

## OVERVIEW OF GEOCHEMICAL PROCESSES CONTROLLING LEACHING CHARACTERISTICS OF MSWI BOTTOM ASH

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### ABSTRACT

In the past few years important progress has been made in understanding the geochemical processes that control leaching of various elements from MSWI bottom ash. An overview of that progress is presented here. Bottom ash leaching has been observed to depend strongly on the ageing/weathering of the solid material. Three major stages in weathering have been 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  $-\text{SO}_4$ . In the first two stages, which are characterised by relatively unweathered bottom ash of  $\text{pH} > 12$  or  $\text{pH} 10\text{-}10.5$  respectively, the general processes are thought to be precipitation/dissolution of relatively soluble minerals. In the third stage, the leaching of several elements has decreased, including the potential contaminants Cd, Pb, Cu, Zn, and Mo. This reduction in leaching is due to (a) the neutralisation of bottom ash pH, (b) sorption processes or formation of more stable mineral species, and (c) reduced leaching of dissolved organic carbon (DOC). The latter process is important for Cu in particular, since  $>90\%$  of the dissolved copper may be associated with DOC. It will be discussed how the obtained knowledge of these geochemical processes can be applied to make reliable predictions of the long-term behaviour of bottom ash in the environment.

### 1. INTRODUCTION

Combustion residues, such as Municipal Solid Waste Incinerator (MSWI) bottom ash and alkaline coal fly ash, are produced world-wide in ever-increasing quantities. Combustion residues, however, may pollute the environment because they are enriched in potentially toxic elements relative to soils and sediments [1,2]. For a proper assessment of the environmental impact of the utilisation and disposal of these ashes it is, therefore, necessary to understand both the short-term and the long-term processes that affect the mobilization of potentially hazardous elements from ash residues. Recently, considerable progress has been made in understanding the behaviour of alkaline (waste) materials in the environment. By considering waste materials as mineral assemblages, similar to rocks and soils, it has been shown (a) that upon weathering the high-temperature solids that form during combustion will transform into naturally occurring secondary minerals [e.g. 3-8], (b) that element leaching can be modelled/predicted by common geochemical processes such as dissolution/precipitation, sorption, redox, and complexation processes [e.g. 1,3,7,9-21], and (c) that element leaching depends strongly on the ageing/weathering of the solid material [5,7,8,19].

This paper gives an overview of geochemical processes that control element leaching from MSWI bottom ash at different stages of weathering. Although we focus on MSWI bottom ash only, the geochemical processes discussed here will contribute to a more general understanding of the behaviour of combustion residues or alkaline (waste) materials in the environment.

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## 2. MSWI BOTTOM ASH

Incineration is a viable management strategy for treating combustible municipal solid waste that cannot be recycled. The waste volume is strongly reduced while exothermic energy is recovered. Incinerators usually operate at temperatures averaging from 850-1000°C, depending on furnace-design and on the caloric value of the waste [22]. 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, 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.

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 [2]. Table 1 gives the order of various element concentrations found in MSWI bottom ash world wide [18].

MSWI bottom ash is a highly reactive material because it consists predominantly (>70%) of X-ray amorphous, glassy constituents [2,14,23] and because it has a relatively high surface area due to internal porosity [11,18,22]. 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 [14,24]:

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

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**Table 1**  
**Element concentrations generally found in MSWI bottom ash world-wide\***

