 1M  $\text{HNO}_3$ . This modification allowed for a > 99 % recovery of Cu from the toluene, compared to approx. 91 % in the single extraction with 2 ml of 1M  $\text{HNO}_3$ . The total concentration of Cu in the combined  $\text{HNO}_3$ -fractions was determined by ICP-AES.

### *Titration*s

To determine the concentrations and stability constants of Cu-DOC complexes at different site occupations, bottom ash leachates were titrated with acac and Cu prior to CLE-SE analysis. Cu was added to 50 ml subsamples of the leachates at concentrations in the range 2 - 20  $\mu\text{mol/L}$ . The subsamples were agitated continuously for 24 hours. After 2 and 22 hours of equilibration the pH was re-adjusted to the value prior to Cu-addition using analytical-grade 1M  $\text{HNO}_3$  or 1M NaOH. The solutions were filtered through pre-washed 0.2  $\mu\text{m}$  membrane filters and subjected to CLE-SE analysis using  $10^{-5}$  M acac. Titrations with acac

were performed in filtered bottom ash leachates with no extra Cu added. Used acac concentrations varied between  $10^{-5}$  -  $10^{-2}$  M.

*Speciation calculations*

Equation 1 gives the mole-balance for Cu and also includes the species that result from the addition of acac and toluene.

$$[Cu]_T = [Cu^*] + [Cu(acac)_2^o] + [Cu^{2+}] + [Cu(acac)^+] + [CuX_i] + [CuL_i] \quad (\text{Eq. 1})$$

$[Cu]_T$  is the total analytical concentration of Cu,  $[Cu^*]$  the  $Cu(acac)_2^o$  transferred to the toluene-phase,  $[CuX_i]$  the sum of the inorganic complexes, and  $[CuL_i]$  the sum of the naturally-occurring Cu-DOC complexes.  $[Cu]_T$  and  $[Cu^*]$  were measured by ICP-AES as described above. The concentrations of the remaining species were calculated from Equations 2-8 given in Table 1, and from the distribution coefficient of  $Cu(acac)_2^o$  between toluene and water (the  $K_{d(Cu)}$ , see below). In addition, the speciation code MINTEQA2, version 3.11 (ALLISON *et al.*, 1991) was used to calculate the aqueous speciation of acetylacetone and the complexation of Cu with inorganic ligands. Input in MINTEQA2 were the total concentrations of inorganic components in the leachates measured by chemical analysis and the concentration of acetylacetone added to the sample. The Davies equation was used for ionic strength corrections and the pH was fixed at the measured value.

The conditional stability constant,  $K_{cond(i)}$  for the reaction  $Cu^{2+} + L_i \rightleftharpoons CuL_i$  as well as the total concentration of ligand  $L_i$  were determined by fitting the experimental data to a Langmuir isotherm with one or more ligands (Eq. 9), the number of ligands depending on the heterogeneity of the DOC. The non-linear least-square regression routine of the computer program PRISM (1997) was used for this purpose.

$$[CuL]_T = \sum_{i=1}^n \frac{[L_i]_T \cdot [Cu^{2+}] \cdot K_{cond(i)}}{1 + [Cu^{2+}] \cdot K_{cond(i)}} \quad (\text{Eq. 9})$$

Subsequently, MINTEQA2 modelling was performed to investigate the processes that control the leaching of Cu from fresh and 1.5-year old MSWI bottom ash. The infinite solids approach described in

**TABLE 1. Equations for calculating the speciation of Cu.**

1	$[Cu]_T = [Cu^*] + [Cu(acac)_2^o] + [Cu^{2+}] + [Cu(acac)^+] + [CuX_i] + [CuL_i]$	
	<b>equation</b>	<b>description</b>
	$[Cu]_T$	total analytical concentration of Cu
2	$[Cu^*] = [Cu]_{acid} \cdot V_{acid} / V_{aq}$	the concentration of $Cu(acac)_2^o$ transferred to the toluene
3	$[Cu(acac)_2^o] = \frac{[Cu^*] \cdot V_{aq}}{K_{d(Cu)} \cdot V_{tol}}$	the concentration of $Cu(acac)_2^o$ that remained in the aqueous phase
4	$[Cu^{2+}] = \frac{[Cu(acac)_2^o]}{\beta_2 \cdot [acac^-]^2}$	the concentration of $Cu^{2+}$ in the aqueous phase
5	$[Cu(acac)^+] = K_1 \cdot [Cu^{2+}] \cdot [acac^-]$	the concentration of $Cu(acac)^+$ in the aqueous phase
6	$[CuX_i] = \alpha_{CuX_i} \cdot [Cu^{2+}]$	the sum of the inorganic complexes in the aqueous phase
7	$[CuL_i] = [Cu]_T - [Cu^*] - [Cu^{2+}] - [Cu(acac)_2^o] - [Cu(acac)^+] - [CuX_i]$	the sum of the naturally occurring Cu-DOC complexes in the aqueous phase

All concentrations are in mol/L

$V_x$  Volume of phase x in ml;

$K_{d(Cu)}$  Distribution coefficient of  $Cu(acac)_2$  between toluene and water, (determined in this study)

$$K_{d(Cu)} = \frac{[Cu(acac)_2^o]_{tol}}{[Cu(acac)_2^o]_{aq}} = \frac{[Cu^*] \cdot V_{aq} / V_{tol}}{\beta_2 \cdot [Cu^{2+}] \cdot [acac^-]^2} \quad (\text{Eq. 8});$$

$[acac^-]$  is calculated by MINTEQA2 for each leachate separately.

$\beta_2$  Formation constant for the reaction  $Cu^{2+} + 2acac^- \rightleftharpoons Cu(acac)_2$ , which is  $1.135 \times 10^{15}$  (SILLEN AND MARTELL, 1964);

$K_1$  Formation constant for the reaction  $Cu^{2+} + acac^- \rightleftharpoons Cu(acac)^+$ , which is  $1.84 \times 10^{18}$  (SILLEN AND MARTELL, 1964);

$\alpha_{CuX_i}$  Side reaction coefficient for the complexation of Cu with inorganic ions, calculated by MINTEQA2 for each bottom ash leachate separately.

MEIMA AND COMANS (1997b) was used to calculate the total concentration of Cu in equilibrium with potential solubility-controlling minerals. Sorption processes were modelled using the Diffuse Layer / Surface Complexation Model for sorption of ions on Hydrous Ferric Oxide (HFO) (DZOMBAK AND MOREL, 1990), which is incorporated in MINTEQA2. In order to model sorption reactions on amorphous Al-minerals, the HFO was used as a surrogate sorbent mineral because there is no complete and systematic database for sorption reactions on amorphous Al-minerals (MEIMA AND COMANS, 1997c). The parameters for the 1.5-year old MSWI bottom ash were determined as part of another study (MEIMA AND COMANS, 1997c), the parameters for the fresh MSWI bottom ash were determined in a similar way for this study (see Table 2). In short, the concentrations of amorphous Fe-(hydr)oxides and amorphous Al-minerals were determined by 'selective' extraction from the bottom ash with ascorbic acid (KOSTKA AND LUTHER, 1994) and oxalic acid (BLAKEMORE *et al.*, 1987), respectively. The concentration of Cu, Pb, and Zn available for sorption was determined by leaching the bottom ash at low pH (pH 2-4).

The following additions and modifications were implemented to the standard MINTEQA2 (version 3.11) databases:  $\log K [\text{Cu}(\text{OH})_2^0] = -16.20$  (MOREL AND HERING, 1993); and  $\log K [\text{Cu}(\text{acac})^+] = 8.265$ ,  $\log K [\text{Cu}(\text{acac})_2^0] = 15.055$ ,  $\log K [\text{HAcAc}^0] = 8.95$ , as well as acac-complexes for Cd, Zn, Mg, Al, and Fe (SILLEN AND MARTELL, 1964). Furthermore, the  $\log K_{\text{cond}(i)}$  for  $\text{CuL}_1$  and  $\text{CuL}_2$  determined in this study were included. Because of the conditional character of these constants, different  $\log K_{\text{cond}(i)} [\text{CuL}_i]$  were added for different pH values (Eq. 10 and 11), and the obtained constants were divided by the activity coefficient of  $\text{Cu}^{2+}$  obtained from an initial MINTEQA2 calculation.

#### *Determination of the $K_{d(\text{Cu})}$*

The distribution coefficient of  $\text{Cu}(\text{acac})_2^0$  between toluene and water,  $K_{d(\text{Cu})}$ , was determined in artificial bottom ash leachates prepared on the basis of major element concentrations found in L/S=5 leachates of fresh and 1.5-year old bottom ash at pH 8.5. Used chemicals were analytical grade  $\text{NaHCO}_3$ ,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{NaCl}$ ,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{SiCl}_4$ ,  $\text{HNO}_3$ ,  $\text{NaOH}$  and  $\text{Ca}(\text{OH})_2$ . The

prepared solutions were equilibrated until the pH remained constant, and were then filtered through pre-washed 0.2  $\mu\text{m}$  membrane filters. Subsequently, various amounts of  $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$  were added to 50 ml subsamples of these solutions, yielding solutions of 0.01 - 1.40 mg Cu/L. The 50 ml solutions were equilibrated for 24 hours and were then filtered through pre-washed 0.2  $\mu\text{m}$  membrane filters. CLE-SE analysis was performed as described above using an acetylacetone concentration of  $2.8 \times 10^{-3} \text{M}$ . A small subsample was acidified for ICP-AES to determine  $[\text{Cu}]_{\text{T}}$ . Equation 8 (Table 1) was subsequently used to calculate the  $K_{\text{d}(\text{Cu})}$ .

**TABLE 2. Parameters used for modelling Cu-sorption to amorphous Fe/Al-(hydr)oxides.**

parameter	dimension	HFO <sup>a</sup> properties	fresh <sup>b</sup> bottom ash	1.5-year old <sup>c</sup> bottom ash
HFO	g/mol	89		
[site 1]	mol/g	5.62E-05		
[site 2]	mol/g	2.25E-03		
surface area	$\text{m}^2/\text{g}$	600		
[sorberent] <sup>d</sup>	g/L		2.53	5.24
[Cu] available	mol/L		2.4E-03	2.2E-03
[Pb] available	mol/L		1.7E-04	4.0E-04
[Zn] available	mol/L		2.5E-03	3.0E-03

<sup>a</sup> data from Dzombak and Morel (1990), <sup>b</sup> this study, <sup>c</sup> data from Meima and Comans (1997c)

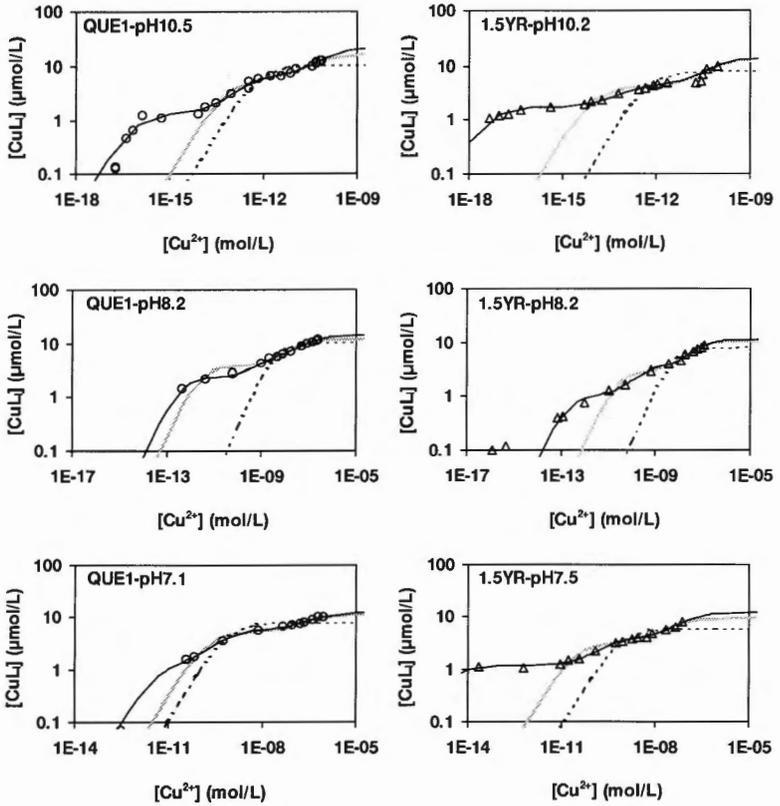
<sup>d</sup> [sorberent] is the concentration of HFO plus that of amorphous Al-minerals. HFO was used as a surrogate sorberent mineral for amorphous Al-(hydr)oxides because of the absence of a complete and systematic database for sorption reactions on amorphous Al-(hydr)oxides (Meima and Comans, 1997c).

## RESULTS AND DISCUSSION

*Determination of  $K_{cond(i)}$  and  $[L_{(i)}]_{\tau}$* 

The distribution coefficient of  $\text{Cu}(\text{acac})_2^{\circ}$  between toluene and water was found to be 4.42 ( $R^2 = 0.992$ ,  $n=22$ ) for artificial leachates of fresh bottom ash and 3.37 ( $R^2 = 0.999$ ,  $n = 12$ ) for artificial leachates of 1.5-year old bottom ash. These  $K_{d(\text{Cu})}$ -values are close to the value of 4.34 which is predicted from reported solubilities of  $\text{Cu}(\text{acac})_2^{\circ}$  in toluene ( $1.65 \cdot 10^{-3}$  M) and neutral water ( $3.8 \cdot 10^{-4}$  M) (STARÝ AND LILJENZIN, 1982). Additional experiments with solutions of NaCl and  $\text{CaCl}_2$  at various ionic strengths (0.003M - 0.3M) were inconclusive about the reason for the slightly lower  $K_{d(\text{Cu})}$  measured for 1.5-year old bottom ash than for fresh bottom ash. However, all  $K_{d(\text{Cu})}$  were in between the values found for fresh and 1.5-year old bottom ash. Because the composition and the ionic strength of the leachates from fresh and 1.5-year old MSWI bottom ash varies with the pH, the averaged  $K_{d(\text{Cu})}$  of  $3.9 \pm 0.5$  was taken as representative for leachates from both fresh and weathered bottom ash. In all calculations, the uncertainty in  $K_{d(\text{Cu})}$  was taken into account implicitly.

Figure 1 shows Langmuir isotherms for titrated leachates of fresh and weathered bottom ash at different pH-values, and the results of the non-linear regression procedure by which the experimental data were fitted to one, two, and three-ligand Langmuir isotherms. At higher  $[\text{Cu}^{2+}]$ , the concentration of  $\text{CuL}_i$  levels to constant values (see Fig. 1), which points to a saturation of the DOC. Figure 1 clearly illustrates that the DOC has sites with different affinity for Cu. The one-site model predicts the complexation of Cu with DOC over a relatively narrow range of site occupations, the two-site model over a considerably broader range, and the three-site model almost over the whole range of possible site occupations. The obtained model parameters are given in Table 3. Although the 3-site model is statistically the better model over the one- and two-site models, we prefer to use the two-site model in subsequent geochemical modelling for two reasons. First, the two-site model gives a very good prediction of the measured complexation of Cu with DOC for site saturations of 14-100%, which is the range relevant to bottom ash leachates. Secondly, the two extra parameters required to give a better



**Figure 1.** The concentration of  $CuL_i$  as a function of  $[Cu^{2+}]$  in titrated leachates from fresh (QUE1,  $\circ$ ), and 1.5-year old (1.5YR,  $\Delta$ ) bottom ash at three pH-values. The indicated pH-values correspond to measured values after filtration. The curves through the data were obtained by non-linear least-square regression analysis on the basis of Langmuir isotherms with one (dashed lines), two (grey lines), and three (solid lines) ligands.

