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Application of Surface Complexation/Precipitation Modeling to Contaminant Leaching from Weathered Municipal Solid Waste Incinerator Bottom Ash

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In this paper, we have successfully applied surface complexation/precipitation modeling 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 unfavorable 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 modeling 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 aluminum (hydr)oxides, are required to describe the leaching of Cu and Pb.

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 (*1*−*3*), MSWI electrostatic precipitator ash (*4*), and coal fly ash (*5*, *6*). 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 it is unlikely to be important in the weathered ash (*7*). 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 neutralization of bottom ash pH and to sorption processes (*7*). Other observations confirm that sorption processes may control contaminant leaching from combustion residues such as MSWI bottom ash and coal fly ash (*5*, *8*−*12*). In particular, amorphous iron and aluminum (hydr)oxides are known to strongly sorb heavy metals and molybdenum (*13*−*15*). Since these types of minerals also form in MSWI bottom ash during weathering (*3*), 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) iron and aluminum (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 (*15*). The leaching of As and Se from acidic coal fly ash could also be modeled with a (simplified) surface complexation model for sorption of ions on hydrous ferric oxide (HFO) (*12*). Dzombak and Morel (*15*) 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 iron-hydroxide or ferrihydrite, is an almost X-ray amorphous solid phase that forms upon rapid hydrolysis of ferric iron solutions at 20−30 °C (*15*). There are no such extensive databases available for (amorphous) aluminum (hydr)oxide or other natural (hydr)oxides. Therefore, researchers sometimes use HFO as a surrogate sorbent mineral in more complex systems (*10, 11*).

The sorption database for HFO (*15*) has been used previously to model the leaching of trace elements from incineration residues (*10, 11*). 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 unfavorable for sorption, which give sorbed concentrations, and (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 (*16*−*18*) and also recently in coal fly ash (*12*). The selectivity of various chemicals for iron minerals has recently been evaluated thoroughly by Kostka and Luther (*16*). These workers have concluded that HFO is most selectively dissolved by extraction with ascorbate. Less is known about the selectivity of various chemicals for aluminum minerals. The oxalate extraction is usually used to dissolve short-range order aluminosilicates, such as amorphous $Al(OH)_3$ and allophane-like minerals (*17*, *18*). 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 aluminum (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 (*15*). A scheme with surface complexation/precipitation reactions was first developed by Farley et al. (*19*).

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 the database with sorption constants for HFO of Dzombak and Morel (*15*), both of which are incorporated in the computer code MINTEQA2.

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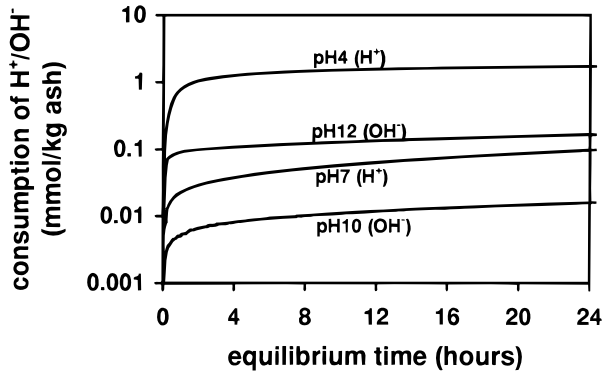

FIGURE 1. Acid/base consumption by the 1.5-year-old MSWI bottom ash suspensions at different pH during the 24-h equilibration period.

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 (*3*). In short, the bottom ash was subjected for 24 h 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 h of equilibration and indicates that the solids had approached "equilibrium" with respect to pH over this period. The equilibrated suspensions were filtered over 0.2-μm membrane filters, and the clear filtrates were analyzed by ICP−AES, GF−AAS, ion chromatography, and a carbon analyzer to obtain the total concentrations of Na, K, Ca, Mg, Al, Si, Fe, Zn, Cu, Mo, Cd, Pb, Cl, SO_4, and CO_3. 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 unfavorable for sorption. In the pH-stat experiments, HNO_3 and NaOH were used to adjust the bottom ash pH. Bulk chemical characteristics of this 1.5-year-old bottom ash are summarized in Table 1.

Surface Complexation Model (SCM). The geochemical speciation code MINTEQA2 version 3.11 (*20*) 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 Table 2.