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

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\* data from Ref 18

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

Element	unweathered (A-type) bottom ash, pH<12 controlling mechanism identified species	quenched/non-carbonated (B-type) bottom ash, pH10-10.5 controlling mechanism identified species	carbonated (C-type) bottom ash, pH8-8.5 controlling mechanism identified species
Ca, SO <sub>4</sub> , CO <sub>3</sub>	solubility-control by portlandite <sup>7</sup> and gypsum <sup>7</sup> anhydrite <sup>7,27</sup> , calcite <sup>7,27</sup> , portlandite <sup>7</sup> , complex-(Ca)silicate <sup>27</sup>	solubility-control by ettringite <sup>5,7,25</sup> and gypsum <sup>5,7,11,12,13,25</sup> ; anhydrite <sup>14</sup> ; solubility-control by calcite <sup>11</sup>	solubility-control by calcite <sup>7</sup> and gypsum <sup>7</sup> anhydrite <sup>7</sup> , gypsum <sup>5</sup> , calcite <sup>5,7,8</sup>
Al	solubility-control by hydrous Al-silicate <sup>7</sup> complex-silicates <sup>27</sup>	solubility-control by gibbsite <sup>7,8,12,14,25</sup> or amorphous Al(OH) <sub>3</sub> <sup>7,8,13</sup>	solubility-control by gibbsite <sup>7</sup> or amorphous Al(OH) <sub>3</sub> <sup>8</sup> amorphous Al(OH) <sub>3</sub> <sup>8</sup>
Fe	magnetite <sup>7,27</sup> , hematite <sup>7</sup> , pseudobrookite <sup>27</sup>	solubility-control by ferrihydrite <sup>7,12-14</sup>	solubility-control by ferrihydrite <sup>7</sup> magnetite <sup>5,7</sup> , hematite <sup>5,7</sup> , wustite <sup>19</sup> , maghemite <sup>19</sup> , iron oxide <sup>19</sup>
Mg	solubility-control by brucite <sup>7</sup> complex-silicates <sup>27</sup>	solubility-control by brucite <sup>7,12,26</sup> or magnesite <sup>14</sup>	solubility-control by Mg-calcite <sup>7</sup> , sepiolite <sup>7</sup> , or dolomite <sup>7</sup> magnesite <sup>14</sup> , dolomite <sup>14</sup> , MgSO <sub>4</sub> ·2H <sub>2</sub> O <sup>14</sup> , sepiolite <sup>7</sup> , complex-silicates <sup>27</sup> , MgAl <sub>2</sub> O <sub>4</sub> <sup>14</sup>
Si	solubility-control by hydrous Al-silicate <sup>7</sup> quartz <sup>7,27</sup> , glasses <sup>27</sup> , complex-silicates <sup>7,27</sup>	solubility-control by wairakite <sup>12</sup> or amorphous SiO <sub>2</sub> <sup>7</sup>	solubility-control by illite <sup>7</sup> or amorphous SiO <sub>2</sub> <sup>7</sup> hydrous Al-silicate <sup>5,6,23</sup> , quartz <sup>27</sup> , illite <sup>5</sup> , complex-silicate <sup>5,7</sup>
Na, K, Cl	complex-(Na/K)silicates <sup>27</sup>	complex-(Na/K)silicates <sup>27</sup>	halite <sup>2</sup> , sylvite <sup>2</sup> , complex-(Na/K)silicates <sup>14,27</sup>
Mo	solubility-control by powellite <sup>19</sup>	solubility-control by powellite <sup>12,19,28</sup>	CaMoO <sub>4</sub> <sup>19</sup> sorption to ferrihydrite <sup>19,20</sup> CaMoO <sub>4</sub> <sup>29</sup> , Pb/Mo-rich particle <sup>29</sup>
Cu	metallic/alloy <sup>19</sup>	organic complexation <sup>12,19,21,28</sup> and solubility-control by tenorite <sup>12,19,21,28</sup> or Cu(OH) <sub>2</sub> <sup>14</sup>	metallic/alloy <sup>14,19,27</sup> , CuCl <sup>14</sup> , NaCuPO <sub>4</sub> <sup>14</sup> , complex-silicate <sup>14</sup> organic complexation <sup>21</sup> and sorption to amorphous Al(OH) <sub>3</sub> <sup>6,20,21</sup> Cu/O-phases (e.g. cuprite, tenorite) <sup>19</sup> , metallic/alloy <sup>19</sup> , complex-silicate <sup>19</sup> , Cu/Ca/O-, Cu/Fe/O-, Cu/Al/O-, Cu/Al/O/Si/Ca-, Cu/S-phases <sup>19</sup> , sorbed to neoformed clays <sup>29</sup>
Pb	metallic/alloy <sup>19</sup>	solubility-control by cerussite <sup>11,19,28</sup> or Pb(OH) <sub>2</sub> <sup>11,12</sup> or sorption-control <sup>28</sup>	complex-silicate <sup>13,14,16</sup> , PbO <sup>14</sup> sorption-control <sup>19,20</sup> or solubility-control by chloropyromorphite <sup>19</sup> metallic/alloy <sup>19</sup> , complex-silicate <sup>19</sup> , Pb/O-, Pb/Ca/O-, Pb/Fe/O-, and Pb/Al/O phases <sup>19</sup> , sorbed to neoformed clays <sup>29</sup>
Zn	solubility-control by zincite <sup>19</sup> metallic/alloy <sup>19</sup>	solubility-control by zincite <sup>12,19</sup> , Zn(OH) <sub>2</sub> <sup>11</sup> , or ZnSiO <sub>3</sub> <sup>11,12,14</sup> ; sorption-control <sup>19</sup>	zincite <sup>14</sup> , ZnSO <sub>4</sub> <sup>14</sup> , ZnCl <sub>2</sub> <sup>14</sup> , elemental Zn <sup>14</sup> , franklinite <sup>14</sup> sorption-control <sup>20</sup> or solubility-control by zincite <sup>19</sup> Zn/O-phases (e.g. zincite) <sup>19</sup> , metallic/alloy <sup>19</sup> , complex-silicate <sup>19</sup> , Zn/Ca/O-, Zn/Fe/O-, Zn/Al/O-, Zn/Al/O/S-phases <sup>19</sup> , sorbed to neoformed clays <sup>29</sup>
Cd	solubility-control by otavite <sup>19</sup> or Cd(OH) <sub>2</sub> <sup>19</sup>	solubility-control by otavite <sup>12,14,16,19,28</sup> or sorption to calcite <sup>12,16</sup>	sorption-control <sup>19,20</sup>
other		possible solubility-controlling minerals for Mn, Ba, and V: MnO(OH) <sup>18</sup> ; barite <sup>14</sup> ; Pb <sub>2</sub> V <sub>2</sub> O <sub>7</sub> <sup>14</sup>	rutile <sup>2,14</sup> , barite <sup>14,19</sup> , graphitic carbon <sup>14</sup> , taenite <sup>14</sup> , (species containing Sb, Sr, Ni, Cr, As, Ag, Rb, Nd <sup>14</sup> , Cr-oxides <sup>27</sup> ) Ni sorbed to neoformed clays <sup>29</sup>

