

Antimony leaching from uncarbonated and carbonated MSWI bottom ash

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Abstract

The recycling potential of municipal solid waste incinerator (MSWI) bottom ash may be limited by the leaching of antimony (Sb). Therefore, treatment methodologies need to be developed. The pH-dependent leaching behaviour of this oxyanion-forming element in fresh and weathered bottom ash is, however, not understood. Sb leaching was investigated in a wide range of both pH and extent of carbonation. Sb came close to equilibrium with calcium antimonate ($\text{Ca}[\text{Sb}(\text{OH})_6]_2$) at acid and neutral pH. Therefore, adsorption experiments with synthetic calcite (CaCO_3), 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 portlandite ($\text{Ca}(\text{OH})_2$) and adsorption modelling to hydrous ferric oxides (HFO) and amorphous aluminium minerals (AAM) were conducted to investigate which minerals decrease Sb leaching below equilibrium with calcium antimonate. At $\text{pH} > 12$, calcium antimonate comes into solution due to portlandite formation, but the subsequent increase in Sb leaching is reduced due to strong interaction of Sb with portlandite and ettringite. Ettringite appears to be an important host mineral for Sb at the natural pH of mildly weathered bottom ash (11.8) because a minimum in leaching is observed. When pH is decreased below 10.5, ettringite dissolves and Sb comes into solution, approaching equilibrium with calcium antimonate near pH 9. Gypsum showed no affinity for Sb. The interaction of calcite with Sb was not clear. Adsorption modelling suggested that HFO, rather than AAM, control Sb leaching when $\text{pH} < 9$. During carbonation, Sb leaching first increased, most likely due to dissolution of ettringite. Then, Sb leaching decreased, since the pH became low enough to allow sorption by HFO.

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1. Introduction

Although landfilling is the predominant solid waste management option for many European countries, municipal solid waste is increasingly being incinerated because the waste volume is reduced down to 10%, waste-to-energy conversion is possible, and some of the produced residues are recyclable [1]. MSWI bottom ash technically has a high recycling potential. However, the leaching of heavy metals sometimes does not comply with legal leaching requirements [2].

Few European countries include Sb in environmental legislation [2] but international attention steadily increases, since Sb is regarded as a potentially harmful element [1,3,4]. At the

European level, new leaching criteria for acceptance on landfills were published in a council decision (2003/33/EC) that include standards for Sb [2]. In Flanders, an informal limit value advises that Sb leaching should not exceed 0.1 mg/kg for recycling of granular material in construction applications. At present, bottom ash does not comply with this or with European regulations [2]. Hence, in order to allow safe deposition or recycling of MSWI bottom ash, treatment methodologies need to be applied. However, it is not known how Sb will be affected, since the mechanisms, which determine its leaching behaviour, are not yet understood.

Sb is assumed to occur as the pentavalent $\text{Sb}(\text{OH})_6^-$ oxyanion in bottom ash leachates and it has been established that it is not in equilibrium with any known Sb-compound [5,6]. Hence, sorption or solid solution phenomena control Sb leaching. Amorphous iron oxides, frequently referred to as hydrous ferric oxides (HFO), and amorphous aluminium minerals (AAM) have a high

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adsorption potential for oxyanions and are the most important phases controlling Sb leaching in soils [7]. They are believed to play an important role in bottom ash too, but only when pH is lower than 9, as is the case in highly weathered bottom ash [5,6]. It is not known which mechanism controls Sb-leachability at the “natural” alkaline pH (11,12) of fresh or mildly weathered bottom ash. Ettringite is likely to be an important host mineral for Sb [6,8] because it occurs in large quantities in bottom ash [9] and various oxyanions can be efficiently immobilised by substituting sulphate in its structure [10–12]. Portlandite, calcite and gypsum also occur in relatively high amounts in MSWI bottom ash [9] and are known to interact with oxyanions such as arsenate (AsO_4^{3-}) or selenite (SeO_3^{2-}) [13–17].

Aging will affect the mineralogy of bottom ash. The most important changes occurring during weathering of MSWI bottom ash that have been identified, are a drop in pH, accompanied by the formation of calcite, the dissolution of metastable (hydr)oxides (e.g. portlandite, ettringite), the precipitation of gypsum and aluminosilicates, and the neoformation of Al and Fe oxides [5,18,19]. This complex weathering sequence results in highly weathered bottom ash with adsorption of Sb mainly to neoformed aluminium oxides [5]. However, the effect of carbonation alone on Sb leaching is not understood. Previously, it has been shown that during carbonation, Sb leaching will rapidly increase followed by a slow decrease as a function of carbonation time [8]. The drop in pH, as a result of the carbonation reactions, may allow $\text{Sb}(\text{OH})_6^-$ to be adsorbed by HFO and/or AAM.