**TABLE 3. Parameters obtained by non-linear least-square regression analysis of the experimental data on the basis of a 2-site and a 3-site Langmuir isotherm.**

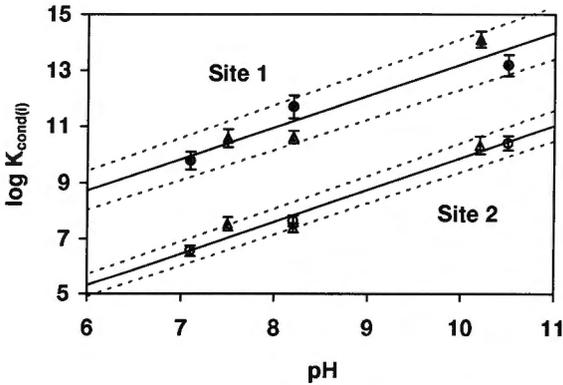
	fresh bottom ash leachate pH			1.5-year old bottom ash leachate pH		
	pH 10.5	pH 8.2	pH 7.1	pH 10.2	pH 8.2	pH 7.5
<b>two-site model</b>						
[L <sub>1</sub> ] <sub>T</sub> (in μmol/L)	6.1±0.8	3.7±0.6	5.5±0.4	4.0±0.5	3.0±0.4	3.3±0.4
[L <sub>2</sub> ] <sub>T</sub> (in μmol/L)	10±2	8±1	6±2	9±4	7±2	6±2
log K <sub>cond(1)</sub>	13.2±0.4	11.7±0.4	9.8±0.3	14.1±0.3	10.6±0.2	10.6±0.3
log K <sub>cond(2)</sub>	10.4±0.3	7.6±0.2	6.6±0.2	10.3±0.3	7.4±0.2	7.5±0.2
n <sup>1</sup>	22	14	12	17	15	15
RSS <sup>2</sup>	8.24x10 <sup>8</sup>	3.52x10 <sup>8</sup>	1.14x10 <sup>8</sup>	1.01x10 <sup>9</sup>	1.84x10 <sup>8</sup>	3.21x10 <sup>8</sup>
<b>three-site model</b>						
[L <sub>0</sub> ] <sub>T</sub> (in μmol/L)	1.3±0.4	2.4±0.5	1.3±0.8	1.7±0.4	1.1±0.3	1.2±0.6
[L <sub>1</sub> ] <sub>T</sub> (in μmol/L)	5.8±3.0	3.6±0.5	4.6±0.6	2.8±0.3	2.4±0.4	2.8±0.3
[L <sub>2</sub> ] <sub>T</sub> (in μmol/L)	15±15	8±2	6±2	9±2	8±3	8±3
log K <sub>cond(0)</sub>	16.2±1.4	12.5±0.2	11.4±1.1	17.4±0.3	12.8±0.4	14.8±0.6
log K <sub>cond(1)</sub>	12.6±0.6	8.9±0.1	9.3±0.2	13.1±0.2	9.7±0.3	9.7±0.1
log K <sub>cond(2)</sub>	10.0±0.3	7.0±0.2	6.4±0.2	10.2±0.1	7.2±0.2	7.1±0.2
n <sup>a</sup>	22	14	12	17	15	15
RSS <sup>b</sup>	3.08x10 <sup>8</sup>	3.58x10 <sup>8</sup>	3.86x10 <sup>7</sup>	7.32x10 <sup>7</sup>	7.04x10 <sup>7</sup>	2.71x10 <sup>7</sup>
The reported standard deviations include the uncertainty in the K <sub>d</sub> (Cu) .						
<sup>a</sup> number of titration data						
<sup>b</sup> residual sum of squares between model and experimental data.						

prediction of the Cu-complexation at site occupations below 14% refer to sites with extremely high  $K_{\text{cond}(i)}$  but with very low capacities (see Table 3); the meaning of such sites is questionable, particularly because the two extra parameters cannot be determined with great accuracy (see Table 3).

The conditional stability constants ( $K_{\text{cond}(i)}$ ) obtained from the fitting procedure on the basis of the 2-site Langmuir model are plotted as a function of pH in Figure 2. Error bars represent the standard deviation in the reported parameters, including the deviation introduced by the uncertainty in the  $K_{d(\text{Cu})}$  (see above). The observed increase in  $K_{\text{cond}(i)}$  towards alkaline pH results from the weaker competition between  $\text{H}^+$  and  $\text{Cu}^{2+}$  at alkaline pH. Within the range of pH-values studied, the data are well described by Equations 10 and 11, which are linear regressions through the combined data of fresh and weathered bottom ash.

$$\log K_{\text{cond}(1)} = (1.126 \pm 0.047) \cdot \text{pH} + (1.96 \pm 0.43) \quad (R^2=0.8876; n=69) \quad (\text{Eq. 10})$$

$$\log K_{\text{cond}(2)} = (1.146 \pm 0.027) \cdot \text{pH} - (1.57 \pm 0.24) \quad (R^2=0.9645; n=69) \quad (\text{Eq. 11})$$



**Figure 2.** Conditional stability constants ( $\log K_{\text{cond}(i)}$ ) for Ligand 1 (●▲) and Ligand 2 (○△), calculated for leachates from fresh (circles) and 1.5-year old (triangles) bottom ash. Error bars represent the standard deviation in the  $\log K_{\text{cond}(i)}$  and also include the deviation introduced by the uncertainty in  $K_{d(\text{Cu})}$  (Eq. 8). Lines represent linear regressions through the combined data of fresh and 1.5-year old bottom ash. The Equations for these lines are given in the text (Eq. 10 and 11).

In general, these  $K_{\text{cond}(i)}$  are within the range found for natural waters (BUFFLE, 1988). Equation 10 and 11 both yield an  $\text{H}^+/\text{Cu}^{2+}$  exchange ratio of 1.1, indicating that approx. one mol of protons is released when one mol of Cu binds to the DOC. For comparison, reported  $\text{H}^+/\text{Cu}^{2+}$  exchange ratios for the complexation of Cu with humic acid are between 1.1 and 1.9 (TIPPING *et al.*, 1995; KINNIBURGH *et al.*, 1996).

**TABLE 4. Concentrations of Cu and DOC in leachates from fresh and weathered MSWI bottom ash, calculated site densities on DOC, and the speciation of Cu in the leachates.**

	fresh bottom ash leachate pH			1.5-year old bottom ash leachate pH		
	pH 10.5	pH 8.2	pH 7.1	pH 10.2	pH 8.2	pH 7.5
<b>direct measurements</b>						
[Cu] <sub>T</sub> (μmol/L)	6.33	5.79	9.10	6.20	3.47	5.85
[DOC] (mg/L)	89.4	103.0	109.1	26.4	15.1	15.9
<b>Calculated site densities on DOC</b>						
S <sub>1</sub> (mol/kg C)	0.07	0.04	0.05	0.15	0.20	0.21
S <sub>2</sub> (mol/kg C)	0.11	0.08	0.06	0.34	0.49	0.39
<b>Calculated Cu-speciation<sup>a</sup></b>						
% CuL <sub>1</sub>	95(-13+5)	64 ± 10	60 ± 5	65 ± 7	86 ± 11	56 ± 7
% CuL <sub>2</sub>	5(-5+7)	35(-9+5)	32(-11+1)	32(-5+0)	13 ± 9	39(-5+0)
% inorganic	1(-1+5)	1(-1+5)	8(-6+15)	3(-3+13)	0(-0+3)	5(-4+13)

<sup>a</sup> The reported standard deviations include the uncertainty in the  $K_{\text{d}(Cu)}$ .

Calculated site-concentrations (μmol/L) and site densities (mol/kg C) are given in Table 3 and 4, respectively. The site with the lower affinity for Cu (L<sub>2</sub>) was found to be generally present at a higher concentration than the site with the higher affinity for Cu (L<sub>1</sub>). The molar concentrations of site 1 were the highest in leachates from fresh MSWI bottom ash, the molar concentrations of site 2 were similar for the two ashes. Due to differences in leached amounts of DOC, the average site density calculated for the 'weathered' DOC (0.59 mol/kg C) is

significantly higher than calculated for the 'fresh' DOC (0.13 mol/kg C). However, both values are approx. one order of magnitude lower than the site densities generally determined for humic acids (BUFFLE, 1988; KINNIBURGH *et al.*, 1996). Apparently, only a small fraction of the DOC in bottom ash leachates is reactive towards Cu. DOC, therefore, may not be a very accurate parameter to estimate the extent of organic complexation in bottom ash leachates.

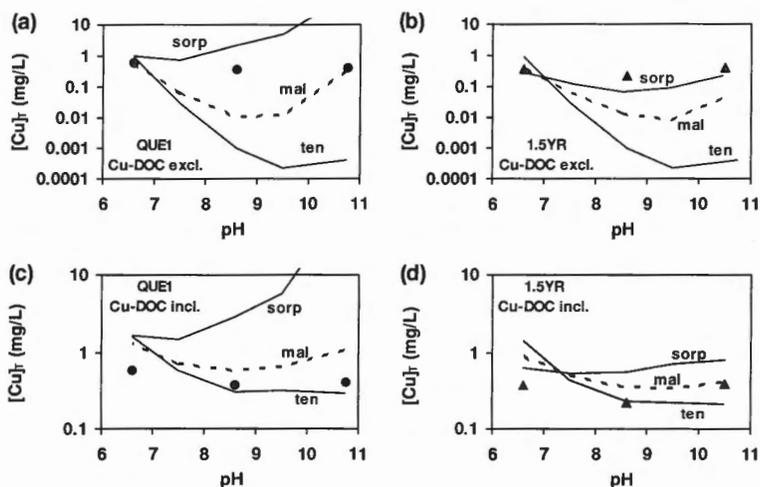
The similar  $K_{\text{cond}(i)}$  that were obtained for DOC from fresh and 1.5-year old MSWI bottom ash suggest that the organic sites are possibly similar in nature. If so, the significant higher binding capacity observed for the 'weathered' DOC relative to the 'fresh' DOC then indicates that these organic sites are retained in the bottom ash during weathering. In preliminary experiments using gel permeation chromatography, Cu was indeed detected in the same molecular-size fraction for leachates from the fresh and the 1.5-year old MSWI bottom ash (VAN ZOMEREN AND COMANS, unpubl. results). Additional research, however, is required to further explain the above results.

#### *Cu-speciation in bottom ash leachates and factors controlling Cu-leaching*

Table 4 gives the aqueous speciation of Cu in bottom ash leachates calculated on the basis of the above determined  $[L_i]_T$  (Table 3) and  $K_{\text{cond}(i)}$  (Eq. 10 and 11). Table 4 shows that 95-100% of the dissolved Cu is bound to DOC in leachates from both fresh (pH 10.5) and weathered (pH 8.2) bottom ash. Site 1 is calculated to be completely saturated with Cu, the weaker site ( $L_2$ ) for up to 50%. MACKEY AND ZIRINO (1994) have proposed that the relatively high concentrations of dissolved Cu found in sea water are not only the result of the complexation of Cu with DOC, but are mainly the result of the presence of colloidal Cu. These authors propose that it is not possible to discriminate between colloidal Cu or organically-bound Cu on the basis of the results of measurements of  $K_{\text{cond}(i)}$  such as described above. The role of colloidal Cu in bottom ash leachates, however, is unlikely to be significant because ultrafiltration of leachates from fresh MSWI bottom ash did not result in a reduction of the dissolved Cu-concentration, whereas it did result in a significant

reduction of the dissolved Fe- and Al-concentrations (COMANS AND GEELHOED, unpubl. results).

Figure 3 shows measured  $[Cu]_T$  as a function of pH in fresh and weathered bottom ash leachates together with predicted  $[Cu]_T$  on the basis of equilibrium with tenorite ( $CuO$ ), malachite ( $Cu_2(OH)_2CO_3$ ), and sorption to amorphous Fe/Al-(hydr)oxides. Tenorite and malachite are among the least soluble Cu-minerals at  $pH > 7.5$ . Since tenorite has also been shown to precipitate from alkaline  $SO_4$ -rich aqueous solutions at atmospheric pressure and temperature (MARANI *et al.*, 1995), tenorite may control the leaching of Cu from fresh MSWI bottom ash. In weathered/carbonated bottom ash, equilibrium with malachite and



**Figure 3.** Measured and predicted Cu-leaching as a function of pH for fresh (QUE1, ●) and 1.5-year old (1.5YR, ▲) MSWI bottom ash. (a) and (b) show the predicted Cu-leaching without taking into account organic complexation reactions. (c) and (d) show the predicted Cu-leaching on the basis of both inorganic and organic complexation reactions. Ten = tenorite ( $CuO$ ), Mal = malachite ( $Cu_2(OH)_2CO_3$ ), sorp = sorption to amorphous Fe/Al-(hydr)oxides (see also Table 2).

sorption to amorphous Fe/Al-(hydr)oxides have been suggested to be potentially important controlling mechanisms for Cu, although the role of tenorite could not be excluded (MEIMA AND COMANS, 1997ac).

If inorganic complexation reactions are taken into account only (Fig 3a,b), measured  $[Cu]_T$  are up to three orders of magnitude oversaturated with respect to tenorite, up to 1.5 orders of magnitude oversaturated with respect to malachite, and within 1-2 orders of magnitude from the predicted Cu-leaching on the basis of sorption to amorphous Fe/Al-(hydr)oxides. However, if inorganic and organic complexation reactions are taken into account (Fig 3c,d), measured  $[Cu]_T$  are within half an order of magnitude from the predicted  $[Cu]_T$  on the basis of equilibrium with tenorite, malachite, and in the case of 1.5-year old bottom ash, also on the basis of sorption to amorphous Fe/Al-(hydr)oxides. Apparently, the differences in Cu-leaching predicted on the basis of solubility-control and sorption are largely masked by the large proportion of Cu bound to DOC. On the basis of these results we may conclude that the leaching of Cu from fresh and 1.5-year old MSWI bottom ash is primarily controlled by the availability of (strong) organic ligands.

The mechanism that binds Cu to the solid phase is likely to be the thermodynamically most stable mineral or sorption process. For the fresh bottom ash, this appears to be equilibrium with tenorite. Above pH 7.5 Cu-concentrations in equilibrium with tenorite describe almost exactly the measured  $[Cu]_T$  in leachates from both fresh and weathered bottom ash. Below pH 7.5, however, equilibrium with tenorite (or any other secondary Cu-mineral listed in the MINTEQA2 version 3.11 databases or in LINDSAY, 1979) would result in a strong increase in Cu-leaching, which is not observed in the data (Fig. 3c,d). Because the sorption model does predict relatively low Cu-leaching down to a pH of 6.5 in the 1.5-year old bottom ash (Fig. 3d), Cu-leaching from weathered bottom ash may be controlled by sorption to amorphous Fe/Al-(hydr)oxides. In fresh MSWI bottom ash, however, the amount of sorption sites seems too low for sorption to be significant, as shown in Fig. 3c.

In conclusion, the leaching of Cu from fresh and 1.5-year old MSWI bottom ash is primarily controlled by the availability of strong organic ligands. In the absence of DOC the predicted Cu-leaching would

be 2-3 orders of magnitude lower. Future research, therefore, should focus on the identification of the nature of the DOC and its binding sites and the role of organic complexation in the long term.

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## **Chapter 7**

**Geochemical processes controlling  
the leaching of contaminants  
in a 20-year old disposal  
of MSWI residues.**

# GEOCHEMICAL PROCESSES CONTROLLING THE LEACHING OF CONTAMINANTS IN A 20-YEAR OLD DISPOSAL OF MSWI RESIDUES

Jeannet A. Meima<sup>1</sup>, Marcel Bus<sup>1</sup>, Chris Zevenbergen<sup>‡</sup>, John Bradley<sup>#</sup>,  
Ole Hjelmar<sup>¶</sup>, Hans A. van der Sloot<sup>1</sup>, and Rob N.J. Comans<sup>1</sup>

<sup>1</sup> Netherlands Energy Research Foundation (ECN), Westerduinweg 3,  
1755 LE Petten, The Netherlands.

<sup>‡</sup> IWACO B.V., Hoofdweg 490, 3067 GK Rotterdam, The Netherlands.

<sup>#</sup> MVA, Inc., 5500 Oakbrook Pkwy, Suite 200, Norcross, Georgia 30093, USA.

<sup>¶</sup> Water Quality Institute, Research Centre, 11 Agern Allé, DK-2970,  
Hørsholm, Denmark.

## ABSTRACT

A 20-year old disposal of naturally weathered MSWI residues was sampled at various depths to collect and analyse both pore waters and solid phase. The geochemical processes controlling solid/liquid partitioning were subsequently investigated by (I) comparing the observed pore water concentrations with concentrations predicted on the basis of aqueous (in)organic complexation, precipitation/dissolution, and/or sorption processes, and (II) by characterising the neoformed minerals with X-ray diffraction and/or electron microscopy. Two major environments were distinguished in the disposal: an (unsaturated) oxidised/carbonated environment down to a depth of 8.3 meters below the surface, and a reducing/alkaline environment below that depth. The dissolved Cu, and possibly the dissolved Pb, was largely organically-bound. The observed metal concentrations in the pore waters were generally consistent with concentrations predicted on the basis of solid/liquid partitioning by sorption to neoformed minerals: towards alkaline pH (increasing depth) the pore water concentrations of Mo and Sb generally increased, whereas pore water concentrations of Cd, Pb, Zn, and Cu generally decreased. Both amorphous Al-minerals (Al(OH)<sub>3</sub>, amorphous aluminosilicates) and crystalline Fe-oxides (goethite,

lepidocrosite) were found to be present in quantities that are potentially large enough to explain the observed pore water concentrations of Zn, Cu, Pb, Cd, Mo, and Sb by surface complexation processes. The potential importance of the amorphous Al-minerals in the retention of minor elements was confirmed by electron microscopic observations of neoformed amorphous aluminosilicates which were significantly enriched in Zn.