**Mineral formulas:**

anhydrite, CaSO<sub>4</sub>; barite, BaSO<sub>4</sub>; brucite, Mg(OH)<sub>2</sub>; calcite, CaCO<sub>3</sub>; cerussite, PbCO<sub>3</sub>; chloropyromorphite, Pb<sub>3</sub>(PO<sub>4</sub>)<sub>3</sub>Cl; chromite, FeCr<sub>2</sub>O<sub>4</sub>; corundum, Al<sub>2</sub>O<sub>3</sub>; cuprite, Cu<sub>2</sub>O; dolomite, CaMg(CO<sub>3</sub>)<sub>2</sub>; 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; ferrihydrite, Fe(OH)<sub>3</sub>; franklinite, ZnFe<sub>2</sub>O<sub>4</sub>; gibbsite, Al(OH)<sub>3</sub>; goethite, FeOOH; gypsum, CaSO<sub>4</sub>·2H<sub>2</sub>O; halite, NaCl; hematite, Fe<sub>2</sub>O<sub>3</sub>; hercynite, FeAl<sub>2</sub>O<sub>4</sub>; illite, K<sub>0.8</sub>Mg<sub>0.25</sub>Al<sub>2.5</sub>Si<sub>3.5</sub>O<sub>10</sub>(OH)<sub>2</sub>; iron oxide, Fe<sub>2</sub>O<sub>3</sub>; jacobsonite, MnFe<sub>2</sub>O<sub>4</sub>; maghemite, Fe<sub>2</sub>O<sub>3</sub>; magnesite, MgCO<sub>3</sub>; magnetite, Fe<sub>3</sub>O<sub>4</sub>; otavite, CdCO<sub>3</sub>; portlandite, Ca(OH)<sub>2</sub>; powellite, CaMoO<sub>4</sub>; pseudobrookite, Fe<sub>2</sub>TiO<sub>5</sub>; pyrite, FeS<sub>2</sub>; quartz, SiO<sub>2</sub>; rutile, TiO<sub>2</sub>; sepiolite, Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>·1.5H<sub>2</sub>O; sylvite, KCl; taenite, Fe<sub>3</sub>Ni; tenorite, CuO; ulvospinel, Fe<sub>2</sub>TiO<sub>5</sub>; wairakite, CaAl<sub>2</sub>Si<sub>4</sub>O<sub>12</sub>·2H<sub>2</sub>O; whitlockite, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>; wustite, FeO; zincite, ZnO.