The aim of the present paper is to improve understanding of the mechanisms controlling pH-dependent Sb leaching in fresh and weathered MSWI bottom ash. At first, the carbonation reaction was accelerated to study the effect of carbonation on Sb leaching. Then, adsorption to HFO and AAM was modeled to explain why Sb leaching can decrease upon prolonged accelerated carbonation as observed by Van Gerven et al. [8]. Finally, the interaction of Sb with several major minerals in MSWI bottom ash at neutral to alkaline pH, that have a known affinity for oxyanions (calcite, ettringite, gypsum, and portlandite), was studied. Thus, Sb leaching in a wide range of both pH and weathering degree is investigated.

2. Experimental

2.1. Bottom ash

The used bottom ash already underwent an on-site treatment after quenching. The light organic fraction and the fraction larger than 50 μm were separated from the main stream by wet sieving. This stream was then further sieved into 0–2, 2–6 and 6–50 μm fractions. The smallest fraction was separated in a sand fraction (0.1–2 mm) and a sludge fraction (0–0.1 mm). Since the sand fraction is the largest one and it usually does not comply with Flemish leaching limit values, it was studied in this paper. It is not expected that wet sieving results in a dramatic shift in mineralogy compared to the original bottom ash. Most probably, only the content of soluble salts and organic matter will be much lower compared to the original bottom ash, since both are

solubilized during wet sieving. For the sake of convenience, the sand fraction is hereafter denominated bottom ash. After collection, the bottom ash was dried at 40 °C and stored in a closed bucket to slow down transformation reactions. Prior to carbonation experiments, the bottom ash was ground to a particle size of less than 2 mm.

2.2. Accelerated carbonation

Carbonation experiments were performed in a CO_2 incubation chamber (Sanyo MCO-17AI) to control CO_2 -percentage at 20% and temperature at 37 °C during carbonation. These parameters were chosen, since in a previous experiment they lead to the most pronounced effect on Sb leaching [8]. On the bottom of the chamber, a water tub was placed to keep constant atmosphere humidity.

Five large plastic plates containing 400 g of bottom ash, brought to initial moisture content of 6% with distilled water, were prepared. The bottom ash was spread out on plastic trays to obtain a layer thickness of less than 0.5 mm. These trays were placed in the CO_2 chamber. After 2 and 6 h and 1 and 7 days, a tray was removed from the chamber for analysis. It was verified that the 6% moisture content remained constant throughout the experiment.

2.3. Determination of total metal concentration and leaching concentration

The total metal content was determined by digesting 0.1 g of dry material with concentrated HNO_3 , HClO_4 and HF consecutively. After digestion, the metal content was measured in the resulting liquid sample with Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Thermo, Xi series).

Leaching of metals was tested using the EN 12457-2 test. About 10 g of dry material was agitated in 100 ml distilled water for 24 h. After filtration over a 0.45 μm filter, the metals in the filtrate were measured with ICP-MS.

In order to evaluate the pH dependence of metal leaching, a set of tests based on the EN-standard was used. Various volumes of concentrated HNO_3 or KOH 60% (w/w) were added to distilled water in order to obtain different leachate pH levels after 24 h. Metal concentration was determined with ICP-MS, sulphate concentration with ion chromatography (Dionex ICS-2000 with an AS-18 column).

To evaluate possible equilibrium with calcium antimonate ($\text{Ca}[\text{Sb}(\text{OH})_6]_2$), the saturation index was calculated in all leachates using the lowest solubility product found in literature ($\log K_{\text{sp}} = -12.55$, [20]).

Sb-speciation in bottom ash leachates (L/S = 10) was analysed using high pressure liquid chromatography coupled to ICP-MS with a 4 mm Dionex AS-17 column and 0.1 M EDTA at pH 4.7 as the mobile phase at a flow of 1 ml/min using In as an internal standard. All sample preparation was performed in a N_2 -atmosphere. Bottom ash suspensions (L/S = 10) were shaken with degassed water for 24 h after which the supernatant was filtrated over 0.45 μm nylon filters and immediately diluted in 0.05 M EDTA to prevent reduced Sb-species from being

oxidized upon exposure to the ambient atmosphere. During preliminary testing, it was verified that Sb^{III} species dissolved in 0.05 M EDTA remained unoxidized for at least 48 h. Hence, the Sb speciation in the bottom ash leachates, diluted in 0.05 M EDTA, could be analysed using this technique.

2.4. Adsorption by HFO and AAM

Adsorption of Sb to HFO and AAM was modelled using a previously described method [6,21]. Ascorbate-extractions of iron (Asc(Fe)) according to the method of Ferdelman et al. described by Kostka and Luther [22] were used to estimate the HFO content of bottom ash. Acid ammonium oxalate extraction in the dark [23] of aluminium (Oxal(Al)) was used to estimate the quantity of AAM. Al and Fe concentrations in extracts were measured with ICP-MS.

