



## Immobilization of antimony in waste-to-energy bottom ash by addition of calcium and iron containing additives



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### ABSTRACT

The leaching of Sb from waste-to-energy (WtE) bottom ash (BA) often exceeds the Dutch limit value of  $0.32 \text{ mg kg}^{-1}$  for recycling of BA in open construction applications. From the immobilization mechanisms described in the literature, it could be concluded that both Ca and Fe play an important role in the immobilization of Sb in WtE BA. Therefore, Ca and Fe containing compounds were added to the samples of the sand fraction of WtE BA, which in contrast to the granulate fraction is not recyclable to date, and the effect on the Sb leaching was studied by means of batch leaching tests. Results showed that addition of 0.5 and 2.5% CaO, 5%  $\text{CaCl}_2$ , 2.5%  $\text{Fe}_2(\text{SO}_4)_3$  and 1%  $\text{FeCl}_3$  decreased the Sb leaching from  $0.62 \pm 0.02 \text{ mg kg}_{\text{DM}}^{-1}$  to  $0.20 \pm 0.02$ ,  $0.083 \pm 0.044$ ,  $0.25 \pm 0.01$ ,  $0.27 \pm 0.002$  and  $0.29 \pm 0.02 \text{ mg kg}_{\text{DM}}^{-1}$ , respectively. Due to the increase in pH from 11.41 to 12.53 when 2.5% CaO was added, Pb and Zn leaching increased and exceeded the respective leaching limits. Addition of 5%  $\text{CaCO}_3$  had almost no effect on the Sb leaching, as evidenced by the resulting  $0.53 \text{ mg kg}_{\text{DM}}^{-1}$  leaching concentration. This paper shows a complementary enhancement of the effect of Ca and Fe, by comparing the aforementioned Sb leaching results with those of WtE BA with combined addition of 2.5% CaO or 5%  $\text{CaCl}_2$  with 2.5%  $\text{Fe}_2(\text{SO}_4)_3$  or 1%  $\text{FeCl}_3$ . These lab scale results suggest that formation of romeites with a high Ca content and formation of iron antimonate (triphyte) with a very low solubility are the main immobilization mechanisms of Sb in WtE BA. Besides the pure compounds and their mixtures, also addition of 10% of two Ca and Fe containing residues of the steel industry, hereafter referred to as R1 and R2, was effective in decreasing the Sb leaching from WtE BA below the Dutch limit value for reuse in open construction applications. To evaluate the long term effect of the additives, pilot plots of WtE BA with 10% of R1 and 5% and 10% of R2 were built and samples were submitted to leaching tests at regular intervals over time. The Sb leaching from untreated WtE BA was just below or above the Dutch limit value. The Sb leaching from the pilot plots of BA with additives first remained stable around  $0.13 \text{ mg kg}^{-1}$  but had a tendency to slightly increase after 6 months, indicating the need for further research on the effect of weathering, and more specifically of carbonation, on Sb leaching from WtE BA.

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### 1. Introduction

Waste-to-Energy (WtE) is a well-established technology and is besides reuse and recycling an important part of municipal solid

waste (MSW) management in many European countries (European Environment Agency, 2015). Combustion of the organic fraction of MSW generates heat that produces steam in the boiler, which can be delivered as such, or converted to electricity. The largest part of the mineral fraction of the MSW remains as bottom ash (BA). BA extracted from WtE plants typically undergoes a size separation and washing step (Vandecasteele et al., 2007) in view of its reuse as construction material. For use as a secondary raw material, the obtained granular and sand fractions of BA have to comply with leaching limit values set in the applicable national

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legislations. In the Netherlands in 2012, a “Green deal” on “sustainable and useful application of bottom ash of WtE installations” was negotiated between the government and the association of waste treatment companies (Dutch Ministry of Infrastructure and Environment, 2012). The Green Deal states that by 2017 at least half of the WtE BA has to be applied in open construction applications, meaning that no barriers such as liners have to be provided to isolate the ash or mixture of ash with other construction materials from the surrounding soil, and that no intensive monitoring or aftercare of the groundwater should be provided. Furthermore, the Dutch government aims at prohibiting by 2020 the use of WtE BA as “Isoleren-Beheersen-Contoleren (IBC)” construction material i.e. in “closed” construction applications with regulated isolation, monitoring and control measures, which was, until the green deal was concluded, the most applied use.