The sequence of reactions during incineration has been compared to a melt of melilite-bearing igneous rock which can be described by a  $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-Na}_2\text{O-FeO}$  system [14]. 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, ref. 14,24). A detailed overview of minerals and species identified in MSWI bottom ash is given in Table 2.

Potentially hazardous elements in MSWI bottom ash include heavy metals (e.g. copper), oxyanions (e.g. molybdenum and antimony), and soluble salts (e.g. sulphate and chloride) (see Table 1).

### 3. WEATHERING

As shown above, MSWI bottom ash consists primarily of metastable solids. Upon weathering these solids transform into naturally occurring secondary minerals. Weathering has been shown to strongly affect the leaching of major and trace elements from MSWI bottom ash [5,7,8,19]. In general, weathering reactions in MSWI bottom ash have been shown to be similar to those observed in alkaline soils and volcanic ashes [4,5] and basalts [4].

Three major stages in weathering have been identified, each stage having a characteristic pH that is controlled largely by Ca minerals and  $\text{pCO}_2$  [7]. Figure 1 illustrates the changes Ca-leaching as weathering continues. Important characteristics of the three weathering stages are discussed below.

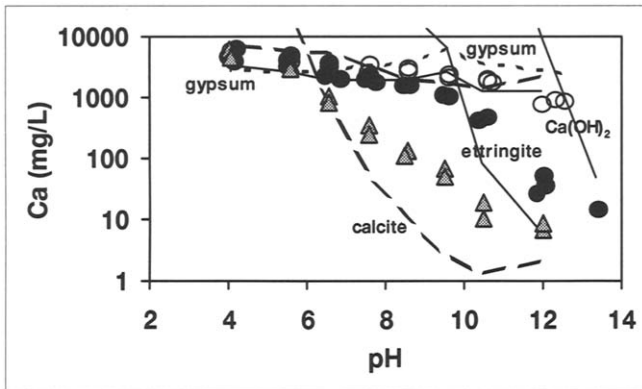


Figure 1. Total dissolved Ca in type A (○), type B (●), and type C (▲) bottom ash leachates at  $L/S=5$  as a function of pH, and MINTQA2 predictions assuming equilibrium with different mineral phases. The style of the lines indicates the category of bottom ash on which the modelling was performed: ----- A-type; ——— B-type; - - - C-type bottom ash. (Modified after Ref. 7.)

**(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 [7,25,30]. The resulting bottom ash pH is strongly alkaline (12.4) and controlled by the solubility of portlandite ( $\text{Ca(OH)}_2$ ) [7].

**(B) quenched/non-carbonated bottom ash, with pH 10-10.5**

In stage B bottom ash pH has been decreased to 10-10.5 by the formation of ettringite ( $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$ ), gibbsite ( $\text{Al(OH)}_3$ ), and gypsum ( $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ ) [7,25]. When the three minerals coexist, no degrees of freedom are left and pH is fixed at pH 10 [7,25]. Due to continuing hydrolysis secondary minerals such as amorphous Fe/Al-(hydr)oxides, hydrous aluminosilicates, and possibly zeolites begin to precipitate [4,5,7]. Soluble salts will be leached rapidly with percolating water [e.g. 4,5,7,11,30]. Biodegradation of residual organic matter and dissolution of reduced mineral phases may create a reducing environment [5,18].