The Diffuse Layer/Surface Complexation Model (DL/SC) [24] for sorption of Sb on HFO was used in which the intrinsic constants are estimated on the basis of linear free-energy relationships. To include sorption on AAM, some assumptions had to be made, since thermodynamic data are generally lacking. The molecular weight of 89 g HFO/mol Fe recommended by Dzombak and Morel [24] was used to calculate both the HFO as well as the AAM content in carbonated and uncarbonated bottom ash. In addition, thermodynamic data used for sorption on HFO were also used for AAM.

The DL/SC model is available in the geochemical speciation program Visual Minteq (version 2.32) [25]. The aqueous species HSbO_3^0 ($\text{p}K_{\text{a}} = 2.72$) [24] was added to the standard thermodynamic database. The maximal experimental leaching value from uncarbonated bottom ash between pH 8 and 10 was chosen to be the Sb fraction available for adsorption, based on the assumption that in this pH range, both adsorption by HFO and AAM or solid solution formation by calcium bearing minerals are minimal. To allow comparison with experimental leaching data, all input parameters were recalculated to represent ion or sorbent concentrations in bottom ash suspensions at L/S = 10 l/kg.

2.5. Occurrence of calcium bearing minerals in bottom ash

The quantity of calcite was estimated on the basis of carbonate content. About 60 ml of distilled water and 40 ml of 5 M HCl was added to 5 g of dry bottom ash. The formed reaction gas, which contains CO_2 , was stripped out using a flow of N_2 -gas and was led through two absorption bottles, each containing 50 ml of 1 M NaOH. After 2 h of reaction time, the carbonate concentration in the absorption bottles was determined by titration with 0.5 M HCl.

The exact mineralogy of bottom ash is hard to reveal using conventional methods such as XRD, due to the complex composition of this residue. Therefore, it was chosen to estimate the quantity of calcium bearing minerals in uncarbonated bottom ash by modelling the pH-dependent leaching of Ca, Al and sulphate in Visual Minteq. This approach was based on the assumption that the leaching of these matrix components in bottom ash is controlled by the minerals calcite, gibbsite ($\text{Al}(\text{OH})_3$), ettringite, gypsum and portlandite as proposed by Meima and Comans [19].

Total concentrations of Ca, Al and sulphate leachability at pH 3 were used as inputs together with the calcite content calculated from carbonate measurements.

2.6. Adsorption experiments with calcium bearing minerals

Commercially available gypsum and calcite powders were used. XRD-analysis (Philips PW1130/90 with a Co-lamp) confirmed that these powders were pure gypsum and calcite, respectively. Calcite-free portlandite was formed by immersing freshly combusted lime in double deionised water. The resulting suspension was immediately filtered and vacuum dried at 40 °C. Subsequently, the powder was ground to a particle size <1 mm. XRD analysis confirmed a pure and calcite-free portlandite phase.

Portlandite was allowed to react with $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ to produce ettringite according to the method of Atkins et al. [26]. XRD analysis confirmed an ettringite phase with only a slight calcite impurity.

Suspensions with a liquid-to-solid (L/S) ratio of 50, 100, 200 and 500 of calcite, ettringite, gypsum or portlandite were prepared and allowed to fully equilibrate with the solution. All actions with portlandite suspensions were performed in a N_2 -atmosphere to avoid carbonate formation. Due to the relatively high solubility of portlandite and gypsum, suspensions of these two minerals were equilibrated in presaturated solutions. About 5 g/l of solid was agitated in water and soluble Ca was measured at regular time intervals with ICP-MS. The suspension was considered to be in equilibrium when a constant Ca concentration was reached. The resulting supernatant was separated from the solid with 0.45 μm membrane filters. Different quantities of fresh portlandite and gypsum were again added to 500 ml of presaturated solution to obtain the correct L/S ratio. Calcite and ettringite were added to 500 ml ultrapure water. Portlandite and calcite suspensions were prepared in gas-tight glass jars, filled with a N_2 -atmosphere in the case of portlandite and a 0.5 bar CO_2 atmosphere in the case of the calcite suspension. Ettringite and gypsum suspensions were left open to the ambient atmosphere. All suspensions were agitated until a constant Ca concentration was reached.

Sb^{V} was then added to a total concentration of 100 ppb in suspensions and blanks. Samples were taken under continuous stirring after 1, 3 and 7 days in which the Sb concentration was measured with ICP-MS. Uptake by calcium bearing minerals was calculated from the concentration difference with the blank.