## INTRODUCTION

Incineration of municipal solid waste results in the production of fly ash and very large quantities of bottom ash. Incineration is economically attractive because it strongly reduces the original volume of the waste while energy is recovered. However, the solid residues, the bottom ash and the fly ash, are enriched in potentially harmful elements relative to soils and sediments. To ensure an environmentally safe utilisation or disposal of these residues, the mechanisms controlling their short-term and long-term release need to be identified, which requires knowledge of both chemical (speciation) and physical (transport) processes. In this study we focus on the chemical processes controlling the partitioning of major and minor elements between the solid phase and pore water in a 20-year old disposal of Municipal Solid Waste Incinerator (MSWI) residues.

In the past few years important progress has been made in our understanding of the chemical processes that control the leaching of major and minor elements from combustion residues in general. The most important findings with respect to MSWI residues are reviewed below. First of all, bottom ash leaching has been observed to depend strongly on the ageing/weathering of the solid material (BELEVI *et al.*, 1992; ZEVENBERGEN AND COMANS, 1994; MEIMA AND COMANS, 1997a,b). Fresh MSWI bottom ash has an alkaline pH and consists primarily of meta-stable minerals that decompose during weathering (e.g. BELEVI *et al.*, 1992; ZEVENBERGEN AND COMANS, 1994; ZEVENBERGEN *et al.*, 1996; CHANDLER *et al.*, 1997; MEIMA AND COMANS, 1997a). With time, the pH will decrease to 8-8.5 by absorption of CO<sub>2</sub> (atmospheric or biogenic)

and subsequent precipitation of calcite (e.g. ZEVENBERGEN AND COMANS, 1994, JOHNSON *et al.*, 1995; MEIMA AND COMANS, 1997a,c). In particular the pH has been shown to be a very important controlling parameter in element leaching (e.g. VAN DER SLOOT *et al.*, 1989; COMANS *et al.*, 1993; EIGHMY *et al.*, 1995; VAN DER SLOOT *et al.*, 1996; CHANDLER *et al.*, 1997). For example, the pH affects the speciation of dissolved elements and the surface speciation of mineral particles. Precipitation/dissolution processes have been found to control the leaching of major elements from fresh and weathered residues (e.g. COMANS *ET AL.*, 1993; KIRBY AND RIMSTIDT, 1994; EIGHMY *et al.*, 1994, 1995; MEIMA AND COMANS, 1997a), and probably also the leaching of minor elements from *relatively unweathered residues* (COMANS *et al.*, 1993; EIGHMY *et al.*, 1994,1995; MEIMA AND COMANS, 1997b). The leaching of Cu from MSWI bottom ash has been suggested to be strongly enhanced by organic complexation (e.g. VAN DER SLOOT *et al.*, 1992; COMANS *et al.*, 1993; JOHNSON *et al.*, 1996); indeed, 95-100% of the dissolved Cu in leachates from fresh and 1.5-year old bottom ash was recently found to be organically-bound (MEIMA *et al.*, 1997d). The leaching of minor elements from *the more weathered residues* is likely to be controlled by sorption processes (JOHNSON *et al.*, 1996; MEIMA AND COMANS, 1997e). Sorption processes are expected to become more important in weathered residues. The weathering of the high-temperature minerals has been shown to result in the formation of mineral species, such as amorphous Fe/Al(hydr)oxides and amorphous aluminosilicates (ZEVENBERGEN AND COMANS, 1994; ZEVENBERGEN *et al.*, 1994; MEIMA AND COMANS, 1997a,c), which can strongly bind both metals and oxyanions.

In this study we investigate the geochemical processes that control the partitioning of major and minor elements between solid phase and pore water at various depth in a 20-year old disposal of mainly MSWI residues. We investigate whether the observed solid/liquid partitioning can be described by the same processes as those identified earlier in the laboratory: aqueous (in)organic complexation, precipitation/dissolution, redox, and/or sorption processes. A geochemical speciation code was used for modelling purposes, and parameters for the modelling of sorption reactions and the complexation of Cu with DOC were obtained

by specific measurements on the ash samples. Neoformed minerals were investigated with X-ray diffraction and electronmicroscopic techniques.

## MATERIALS AND METHODS

### *Description of the disposal*

The disposal site is located in the vicinity of Copenhagen (Denmark) and was filled up over the period 1974-1978 with 60.000 m<sup>3</sup> of mainly incinerator residues (bottom ash, fly ash, scrap metal) from a large MSWI located in the Copenhagen area. In addition, some unknown amounts of incompletely combusted residues and mercury-treated seed corn were also disposed at this site. During the period of deposition, leachate from another MSWI disposal was sprayed into the air above the surface of this site. The disposal was constructed as an artificial hill with a surface area of 8300 m<sup>2</sup> and a maximum depth/height of 18.5 meters, and was covered in 1978 by a 1-meter layer of topsoil with grass and other self-sown plants. The disposal was equipped with a PVC bottom liner and a drainage system for containment and collection of leachate. Both the water balance and the quality of the leachate have been monitored continuously (HJELMAR, 1989). At the time of sampling, the cumulative volume of leachate that was collected at the base of the disposal corresponded to a Liquid to Solid (L/S) ratio of approximately 0.5 L/kg (Hjelmar, pers. comm.)

### *Sampling*

Samples were taken in November 1996 using 7.5 cm diameter stainless steel tubes of 50 cm length. Samples were taken down to a depth of 10.30 meter. The tubes were driven mechanically as far as possible into the disposal. Filled tubes were closed tightly on top and bottom ends with stainless steel caps and were taken to the laboratory for slicing and further analyses. The tubes were stored at 4°C until use.

Additional samples were collected from a 25 cm diameter drill, which was used to widen the hole for engineering purposes. These samples were used for direct measurement of pH, E<sub>H</sub>, and temperature. In addition, samples deviating in colour and/or morphology were collected

and taken to the laboratory for mineralogical analyses. All samples were stored at 4°C until use.

#### *Analysis of pore water and solid*

The cores were sectioned into slices on the basis of (I) transitions between bottom ash and fly ash, (II) transitions in pH and/or  $E_H$  measured in the field, and (III) major transitions in colour and/or structure of the material. Cores from depths between 8.25 and 10.30 meter were sliced in a glove-bag under a  $N_2$ -atmosphere to maintain the relatively low redox potentials measured in the field. The number of slices was 47.

The pore water of the core slices was extracted by means of centrifugation (6000 g, 20 min) through 0.20  $\mu m$  membrane filters, using 300 ml custom-made Deldrin/Teflon (PTFE) centrifuge tubes. Pore waters from low- $E_H$  sections, i.e. slices from depths between 8.25 and 10.30 meter, were extracted within 1 week of sampling, and from the remaining sections within 3 weeks of sampling. Pore water and solids from low- $E_H$  samples were further handled in a glove-box under a  $N_2$ -atmosphere. For further analysis, one half of the pore waters was acidified with concentrated suprapure  $HNO_3$  for the analysis of Na, K, Ca, Mg, Al, Si, Fe, P, Cu, Mo, Pb, Zn, Cd, and Sb by ICP-AES, or GF-AAS in case element concentrations were below the limit of detection of ICP-AES. The remaining sample was left untreated for the measurement of Cl and  $SO_4$  by means of ion chromatography, and total inorganic carbon (TIC) and dissolved organic carbon (DOC) with a carbon analyser. Residual solid samples were sieved through a 3.35 mm-sieve and stored in gas-tight glass bottles at 4°C. Low- $E_H$  samples were stored under  $N_2$ .

The bulk chemical composition of the solid samples was determined by Neutron Activation Analysis (Na, K, Ca, Mg, Al, Fe, Mo, Zn, Cd, and Sb), or destruction with concentrated  $HNO_3/H_2SO_4$  followed by ICP-AES analysis (Cu, Pb, S, P, Si).

#### *Mineralogical analysis*

An X-ray diffractometer was used to investigate the crystalline minerals in 13 bulk samples of bottom and/or fly ash which were assumed to be representative for the entire profile. In addition, XRD was

used to investigate the mineralogy of the samples that were collected in the field because of deviating colour and/or morphology (30 samples in total). Amorphous precipitates were characterised by scanning electron microscopy (SEM) in combination with energy dispersive X-ray spectroscopy (EDS).

Transmission electron microscopy (TEM) was used to further characterise secondary phases that were found to be enriched in minor elements. This analysis was performed on ultramicrotomed thin-sections of material from (a) the interface between reducing and oxidising conditions (8.25-8.30 m), (b) a bulk bottom ash sample from the upper, carbonated/oxidised part of the profile (2.35-3.15 m), and (c) a bulk bottom ash sample from the lower, water-saturated part of the profile (9.90-10.30 m). A quantitative (<2% relative error) estimate of the composition of specific particles was made by EDS. Selected area electron diffraction (SAED) was used to identify structural and mineralogical properties. Details on the electron microscopic methods are given elsewhere (BRADLEY, 1988).

#### *Sorption parameters*

The amount of sorbent minerals in the ash and the amount of minor elements available for solid/liquid partitioning were determined for 17 samples which were considered to be representative for the entire profile. The same approach was followed as outlined in MEIMA AND COMANS (1997e):

Concentrations of amorphous iron hydroxides (Hydrous Ferric Oxide), crystalline iron oxides, and amorphous Al-minerals were obtained from 'selective' chemical extractions on the ash samples. Hydrous Ferric Oxide (HFO) was extracted from 3 g ash with 60 ml ascorbic acid solution (20 g/L) at pH 8 for 24 hours at room temperature (KOSTKA AND LUTHER, 1994). Crystalline+amorphous iron oxides were extracted from 3 g ash with 60 ml dithionite solution (50 g/L) at pH 4.8 for 4 hours at 60°C (KOSTKA AND LUTHER, 1994). Short-range ordered (hydrated) aluminosilicate minerals were extracted from 3 g ash with 300 ml 0.2M ammonium oxalate at pH 3 for 4 hours in the dark (BLAKEMORE *et al.*, 1987). Concentrations of Fe, Al, and Si in the extracts were determined by ICP-AES analysis.

Sorbed concentrations of Cu, Pb, Cd, Zn, Mo, and Sb were obtained from pH-static leaching experiments at pH values unfavourable for sorption. Samples were leached for 24 hours at a Liquid to Solid (L/S) ratio of 5 at pH 2 to obtain sorbed concentrations of Cu and Pb, at pH 4 in case of Cd and Zn, at pH 10.5 in case of Mo, and at pH 8 in case of Sb. N<sub>2</sub>-gas was bubbled through the suspensions of samples from below the redox interface to preserve the relatively low redox potentials.

*Parameters for organic complexation of Cu*

The competitive ligand-exchange solvent extraction (CLE-SE) technique described in MEIMA *et al.* (1997d) was used to analyse and determine parameters for organic complexation of Cu. Three samples from above the redox interface (average depths -1.3, -2.8, and -6.1 meters) and three samples from below the redox interface (average depths -8.35, -8.9, and -9.5 meters) were subjected to this analysis. The samples were suspended in water at a relatively low Liquid to Solid (L/S) ratio of 2.5, and were tumbled continuously in polyethylene vessels for 24 hours. After these 24 hours, the pH of the suspensions was measured and the suspensions were filtered through 0.2 µm membrane filters. A subsample was taken for analysis of CO<sub>3</sub>, DOC, Cl, Na, K, Ca, S, Mg, Al, Si, Fe, and Cu as described above. The remaining volume of the clear filtrate was used for CLE-SE analysis.

In the CLE-SE procedure, originally based on the analysis of organic copper complexes in sea water (MOFFET AND ZIKA, 1987), acetylacetonone (at concentrations specified below) and toluene (1.75 ml) were added to 17.5 ml of leachate. The acetylacetonone reacts with the Cu to a neutrally charged Cu(acac)<sub>2</sub><sup>0</sup>-complex, which is distributed between the water phase and the toluene phase. The concentration of the Cu(acac)<sub>2</sub><sup>0</sup> in the toluene phase is measured by quantitative dissolution into diluted HNO<sub>3</sub> and subsequent ICP-AES analysis. Subsequently, the concentrations of all species in the water phase can be calculated as outlined in Meima *et al.* (1997d), using a distribution coefficient of the Cu(acac)<sub>2</sub><sup>0</sup> between toluene and water of 3.9 ± 0.5 as determined earlier for artificial bottom ash leachates (MEIMA *et al.*, 1997d).

Finally, to determine the concentrations and the conditional stability constants of Cu-DOC complexes at different site occupations,

bottom ash leachates were titrated with acetylacetone ( $10^{-5}$  -  $10^{-2}$  mol/L) and Cu (2 - 50  $\mu$ mol/L), prior to CLE-SE analysis. NaOH was added to neutralise excessive acid resulting from the addition of  $>5.10^{-4}$ M acetylacetone concentrations. The conditional stability constant,  $K_{\text{cond}(i)}$ , for the reaction  $\text{Cu}^{2+} + \text{L}_i \rightleftharpoons \text{CuL}_i$  as well as the total ligand concentration  $[\text{L}_i]_{\text{T}}$  were determined by fitting the titration data to a Langmuir isotherm with one or more ligands. The number of ligands needed in the analysis depends on the heterogeneity of the DOC.

### *Geochemical modelling*

The speciation code MINTEQA2 version 3.11 (ALLISON *et al.*, 1991) was used to calculate (I) the aqueous speciation of the different components in the pore water samples, (II) the concentration of an element/component in equilibrium with potential solubility-controlling minerals, as described in detail in Meima and Comans (1997a), and (III) the concentration of an element as controlled by sorption to neoformed minerals. pH and  $E_{\text{H}}$  were fixed at the values measured in the field, and the Davies equation was used to calculate activity coefficients. For the sorption modelling the same approach was followed as outlined in MEIMA AND COMANS (1997e). In short, the sorption modelling was based on the Diffuse Layer Model and the database with surface complexation reactions and associated equilibrium constants for the sorption of ions on Hydrrous Ferric Oxide (HFO). Both are included in MINTEQA2 and are based on the work of DZOMBAK AND MOREL (1990). We used values recommended by DZOMBAK AND MOREL (1990) for molar weight of the HFO (89 g/mol Fe), specific surface area (600  $\text{m}^2/\text{g}$ ), concentration of low-capacity/high-affinity sites (5mmol/mol Fe), and concentration of high-capacity/low-affinity sites (0.2 mol/mol Fe). For modelling purposes, HFO was taken as a surrogate sorbent mineral for amorphous Al-minerals and crystalline Fe-oxides, in the absence of a complete and systematic database for sorption reactions on these minerals. One mol of Al was assumed to be representative of one mol of Fe. Additions and modifications to the standard MINTEQA2 (version 3.11) databases are summarised in Table 1.

**TABLE 1. Additional or modified thermodynamic data used in the MINTEQA2 calculations**

<b>aqueous species</b>	<b>log K</b>	<b>source</b>
$\text{Cu}(\text{OH})_2^{\circ}$	-16.20	MOREL AND HERING, 1993
$\text{HMoO}_4^-$	4.24	RAI AND ZACHARA, 1984
$\text{H}_2\text{MoO}_4^{\circ}$	8.24	RAI AND ZACHARA, 1984
$\text{CaMoO}_4^{\circ}$	2.57	ESSINGTON, 1992
$\text{MgMoO}_4^{\circ}$	3.03	ESSINGTON, 1992
$\text{HSbO}_3^{\circ}$	5.65	DZOMBAK AND MOREL, 1990
$\text{Cu}(\text{acac})^+$	8.265	SILLEN AND MARTEL, 1964
$\text{Cu}(\text{acac})_2^{\circ}$	15.055	SILLEN AND MARTEL, 1964
$\text{Hacac}^{\circ}$	8.95	SILLEN AND MARTEL, 1964
$\text{Me-acac}^{\text{a}}$		SILLEN AND MARTEL, 1964
$\text{CuL}_1^{\text{b}}$		this study
$\text{CuL}_2^{\text{b}}$		this study
<b>minerals</b>		
$\text{CdCO}_3$ (c) (otavite)	12.10	STIPP <i>et al.</i> , 1993
$\text{CuOH}$ (c)	0.70	LINDSAY, 1979
various Mo-containing minerals		RAI AND ZACHARA, 1984
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum)	4.62	MOREL AND HERING, 1993
$\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$ (ettringite)	-56.7	ATKINS <i>et al.</i> , 1991
<b>sorbed species</b>		
$=\text{X}_1\text{SbO}_3^{\circ}$	11.33 <sup>c</sup>	DZOMBAK AND MOREL, 1990
$=\text{X}_2\text{SbO}_3^{\circ}$	11.33 <sup>c</sup>	DZOMBAK AND MOREL, 1990
$=\text{X}_1\text{HSbO}_3^-$	4.23 <sup>c</sup>	DZOMBAK AND MOREL, 1990
$=\text{X}_2\text{HSbO}_3^-$	4.23 <sup>c</sup>	DZOMBAK AND MOREL, 1990
$=\text{X}_1\text{MoO}_4^-$	9.50 <sup>c</sup>	DZOMBAK AND MOREL, 1990
$=\text{X}_2\text{MoO}_4^-$	9.50 <sup>c</sup>	DZOMBAK AND MOREL, 1990

<sup>a</sup> Complexes of Cd, Zn, Mg, Al, and Fe with acetylacetone.

