Investigation of washing, heating and carbonation as treatment techniques for the improvement of environmental characteristics of MSWI-bottom ash, in view of recycling

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Abstract

MSWI-bottom ash often may not be recycled as construction material in Flanders, because leaching of Cu exceeds the limit value of 0.5 mg/kg. Leaching of other components such as Mo and Sb is critical as well, but limit values for these elements are to date only informal.

Three treatment techniques were investigated to lower Cu leaching: thermal treatment destroying organic matter still present in the incinerator residue and ligands that may form complexes with Cu and enhance leaching, washing with solutions of organic complexants to extract Cu and accelerated carbonation. Carbonation decreases pH and causes metal hydroxides to react to carbonates.

Heating the bottom ash to 400°C decreases Cu leaching to 0.1 mg/kg. Washing was performed with six solutions, of which washing with citric acid and ammoniumcitrate decreases Cu leaching to below the limit value. Carbonation decreased Cu leaching from 3.3 mg/kg to 1.0 mg/kg, but further improvement should be possible. Although heating and washing gave better results in the laboratory, accelerated carbonation seems to be the most promising technique.

Keywords: MSWI-bottom ash, leaching, heavy metals, recycling, carbonation, washing, heating.
1 Introduction

Recycling is a topic of growing importance in the field of waste management. Bottom ash, originating in the grate furnace of a municipal solid waste incinerator (MSWI), is an example of a material with a high recycling potential: it can replace the sand or gravel fraction in concrete bricks or can be used as such in foundations [1]. For bottom ash to be recycled, the material must comply with strict regulations, comprising civil-technical (strength, grain size distribution, …) and environmental requirements. While the former requirements do not seem to be a problem for bottom ash, the latter are. Worldwide, leaching of heavy metals such as Cu, Pb and Zn is reported to exceed the limit values substantially, to an extent depending on the incineration process parameters and the local limit values.

In Flanders MSWI-bottom ash can be recycled when limit values for the total element concentration and leaching are not exceeded (Table 1). The limit values for total concentration are however only indicative. Besides the eight regulated metals, seven others are up to now not regulated, but (informal) limit values have been suggested. Civil-technical requirements are regulated as well, but depend on the specific recycling option. For MSWI-bottom ash, Cu leaching is the main problem. Leaching of Ba, Mo and Sb is critical as well, but for these elements limit values to date are only informal.

Table 1: Flemish limit values (mg/kg DM) for recycling of granular material in construction applications.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Total concentration(a) (mg/kg DM)</th>
<th>Leaching</th>
<th>Total concentration(a) (mg/kg DM)</th>
<th>Leaching</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>250</td>
<td>0.8</td>
<td>Ba</td>
<td>7500</td>
</tr>
<tr>
<td>Cd</td>
<td>10</td>
<td>0.03</td>
<td>Co</td>
<td>250</td>
</tr>
<tr>
<td>Cu</td>
<td>375</td>
<td>0.5</td>
<td>Mo</td>
<td>185</td>
</tr>
<tr>
<td>Cr</td>
<td>1250</td>
<td>0.5</td>
<td>Sb</td>
<td>50</td>
</tr>
<tr>
<td>Hg</td>
<td>5</td>
<td>0.02</td>
<td>Se</td>
<td>5</td>
</tr>
<tr>
<td>Ni</td>
<td>250</td>
<td>0.75</td>
<td>V</td>
<td>1250</td>
</tr>
<tr>
<td>Pb</td>
<td>1250</td>
<td>1.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>1250</td>
<td>2.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(a\) indicative values only

Leaching of metals from bottom ash and the reduction of its importance has been the subject of several investigations. Several techniques have been proposed ranging from physical ones such as sieving and (dia-)magnetic separation to chemical ones such as washing and carbonation [2].

For Cu leaching, a predominant mechanism is the formation of highly soluble organo-copper complexes. Bottom ash typically has a TOC of 1-4 % [1, 3]. Although the exact speciation of this organic material and of the complexes formed was not yet identified in MSWI-bottom ashes, it is clear that a high organic carbon content is correlated with high Cu leaching [2, 4]. Heating of the sample will volatilize and/or decompose organic matter. As a consequence Cu will not be able anymore, or at least to a lesser extent, to form organo-copper...
complexes, so that leaching decreases. Washing with organic complexants on the other hand increases leaching, thus allowing (partial) removal of the Cu fraction. This Cu will for sure not be released in a subsequent leaching step.