3. Results and discussion

3.1. Characterization of uncarbonated bottom ash

Table 1 shows the results of the destruction and EN-leaching tests of uncarbonated bottom ash. Although the total Sb-concentration is well above the Flemish indicative value of 50 mg/kg, it is probably still an underestimation since SbF_5 , which can be formed during destruction with HF, is highly volatile. The pH of the leachate of the EN test was 10.8, which indicates a mildly weathered bottom ash. During storage prior to sampling, the bottom ash already underwent carbonation due to

Table 1
Total and leachable (EN 12457-2) element concentration in uncarbonated bottom ash (mg/kg)

Element	Total	Leachable
Fe	99299	5.70
Ca	70692	2421
Al	27735	723
Cd	7975	0.010
Cr	96.8	0.50
Cu	3248	6.72
Ni	304	0.040
Zn	7975	3.92
Pb	1710	0.62
Mo	18.7	0.68
Sb	132.6	0.17

contact with atmospheric CO₂. Sb leaching (0.17 ± 0.03 mg/kg) exceeds the Flemish indicative value for recycling (0.1 mg/kg) but complies with the European limit value for landfilling of non-hazardous waste (0.7 mg/kg).

Speciation analysis indicated that all leachable Sb at the natural pH of uncarbonated bottom ash occurred as Sb^V. It was previously postulated that Sb in bottom ash leachates should always occur as Sb^V [6]. Given the Eh values typically measured in leachates (100–250 mV [18]), Sb(OH)₆⁻ should indeed dominate Sb speciation in alkaline bottom ash leachates according to Eh–pH diagrams [7].

3.2. Accelerated carbonation

Fig. 1 shows the evolution of Sb leaching as a function of carbonation time. The same trend was observed in a previous experiment [8]. A sudden increase from 0.17 up to 1.67 mg/kg after 24 h was followed by a gradual decrease down to 1.23 mg/kg after 7 days, still higher than the EU-limit value for non-hazardous waste. The pH, carbonate content, Asc(Fe), and Oxal(Al) evolution as a function of carbonation time are given in

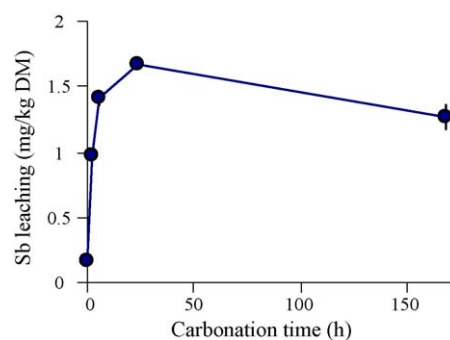


Fig. 1. Sb leaching as a function of carbonation time (DM refers to dry material).

Fig. 2. As a result of the carbonation reaction, a sudden decrease in pH was observed from 11.8 to 9.0 after 24 h followed by a more gradual decrease to 8.6. Fully carbonated bottom ash has a pH of 8.5, since it is controlled by calcite only [19]. The calcite content was 30.6 g/kg in uncarbonated bottom ash, increased to 63.3 g/kg after 6 h carbonation and remained relatively constant, which also indicates that in this case, carbonation was virtually complete after 7 days.

No significant change in the amount of Asc(Fe) and Oxal(Al) was found between differently carbonated fractions, on average 3.9 g Fe/kg and 24.6 g Al were extracted. The amount of Oxal(Al) corresponds well to what previously has been found in highly weathered bottom ash [5] but the amount of HFO in the present material is higher than what was found in highly weathered samples by Meima [5] (1 g Fe/kg) since during weathering, HFO are transformed to more crystalline iron oxides.

3.3. pH-dependent leaching

Fig. 3 shows the evolution in pH-dependent leaching as a function of carbonation time. At the “natural” pH of uncarbonated bottom ash (10.8), a minimum in leaching is found. When pH is decreased, Sb leaching increases to reach a maximum

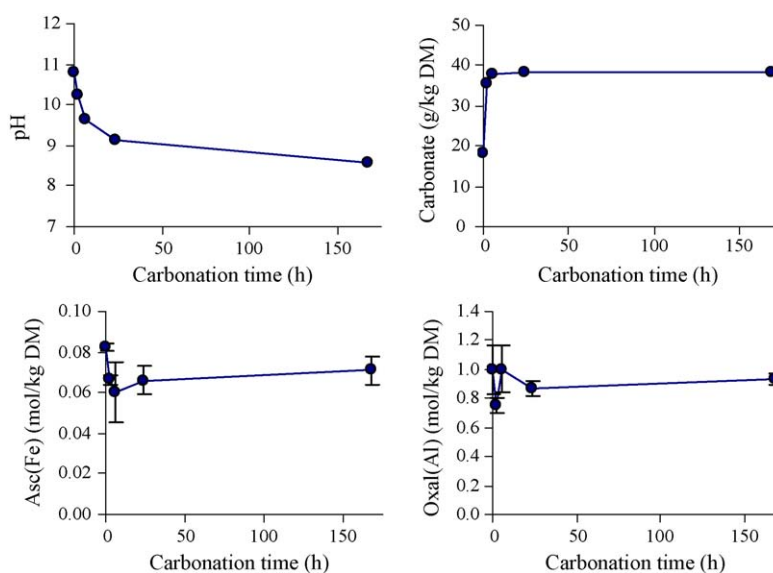


Fig. 2. The evolution of pH, carbonate content, Asc(Fe), and Oxal(Al) as a function of carbonation time. Vertical lines indicate standard deviation (three replicates).