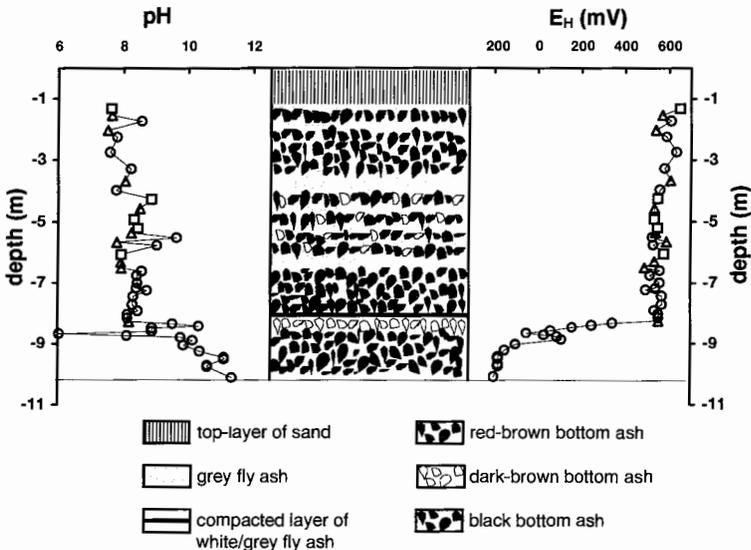
<sup>b</sup> The conditional stability constants determined in this study were included in MINTEQA2. Because of the conditional character of the constants, different  $\log K_{\text{cond}(i)}$  were added for different pH values (see Table 2). Before incorporation in MINTEQA2, the constants given in Table 2 were divided by the activity coefficient of  $\text{Cu}^{2+}$  obtained from an initial MINTEQA2 calculation.

<sup>c</sup> These sorption constants, now written in the MINTEQA2 format, were estimated on the basis of linear free-energy relationships by DZOMBAK AND MOREL (1990).

## RESULTS AND DISCUSSION

*Material characteristics*

Figure 1 gives a schematic representation of the material that was found down to a depth of 10.3 meter as well as the pH and  $E_H$  measured in the field. Down to a depth of 8.25 meters the material was unsaturated (moisture 15-25%) and largely carbonated and oxidised, whereas below this depth the conditions became alkaline and reducing. At the time of sampling, the “groundwater” level in the disposal was situated between depths of 10.0 and 10.3 meters. The material in the upper part of the disposal consisted of successions of layers of grey fly ash and layers of reddish-brown bottom ash. The reddish-brown colour of the bottom ash came from extensive oxidation of iron particles. In the lower part of the disposal only bottom ash was found, which colour changed into black in the reducing layers.



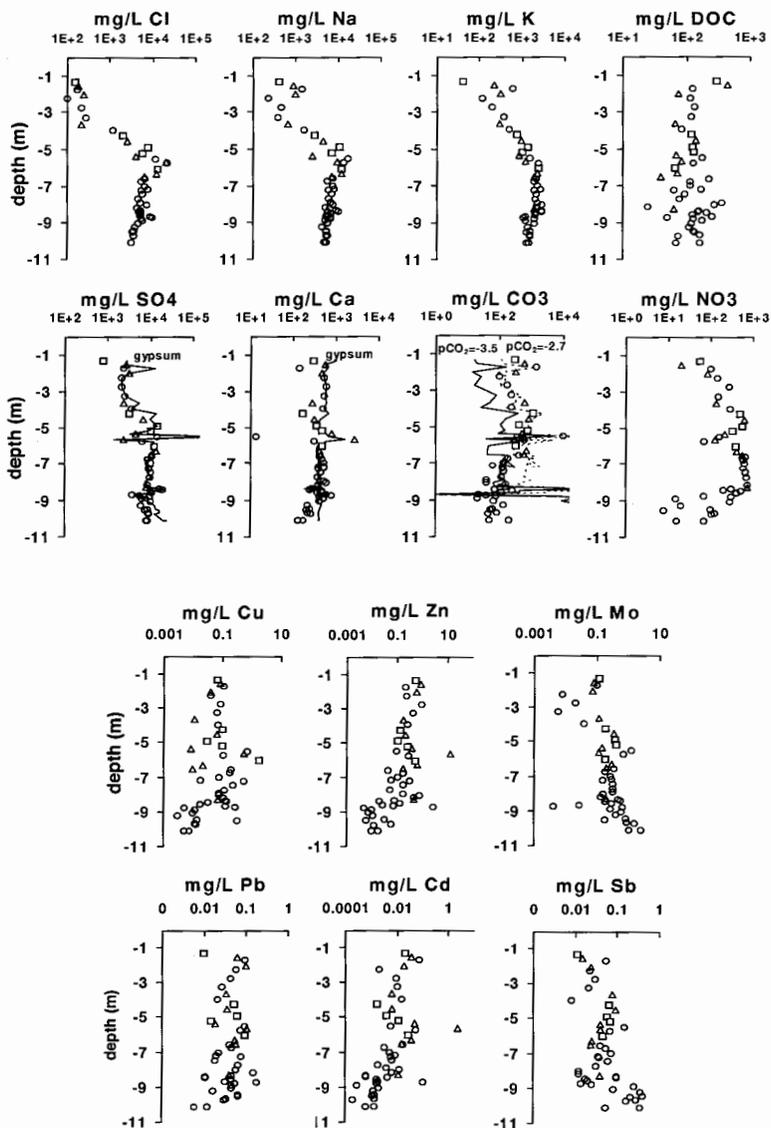
**Figure 1.** Schematic representation of the samples collected at the MSWI disposal site, and field measurements of pH and  $E_H$  (in mV relative to  $H_2$ ).

Additional physical characteristics of the profile are given in the Appendix, as well as bulk chemical and mineralogical compositions, a characterisation of the material from the pH/redox interface, a characterisation of neoformed Fe, Al, and Si minerals, and an overview of identified phases that are enriched in minor elements.

### ***Processes controlling the leaching of major elements***

Pore waters largely consist of Cl, Na, K, SO<sub>4</sub>, Ca, Mg, NO<sub>3</sub>, DOC, and CO<sub>3</sub>. Figure 2 shows their concentrations as a function of depth. Below a depth of 5 meters, pore waters become very saline due to high concentrations of Cl, Na, and SO<sub>4</sub>. Ionic strengths vary from 0.041 in the upper part of the profile to 0.30 in the lower part of the profile. Between depths of 5.5 and 6.5 meters, however, ionic strengths were considerably higher (0.65-0.8) due to the presence of large amounts of fly ash (see Fig. 1). The profiles for Na, K, and Cl are similar in shape, and illustrate the effect of percolating water on elements that have little or no retention in the solid phase.

Concentrations of SO<sub>4</sub> and Ca are controlled by equilibrium with gypsum down to a depth of 9 meters (see Fig. 2), and below this depth probably by ettringite (Ca<sub>6</sub>Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>(OH)<sub>12</sub>·26H<sub>2</sub>O). Gypsum was detected by XRD in bulk fly ash samples. Pore waters are oversaturated with respect to calcite, which was also observed for artificially and naturally carbonated MSWI bottom ash (V.D. WEIJDEN, 1995; MEIMA AND COMANS, 1997a,c) and for carbonated coal fly ash (SCHRAMKE, 1992). Oversaturation with respect to calcite has been explained by incorporation of SO<sub>4</sub> and/or Mg in the calcite lattice (SCHRAMKE, 1992), and/or by organic complexation reactions (REDDY *et al.*, 1990; V.D. WEIJDEN, 1995). Calcite was detected by XRD in both bulk fly ash and bulk bottom ash samples. Equilibrium with the atmospheric CO<sub>2</sub>-pressure is obtained in the lower part of the oxidised/carbonated zone (6.5 - 9 meters), but at shallower depths pore waters were found to be in equilibrium with a slightly higher CO<sub>2</sub>-pressure (10<sup>-2.7</sup> atm.) (see Fig. 2). These relatively high CO<sub>2</sub>-pressures indicate that the oxidation of organic matter is a significant source of CO<sub>2</sub>. Mg-leaching is likely to be



**Figure 2.** Pore water profiles for Cl, SO<sub>4</sub>, Na, Ca, K, CO<sub>3</sub>, DOC, and NO<sub>3</sub> (upper graphs), and Cu, Pb, Zn, Cd, Mo, and Sb (lower graphs). Symbols: ○ bottom ash, △ fly ash, □ mixed fly & bottom ash. Lines represent the predicted concentrations of Ca and SO<sub>4</sub> in equilibrium with gypsum, and the predicted CO<sub>3</sub>-concentration in equilibrium with pCO<sub>2</sub>=-3.5 and -2.7 atm., respectively.

controlled by a carbonate (possibly Mg-calcite) in the oxidised/carbonated layer, and by brucite ( $\text{Mg}(\text{OH})_2$ ) in the reducing/alkaline layer (not shown). The factors that control the observed fluctuations in DOC-leaching are not understood.

The pH of the material in the upper 8.3 meters is generally in the range of pH values predicted on the basis of equilibrium with calcite and  $\text{pCO}_2 = -2.7$  (pH 7.7) and  $\text{pCO}_2 = -3.5$  (pH 8.3), respectively. The alkaline pH values (10-11) observed at depths below 9 meters result from the dissolution of residual alkaline minerals. The occurrence of pH values of  $>10.5$  indicates that the three minerals ettringite, gypsum, and gibbsite ( $\text{Al}(\text{OH})_3$ ) may not coexist, because coexistence of these minerals would control the pH to values of  $\sim 10$  (MEIMA AND COMANS, 1997a). Indeed, at  $\text{pH} > 9.5$ , the pore waters are strongly undersaturated with respect to gibbsite (not shown); amorphous aluminosilicates instead may control the Al-concentrations to relatively low values at alkaline pH.

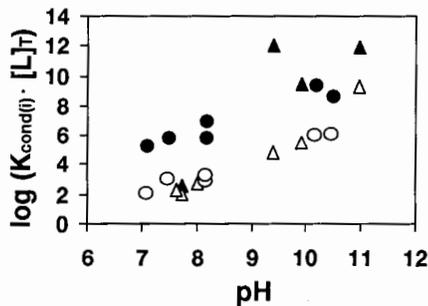
### ***Processes controlling the leaching of Cu, Zn, Pb, Cd, Mo, and Sb***

Pore water concentrations of Cu, Zn, Pb, Cd, Mo, and Sb as a function of depth are shown in Figure 2. Most concentrations fall within a range of 1-2 orders of magnitude. In general, the concentrations of Mo and Sb tend to increase with depth, whereas concentrations of Cd, Pb, Zn, and Cu tend to decrease. On the basis of measured pH and  $E_H$  in the field, the dominant valence states of Mo and Sb were calculated to be Mo(VI) and Sb(V). The dominant valence state of Cu depends on the role of organic complexation. On the basis of inorganic complexation reactions, it was calculated that Cu(I) species are dominant over Cu(II) species at depths below 8.5 meters. Below, we first discuss the complexation of Cu with DOC, followed by a discussion of possible mechanisms (precipitation/dissolution, sorption) controlling the leaching of Cu, Zn, Pb, Cd, Mo, and Sb.

#### ***The complexation of Cu with DOC***

The complexation of Cu with DOC was investigated for 3 samples from above the redox interface and for 3 samples from below the redox

interface. In general, a Langmuir model with one or with two sites gave the statistically best fit through the experimental titration data. The obtained  $K_{\text{cond}(i)}$ ,  $[L_i]_{\text{T}}$ , and site densities on DOC are summarised in Table 2. The results were compared to results obtained for DOC from fresh and 1.5-year old MSWI bottom ash (MEIMA *et al.*, 1997d) by plotting the product  $K_{\text{cond}(i)} \cdot [L_i]_{\text{T}}$  as a function of the pH (Figure 3). The product of  $K_{\text{cond}(i)}$  and  $[L_i]_{\text{T}}$  was used rather than  $K_{\text{cond}(i)}$  only, because  $K_{\text{cond}(i)}$  and  $[L_i]_{\text{T}}$  are not completely independent in the above analysis. Table 2 and Figure 3 indicate that the  $K_{\text{cond}(i)}$  obtained for samples from below the redox interface are considerably higher than obtained for samples from above the redox interface. Furthermore, the values corresponding to the low affinity sites all plot on a single line, indicating that these sites have possibly general characteristics, whereas the values corresponding to the high-affinity sites are more variable. Site densities of DOC from the reducing/alkaline layer resemble the site densities found for fresh and 1.5-year old bottom ash (MEIMA *et al.*, 1997d), whereas the site densities of the DOC from the oxidised/carbonated layer are considerably higher and similar in magnitude as those found for humic acids (BUFFLE, 1988; KINNIBURGH *et al.*, 1996).



**Figure 3.** Comparison of  $\log[K_{\text{cond}(i)} \cdot [L_i]_{\text{T}}]$  of bottom ash from the 20-year old disposal ( $\Delta$  low-affinity sites;  $\blacktriangle$  high-affinity sites) and of leachates from fresh and 1.5-year old MSWI bottom ash ( $\circ$  low-affinity sites;  $\bullet$  high-affinity sites; from MEIMA *et al.*, 1997d).  $[L_i]_{\text{T}}$  were expressed in mol/kg ash.

**TABLE 3. Parameters for the complexation of Cu with DOC.**

Depth (m)	1.1-1.5	2.4-3.2	6.0-6.2	8.3-8.4	8.8-9.0	9.4-9.6
<b>CLE-SE data based on L/S=2.5 leachates<sup>1</sup></b>						
pH	7.75	7.65	8.03	9.42	9.93	11.00
[DOC] (mg/L)	7.17	3.04	6.50	15.58	10.64	25.57
[L <sub>1</sub> ] <sub>T</sub> (μmol/L)	0.7(-0.6+2.5)			0.45±0.08	0.18±0.02	2.0±1.6
[L <sub>2</sub> ] <sub>T</sub> (μmol/L)	13(-0.8+23)	9.7±1.7	14.1±0.5	9.3±0.6	3.3±0.3	2.3±1.5
logK <sub>cond(1)</sub>	8.4±1.5			18.0±0.6	15.8±0.2	17.2±2.9
logK <sub>cond(2)</sub>	6.5±0.3	7.00±0.04	7.23±0.14	9.53±0.11	10.62±0.06	14.6±0.4
n <sup>2</sup>	16	16	12	12	11	7
RSS <sup>3</sup>	5.04x10 <sup>f</sup>	1.68x10 <sup>b</sup>	9.62x10 <sup>f</sup>	2.76x10 <sup>f</sup>	6.58x10 <sup>b</sup>	1.12x10 <sup>f</sup>

**Calculated site densities on DOC**

site 1 (mol/kgC)	0.10			0.03	0.02	0.08
site 2 (mol/kgC)	1.86	3.20	2.17	0.60	0.31	0.09

**Pore water data**

pH	7.62	7.59	7.95	9.53	10.15	11.15
L/S	0.27	0.21	0.27	0.17	0.34	0.25
[Cu] <sub>T</sub> (mg/L)	0.066	0.082	1.796	0.126	0.012	0.333
[DOC] (mg/L)	295.3	133.2	66.3	159.5	176.6	136.8

**Calculated Cu-speciation in the pore waters<sup>4</sup>**

% inorganic	1-17%	1-10%	1-54%	0-1%	0%	0-18%
% CuL <sub>1</sub>	46-76%			23-100%	94-100%	39-100%
% CuL <sub>2</sub>	23-38%	91-99%	47-99%	0-76%	0-6%	0-43%

<sup>1</sup> The reported standard deviations include the uncertainty in the distribution coefficient of the Cu(acac)<sub>2</sub><sup>o</sup> between toluene and water, which is 3.9 ± 0.5 (MEIMA *et al.*, 1997d).

<sup>2</sup> Number of titration data.

<sup>3</sup> Residual Sum of Squares between model and experimental data.