Carbonation seems to be one of the most promising techniques for a whole range of metals [5]. The carbonation process is the reaction of CO₂ from the air with hydroxides in the bottom ash, giving carbonates. This reaction is accompanied by a decrease of the material pH from 11-12 to 8-9. In several MSWI's bottom ash is left to mature for 6-12 weeks after quenching. After this natural maturation, leaching of several metals appears to be less important than from fresh bottom ash. It is believed that carbonation plays an important role during this maturation [6, 7, 8, 9].

Accelerated carbonation using the CO₂ from the stack gas of MSW-incinerators that contains around 10% CO₂, might be a realistic technique for the treatment of bottom ash. This could be achieved in different ways: the stack gas could be led in counter-current over a thin layer of bottom ash on a moving-belt or the gas could be blown through tubes in the bottom ash heaps [10].

2 Materials and methods

2.1 Bottom ash and leaching test

The bottom ash studied in this paper already underwent an on-site treatment after quenching. The material went through several wet-sieving steps to separate the light organic fraction and the fraction larger than 50 mm from the main stream, and send these back into the incinerator. The main stream again went through a wet sieving process to produce three fractions: 0-2 mm, 2-6 mm and 6-50 mm. Magnets removed ferrous material from the granulate fractions of 2-6 mm and 6-50 mm. The Eddy current technique was used to separate non-ferrous material from the 6-50 mm granulate fraction. The smallest fraction was separated in a sand fraction (0.1-2 mm) and a sludge fraction (0-0.1 mm). It is the sand fraction that is studied in this investigation because of its non-compliance with the Flemish environmental limit values, whereas the two granulate fractions comply in general with these limit values. After collection, the sand fraction was dried in an oven at 40°C for 6 days and was stored in a closed bucket so as to slow down transformation reactions.

Leaching of metals from the granular material was determined using the EN 12457-2 test and measuring the resulting liquid sample for its metal content using a VG PlasmaQuad PQ-2 Plus ICP-mass spectrometer. More details are provided elsewhere [11]. The samples used in the heating, extraction and carbonation tests originate from different batches, giving slightly different leachate concentrations. The concentrations of each batch is given in the specific paragraph.

2.2 Heating

50 grams of bottom ash was dried for 24 hours at 105°C. Then subsamples of 4 grams of dry matter (DM) were heated for 2 hours at different temperatures (220, 300, 400, 500, 600 and 700°C).
2.3 Extraction with a solution of organic complexants

Extraction tests were performed initially on the raw bottom ash (not sieved). Ferrous material was removed with a hand magnet and the bottom ash was dried and milled to particles smaller than 4 mm. Citric acid, \((\text{NH}_4)_2\text{-citrate}\), Na\(_2\)-EDTA, tartaric acid, oxalic acid and acetic acid were used in extracting solutions. The procedure was as follows: dry material is extracted for 1 hour with a 0.1 M solution of the complexing agent at \(L/S = 5\); the slurry is filtered over a membrane filter (0.45 \(\mu\)m) and the residue on the filter is washed with distilled water for 1 hour at \(L/S = 5\) in order to remove remaining complexing reagent; after filtration the residue is leached.

In a second investigation 0.2 M solutions of Na\(_3\)-citrate, \((\text{NH}_4)_2\text{-citrate}\) and Na\(_2\)-EDTA were used on the sand fraction of the bottom ash. The extraction was performed for 1 hour at \(L/S = 10\). After filtration, a second extraction was performed. The complexing agents were then removed from the residue by two short washing steps at \(L/S = 1\) each. After filtration, the residue was leached.

2.4 Carbonation

The carbonation tests were carried out in a Sanyo MCO-17AI chamber to control the \(\text{CO}_2\)-percentage and the temperature in the atmosphere. The tested \(\text{CO}_2\)-percentages were 10 and 20%, the tested temperatures were 30, 37 and 50°C. On the bottom of the chamber a water tub was placed to keep a constant atmospheric humidity for a given temperature. Bottom ash samples of about 25 g were spread out in Petri-dishes (\(\phi\) 150 mm), resulting in layers of 1-2 mm thickness. To some samples distilled water was added to vary the moisture content of the samples and the material was gently mixed. The different ash moisture contents obtained were 2.3, 6, 13, 25, 37 and 50% (w/w). Samples were removed from the chamber after 1h, 2h, 3h, 1d, 2d, 3d and 6d (in some cases 7 days) and subsequently tested. Besides using the carbonation chamber technique, samples were also put in an oven at 40°C with an initial material humidity of 6% in contact with air (\(\text{CO}_2\) percentage of 0.03%).