In the Netherlands, BA applied as secondary raw material in open applications has to comply with the leaching limits for heavy metals and for halogenides and sulfates set in the Dutch Decree on soil quality and its regulations (Decree on Soil Quality, 2007). Of all the regulated heavy metals, Sb is the most problematic since its leaching from BA e.g. as reported by Cornelis et al. (2012b, 2006) often exceeds the limit of  $0.32 \text{ mg kg}_{\text{DM}}^{-1}$  set in the Dutch regulations. However, only very little is known about the leaching mechanisms of Sb compared to other oxyanion forming metals such as Cr and As. Recent studies suggest four mechanisms that control the mobility of Sb in inorganic alkaline matrices such as WtE BA. In all these mechanisms, the pH of the matrix and the oxidation state of Sb, either Sb(III) or Sb(V), play an important role. At the intrinsic pH of WtE BA (i.e. between 8 and 12) Sb(III) is predominantly present as  $\text{Sb(OH)}_3$  and Sb(V) as the oxyanion  $\text{Sb(OH)}_6^-$  (Tella and Pokrovski, 2012). It is generally assumed that in WtE BA, Sb(V) is the dominant oxidation state given the oxidizing conditions in the furnace (Paoletti et al., 2001; Meima and Comans, 1998), but local reducing conditions can develop where Sb(III) may still persist e.g. if oxygen is depleted locally. Cornelis et al. (2012a) indeed detected both Sb(V) and Sb(III) in the leachate of WtE BA. However, when the leachate pH is lower than that of the original BA, e.g. for carbonated BA, Sb(III) leaching is much lower than that of Sb(V). At pH values above 10, the leaching of Sb(III) increases rapidly to reach the same order of magnitude as the Sb(V) leaching.

The reaction of  $\text{Sb(OH)}_6^-$  with  $\text{Ca}^{2+}$  is considered important in controlling Sb(V) leaching in alkaline matrices. Indeed, the presence of a calcium (Ca) antimonate in WtE BA was reported by Paoletti et al. (2001) and the structure was hypothesized to be  $\text{Ca}[\text{Sb(OH)}_6]_2$ . Cornelis et al. (2006) however showed that the concentration of Sb(V) in the leachate of WtE BA was lower than could be expected based on the solubility of  $\text{Ca}[\text{Sb(OH)}_6]_2$ . Different mechanisms have been proposed to account for this discrepancy. In more recently reported work, Cornelis et al. (2012b) still suggest that Ca antimonate plays the most important role, but found that Ca antimonates, also called romeites have a flexible structure with the general formula  $\text{Ca}_{1+x}\text{Sb}_2\text{O}_6(\text{OH})_{2-2x}$  of which  $\text{Ca}[\text{Sb(OH)}_6]_2$  is only one possible form. The specific composition of the romeites depends on the pH and the amount of Ca available at the time of their formation. The solubility of romeites decreases as they contain more Ca and the pH is higher, leading to a relatively low Sb concentration in equilibrium with romeite (Cornelis et al., 2011).

A second often proposed mechanism is incorporation of Sb  $(\text{OH})_6^-$  in ettringite naturally present in WtE BA to form a solid solution (Meima and Comans, 1998; Cornelis et al., 2006). Ettringite is a mineral with general structure  $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$ , shown to be able to incorporate different oxyanions by replacing sulfates between the  $(\text{Ca}_6[\text{Al}(\text{OH})_6]_4\cdot 24\text{H}_2\text{O})^{6+}$  columns. In a later study, Cornelis et al. (2012b) found though that incorporation in the ettringite structure is well described for multiple negatively

charged tetragonal oxyanions such as chromates, but is unlikely for  $\text{Sb(OH)}_6^-$  that is single negatively charged and has a large octahedral structure. According to the same authors, adsorption of Sb  $(\text{OH})_6^-$  on the ettringite surface instead of incorporation in the structure is however a valid immobilization mechanism.