<sup>4</sup> The calculated range in Cu-speciation is based on two limiting scenario's with respect to the solubility of the organic ligands:

(1) [L<sub>0</sub>]<sub>T</sub> in the pore waters is equal to the measured [L<sub>0</sub>]<sub>T</sub> at L/S=2.5;

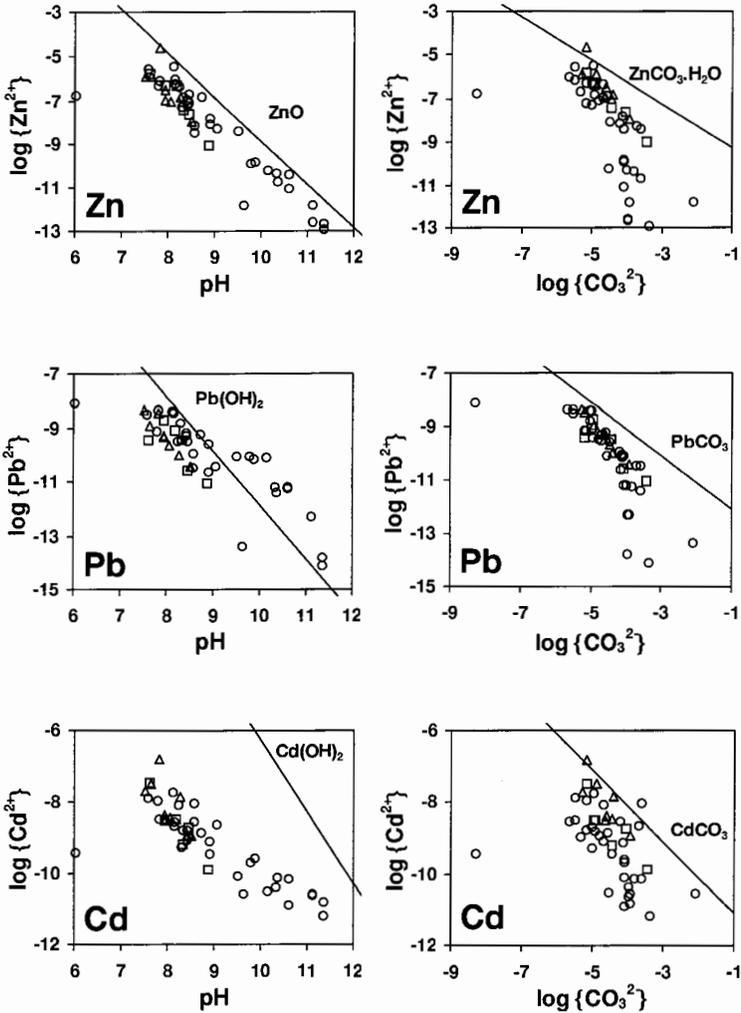
(2) [L<sub>0</sub>]<sub>T</sub> increases linearly and inversely with the L/S-ratio, i.e. [L<sub>0</sub>]<sub>T</sub> in the pore waters is approx. 10 times the [L<sub>0</sub>]<sub>T</sub> at L/S=2.5.

In order to calculate the aqueous speciation of Cu in the pore waters, the ligand concentrations determined at L/S=2.5 need to be extrapolated to the L/S ratio of the pore waters, which is approximately 0.25 (see Table 2). Since the processes controlling the solubility of the identified ligands are not known, two limiting scenarios were investigated: (I) a scenario in which  $[L_{(i)}]_T$  was assumed to be independent of the L/S ratio, and (II) a scenario in which  $[L_{(i)}]_T$  was assumed to depend (inversely and linearly) on the L/S ratio. On the basis of these 2 scenarios it was calculated that 82-100% of the dissolved copper is organically-bound in the reduced/alkaline layer (see Table 2). In the upper two samples of the oxidised/carbonated layer, 83-99% of the dissolved copper was calculated to be organically-bound. In the sample with the highest dissolved Cu-concentrations (depth -6.1 meters) between 45-99% is organically bound; the uncertainty in this sample is relatively large because  $[Cu]_T \gg [L_i]_T$  in scenario I. Due to large fraction of the dissolved Cu that is organically-bound, Cu(II)-species are dominant over Cu(I) species in the entire profile.

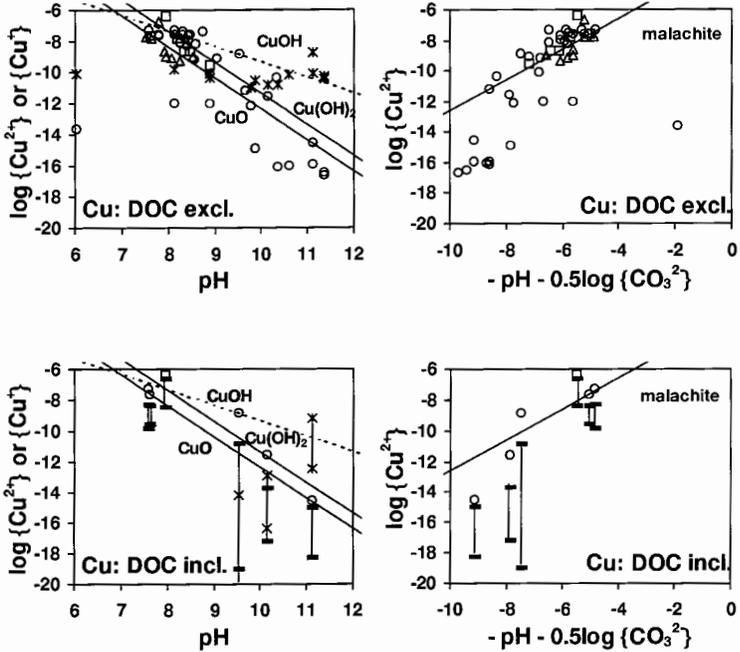
#### *Precipitation/dissolution processes*

Figure 4 and 5 show the activities of  $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$ ,  $Cu^{2+}$ , and  $Cu^+$  as a function of both pH and  $CO_3^{2-}$ -activity. Activities of  $Cu^{2+}/Cu^+$  were calculated on the basis of both organic and inorganic complexation reactions (Fig. 5, lower panels), and on the basis of inorganic complexation only (Fig. 5, upper panels). For comparison, predicted activities on the basis of equilibrium with relatively insoluble metal-(hydr)oxide and carbonate minerals are also given. Pore water concentrations of Sb and Mo were calculated to be too low to be controlled by the precipitation/dissolution of pure mineral phases. One exception is the mineral wulfenite ( $PbMoO_4$ ) for pH values below 10, but the observed fluctuations in Pb and Mo leaching cannot be explained by equilibrium with this mineral (not shown).

Fig. 4 shows that the pore waters with the highest concentrations of Cd and Zn (see Fig. 2), which are in particular fly ash samples, approach equilibrium with otavite ( $CdCO_3$ ), zincite ( $ZnO$ ), and/or  $ZnCO_3 \cdot H_2O$ . The majority of the pore waters, however, are (slightly) undersaturated with respect to these minerals. Similarly, pore waters with the highest



**Figure 4.** Calculated activities of  $Zn^{2+}$ ,  $Pb^{2+}$ , and  $Cd^{2+}$  vs pH and  $CO_3^{2-}$ -activity. Symbols:  $\circ$  bottom ash,  $\Delta$  fly ash,  $\square$  mixed fly & bottom ash. Lines represent activities predicted from control by the following minerals: ZnO (zincite),  $ZnCO_3 \cdot H_2O$ ,  $Cd(OH)_2$ ,  $CdCO_3$  (otavite),  $Pb(OH)_2$ ,  $PbCO_3$  (cerussite).



**Figure 5.** Calculated activities of  $\text{Cu}^{2+}$  and  $\text{Cu}^+$  vs pH and  $\text{CO}_3^{2-}$ -activity. The plots in the upper panel are based on inorganic complexation reactions only. The plots in the lower panel include the effect of organic complexation, which is denoted by vertical lines. The boundaries of these vertical lines are set by the lower and higher limit of ligand concentrations (see footnote Table 2). Diagonal lines represent activities predicted from control by the following minerals:  $\text{CuO}$  (tenorite),  $\text{Cu}(\text{OH})_2$ ,  $\text{CuOH}$ , and  $\text{Cu}_2(\text{OH})_2\text{CO}_3$  (malachite). Symbols:  $\circ$  bottom ash ( $\text{Cu}^{2+}$ ),  $\Delta$  fly ash ( $\text{Cu}^{2+}$ ),  $\square$  mixed fly & bottom ash ( $\text{Cu}^{2+}$ ), \* bottom ash ( $\text{Cu}^+$ ). In all MINTEQA2 calculations the pH and  $E_H$  were fixed to the values measured in the field.

concentrations of Pb are close to equilibrium with  $\text{Pb(OH)}_2$  or cerussite ( $\text{PbCO}_3$ ). However, all pore waters from the reduced/alkaline layer were calculated to be strongly oversaturated with respect to  $\text{Pb(OH)}_2$ , indicating that the leaching of Pb was possibly enhanced significantly by organic complexation. Organic complexation of Cu was also found to be more significant in the reduced/alkaline than in the oxidised/carbonated layer (Table 2). Pore waters were also found to be strongly oversaturated with respect to chloropyromorphite ( $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$ ) (not shown). Figure 5 shows that the level of saturation with respect to Cu(II)-(hydr)oxides and Cu(II)-carbonates varies between saturation and undersaturation, depending on the concentration of organic ligands (scenario I or II) used in the modelling. Pore waters remain generally undersaturated with respect to Cu(I)-hydroxide (Figure 5, lower panel).

In the water-saturated part of the disposal sulphide precipitates of Cu, Pb, and Zn were detected by TEM-analysis. Sulphide precipitation has earlier been suggested as a possible mechanism to explain the relatively low concentrations of heavy metals in percolate from this disposal (HJELMAR, 1989). MINTEQA2 modelling on the basis of bulk  $\text{pH}/E_{\text{H}}$  measured in the field, however, indicated that the pore waters are strongly undersaturated (saturation indices  $\ll -20$ ) with respect to these metal sulphides, and that redoxpotentials as low as  $-350\text{mV}$  (or  $-450\text{mV}$  in the case of ZnS) are required to obtain equilibrium with PbS, CuS, and CdS. Since bulk redoxpotentials measured in the field were only  $-200\text{mV}$ , it is unlikely that metal sulphides control bulk pore water concentrations of Cd, Zn, Cu, or Pb.

In conclusion, the solubility of carbonate/hydroxide minerals may control metal leaching in the sections with relatively high metal concentrations, which seems in particular to be the case for fly ash. However, precipitation/dissolution processes cannot generally explain the measured pore water concentrations.

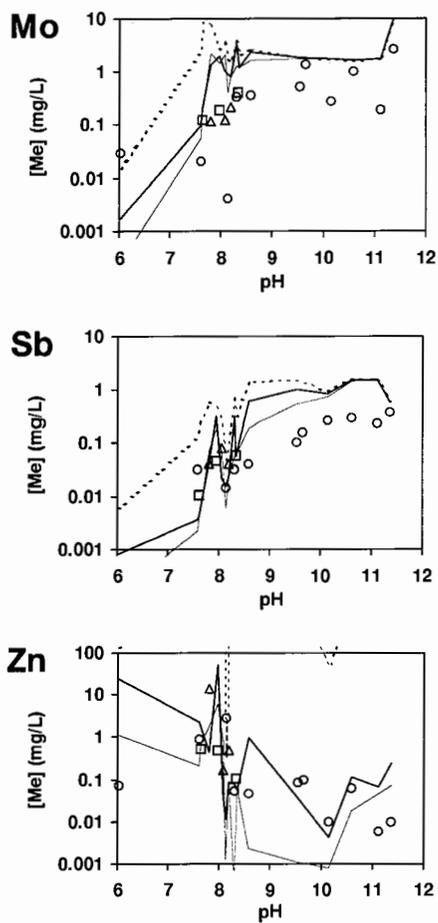
### *Sorption processes*

As has been shown recently (MEIMA AND COMANS, 1997e), sorption processes are likely to control the leaching of metals and molybdate from weathered MSWI bottom ash in the laboratory. Three parameters are very important in modelling solid/liquid partitioning by

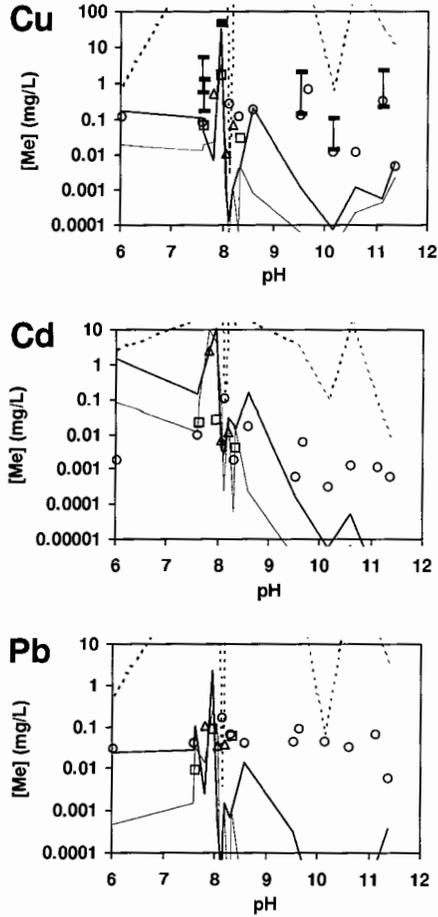
sorption, i.e. the pH, the amount of sorbent minerals (surface sites) in the ash and the amount of metals and oxyanions available for sorption. The latter two parameters were obtained from the data in Figure 9 (Appendix). Figure 6 gives the predicted pore water concentrations of Cd, Pb, Zn, Cu, Mo, and Sb as a function of pH on the basis of surface complexation with HFO, HFO + amorphous Al-minerals, and HFO + crystalline Fe oxides. In the modelling, HFO was used as a surrogate sorbent mineral for amorphous Al-minerals and crystalline Fe oxides. This was done by using the Diffuse Layer Model, and sorption parameters for HFO of DZOMBAK AND MOREL (1990), as further detailed in MEIMA AND COMANS (1997e). Although the absolute level of the predicted concentrations may not be very accurate, the model should be able to predict reasonably well the effects of variations in pH, metal availability, and sorbent mineral concentrations on the pore water concentrations in the different sections of the profile. Variations in the amount of a metal available for sorption also affect the sorption of other elements, e.g. the extremely high availability of Cu at a depth of 6.1 meters (pH7.95-data point in Fig. 6) resulted in considerably less sorption of Pb, Zn, and Cd.

Fig. 6 demonstrates that the concentration of HFO is generally too low to result in sufficient sorption, except for the sample at pH 8.13, which came from the zone of alternating redox conditions (depths 8.5-8.75 meters). The concentrations of amorphous Al-minerals and crystalline Fe-oxides (Fig. 9), however, are potentially large enough to explain the observed pore water concentrations of Cd, Pb, Zn, Cu, Mo, and Sb by surface complexation. The predicted curves for sorption on amorphous Al-minerals and crystalline Fe-oxides are similar in shape since we used HFO as a surrogate sorbent mineral for both amorphous Al-minerals and crystalline Fe-oxides. Therefore, the results of this modelling approach do not give clues as to the contribution of individual sorbent minerals.

Sorption predicts reasonably well the observed reduction in the leaching of the oxyanions (Mo, Sb) towards neutral pH values as well as the observed reduction in the leaching of the cationic metals towards alkaline pH values. In quantitative terms, the model based on amorphous Al-minerals gives generally the best predictions, particularly for Mo, Sb,



**Figure 6.** Predicted pore water concentrations of Mo, Sb, Zn, Cu, Cd, and Pb on the basis of sorption to amorphous  $\text{Fe}(\text{OH})_3$  (HFO) (dashed lines), HFO plus amorphous Al-minerals (regular lines); HFO plus crystalline Fe oxides (thin lines). Symbols: ○ bottom ash, □ mixed fly & bottom ash.



**Figure 6.** (continued) Vertical lines represent the effect of organic complexation on predicted Cu-concentrations on the basis of sorption to HFO + amorphous Al-minerals. The boundaries of the vertical lines are set by the lower and higher limit of ligand concentrations (see footnote, Table 2).

and Zn. The observed and predicted concentrations of these elements were generally within one order of magnitude. The generally higher predicted than observed concentrations of Mo and Sb at alkaline pH may point to an overestimation of total available metal concentrations. The model also predicts reasonably well the observed trend in the leaching of Cu. In general, predicted and measured concentrations were within one order of magnitude when taking account of complexation with DOC and using the model based on amorphous Al-minerals. Furthermore, the observed trend in the leaching of Cd is also consistent with the predicted concentrations. Measured and predicted concentrations are generally within one order of magnitude for the oxidised/carbonated samples both on the basis of crystalline Fe oxides and amorphous Al-minerals. However, the dissolved Cd-concentrations in the reduced/alkaline samples remain underestimated on the basis of these models. The leaching of Pb is relatively pH-independent, which is not consistent with the general shape of the sorption curves. On the basis of sorption to both crystalline Fe oxides and amorphous Al-minerals the leaching of Pb was largely underpredicted. Since the alkaline pore waters were also calculated to be oversaturated with  $\text{Pb}(\text{OH})_2(\text{s})$ , the dissolved Pb is possibly largely organically-bound. Further research is required to confirm this hypothesis.