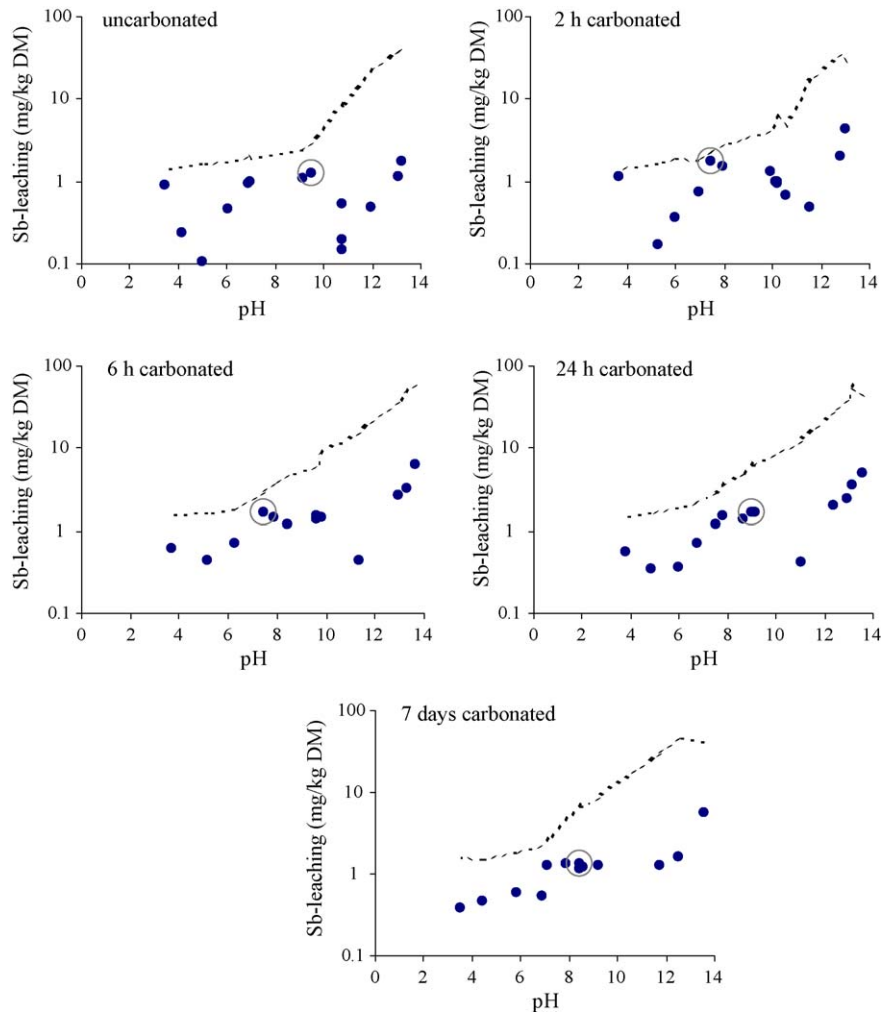


Fig. 3. pH-dependent leaching of Sb from uncarbonated and carbonated MSWI bottom ash. Sb in equilibrium with $\text{Ca}[\text{Sb}(\text{OH})_6]_2$ is indicated with the dotted line. Available Sb for adsorption by HFO and AAM are indicated with circles.

between pH 7 and 9. A further decrease in pH now results in a decline in Sb leaching until another minimum is reached at pH 5. Sb leaching largely is controlled by adsorption and solid solution phenomena because Fig. 3 shows that Sb concentrations approached equilibrium with calcium antimonate at neutral and acid pH values only. Especially at high pH, Sb is far from equilibrium.

It can be argued that Sb-speciation is not necessarily pentavalent at low pH. The Eh of bottom ash typically varies between 100 and 250 mV [18], which implies that, according to its Eh–pH diagram [7], at pH-values below 8 Sb^{V} theoretically can be reduced to Sb^{III} . However, Sb^{III} is easily oxidized to Sb^{V} in the presence of HFO [27], and reduction of Sb^{V} to Sb^{III} is a relatively slow reaction [28]. It is therefore assumed that soluble Sb is pentavalent, independent of pH, as also previously proposed by Meima and Comans [6].

Accelerated carbonation clearly has an effect on the pH-dependent leaching behaviour. Compared to uncarbonated bottom ash, the minimum in leaching at alkaline pH is less pronounced compared to carbonated fractions. Alternatively, the leaching at acid pH is much less pronounced in the 7

days carbonated bottom ash compared to uncarbonated bottom ash.