For surface complexation modeling, 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 (*15*). Equation 1 gives the general surface complexation reaction for the sorption of divalent cations on HFO:

$$\equiv Fe{-}OH^0 + Me^{2+} \leftrightarrow \equiv Fe{-}OMe^+ + H^+ \qquad K_{Me} \quad (1)$$

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 vs pH, which maintains the characteristic shape and concentration levels of general leaching curves.

TABLE 1. Bulk Chemical Characteristics of the 1.5-Year-Old MSWI Bottom Ash[a]

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_H (Suspension at L/S = 5; t = 24 h)

pH	8.53
E_H (mV)	301

Bulk Crystalline Minerals

quartz (SiO_2), calcite ($CaCO_3$),[b] anhydrite ($CaSO_4$), feldspar, magnetite (Fe_3O_4), and hematite (Fe_2O_3)

Solubility Controlling Minerals

calcite, gypsum ($CaSO_4{\cdot}2H_2O$), ferrihydrite ($Fe(OH)_3$), gibbsite ($Al(OH)_3$)

[a] Data taken from ref 3. [b] The calcite content is 7.9 (m/m) % measured by acid addition and subsequent determination of the CO_2 released (this study).

TABLE 2. Additional or Modified Thermodynamic Data Used in the MINTEQA2 Calculations[a]

	log K	source
aqueous species		
$Cu(OH)_2^0$	−16.20	21
$HMoO_4^-$	4.24	*22*
$H_2MoO_4^0$	8.24	*22*
$CaMoO_4^0$	2.57	*23*
$MgMoO_4^0$	3.03	*23*
minerals		
$Fe_2(MoO_4)_3$(s)	35.29	*24*
sorbed species		
$\equiv X_1MoO_4^-$	9.50[b]	*15*
$\equiv X_2MoO_4^-$	9.50[b]	*15*
$Fe(OH)_3$(s)	−2.50	*15*
$Zn(OH)_3$(s)	−11.70	*15*
$Cu(OH)_2$(s)	−8.64	*20*
$Pb(OH)_2$(s)	−8.15	*20*
$Cd(OH)_2$(s)	−13.73	*20*
$Fe_2(MoO_4)_3$(s)	35.29	*24*

[a] The components of the reactions are H_2O, H^+, Me^{2+}, Fe^{3+}, MoO_4^{2-}, $\equiv X_1OH^0$, and $\equiv X_2OH^0$. All constants refer to formation reactions. [b] This constant was estimated on the basis of linear free-energy relationships.

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 $Me(OH)_2$(s) and $Fe(OH)_3$(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 (*15*):

$$\equiv Fe{-}OH^0 + Me^{2+} + 2H_2O \leftrightarrow Fe(OH)_3(s) + \equiv Me{-}OH_2^+ + H^+ \qquad K_{Me} \quad (2)$$

$$=Me{-}OH_2^+ + Me^{2+} + 2H_2O \leftrightarrow Me(OH)_2(s) + =Me{-}OH_2^+ + 2H^+ \qquad 1/K_{spMe} \quad (3)$$

$$\equiv Fe{-}OH^0 + Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_3(s) + \equiv Fe{-}OH^0 + 3H^+ \qquad 1/K_{spFe} \quad (4)$$

The symbols ≡ and = denote bonds at the surface; $\equiv Fe{-}OH^0$ represents $[Fe(OH)_3]_n$, and $=Me{-}OH^0$ represents $[Me(OH)_2]_n$, which means that reaction 2 is balanced with respect to H and O. The assumption of ideal solid-solution behavior 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 (*15*). The precipitation constants used for surface precipitation modeling are given in Table 2.

The surface precipitation model is not incorporated in the standard 3.11 version of MINTEQA2 (*20*). Therefore, we implemented the scheme of reactions worked out by Dzombak and Morel (*15*) by adding to the sorption database reactions for the sorption (eq 5a) and subsequent precipitation (eqs 6a and 7) of Cd, Pb, Zn, and Cu on HFO. The same approach was used for Mo (eqs 5b, 6b, and 7).