3 Results and discussion

3.1 Heating

The leaching results of heated bottom ash are shown in Table 2 for selected metals. After heating at 300°C leaching of Cu decreases significantly, while the other metals are almost unaffected. At 400°C Cu leaching is below the limit value of 0.5 mg Cu/kg. Between 500 and 600°C the leaching characteristics of Cu, Zn, Pb and Al change: more of these elements is leached. This is the temperature range where carbonates are transformed into oxides. This increases the pH of the leaching solution to a value of 12.4. At this high pH amphoteric metals (Pb, Zn, Al, and to a lesser extent Cu) form soluble hydroxide-complexes in the leachates, so that leaching increases. In the leachates of bottom ash treated at 600 and 700°C a white precipitation formed. After filtration and measuring
the metals in the new filtrate, it became clear that this precipitation consists of an Al-phase, with which Cu co-precipitates or on which it adsorbs.

Table 2: Leaching results (mg/kg DM) of thermally treated bottom ash fraction.

<table>
<thead>
<tr>
<th>pH</th>
<th>Cu</th>
<th>Cr</th>
<th>Zn</th>
<th>Pb</th>
<th>Fe</th>
<th>Al</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>limit value</td>
<td>0.5</td>
<td>0.5</td>
<td>2.8</td>
<td>1.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Untreated</td>
<td>10.6</td>
<td>6.48</td>
<td>0.42</td>
<td>0.09</td>
<td>0.02</td>
<td>0.3</td>
<td>29.2</td>
</tr>
<tr>
<td>105°C</td>
<td>10.4</td>
<td>7.94</td>
<td>0.34</td>
<td>0.41</td>
<td>0.12</td>
<td>&lt;0.1</td>
<td>275</td>
</tr>
<tr>
<td>220°C</td>
<td>10.2</td>
<td>8.42</td>
<td>0.24</td>
<td>0.15</td>
<td>0.02</td>
<td>&lt;0.1</td>
<td>496</td>
</tr>
<tr>
<td>300°C</td>
<td>9.9</td>
<td>0.94</td>
<td>0.19</td>
<td>0.13</td>
<td>0.02</td>
<td>&lt;0.1</td>
<td>620</td>
</tr>
<tr>
<td>400°C</td>
<td>9.7</td>
<td>0.08</td>
<td>0.25</td>
<td>0.14</td>
<td>0.01</td>
<td>&lt;0.1</td>
<td>449</td>
</tr>
<tr>
<td>500°C</td>
<td>9.8</td>
<td>0.03</td>
<td>0.56</td>
<td>0.14</td>
<td>0.02</td>
<td>&lt;0.1</td>
<td>459</td>
</tr>
<tr>
<td>600°C</td>
<td>12.4</td>
<td>0.15</td>
<td>0.37</td>
<td>2.42</td>
<td>6.02</td>
<td>&lt;0.1</td>
<td>57.4</td>
</tr>
<tr>
<td>600°C +</td>
<td>12.4</td>
<td>0.03</td>
<td>0.37</td>
<td>2.17</td>
<td>5.70</td>
<td>&lt;0.1</td>
<td>3.93</td>
</tr>
<tr>
<td>700°C</td>
<td>12.5</td>
<td>3.06</td>
<td>0.17</td>
<td>5.45</td>
<td>63.6</td>
<td>&lt;0.1</td>
<td>62.5</td>
</tr>
<tr>
<td>700°C +</td>
<td>12.5</td>
<td>0.25</td>
<td>0.18</td>
<td>5.24</td>
<td>59.1</td>
<td>&lt;0.1</td>
<td>4.74</td>
</tr>
</tbody>
</table>

+ white precipitation formed in the filtrated leachate; after 24 hours the leachate was again filtrated and metals were measured.