The possibly important role of amorphous Al-minerals in the sorption of minor/trace elements is supported by electron microscopic observations. First of all, the amorphous aluminosilicates from the oxidised/carbonated and reduced/alkaline ash layers were found to be significantly enriched in Zn (see Fig. 8 and Fig. 10 in the Appendix). In addition, individual samples of amorphous aluminosilicates were found which were enriched in Cu and Zn (SEM/EDS), respectively Pb (TEM/EDS) (see appendix). Furthermore, in 1.5-year old MSWI bottom ash both Cu and Zn were detected in amorphous gel-like precipitates consisting mainly of Al and O (MEIMA AND COMANS, 1997b), and in 12-year old MSWI bottom ash neoformed poorly-crystallised clay-minerals were found which were enriched in Cu, Zn, Pb, and Ni (ZEVENBERGEN *et al.*, 1994). Whether or not the other metals (e.g. Cu, Pb, Cd, Mo, Sb) are associated to a significant degree with the amorphous Al-minerals in the 20-year old disposal remains unclear from the electron microscopic

analyses. The limit of detection for these metals is too high. (The detection of Zn was facilitated by its considerably higher bulk concentration compared to the other metals, see appendix).

## GENERAL DISCUSSION

### *Evaluation of the geochemical modelling approach*

The material that we obtained from the 20-year old disposal of MSWI residues was extremely heterogeneous. Variations in input material (fly ash, bottom ash, metal scrap) and variations in physical/chemical conditions down the profile (pH,  $E_H$ , ionic strength, water content) have made the analysis presented in this paper very complex. In general, two major environments can be distinguished in the disposal: an oxidised/carbonated (down to a depth of 8.25 meter) and a reduced/alkaline (below depths of 8.8 meters) environment, which are separated by an interface consisting of compacted fly ash, iron oxides, and secondary amorphous aluminosilicates (see Appendix). The lower part of the reduced/alkaline layer was water-saturated.

In general, we were able to describe the leaching of major and minor elements reasonably well by the same processes as those identified earlier in the laboratory. These processes are aqueous complexation, redox, and precipitation/dissolution processes in case of the major elements and, additionally, sorption processes in the case of the minor elements. The most important findings regarding the controlling processes for Cu, Zn, Pb, Cd, Mo, and Sb are summarised below.

The dissolved Cu appears to be largely organically-bound in both the oxidised/carbonated and reduced/alkaline layers. In addition, our modelling results suggest that organic complexation may also be important for Pb.

The observed range in pore water concentrations of Pb, Zn, Cd, Cu, Mo, and Sb generally varies over 1-2 orders of magnitude. In the sections with higher pore water concentrations heavy metal concentrations are likely to be controlled by equilibrium with carbonate

and maybe (hydr)oxide minerals. This seems particularly to be the case for fly ash. In addition, in the reduced/alkaline layer the leaching of Pb may be controlled by equilibrium with  $\text{Pb(OH)}_2(\text{s})$ . Except for these specific samples, pore waters were generally calculated to be undersaturated with respect to common solubility-controlling minerals for Mo, Sb, Cu, Zn, Cd, and Pb.

Sorption is considered to be the major controlling process in this 20-year old disposal. Potentially important sorbent minerals in the ash are amorphous Al-minerals and crystalline Fe oxides, which are both present in quantities that are large enough to explain the observed pore water concentrations of Zn, Cu, Pb, Cd, Mo, and Sb by surface complexation. Amorphous  $\text{Fe(OH)}_3$  was present in too small amounts to bind these elements sufficiently, except in the zone of alternating redox conditions (depth 8.5-8.75 meters). On the basis of sorption to crystalline Fe oxides or amorphous Al-minerals, we were indeed able to predict the general trend in measured pore water concentrations of Mo, Sb, Zn, Cu, and Cd. The approach which was used to model sorption on these (hydr)oxide minerals does not allow for conclusions as to the relative importance of the Fe- and Al-sorbent minerals. The potential importance of the amorphous Al-minerals in the retention of minor elements was confirmed by electron microscopic observations: neoformed amorphous aluminosilicates were found which were significantly enriched in Zn.

The results presented in this paper illustrate that the geochemical modelling approach is very promising, but that there is also a large potential for improvement. Essential in geochemical modelling are (a) well-developed databases containing thermodynamic constants for the above mentioned processes, (b) knowledge of the pH,  $E_{\text{H}}$ , and major element concentrations in the pore waters, and (c) in the case of sorption modelling knowledge of the types and concentrations of available sorbent minerals and their site densities, and (total) available concentrations of minor elements. Because of the potential importance of sorption processes and organic complexation reactions, these processes in particular deserve more attention in future research.

With respect to sorption modelling, for a more thorough evaluation of the role of amorphous Al-minerals and crystalline Fe-oxides a general

surface complexation model (e.g. the Diffuse Layer Model of DZOMBAK AND MOREL (1990) which was used for HFO) with sorption constants for these minerals is required. Furthermore, the identity and sorptive capacity of the secondary amorphous Al-minerals in bottom ash need to be further characterised.

With respect to organic complexation, there is a need for a thorough and less conditional characterisation of the complexing properties of DOC from fresh and weathered bottom ash with respect to Cu as well as other metals. In addition, the leaching/solubility, and long-term stability of DOC itself needs further investigation.

For the prediction of the short-term and long-term leaching of elements from disposed or utilised combustion residues, the role of transport processes needs to be taken into account, in addition to the geochemical processes that control the partitioning of elements between pore water and solid phase, as were investigated in this paper. Furthermore, in relation to the prediction of the long-term leaching, the kinetics of the different weathering processes also become important, such as the rate of carbonation and of secondary mineral formation.

*Implications for the long-term leaching of heavy metals and oxyanions from MSWI bottom ash*

MSWI bottom and fly ash are materials that are highly susceptible to weathering. The secondary phases that precipitate as a result of weathering may bind significant amounts of contaminants, resulting in the retention of these elements. However, this immobilisation mechanism fails for oxyanions if the pH of the material remains alkaline. The mobility of oxyanions in the reduced/alkaline layer was found to be significantly higher than in the oxidised/carbonated layer. This difference is explained by the strong decrease in the affinity of oxyanions for sorption to Fe/Al-hydroxides towards alkaline pH. Heavy metals, on the other hand, show significant sorption and generally relatively low leaching in both the oxidised/carbonated and the reduced/alkaline layer. Neutral pH values (e.g. after carbonation), therefore, are considered to be

the most favourable for a relatively low leaching of both heavy metals and oxyanions.

The neutralisation (carbonation) of MSWI bottom ash proceeds best under unsaturated conditions. In a water-saturated disposal, the rate of carbonation is very low, and at the interface between saturated (generally reducing) and unsaturated (generally oxidising) conditions a relatively impermeable layer of Fe-oxides may form, which will further reduce the rate of carbonation. Atmospheric CO<sub>2</sub>, biogenic CO<sub>2</sub>, and weak organic acids contribute to the neutralisation (carbonation) of the bottom ash. The final pH is buffered by CaCO<sub>3</sub>, which is usually present in relatively large amounts (5-10 (m/m)%: JOHNSON *et al.*, 1995). In well-burned MSWI bottom ash this amount of CaCO<sub>3</sub> is expected to be sufficient to maintain an equilibrium pH of 8-8.5 for a very long time, which favours relatively low leaching of both metals and oxyanions. An additional effect of the presence of organic matter, however, is that dissolved organics will significantly enhance the leaching of Cu for >20 years, and possibly also of other metals. In summary, the most environmentally safe utilisation or disposal would consist of only bottom ash<sub>2</sub> which is well-burned and applied/disposed under unsaturated and well-aerated conditions.

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## APPENDIX

### *Additional physical characteristics of the profile*

In the upper part of the disposal concretions of reddish-iron were frequently found, and at depths between 5.0 and 6.5 meters three horizontal Fe-pans were found, which acted as relatively impermeable layers. The pH/redox-interface at a depth 8.25-8.30 meters consisted of a layer of very compact white-grey coloured fly ash. Iron concretions and pH/redox interface are further characterised below.

In the lower part of the disposal spots of dark grey and reddish-brown bottom ash were observed, indicating that the groundwater table (and as a result the  $E_H$ ) had been subject to fluctuations. Between depths of 8.50-8.75 meters pH and temperature deviated significantly from the surrounding material: pH-values were very low (6-8) and the temperature very high (30°C, whereas the average in the disposal was 20°C), which points to a very active biological zone. It is possible that incompletely combusted residues with a relatively high concentration of residual organic matter were disposed at these depths.

### *Bulk chemical and mineralogical composition*

The averaged bulk elemental composition of analysed bottom and fly ash samples is given in Table 3. In comparison with bottom ash, fly ash is significantly depleted in Fe and Cu, and generally more than a factor of 2 enriched in Ca, Al, Zn, S, P, Ti, Pb, Cd, and Sb. Depth profiles for bulk concentrations of major elements (Si, Fe, Ca, Al, Cl, Na, K, S, and P) and minor elements (Cu, Zn, Pb, Cd, Mo, and Sb) are given in Figure 7. Systematic changes in elemental composition with depth were only observed for Fe, Si, Al, Na, Ca, and Cl. Between depths of 7 and 9 meter the bottom ash is up to a factor of 2 enriched in Fe, and up to a factor of 2 depleted in Na, Si, Al, and Ca. These variations in bottom ash composition may have resulted from variations in input during disposal. The observed depletion of the solid material in Cl down to a depth of 5.5 meters, is the result of percolating water.

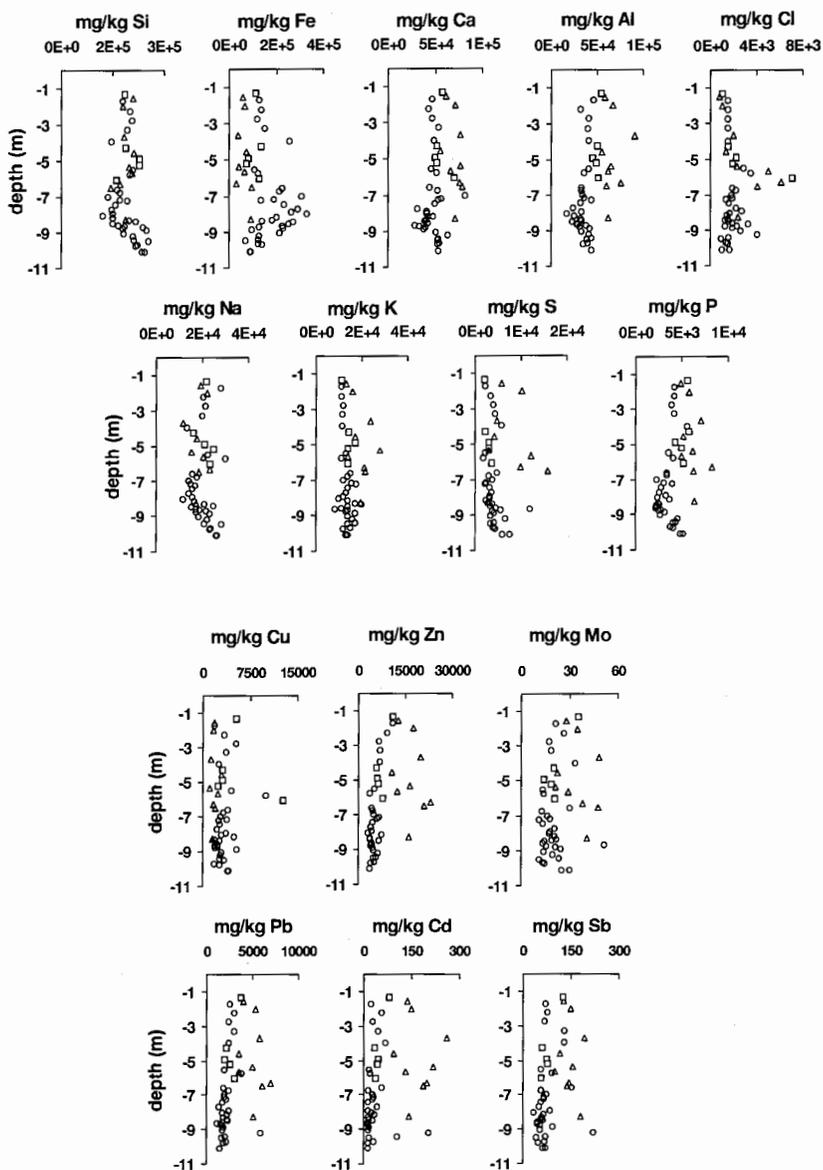
The principal minerals identified by X-ray diffraction analysis in bulk ash samples were quartz ( $\text{SiO}_2$ ), plagioclase feldspar, calcite ( $\text{CaCO}_3$ ), magnetite ( $\text{Fe}_3\text{O}_4$ ), and goethite ( $\text{FeOOH}$ ). Additionally,

gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) was identified in fly ash samples. The concentration of goethite in the oxidised/carbonated part of the disposal was significantly higher than in the reduced/alkaline part. In addition, quartz, feldspar, goethite, lepidocrosite ( $\text{FeOOH}$ ), calcite, gypsum, and/or hydroxylapatite ( $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ ) were the most frequently detected in the 30 samples which were collected in the field on the basis of deviating colour/morphology.

**TABLE 3. Average bulk chemical composition of 33 bottom and 9 fly ash samples.**

	Bottom ash		Fly ash	
	average	min - max	average	min - max
<b>Si</b> (m/m%)	19.0%	(12%-26%)	18.8%	(14%-21%)
<b>Fe</b> (m/m%)	18.0%	(7%-33%)	6.0%	(3.1-9.8)
<b>Ca</b> (m/m%)	4.7%	(2.8%-8.1%)	7.0%	(5.5%-7.8%)
<b>Al</b> (m/m%)	3.5%	(1.7%-4.6%)	6.7%	(5.5%-9.0%)
<b>Na</b> (m/m%)	2.0%	(1.2%-3.0%)	1.9%	(1.2%-2.3%)
<b>K</b> (m/m%)	1.4%	(0.8%-2.0%)	1.9%	(1.3%-2.8%)
<b>Zn</b> (m/m%)	0.5%	(0.3%-1.1%)	1.7%	(1.1%-2.3%)
<b>S</b> (m/m%)	0.4%	(0.2%-1.2%)	0.8%	(0.3%-1.6%)
<b>P</b> (mg/kg)	3500	(2200 - 5600)	6100	(4900 - 8000)
<b>Cu</b> (mg/kg)	3400	(1800 - 9900)	1900	(1000 - 3000)
<b>Ti</b> (mg/kg)	2900	(1800 - 4100)	6400	(4800 - 8000)
<b>Pb</b> (mg/kg)	2200	(1200 - 5900)	5000	(3500 - 7000)
<b>Cl</b> (mg/kg)	1900	(1000 - 4000)	2800	(800 - 6100)
<b>Mn</b> (mg/kg)	1700	(900 - 4200)	1900	(1600 - 2500)
<b>Sb</b> (mg/kg)	70	(40 - 200)	140	(100 - 200)
<b>Cd</b> (mg/kg)	30	(10 - 200)	170	(90 - 300)
<b>Mo</b> (mg/kg)	20	(10 - 50)	30	(20 - 50)

field investigation



**Figure 7.** Bulk concentrations (in mg/kg ash) of Si, Na, Fe, K, Ca, S, Al, P, and Cl (upper graphs) and Cu, Pb, Zn, Cd, Mo, and Sb (lower graphs). Symbols: ○ bottom ash, △ fly ash, □ mixed fly & bottom ash.