$$\equiv Fe{-}OH^0 + Me^{2+} + 2H^+ + P \leftrightarrow =Me{-}OH_2^+ + Fe^{3+} + H_2O \qquad K_{Me}^{int}K_{spFe} \quad (5a)$$

$$\equiv Fe{-}OH^0 + MoO_4^{2-} + H^+ \leftrightarrow =FeMoO_4^- + H_2O + P \qquad K_{Mo}^{int} \quad (5b)$$

$$Me^{2+} + 2H_2O + T_s \leftrightarrow Me(OH)_2(s) + 2H^+ \qquad 1/K_{spMe} \quad (6a)$$

$$3MoO_4^{2-} + 2Fe^{3+} + T_s \leftrightarrow Fe_2(MoO_4)_3(s) \qquad 1/K_{spMo} \quad (6b)$$

$$Fe^{3+} + 3H_2O + T_s \leftrightarrow Fe(OH)_3(s) + 3H^+ \qquad 1/K_{spFe} \quad (7)$$

The symbol P represents the Coulombic term $\exp(-F\Psi/RT)$, 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 eqs 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.

Parameters for the Surface Complexation/Precipitation Model (SCM/SPM). (a) Leachate Composition. The concentrations of Na, K, Ca, Mg, Al, Si, Fe, PO_4, Cl, SO_4, CO_3, and NO_3 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 ≥ 6.5, and $0.1 < I < 0.5$ for pH 4−5.5).

(b) 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 were used 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: pH(Pb) < pH(Cu) < pH(Zn) < pH(Cd), whereas for Mo the reverse holds (*15*). 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 aluminum (hydr)oxides (see below). Table 3 gives the obtained total sorbate concentrations, which were used in subsequent modeling. All model calculations were run with all sorbates present at the appropriate concentrations.

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 of 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 of 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 pH 4)	4.6E−06
Pb (concentration at pH 2)	4.0E−04
Zn (concentration at pH 4)	3.0E−03
Cu (concentration at pH 2)	2.2E−03

(c) Sorbent Mineral Concentration. The HFO content of the bottom ash was measured by ascorbate extraction and is referred to as ASC(Fe). The amorphous aluminum (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 h at four different pH values in the pH-stat, at pH 4, pH 6.5, pH 8.5, and pH 10.5. The equilibrated suspensions were filtered over 0.2-μm membrane filters, and the remaining solid material was extracted as described below. HFO was extracted from 15 g of bottom ash with 300 mL of ascorbic acid solution (20 g/L) according to the method of Ferdelman (*25*) described in Kostka and Luther (*16*). The extractions were performed at pH 8 and took 24 h at room temperature. Amorphous aluminum (hydr)oxides were extracted from 3 g of bottom ash with 300 mL of 0.2M ammonium oxalate at pH 3 for 4 h in the dark (*26*). All Fe and Al-extracts were analyzed 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 second, on the assumption that amorphous aluminum (hydr)oxides also play an important role in the sorption process. For modeling purposes, HFO was taken as a surrogate sorbent for amorphous aluminum (hydr)oxides because of the absence of a complete and systematic database for sorption reactions on amorphous aluminum (hydr)oxides. We believe that the use of HFO as a surrogate for amorphous aluminum (hydr)oxides is justified for the following reasons: The most reactive aluminum and iron (hydr)oxides are $Fe(OH)_3$ (ferrihydrite/HFO) and $Al(OH)_3$. 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