A third immobilization mechanism is adsorption of Sb-species on the surface of iron (Fe) (hydr)oxides present in the BA. Leuz et al. (2006) studied the adsorption of Sb(III) on goethite ( $\text{FeO}(\text{OH})$ ) in a synthetic solution at different ionic strengths and pH values. Verbinen et al. (2013) studied the adsorption of Sb(III) on magnetite ( $\text{Fe}_3\text{O}_4$ ) in a similar way. In both cases, the Sb(III) adsorption was almost independent of the leachate pH and confirmed the possibility for adsorption in WtE BA with a pH typically between 8 and 12. In contrast to Sb(III), the adsorption of Sb(V) to iron (hydr)oxides strongly depends on the pH (Verbinen et al., 2013; McComb et al., 2007; Leuz et al., 2006). McComb et al. (2007) showed that adsorption of  $\text{Sb(OH)}_6^-$  on an amorphous Fe (III)oxide film reached a maximum at pH 3. When, after adsorption, the pH of the solution was brought to 10, rapid desorption occurred. The results of Verbinen et al. (2013), McComb et al. (2007), Johnson et al. (2005) and Leuz et al. (2006), confirm that at the intrinsic pH of WtE BA (i.e. between 8 and 12) adsorption of  $\text{Sb(OH)}_6^-$  on iron oxides or hydroxides can occur, but that only small amounts of  $\text{Sb(OH)}_6^-$  i.e. <20% of the initial concentration will be adsorbed.

Okkenhaug et al. (2013) suggested a fourth immobilization mechanism for Sb in alkaline matrices, studying the leaching of Sb from WtE air pollution control (APC) residue. In some samples with pH above 10, the Sb concentration in the leachate was almost one order of magnitude lower than could be expected based on the solubility of the least soluble romeite  $\text{Ca}_{1.13}\text{Sb}_2\text{O}_6(\text{OH})_{0.26}\cdot 0.74\text{H}_2\text{O}$ . Okkenhaug et al. (2013) explain this discrepancy by the formation of tripuhyte, an iron antimonate mineral ( $\text{FeSbO}_4$ ) with very low solubility. The formation of tripuhyte appeared a rather slow process, taking up to several months. Leverett et al. (2012) showed that, in the redox potential and pH zone corresponding to that of WtE BA, goethite ( $\text{FeO}(\text{OH})$ ) can react with  $\text{Sb(OH)}_6^-$  to form tripuhyte, even at very low Sb and Fe concentrations.

From the above described mechanisms, it can be concluded that Ca and Fe play an important role in the immobilization of Sb in WtE BA. Therefore this paper studies, as the first of its kind, the effect of the addition of Ca and/or Fe containing additives specifically on the leaching of Sb from WtE BA, and the temporal influence of the altered composition on this leaching. Furthermore, this study investigates if, by adding additives, it is possible to decrease the Sb leaching from WtE BA below the limit for application of BA in open construction applications ( $0.32 \text{ mg kg}_{\text{DM}}^{-1}$ ). The obtained results are also interpreted to establish which of the described mechanisms most likely apply to WtE BA.

## 2. Materials and methods

### 2.1. WtE bottom ash

The WtE BA used in the experiments was provided by HVC Noord-Holland, the Netherlands. The BA was first treated in a dry bottom ash plant, where it was screened and crushed for the production of a granular material 0–32 mm. Magnets, eddy current separators and sieves were used to separate iron and non-ferrous metals, such as aluminum, copper and zinc for recycling. Also the coarse unburned material was removed.

The BA used in this project was further treated in a wet installation to leach the mobile components, such as chloride, molybdenum and sulfate to the washing water. The installation contains several washers, upstream columns and cyclones to separate the

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