3.2 Extraction with a solution of organic complexants

Several solutions of organic complexants were used for extracting Cu from the raw bottom ash. The results are shown in Figure 1. Cu leaching from untreated raw bottom ash is 13.4 mg/kg. Citric acid, (NH₄)₂-citrate and Na₂-EDTA extract the most Cu. After two leaching steps, the limit value for Cu is almost attained with citric acid and (NH₄)₂-citrate (in both cases a Cu-concentration of 0.81 mg/kg in the leachate).

![Figure 1: Release of Cu during extraction (E) of raw bottom ash with different organic complexants and subsequent washing (W) steps. Release during two subsequent leaching steps is also shown (L1 and L2).](image)

When focusing on the sand fraction of the bottom ash, the best results are achieved with Na₃-citrate and (NH₄)₂-citrate: Cu leaching in the second leaching step is resp. 0.51 and 0.53 mg/kg (Figure 2). The concentration of Cu in a
The leachate of the untreated bottom ash sand fraction is 7.4 mg/kg. An extraction procedure consisting of one extraction step with a 1 M (NH₄)₂-citrate solution (L/S = 5 during 1 hour) followed by three washing steps (L/S = 5, during 1 hour each) results in a release of Cu during a subsequent leaching test of 0.36 mg/kg, below the limit value of 0.5 mg/kg.

Although this technique gives satisfying results in laboratory, it remains to be investigated if this can be applied in a practical installation. The amount of steps to be performed, the use of expensive reagents and the production of wastewater are obvious drawbacks.

![Figure 2](image)

**Figure 2:** Release of Cu during extraction, washing and leaching steps of the sand fraction of the bottom ash.

### 3.3 Carbonation

#### 3.3.1 Evolution of carbonate content of the material and of pH of the leachates during carbonation

After 6 days of storage the carbonate concentration was 41.4 g/kg DM. During storage this concentration increased slightly to 46.2 g/kg DM after four months. Figure 3a shows the carbonate concentration as a function of accelerated carbonation time for some selected process parameters. The carbonate concentration increases drastically within the first 6 hours. Afterwards the concentration increases slowly to about 70 g/kg DM where it stabilizes. Overall the carbonate concentration nearly doubles.

![Figure 3a](image)

**Figure 3a:** Carbonate concentration of samples as a function of (accelerated) carbonation time.

![Figure 3b](image)

**Figure 3b:** pH of leachates as a function of (accelerated) carbonation time.
The pH of the leachates for samples subjected to accelerated carbonation shows an important decrease from about 11.5 to 8.5-9 within the first 24 hours (Figure 3b) and then slowly decreases further to 8-8.5. The pH of a leachate from material that was in contact with normal air (0.03% CO₂) in an oven at 40°C and with a humidity of 6% is shown as a reference. Under these conditions a very slow decrease of pH is observed.

Both Figures 3a and 3b indicate that the accelerated carbonation reaction is relatively rapid and alters the material significantly within the first 24 hours.

3.3.2 Evolution of metal leaching during carbonation

Figure 4 gives an overview of the leaching results of Cu, Cr, Mo and Sb for samples subjected to accelerated carbonation with varying process parameters (CO₂ percentage, temperature, humidity). This paper will only focus on these elements because the corresponding limit values are exceeded. Leaching of other elements, as well as the influence of the process parameters themselves on leaching is discussed in detail elsewhere [11].

![Figure 4: Overall view on leaching results as a function of carbonation time.](image)

The overall influence of accelerated carbonation on Cu leaching is a significant decrease from about 3.3 mg/kg DM to between 1.0 and 2.0 mg/kg DM, which still exceeds the limit value. Leaching of Cr increases from 0.2 mg/kg DM to well above the limit value within 6 hours and then decreases again, in some cases to below the limit value. Leaching of Mo remains fairly constant during carbonation: it goes from 1.1 mg/kg DM to between 0.8 and 1.2 mg/kg DM, but the informal limit value is still significantly exceeded. Leaching of Sb
also exceeds the informal limit value and even increases with carbonation from 0.6 mg/kg DM to between 1.0 and 2.0 mg/kg DM.