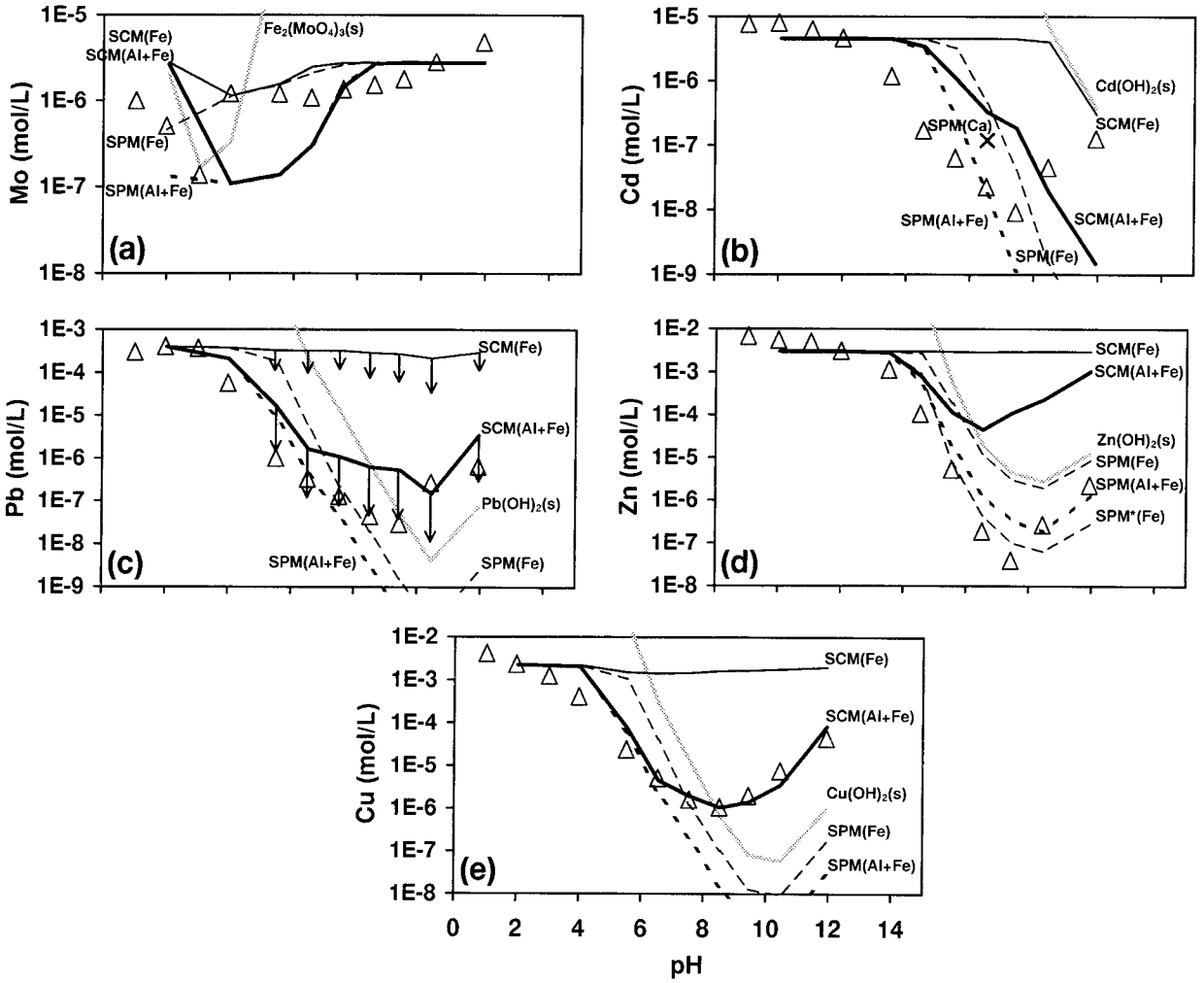

FIGURE 2. Total dissolved Mo (a), Cd (b), Pb (c), Zn (d), and Cu (e) in L/S = 5 leachates of 1.5-year-old MSWI bottom ash vs pH, and MINTEQA2 predictions on the basis of surface complexation/precipitation modeling. The symbol △ represents the leaching data. Model-predicted concentrations on the basis of surface complexation are represented by solid lines [thin lines for HFO, thick lines for amorphous iron + aluminum (hydr)oxides]. Model-predicted concentrations on the basis of surface precipitation are represented by dashed lines (thin lines for HFO, thick lines for amorphous iron + aluminum (hydr)oxides). Gray lines represent equilibrium with bulk $Me(OH)_2$(s) or $Fe_2(MoO_4)_3$(s). The symbol X (in panel b) represents model-predicted Cd concentrations on the basis of surface precipitation with calcite. The arrows in the model-predicted Pb concentrations indicate the effect of a higher sorption constant for low-affinity sites (log K_2^{int} = 1.7 instead of 0.3, see text). The line marked 'SPM*(Fe)' (in panel d) has been modeled on the basis of log $K_{sp(Zn)}$ = 10.2 (from ref 19).

principles, outlined in ref *27*, 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 (*27*). As both the charge and coordination number of Fe(III) and Al(III) in these (hydr)oxides are the same, these principles suggest that aluminum and iron (hydr)oxides have a similar reactivity (*28*). 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, 1 mol of Al was assumed to be representative of 1 mol of Fe. The molecular weight of 89 g of HFO/mol of Fe recommended by Dzombak and Morel (*15*) 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 of the bottom ash only, and from OX(Al) + ASC(Fe), representing the amount of HFO plus amorphous aluminum (hydr)oxides present in the bottom ash. Resulting total sorbent mineral concentrations are given in Table 3.