3.4. Adsorption modelling

The input parameters for the adsorption model are summarized in Table 2. From Fig. 3 it can be seen that the available Sb fractions (i.e. maximal leaching value between pH 8 and 10) were always close to equilibrium with calcium antimonate. Indeed, when adsorption and solid solution controls are lacking, Sb can only be solubility controlled. No clear explanation can be given as to why there is some variation in available Sb between the materials with a different degree of carbonation. Furthermore, as stated above, the variations in HFO and AAM content

Table 2
Input parameters for adsorption modelling of uncarbonated bottom ash

Available Sb ($\mu\text{mol/l}$)	1.043
HFO (g/l)	0.741
AAM (g/l)	8.906

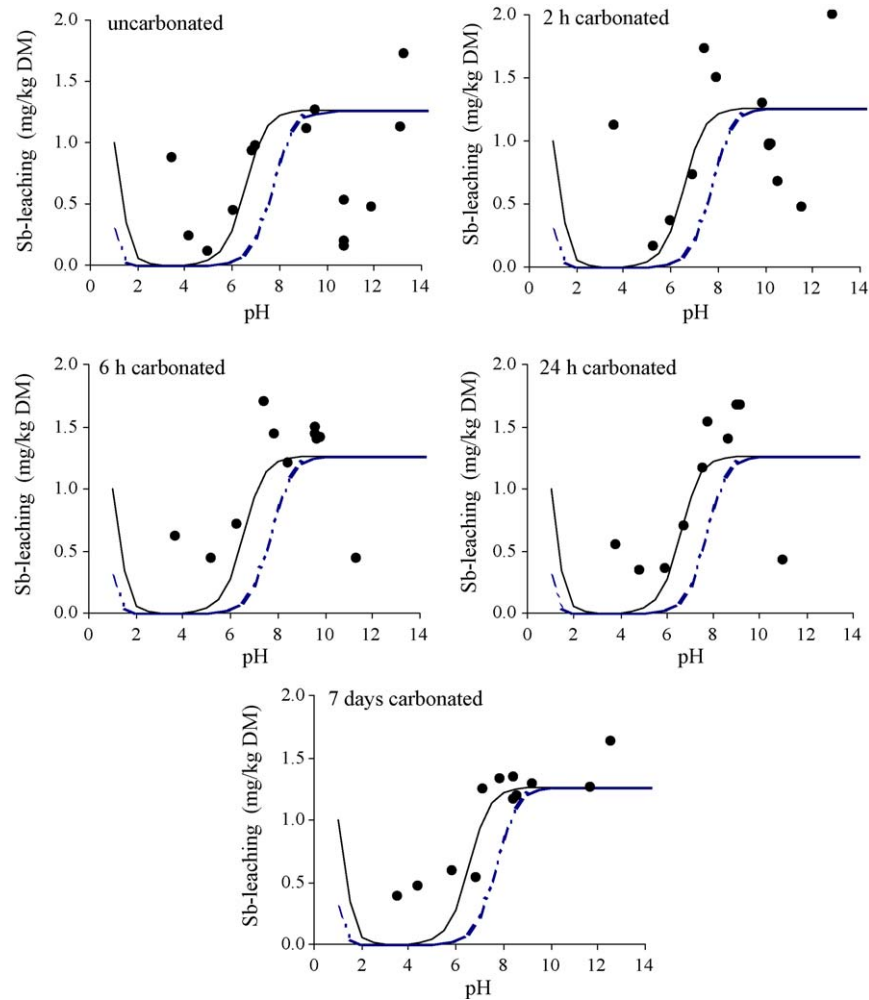


Fig. 4. Experimental and modelled pH-dependent leaching behaviour of Sb from uncarbonated and carbonated MSWI bottom ash suspensions at L/S = 10. Solid lines represent predicted leaching values assuming only HFO as adsorbents, the dotted lines represent predicted leaching values assuming both HFO and AAM as adsorbents.

were not significant. Modelling was therefore only performed using the parameters of uncarbonated bottom ash (Table 2). Adsorption was first modelled assuming adsorption by HFO only and subsequently assuming adsorption by both HFO and AAM. Meima and Comans [6] advocate the latter but it can be seen in Fig. 4 that the addition of AAM as sorbent makes the fit of model calculations with experimental data worse. Assuming sorption by HFO only, provides an excellent fit between pH 6 and 9.5 for uncarbonated bottom ash. Sb forms strong inner-sphere complexes with iron oxides [29], but the adsorption of Sb by AAM has not yet been investigated thoroughly. These results suggest minor sorption of Sb by AAM but more exact models need to be developed for adsorption of Sb to both HFO and AAM, given the many assumptions made for Sb sorption to AAM and given the fact that adsorption modelling of Sb to HFO is based on free-energy relationships [24]. During weathering, HFO are gradually transformed to more crystalline Fe-oxides, which have a much smaller specific surface and hence, show less strong adsorption of trace components [5]. It was demonstrated that in highly weathered bottom ash, adsorption to AAM rather than to HFO controls Sb leaching [5].