**(C) carbonated bottom ash, with pH 8-8.5**

In stage C bottom ash pH has further decreased to equilibrium values of 8-8.5 by absorption of  $\text{CO}_2$  and subsequent precipitation of calcite ( $\text{CaCO}_3$ ) [e.g. 5,7,8]. The  $\text{CO}_2$  required for this carbonation may infiltrate from the atmosphere or come from biodegradation of organic residues [5,26,30]. The neof ormation 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 [6]. The 2:1 clay mineral illite seems to be the final product of glass weathering in MSWI bottom ash [6].

Weathering has been shown to have a significant effect on the leaching of trace elements from MSWI bottom ash [8,19]. 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 [8,19]. A potentially important mechanism is the sorption of trace elements to neof ormed (amorphous) Fe/Al-minerals [8,19,20,29]. Furthermore, the neutralisation of bottom ash pH from >10 to 8-8.5 and the formation of less soluble secondary minerals of trace-elements also contribute to reduce leaching [19]. Lower trace-element leaching from weathered bottom ash does not seem to be caused primarily by a prior release of these elements from the residues during storage [19,31].

#### 4. 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 [13]. Kirby and Rimstidt [13] have identified 3 basic types of solution behaviour during batch leaching of MSWI bottom ash:

1. availability, which 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 [5,7,13,18]. Furthermore, molybdenum may show this type of behaviour at strongly alkaline pH [7,18]. In general, the higher the Liquid to Solid (L/S) ratio, the more elements will show this type of behaviour.

2. kinetic, which 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 [5,8,13]. The leaching of silicon, for example, is strongly influenced by slow dissolution/precipitation kinetics of silicate-minerals [5,8,13]. 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 [7,19]. Little is 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 [18,32].
3. equilibrium, which 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 complex formation, dissolution/precipitation, sorption and redox reactions, which control element leaching from MSWI bottom ash.

## 5. 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 [33]. Figure 2 illustrates the effect of hydrolysis on the solubility of Zn. As a result, pH is a dominant controlling parameter in element leaching from (waste) materials, which is in correspondence with experimental data [e.g. 7,12,16,19,30,34,35]. Other potentially important inorganic complexes include Cd-Cl complexes, which may become significant in leachates from fresh bottom ash [16].

MSWI bottom ash releases substantial amounts of dissolved organic carbon (DOC) originating from incomplete burning of the original waste and/or subsequent biodegradation processes [7]. Copper, which is known to have a very high affinity for organic material [36], has been shown to be bound for >90% to DOC in leachates of both fresh and 1.5-year old MSWI bottom ash [21]. The conditional stability constants of these Cu-DOC complexes have been determined using a competitive ligand exchange / solvent extraction technique [21]. Figure 3 illustrates the importance of this organic complexation on the leaching of Cu from fresh MSWI bottom ash, and shows that Cu-leaching under environmental conditions ( $\text{pH} > 7$ ) is dominated by this process.

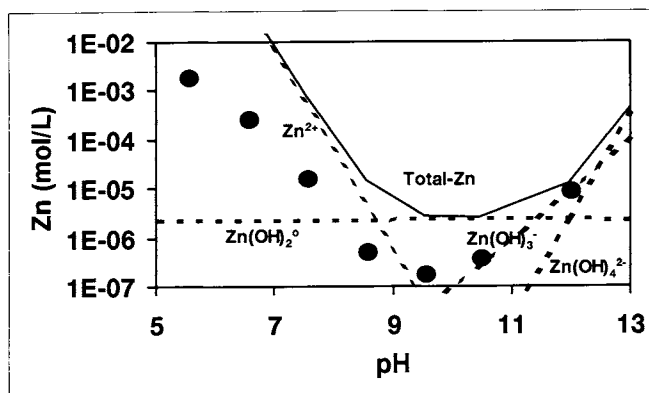


Figure 2. The effect of inorganic complexation on the solubility of zinc. The solid line represents the predicted total concentration of zinc in equilibrium with the mineral zincite ( $\text{ZnO}$ ). Dashed lines represent concentrations of corresponding Zn-species. Symbols represent total dissolved Zn in type B bottom ash leachates at  $L/S=5$ . Data were taken from Ref. 19.