3.3.3 Effect of carbonate formation and pH on metal leaching
Carbonation modifies hydroxide-containing bottom ash at pH 11.5 into carbonate-containing bottom ash at pH 8-9. To evaluate whether the pH decrease or the formation of carbonate causes the change of metal leaching, both uncarbonated and carbonated samples were subjected to leaching tests at different pH. The results are shown in Figure 5 for Cu, Cr, Mo and Sb. In the uncarbonated material, decreasing pH from 11.5 to 8-9 increases Cu, Mo, Cr and Sb leaching (at least down to pH 9 for Cr and pH 8 for Mo and Sb). In the carbonated sample, decreasing pH (slightly) decreases leaching of Cu, Mo and Sb, but increases Cr leaching. The influence of carbonate formation can be assessed by comparing leaching from uncarbonated and carbonated material at the same pH: carbonate formation decreases leaching of all four metals, except for Mo and Sb at pH>11.

Figure 4 showed that carbonation decreases Cu leaching. The results in Figure 5 indicate that the effect on Cu leaching of the pH decrease, increasing Cu leaching in the uncarbonated sample and decreasing Cu leaching only slightly in the carbonated sample, is smaller than the effect of carbonate formation, which decreases Cu leaching significantly both at pH 8-9 and 11.5. Dissolved Cu behaves indeed as a cation, which can precipitate with carbonate. The effect of carbonation on Cr leaching was unclear in Figure 4. Figure 5 shows that the pH decrease increases Cr leaching both for uncarbonated and carbonated material whereas there is almost no effect on Cr leaching of carbonate formation both at pH 8-9 and 11.5. Figure 4 showed that carbonation does not affect Mo leaching, but increases Sb leaching. Figure 5 shows that the pH decrease and carbonate formation have a complex effect on leaching of these two metals: the pH decrease increases leaching from an uncarbonated sample, but decreases leaching from a carbonated sample; the carbonate formation increases leaching at pH 11.5, but decreases leaching at pH 8-9. Cr, Mo and Sb behave as oxyanions in alkaline conditions, forming chromate, molybdate and antimonate. Their leaching behaviour is well described for uncarbonated bottom ash [12]. At high pH solubility of Cr is controlled by BaCrO₄, and the solubilities of Mo and Sb are controlled by oxyanion substitution of sulphate in ettringite, Ca₆Al₂(SO₄)₃(OH)₁₂ · 26H₂O. When pH decreases, ettringite dissolves and sulphate, Mo and Sb ions come into solution. Sulphate then precipitates with Ba, dissolving Cr as a result. In acid conditions oxyanions undergo sorption to amorphous iron and aluminium oxides. Leaching of oxyanions from carbonated bottom ash is less well understood. At high pH, oxyanion leaching can be understood as follows: the carbonate-ion competes with the oxyanions in precipitation or sorption reactions, resulting in a higher Mo and Sb leaching at pH 11.5 from carbonated ash than from uncarbonated ash. At lower pH, however, one expects a more limited increase of Mo and Sb leaching, because now mainly bicarbonate is present which does not form insoluble compounds. Instead a small decrease of Mo and Sb leaching is noticed.
Figure 5: Leaching as a function of pH from an uncarbonated and a carbonated sample.

4 Conclusions

In order to reuse MSWI-bottom ash as granular construction material in Flanders, treatment is necessary to lower the Cu-leaching. Limit values are exceeded also for Ba, Mo and Sb, but these are to date only informal.

Three treatment options were investigated. Heating of the bottom ash to 400°C decreased Cu leaching to well below the limit value. Extraction of Cu with complexing agents such as citric acid and (NH₄)₂-citrate decreased leaching of Cu to around or just below the limit value. Carbonation decreases leaching of Cu and other metals but the limit value for Cu is not attained. Although heating and extraction give better results in the laboratory than carbonation, these techniques have obvious drawbacks. Maintaining the waste in the grate furnace at a higher temperature or during a longer residence time to achieve better burn-out of the residues, decreases resp. the life time of the grate or the capacity of the installation. Introducing a second heating step after the initial incineration, involves huge energy costs. Extraction requires several subsequent treatment steps, input of expensive organic solvents and produces wastewater that has to be treated. Accelerated carbonation on the other hand can be performed using the stack gas of the incinerator containing 10% CO₂, thereby lowering the emission of the greenhouse gas. The carbonation technique also has positive effects on several other metals besides Cu. More research is however needed to optimize the accelerated carbonation treatment.

References