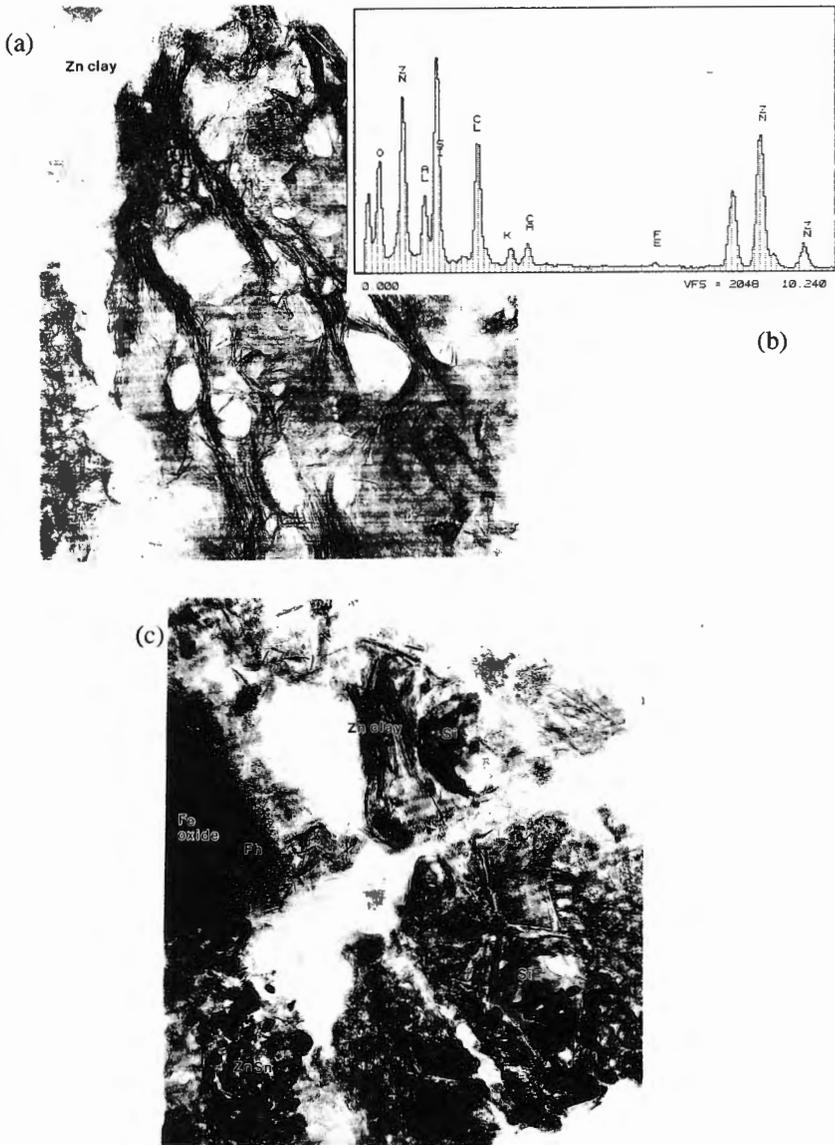
### *Characterisation of the pH/redox interface*

The white-grey coloured fly ash found at the pH/redox interface was further characterised by XRD and TEM. XRD-analysis of the bulk sample revealed the presence of relatively large amounts of Fe-(hydr)oxides (goethite, lepidocrosite, magnetite), whereas quartz, calcite, and feldspars were also found to be present. The white-coloured material was found to consist largely of poorly-crystallised aluminosilicates, and with major elements in decreasing abundance: Al, Si, S, Ca, Na, K, Fe, and Zn. Typically, zinc was found to be largely incorporated in these amorphous aluminosilicates. The neoformation of secondary Al-minerals is discussed in more detail below.

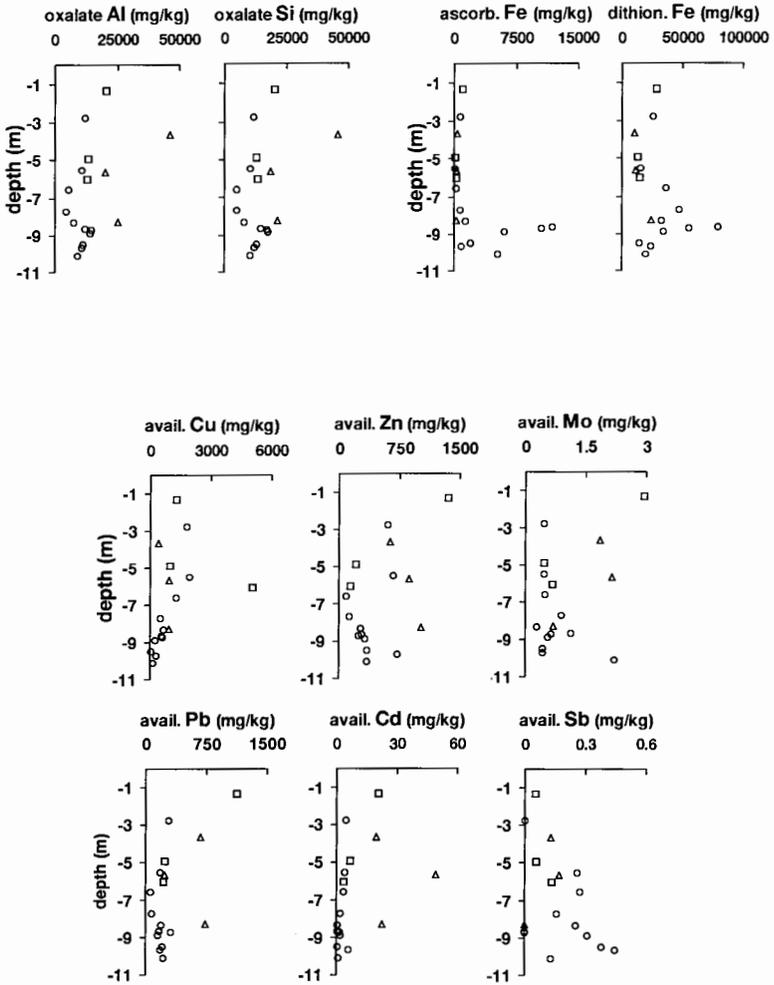
### *Characterisation of neoformed Fe, Al, and Si minerals*

Neoformed secondary Fe, Al, and Si minerals were investigated and characterised in more detail because of their potentially important role in the sorption of minor elements. Figure 8 shows a transmission electron micrograph of a typical field of view of bottom ash from the oxidised/carbonated layer. This TEM-image indicates that there is an extensive neoformation of secondary aluminium- and iron minerals (e.g. aluminosilicates, ferrihydrite, goethite). Most of the silicate grains, for example, were found to have secondary aluminosilicates on their surfaces. Figure 9 gives for various depths the concentrations of ascorbate-extractable Fe (representing amorphous Fe-(hydr)oxides), dithionite-extractable Fe (representing amorphous plus crystalline Fe-(hydr)oxides), and oxalate-extractable Al and Si (representing amorphous Al-(hydr)oxides and amorphous aluminosilicates).

Amorphous Fe-(hydr)oxides were found to be present in relatively low concentrations (1 g Fe/kg ash), except for the zone of alternating redox conditions at depths between 8.5 - 8.75 meters (12 g Fe/kg ash). Apparently, on ageing, amorphous Fe(OH)<sub>3</sub> was transformed into more stable, crystalline Fe-oxides. In terms of quantities, crystalline Fe-oxides are much more abundant than amorphous Fe-(hydr)oxides. The highest concentrations of crystalline Fe oxides (80 g Fe/kg ash) were also found in the zone of alternating redox conditions. The lowest concentrations (15 g Fe/kg ash) were found in samples of fly ash, which were depleted in Fe relative to the bottom ash.



**Figure 8.** (a) Transmission electron micrograph and (b) corresponding EDS analysis showing a typical amorphous (Zn-rich) aluminosilicate from the oxidised/carbonated sample. (c) Transmission electron micrograph showing a typical field of view of bottom ash from the oxidised/carbonated sample: ferrihydrite (Fh), amorphous (Zn-rich) aluminosilicates, Fe oxides (goethite), Zn/Sn-rich crystals (probably stannates), and silicate crystals (Si) heavily decorated with amorphous aluminosilicates.



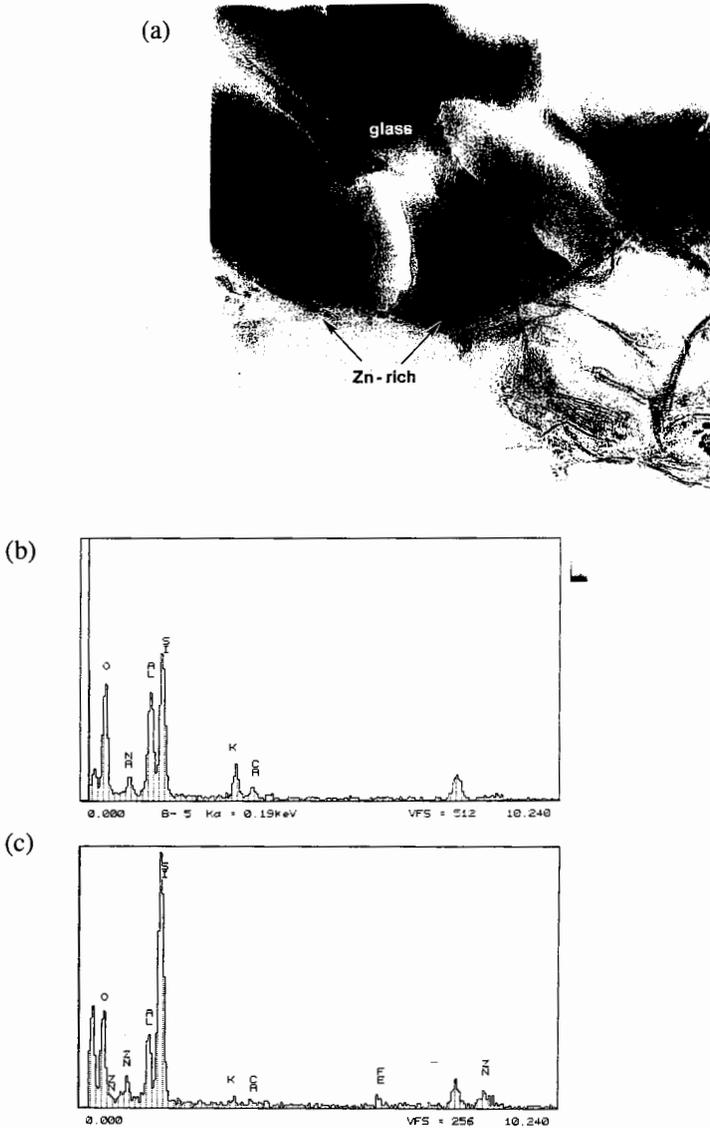
**Figure 9.** Depth profiles for oxalate-extractable Al and Si, ascorbate-extractable Fe, and dithionite-extractable Fe (upper graphs), and total concentrations of Cu, Pb, Zn, Cd, Mo, and Sb available for sorption (lower graphs). Concentrations are expressed in mg/kg ash. Symbols: ○ bottom ash, △ fly ash, □ mixed fly & bottom ash.

An XRD-analysis of secondary iron particles (in bulk ash samples and in iron concretions) indicated that goethite and lepidocrosite were the most abundant iron oxides.

The highest concentrations of amorphous Al-minerals (30 g Al/kg ash) were found in samples of fly ash, which are enriched in bulk Al relative to the bottom ash. In general, the observed variation in oxalate-extractable Al with depth correlates well with the bulk Al-content of the samples (Fig. 9, Fig. 7). The identity of the amorphous Al-minerals was investigated in more detail by TEM-analysis. In general, neoformed Al-minerals were found to consist largely of aluminosilicates, with a composition similar to the composition of smectites. However, basal spacings were not observed, indicating that the material was poorly crystallised. The composition of the neoformed aluminosilicates was generally similar for samples from the oxidised/carbonated layer, the redox interface, and the reduced/alkaline layer. The composition of the neoformed amorphous aluminosilicates did not seem to depend on the composition of the original silicate grains, which is consistent with previous work by ZEVENBERGEN *et al.* (1996). Figure 10 shows a typical example of an image of a glass sphere of a weathered fly ash particle from the upper part of the disposal: Si/Al-ratios increase from 1.3 (glass sphere) to 2.5-3 (rim). Since the Si/Al-ratio of the amorphous aluminosilicates (Si/Al-ratio 2.5-3) is much higher than the Si/Al-ratio obtained by oxalate extraction (Si/Al=1), an additional amount of aluminium is likely to be present as amorphous Al-(hydr)oxide.

#### *Phases enriched in minor elements*

In general, neoformed amorphous aluminosilicates were found to be significantly enriched in Zn. TEM analysis indicated that Zn-rich amorphous aluminosilicates are wide-spread in samples from the oxidised/carbonated layer, the redox interface, and the reduced/alkaline layer. Figure 8 and 10 show typical examples. One example of a Pb-rich amorphous aluminosilicate was found (not shown). In addition, an aluminosilicate enriched in both Cu and Zn was detected by SEM/EDS in one of the samples collected in the field on the basis of deviating colour/morphology (not shown). Formation of Zn-rich amorphous aluminosilicates has not been observed before in MSWI residues, but has



**Figure 10.** (a) Transmission electron micrograph showing an image of a glass sphere of a fly ash particle from the upper part of the disposal, which alteration rim is enriched in Zn; (b) EDS-spectrum of the glass sphere; (c) EDS-spectrum of the rim on the sphere.

*field investigation*

been observed in volcanic ashes (BAJWA, 1984). BAJWA (1984) has shown that the formation of smectite clays in soils of volcanic origin is strongly correlated with the severe Zn deficiencies observed in these soils. In general, the higher the crystallinity of the smectite-clays, the higher the observed Zn-deficiency in the soils (BAJWA, 1984).

In the water-saturated part of the disposal sulphide precipitates of Cu, Pb, and Zn were detected by TEM-analysis (not shown). In individual samples which were collected in the field on the basis of deviating colour and/or structure, we detected by SEM/EDS-analysis a Pb-carbonate, metallic Cu, cuprite ( $\text{Cu}_2\text{O}$ ), Cu-(hydroxyl)chloride, aluminosilicates enriched in Zn, and aluminosilicates enriched in both Cu and Zn.

## SUMMARY

Municipal Solid Waste Incinerator (MSWI) bottom ash is the major residue that remains after the incineration of Municipal Solid Waste. The slag-like material is produced world-wide in very large and ever-increasing quantities. In the past the bottom ash was usually disposed, nowadays it is increasingly being used as a construction material. Incineration concentrates the mineral components of the original waste, including elements of environmental concern such as heavy metals, oxyanions, and salts. To ensure an environmentally safe utilisation or disposal of MSWI bottom ash it is, therefore, necessary to investigate its leaching properties. It is in particular necessary to identify the mechanisms that control leaching, because only then reliable predictions of the *long-term* leaching can be made.

This thesis focuses on the geochemical processes that control the short-term and long-term leaching of major and minor elements from MSWI bottom ash. The research is based on (I) carefully controlled laboratory leaching experiments on MSWI bottom ash at different stages of weathering, (II) geochemical modelling of aqueous (in)organic complexation, precipitation/dissolution, and sorption processes, (III) specific experiments to obtain parameters for the modelling of sorption reactions and organic complexation reactions, (IV) spectroscopic analyses of bottom ash samples, and (V) a field investigation of a 20-year old disposal of MSWI residues.

Fresh MSWI bottom ash is alkaline and consists primarily of minerals that are not stable under atmospheric conditions. As a result of weathering the mineralogical characteristics of the bottom ash will change, which in turn will affect its leaching properties. **Chapter 2** describes the processes controlling the leaching of major elements from MSWI bottom ash at different stages of (natural) weathering. Major elements control the parameters that are also important in the leaching of minor elements: pH, availability of reactive mineral surfaces for sorption of minor elements, redox potential, and ionic strength. On the basis of bottom ash pH, three major stages in weathering have been identified:

## Summary

**Type A** Unweathered bottom ash, which is bottom ash that has not been in contact with water before (“unquenched bottom ash”). The pH is strongly alkaline (12.4), as controlled by equilibrium with portlandite ( $\text{Ca}(\text{OH})_2$ ). Initial alteration processes include hydrolysis reactions and dissolution/precipitation reactions involving (hydr)oxides and salts.

**Type B** Freshly quenched/non-carbonated bottom ash. The pH has decreased to 10-10.5 by simultaneous precipitation of ettringite ( $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$ ), gypsum ( $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ ), and gibbsite ( $\text{Al}(\text{OH})_3$ ). In water-saturated conditions, alkaline pH-values may be maintained for a long time. Due to continuing hydrolysis, secondary minerals such as amorphous Fe/Al(hydr)oxides and amorphous aluminosilicates begin to precipitate. The surfaces of these minerals in particular are very reactive in sorption processes.

**Type C** Carbonated bottom ash, which is neutralised to 8-8.5 by absorption of (atmospheric or biogenic)  $\text{CO}_2$  and subsequent precipitation of calcite. The neoformation of Fe/Al-(hydr)oxides and amorphous aluminosilicates continues.