Experimental and modelled results correspond less satisfactory below pH 6 and diversion between experimental and modelled results increases with carbonation time. This is most probably due to the dissolution of calcite at pH < 6 (Fig. 5) and the subsequent competition of bicarbonate with antimonate for sorption to HFO since bicarbonate also forms inner-sphere complexes with HFO [30]. In addition, the low quality of fit at pH < 4

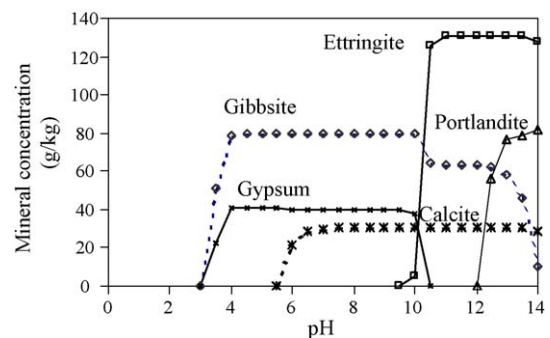


Fig. 5. The occurrence of Ca-bearing minerals in uncarbonated bottom ash.

is most likely caused by the fact that the DL/SC model in Visual Minteq does not account for the dissolution of HFO. In preliminary experiments (results not shown) it was found that after 24 h, HFO started to dissolve below pH 4 thereby releasing adsorbed Sb into solution.

After 24 h of carbonation, Sb leaching again decreased. HFO and AAM content did not change significantly with carbonation time. Adsorption modelling, however, indicated that near a pH of 8.6, HFO surfaces start to develop enough positive charge to adsorb $\text{Sb}(\text{OH})_6^-$. A leaching concentration of 1.25 mg/kg at pH 8.6 was predicted by the model, which corresponds quite well with the experimental value of 1.27 mg/kg at this pH. Carbonation therefore lowered pH enough to allow adsorption by HFO.

3.5. Interaction of Sb with calcium bearing minerals

3.5.1. Occurrence of calcium bearing minerals

Fig. 5 shows the modelled occurrence of calcium-bearing minerals in uncarbonated bottom ash as a function of pH. On a weight basis, ettringite appeared to be the most important Ca-bearing mineral at the natural pH of uncarbonated bottom ash (i.e. pH 10.8) followed by calcite. Piantone et al. [9] confirmed this experimentally. These authors also found significant amounts of anhydrite (CaSO_4), which is a relatively soluble mineral ($\text{p}K_{\text{sp}} = 4.36$) and is probably completely dissolved in bottom ash suspensions of L/S = 10. In carbonated bottom ash fractions, the amount of ettringite is expected to be much lower since upon reaction with CO_2 , ettringite dissolves and is transformed into calcite.

3.5.2. Adsorption experiments

Fig. 6 shows the Sb removal from solution by calcite, ettringite, gypsum and portlandite as a function of time. The Sb concentration found in solution depends on L/S in the case of

ettringite and portlandite. The Ca concentration in solution did not, since the suspensions were in equilibrium with the calcium bearing precipitate prior to Sb addition. The resulting Sb removal can hence not be explained by simple precipitation as calcium antimonate because in that case, Sb removal would be independent of L/S. Furthermore, equilibrium calculations showed that calcium antimonate saturation was not attained. Thus, it is evident that Sb interacted with ettringite and portlandite through adsorption, solid solution formation or both.

In the case of calcite, no relation developed between the Sb uptake and L/S although calcium antimonate saturation was not attained. Adsorption of oxyanions like selenite by calcite surfaces is known to be a complex mechanism because not only by pH and ionic strength influence it, but also calcium and carbonate concentrations in solution, since these ions are potential determining for the calcite surface [31,32]. It has been postulated earlier that calcite should at least have some affinity for antimony ions [20,33]. Further experiments will be conducted in which pH, Ca and carbonate content will be varied. Gypsum showed no affinity for Sb. Interactions of oxyanions with gypsum are not well studied and gypsum, to date, has only been shown to interact with arsenate [14].