(d) Specific Surface Area of HFO. We used the general value of 600 m^2/g recommended by Dzombak and Morel (*15*).

(e) 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 (*15*), i.e., 5 mmol/mol Fe and 0.2 mol/mol Fe, respectively.

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 pH ≥4 were taken from ref 7). For comparison, the solubilities of pure $Me(OH)_2$(s) minerals and $Fe_2(MoO_4)_3$(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 (*7*). Over a large range in pH values, leachates were generally calculated to be undersaturated with respect to common secondary minerals such as (hydr)oxides, carbon-

ates, sulfates, and phosphates. Exceptions were copper (hydroxy)carbonates [e.g., azurite, $Cu_3(OH)_2(CO_3)_2$] and lead phosphates [e.g., chloropyromorphite, $Pb_5(PO_4)_3Cl$], but further evidence for their possible role in controlling the leaching of Cu and Pb from weathered MSWI bottom ash was not found (*7*).

Qualitatively, the observed leaching-trends (Figure 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 (*15*). 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 modeling 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 pH > 9 (*3*), 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 (*29*). Recently, we have started a specific investigation of the role of DOC in Cu leaching from MSWI bottom ash (*30*).

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 summarizes 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 unfavorable 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 aluminum (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 (*15*). Following these criteria, surface precipitation must be considered (see Table 3).

Results of Sorption Modeling. The results of this approach to sorption modeling are shown in Figure 2 together with the leaching data.

Mo leaching (Figure 2a) is described quite well by surface complexation with HFO over a large range of pH values (pH 4−10). If amorphous aluminum (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 $Fe_2(MoO_4)_3$(s) seems more likely to control Mo leaching at these low pH values.

The modeling results for Cd, however, are inconclusive. Cd concentrations are too low to be explained by surface complexation with HFO or amorphous aluminum (hydr)oxides (Figure 2b). The model based on HFO shows significant Cd-sorption above pH 10 only, and if amorphous aluminum (hydr)oxides are included, predicted Cd concentrations still remain 1 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 (*31, 32*), and the mineral is known to have precipitated in large amounts during carbonation of the fresh alkaline bottom ash (*33*). 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 that were estimated by Comans and Middelburg (*32*) for pH ≈ 8−8.5. 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 modeled at this pH, using otherwise the same approach as described above for HFO. Site concentrations were estimated from the $CaCO_3$ content of the bottom ash (Table 1) and the general site densities used by Comans and Middelburg (*32*). However, this model strongly overpredicts the leaching of Cd at pH 8.5 (see Figure 2b) and cannot, at this stage, lend support to the potential role of calcite in controlling Cd leaching.

Pb leaching is described reasonably well by surface complexation if the sorbent mineral concentration is estimated by ASC(Fe) + OX(Al) (Figure 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 relationship, and was considered by Dzombak and Morel (*15*) 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 (*15*). 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 (Table 3); (b) surface complexation largely underestimates Zn sorption, even if amorphous aluminum (hydr)oxides are included (Figure 2d); and (c) the shape of the surface precipitation curves in Figure 2d follows the pattern of the leaching data closely. However, measured Zn concentrations between pH 6 and pH 10 are up to 1 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. (*19*), 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 (Figure 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 (Figure 2e). If amorphous aluminum (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 aluminum (hydr)oxides is supported by mineralogical observations: Cu was detected in an amorphous gel-like precipitate consisting mainly of Al and O that was found in the bottom ash at the 1.5-year-old disposal site (*7);* during carbonation of filtered MSWI bottom ash leachates, a significant amount of Cu coprecipitated with amorphous aluminum (hydr)oxides (*33*); and in 12-year-old MSWI bottom ash, Cu has been found to be incorporated in neoformed clays (*34*). We emphasize 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 (*30*).

In summary, the combination of selective chemical extractions performed on the bottom ash and leaching at pH values unfavorable 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 modeling 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 aluminum (hydr)oxides, are required to describe the leaching of Cu and Pb. Our results for Cd are inconclusive.

The amount of amorphous aluminum (hydr)oxides exceeds the HFO content of the bottom ash by a factor of 10. Considering the high affinity of trace elements for amorphous $Al(OH)_3(s)$ (*13*), amorphous aluminum (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 aluminum (hydr)oxides that can be applied to heterogeneous systems such as MSWI bottom ash.

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