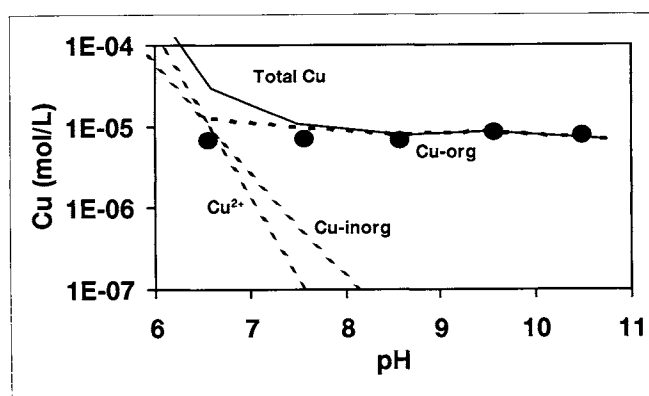


Figure 3. The effect of organic complexation on the leaching of Cu (●) from fresh MSWI bottom ash at  $L/S=5$ . The solid line represents the predicted total concentration of Cu in equilibrium with the mineral tenorite ( $\text{CuO}$ ). Dashed lines represent corresponding concentrations of  $\text{Cu}^{2+}$ , the sum of the inorganic Cu-complexes, and the sum of the organic Cu-complexes. (Modified after Ref. 21.)

### 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, Figure 1). In the case of major elements, solubility-controlling minerals indicated by geochemical modelling generally correspond to minerals detected by spectroscopic analysis of the bottom ash (Table 2). Precipitation/dissolution processes may also control the leaching of trace elements from A- and B-type bottom ash. Proposed controlling processes for trace-element leaching, however, are often indicated by geochemical modelling only (Table 2) because low bulk concentrations hamper the detection of trace-element species by means of spectroscopic techniques [2,19]. A

step-wise approach for the geochemical modelling of element-concentrations in equilibrium with potential solubility-controlling minerals is given in Meima and Comans [7].

### **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 [8,20].

Recent studies have shown that surface complexation reactions can successfully describe the leaching of trace-elements from combustion residues, such as MSWI bottom ash and coal fly ash [9,20,37-39]. In addition, trace-elements have been found to be associated with secondary and potential sorbent minerals in weathered MSWI bottom ash (Table 2).

A step-wise approach for the modelling of surface complexation or surface precipitation processes in heterogeneous systems such as MSWI bottom ash is described by Meima and Comans [20]. 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 [40], (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 trace-element concentrations.

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

### **redox processes**

In fresh MSWI bottom ash the prevailing redox conditions are oxidizing [7,11]. During disposal or utilization 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 [5,18]. Relatively low redox potentials were recorded, for example, in percolate from landfilled combined MSWI bottom and fly ash [41] and in a 6-week old storage of fresh MSWI bottom ash [7]. 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 [18,35,42,43], Cr [18,43], As [43], and V [43], for example, has been shown to increase toward more oxidizing conditions, whereas the leaching of Fe was decreased [7,35,43].
- changing the amount of redox sensitive metal surfaces (Fe/Mn-(hydr)oxides) available for sorption [35].
- changing the degree of (co)-precipitation or complexation with other redox sensitive cations and anions, e.g. the precipitation of heavy-metal sulphides [18,35,41,43].

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

The leaching of major and trace elements from MSWI bottom ash has successfully been described on the basis of geochemical processes such as complexation, precipitation/dissolution, and sorption processes. For the prediction of the long-term behaviour of MSWI bottom ash in the environment the results imply that:

- materials should be tested at pH 10 and/or pH 8.3, depending on whether or not the materials are used in contact with air and may become carbonated;
- the concentrations of toxic elements 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 trace elements may not be large enough. Furthermore, molybdenum is very mobile at alkaline pH. These problems may be overcome by (1) neutralising the pH of the bottom ash, and (2) by adding sorbent minerals to the bottom ash [44].
- on the long-term, the leaching of toxic elements is likely to be reduced by the neutralisation of bottom ash pH and by sorption to neoformed minerals. Future research should concentrate (a) on a further identification/modelling of these sorption processes and (b) on the kinetics of these weathering/sorption reactions, i.e. the period of time that is required to obtain a sufficient reduction in trace-element leaching.
- Little is known about the processes that control element leaching from MSWI bottom ash in reducing environments, which, therefore, also requires further research.

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