More trace ions are incorporated at high precipitation rates of a particular mineral [34]. When mineral suspensions are, however, fully equilibrated, solid solution formation is slow compared to adsorption reactions. Stable suspensions of ettringite, for example, dissolve and precipitate at a very slow rate: $10^{-12.2}$ to $10^{-11.5}$ mol/m²/day whereas adsorption reactions on the other hand are comparably fast [35]. Care was taken in the adsorption reactions to maximize equilibrium of the suspensions prior to Sb addition to have at least some indication which reaction mechanism prevails. As a rule of thumb, adsorption reactions can be considered completed after 24 h [12]. Sb uptake by portlandite mounts to 76% within 24 h (Fig. 6) and then stays relatively constant as a function of time. It is

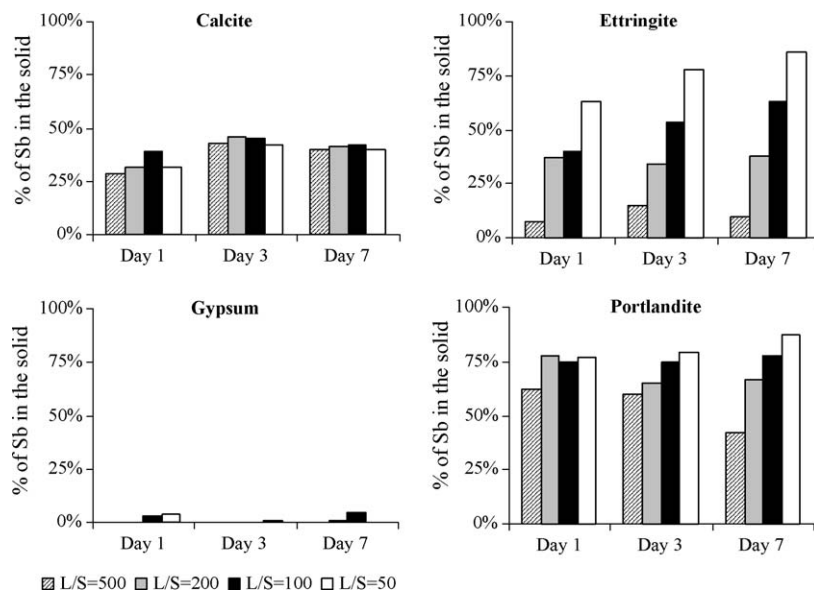


Fig. 6. The uptake of Sb^{V} by calcite, ettringite, gypsum and portlandite as a function of time and L/S.

therefore hypothesized that Sb interacts with portlandite mainly by surface adsorption. In the case of ettringite, still a considerable increase of Sb removal is observed after 24 h. Hence, it appears that the $\text{Sb}(\text{OH})_6^-$ anion adsorbed on the ettringite surface but also formed a solid solution, given the fact that adsorption on ettringite can be considered complete after 24 h [12].

3.5.3. Implications for Sb leaching from MSWI bottom ash

The minimum in Sb leachability at the natural pH of mildly weathered bottom ash (i.e. pH 10.8) can be explained by the interaction of Sb with ettringite. During weathering of a freshly quenched bottom ash (pH > 12) portlandite dissolves and ettringite precipitates [19]. Sb can be incorporated during ettringite precipitation and thus its solubility is lowered below calcium antimonate saturation. When an alkaline solution is added to increase the alkalinity above pH 12, soluble calcium precipitates as portlandite and calcium antimonate comes into solution. In Fig. 3 it can, however, be seen that in this pH region, Sb is far from equilibrium with calcium antimonate. Interaction with both portlandite and ettringite decreases the soluble Sb concentration well below the saturation limit. In carbonated fractions, the minimum at pH 10.8 is less pronounced than in uncarbonated bottom ash since Ca is not present as ettringite or portlandite but as calcite.

When carbonation proceeds, ettringite dissolves and transforms into gypsum and calcite. In Figs. 1–3 it can be seen that when pH is lowered below 10.8 by adding acid as well as by carbonation, Sb leaching increases, reaching a maximum around pH 9. Because gypsum will not immobilize Sb, Sb approaches calcium antimonate saturation. The influence of calcite is not clear.

4. Conclusion

At neutral to alkaline pH, calcium bearing minerals play an important role in the mechanisms controlling Sb leaching from both uncarbonated and carbonated bottom ash. Portlandite and ettringite limit Sb solubility at pH > 12. With portlandite dissolving at pH < 12, ettringite remains the only important host mineral for Sb at 10.8, the natural pH of mildly weathered bottom ash. When the pH is lowered below 10, ettringite dissolves too and calcite and gypsum become the main calcium bearing minerals. Because these minerals show a much less pronounced interaction with Sb or none at all, Sb approaches equilibrium with calcium antimonate. Carbonation of MSWI bottom ash will thus result in an elevated Sb leachability, which exceeds the European leaching limit value for non-hazardous waste.

When pH is lowered to below 9, HFO and AAM surfaces start to develop enough positive charge to adsorb $\text{Sb}(\text{OH})_6^-$ and Sb-leachability decreases again. This is the case in fully carbonated bottom ash: the pH is lowered enough to allow adsorption on originally present HFO. The model results suggest that, contrary to naturally weathered bottom ash [5], AAM appear not to be relevant as adsorbents for Sb in uncarbonated or artificially carbonated bottom ash.

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