The minor elements that are investigated in this thesis include heavy metals (Cd, Pb, Zn, Cu) and oxyanions (Mo), of which in particular Cu and Mo are of environmental concern in Dutch MSWI bottom ash. Processes controlling the leaching of minor elements from the above categories of bottom ash are discussed in **Chapter 3**. In relatively unweathered A- and B-type bottom ash, the general controlling processes appear to be precipitation/dissolution of relatively soluble minerals or, particular in the case of Cu, extensive complexation with dissolved organic carbon. An important result in this chapter is that the leaching of Cd, Pb, Cu, Zn, and Mo from 1.5 and 12-year old (C-type) bottom ash is generally significantly lower than from less weathered types of bottom ash. This reduction in leaching is due to (I) the neutralisation of bottom ash pH, which positively affects the aqueous speciation of heavy metals as well as the speciation of mineral surfaces with respect to oxyanion sorption, and (II) the formation of less soluble species of these elements.

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In the more weathered (C-type) bottom ash minor element leaching does not seem to be controlled by precipitation/dissolution processes; in those samples the controlling mechanism is probably sorption to neoformed minerals.

In **Chapter 4** the interaction of the initially alkaline bottom ash with CO<sub>2</sub> (carbonation) was investigated in more detail by simulating this process in the laboratory. Changes in pH and bottom ash mineralogy were investigated as well as the impact that these changes have on the mobility of Cu and Mo. During the carbonation experiments, a precipitate was formed that consisted mainly of Al-rich amorphous material, calcite, and possibly gibbsite (Al(OH)<sub>3</sub>). Carbonation to pH~8.3 resulted in a reduction of more than 50% in Cu-leaching, and a reduction of approximately 3% in Mo-leaching. The reduction in Cu leaching is attributed to sorption to the neoformed amorphous Al-minerals. On a time scale of months to years (natural weathering/carbonation), the leaching of Cu and Mo is further reduced by the formation of additional sorption sites.

The role of sorption processes in 1.5-year old (C-type) bottom ash was investigated in **Chapter 5**, using a surface complexation model for the sorption of ions on amorphous iron hydroxide. The concentration of sorbent minerals in the bottom ash as well as the available concentrations of metals and oxyanions were determined by specific measurements on the bottom ash. The leaching of Mo, Pb, and Cu from weathered MSWI bottom ash could successfully be described on the basis of the surface complexation model. For Zn, it was necessary to extend the surface complexation model with surface precipitation reactions. Furthermore, the data suggest that Mo and Zn are bound mainly to amorphous iron hydroxides, whereas additional sorbent minerals, probably amorphous Al-minerals, are required to describe the leaching of Cu and Pb.

In **Chapter 6** the role of organic complexation of Cu in leachates from fresh (B-type) and 1.5-year old (C-type) bottom ash was investigated. At least two different sites appear to be involved in the complexation of copper with DOC. Conditional stability constants are in the range found

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for natural waters, but site densities on bottom ash-DOC are much lower. The dissolved Cu appears to be 95-100% organically-bound in leachates from both the fresh and the weathered bottom ash, and geochemical modelling indicates that the leaching of Cu from these ashes is primarily controlled by the availability of the organic ligands in the bottom ash. The mechanism that binds Cu to the solid phase is likely to be solubility-control by a Cu-oxide mineral in the fresh bottom ash, and sorption to amorphous Fe/Al-(hydr)oxides in the 1.5-year old bottom ash.

In **Chapter 7** it was investigated whether the geochemical processes/techniques described in the preceding chapters can be applied to describe the partitioning of major and minor elements between the solid phase and pore water in a 20-year old disposal of MSWI residues. Thereto, samples of solid and pore water were taken at various depth from the disposal. The lower, water-saturated part of the disposal was alkaline and reducing, the upper unsaturated 8.3 meters was carbonated and oxidising. The dissolved Cu, and possibly the dissolved Pb, was found to be largely organically-bound. The observed minor element concentrations in the pore waters were generally consistent with concentrations predicted on the basis of solid/liquid partitioning by sorption to Fe/Al-(hydr)oxides: towards alkaline pH (increasing depth) the pore water concentrations of Mo and Sb generally increased, whereas pore water concentrations of Cd, Pb, Zn, and Cu generally decreased. Both amorphous Al-minerals and crystalline Fe-oxides were found to be present in quantities that are potentially large enough to explain the observed pore water concentrations of Zn, Cu, Pb, Cd, Mo, and Sb by surface complexation processes. The potential importance of the amorphous Al-minerals in the retention of minor elements was confirmed by electron microscopic observations of neofomed amorphous aluminosilicates which were significantly enriched in Zn.

The results in this thesis imply that the leaching of salts, heavy metals, and oxyanions from MSWI bottom ash is likely to be greatest in the earliest stages of disposal/utilisation: the most soluble phases dissolve rapidly, while the capacity of secondary minerals to bind heavy metals and oxyanions may not be large enough. In addition, the presence of

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dissolved organic carbon may significantly enhance the leaching of Cu in particular. On the long term, the leaching of both heavy metals and oxyanions from well-burned bottom ash is likely to be reduced in a natural way by the neutralisation of bottom ash pH and by sorption to neoformed minerals. However, in an alkaline (water-saturated) environment the mobility of oxyanions (Mo, Sb) will remain high. Complexation with dissolved organic carbon may remain significant over time-scales of > 20 years.

## SAMENVATTING

Huishoudelijk afval wordt in toenemende mate verbrand in Afval Verbrandings Installaties. Wat na verbranding op het rooster achterblijft is een slakachtige reststof die AVI-bodemas genoemd wordt. Wereldwijd worden steeds grotere hoeveelheden AVI-bodemas geproduceerd. In het verleden werd de bodemas voornamelijk gestort, tegenwoordig wordt het materiaal in toenemende mate gebruikt als constructie materiaal. Na verbranding blijven de anorganische componenten, inclusief de zware metalen, oxyanionen en zouten, in geconcentreerde vorm achter. Om er zeker van te zijn dat de zware metalen en oxyanionen het milieu niet zullen gaan belasten door uitspoeling (uitloging), is onderzoek nodig naar de mechanismen die uitloging controleren.

Dit proefschrift gaat over de geochemische processen (mechanismen) die de uitloging controleren van hoofd en sporenelementen uit AVI-bodemas op zowel de korte als de lange termijn. Het onderzoek is gebaseerd op (I) gecontroleerde uitloogexperimenten met AVI-bodemas in verschillende stadia van veroudering, (II) geochemische modellering van (an)organische complexatie reacties in de water fase, van oplos/precipitatie reacties, en van de binding (sorptie) van elementen aan reactieve minerale oppervlakken, (III) specifieke experimenten om parameters te verkrijgen voor de modellering van organische complexatie en sorptie reacties, (IV) spectroscopische analyses van bodemas monsters, en (V) onderzoek van een 20-jaar oude stort van AVI-residuen.

Verse AVI-bodemas heeft een basische pH en bestaat hoofdzakelijk uit mineralen die niet stabiel zijn onder atmosferische condities. Door verwerking zal de mineralogische samenstelling van de bodemas veranderen, en daardoor ook de uitloog eigenschappen van het materiaal. **Hoofdstuk 2** gaat in op de processen die de uitloging van hoofdelementen controleren uit AVI-bodemas in verschillende stadia van veroudering. Hoofdelementen controleren de parameters die ook belangrijk zijn voor de uitloging van sporenelementen: pH, beschikbaarheid van reactieve minerale oppervlakken waaraan

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sporenelementen zich kunnen binden, redox potentiaal, en ionsterkte. Op basis van pH kunnen bodemmassen in drie categorieën ingedeeld worden:

**Type A** Onverweerde bodemas. Deze categorie bestaat uit bodemas die nog niet eerder in contact met water is geweest ('ongequenchte bodemas'). De pH is sterk basisch (12.4) en wordt gecontroleerd door het mineraal portlandiet ( $\text{Ca}(\text{OH})_2$ ). Initiele reacties bij contact met water zijn o.a. hydrolyse reacties en oplos/precipitatie reacties van (hydr)oxides en zouten.

**Type B** Vers gequenchte/niet-gecarbonateerde bodemas. De pH van dit type bodemas is afgenomen tot 10-10.5 door gelijktijdige precipitatie van ettringiet ( $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$ ), gips ( $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ ), en gibbsiet ( $\text{Al}(\text{OH})_3$ ). Onder water-verzadigde condities kan de pH voor langere tijd basisch blijven. Verdere hydrolyse reacties leiden tot nieuwvorming van amorfe Fe/Al(hydr)oxides en amorfe aluminiumsilicaten. De oppervlakken van met name deze mineralen zijn zeer reactief in sorptie processen.

**Type C** Gecarbonateerde bodemas. De pH van gecarbonateerde bodemas is geneutraliseerd tot 8-8.5 door de absorptie van  $\text{CO}_2$  (van atmosferische of biologische oorsprong) en de daaropvolgende precipitatie van calciet. Nieuwvorming van Fe/Al-(hydr)oxiden en amorfe aluminiumsilicaten gaat door.

De sporenelementen die in dit proefschrift aan bod komen zijn zware metalen (Cd, Pb, Zn, Cu) en oxyanionen (Mo), waarvan vooral de uitloging van Cu en Mo uit verse bodemas regelmatig de normen van de Nederlandse regelgeving overschrijdt. **Hoofdstuk 3** beschrijft de processen die de uitloging van sporenelementen controleren uit bodemas van de verschillende stadia van veroudering. In relatief onverweerde type-A en -B bodemmassen lijken de processen die uitloging controleren vooral te bestaan uit het oplossen/precipiteren van relatief oplosbare mineralen of, in het geval van met name Cu, sterke complexatie met opgelost organisch materiaal. Een belangrijk resultaat in dit hoofdstuk is dat de uitloging van Cd, Pb, Cu, Zn, en Mo uit 1.5 en 12-jaar oude (type-

C) bodemas in het algemeen significant lager is dan uit minder verweerde type-A en -B bodemmassen. Deze lagere uitloging is te verklaren door (I) de neutralisatie van de bodemas pH, hetgeen positieve effecten heeft op de speciatie van metalen in oplossing en op de speciatie van minerale oppervlakken met betrekking tot de sorptie van oxyanionen, en (II) de vorming van minder oplosbare verbindingen van deze elementen. In de meer verweerde type-C bodemas lijkt de uitloging van sporenelementen niet gecontroleerd te worden door oplos/precipitatie reacties, maar waarschijnlijk door binding aan nieuwgevormde minerale oppervlakken.

In **Hoofdstuk 4** wordt in meer detail de interactie van de initieel basische bodemas met CO<sub>2</sub> (carbonatatie) onderzocht door dit proces te simuleren in het laboratorium. Onderzocht worden veranderingen in pH en bodemas mineralogie en de effecten die deze veranderingen hebben op de mobiliteit van Cu en Mo. Tijdens de carbonatatie experimenten werd een precipitaat gevormd van voornamelijk Al-rijk amorf materiaal, calciet, en mogelijk gibbsiet (Al(OH)<sub>3</sub>). Na carbonatatie was de pH ~8.3, was de uitloging van Cu met meer dan 50% afgenomen en de uitloging van Mo met ca. 3%. De lagere Cu-uitloging wordt verklaard door de sorptie van Cu aan de vers geprecipiteerde amorfe Al-mineralen. Op een tijdschaal van maanden tot jaren (natuurlijke verwerking/carbonatatie) neemt de uitloging van Cu en Mo nog verder af door continue nieuwvorming van reactieve minerale oppervlakken.

De rol van sorptie processen in 1.5-jaar oude (type-C) bodemas wordt verder onderzocht in **Hoofdstuk 5** door gebruik te maken van een bestaand oppervlakte complexatie model voor de sorptie van ionen aan amorf ijzer hydroxide. Parameters zoals de concentratie van bindingsplaatsen en beschikbare concentraties van de sporenelementen in de bodemas werden apart gemeten. De uitloging van Mo, Pb en Cu uit type-C bodemas kon succesvol worden beschreven op basis van dit oppervlakte complexatie model. Voor Zn was het nodig het oppervlakte complexatie model uit te breiden met een oppervlakte precipitatie model. De resultaten van het onderzoek laten verder zien dat Mo en Zn voornamelijk aan amorf ijzer hydroxide binden, en dat additionele

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reactieve mineralen nodig zijn, waarschijnlijk amorfe Al-mineralen, om de uitloging van Cu en Pb goed te kunnen beschrijven.

In **Hoofdstuk 6** wordt voor koper de rol van organische complexatie onderzocht in uitloogoplossingen van verse (type-B) en 1.5-jaar oude (type-C) bodemas. Ten minste twee typen organische liganden blijken een rol te spelen in de organische complexatie van Cu. De gemeten conditionele stabiliteitsconstanten komen overeen met die van natuurlijk organisch materiaal, maar de hoeveelheid bindingsplaatsen op het organisch materiaal van de bodemas is lager. Het opgeloste Cu in uitloogoplossingen van verse en verweerde bodemas blijkt voor 95-100% organisch gebonden, en geochemische modellering laat zien dat de uitloging van Cu uit deze bodemassen voornamelijk gecontroleerd wordt door de beschikbaarheid van de organische liganden in de bodemas. Het mechanisme dat Cu aan de vaste fase bindt is waarschijnlijk oplosbaarheidscontrole door een Cu-oxide mineraal in de verse bodemas, en sorptie aan amorfe Fe/Al-(hydr)oxiden in de 1.5-jaar oude bodemas.

In **Hoofdstuk 7** wordt onderzocht in hoeverre de geochemische inzichten/technieken uit de voorgaande hoofdstukken toegepast kunnen worden in een praktijk situatie. Het gaat hierbij met name om het begrijpen/modelleren van de wijze waarop hoofd- en sporenelementen zich verdelen tussen vaste stof en poriënwater. Voor dit doel werden monsters genomen van vaste stof en poriënwater op verschillende diepten in een 20-jaar oude stort van AVI-residuen. De diepere, water verzadigde delen van de stort waren basisch en reducerend. De bovenste onverzadigde 8.3 meter van de stort waren gecarbonateerd en geoxideerd. Het opgeloste Cu, en mogelijk ook het opgeloste Pb, bleek grotendeels gebonden aan opgelost organisch materiaal. De gemeten concentraties sporenelementen in het poriënwater kwamen over het algemeen overeen met voorspelde concentraties op basis van sorptie aan Fe/Al-(hydr)oxides: met toenemende pH (toenemende diepte) over het algemeen een toename in de poriënwater concentraties van Mo en Sb en een afname in de concentraties van Cd, Pb, Zn en Cu. Zowel amorfe Al-mineralen als crystallijne ijzer oxides bleken in voldoende mate aanwezig om de waargenomen poriënwater concentraties van Zn, Cu, Pb, Cd, Mo

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en Sb te verklaren op basis van oppervlakte complexatie processen. De potentieel belangrijke rol van amorfe Al-mineralen in de retentie van sporenelementen in bodemas wordt bevestigd door electronen microscopische waarnemingen van amorfe Zn-rijke aluminiumsilicaten.

De resultaten in dit proefschrift impliceren dat de initiële uitloging van zouten, zware metalen en oxyanionen uit een stort/toepassing van AVI-bodemas waarschijnlijk het hoogst is: de meest instabiele fasen lossen op, terwijl de capaciteit van de bodemas om zware metalen en oxyanionen te binden nog onvoldoende is. Daarnaast kan de aanwezigheid van opgeloste organische stof de uitloging van met name Cu sterk doen toenemen. Op de lange termijn is het waarschijnlijk dat de uitloging van zowel zware metalen als oxyanionen uit goed uitgebrande bodemas op natuurlijke wijze zal afnemen door de neutralisatie van de pH en door sorptie aan nieuwgevormde mineralen. In een basische (waterverzadigde) omgeving echter, blijven oxyanionen (zoals Mo, Sb) mobiel. Organische complexatie kan ook na 20 jaar nog een rol van betekenis spelen in de mobilisatie van met name Cu.

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## CURRICULUM VITAE

- 29 aug. 1968      Geboren in Wezep
- Juni 1986          diploma VWO  
(Johannes Calvijn Lyceum in Kampen)
- Juni 1990          diploma Hoger Laboratorium Onderwijs,  
studierichting algemene/analytische chemie  
(Rijkshogeschool IJsselland in Deventer)
- Juni 1991          propadeuse Geologie  
(Vrije Universiteit van Amsterdam)
- Aug. 1993          doctoraal diploma Geochemie, specialisatie  
milieugeochemie  
(Rijksuniversiteit Utrecht)
- 1993-1997          Promovenda bij de groep Milieu Analyse van de unit  
Brandstofcellen, Conversie en Milieu van het  
Energieonderzoek Centrum Nederland (ECN) in  
Petten.

