Investigating washing treatment to minimize leaching of chlorides and heavy metals from MSWI bottom ash

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Abstract

Bottom ash residues are one of the major products of Municipal Solid Waste Incineration (MSWI). The application of these residues in building materials is undermined by high content of heavy metals (Pb, Zn, Cu, Mn, Sb, Mo, Cr, Ni and Cd), chlorides and sulphates. Bottom Ash (BA) 0-4 mm was investigated for the distribution pattern of these constituents. Fractionation and washing treatment were applied to bring the emission of these contaminants under the limit established by Soil Quality Decree. Two steps washing treatment was investigated to remove soluble contaminants and to liberate fine particles ($\leq 0.125$ mm) rich in heavy metals and chlorides from BA fractions. Different washing parameters were investigated such as washing time, liquid to solid (L/S) ratio and mass of liberated fine particles for the optimization of the treatment. BA was washed twice with the L/S=3 for the duration of 60 min in order to remove soluble chlorides and concentrate heavy metals in the fine particles liberated during washing.
1 Introduction

In the Netherlands, the waste management strategy prioritizes the prevention and recycling of waste materials, which is followed by waste incineration and the least favorable option of landfilling. Due to the land scarcity and stringent state regulations, the number of the operational landfills in the Netherlands decreased by two-thirds over the last two decades. Nevertheless, a significant amount of waste cannot be recycled and reused, due to which incineration offers an effective alternative. In 2014 alone, 7601 kilotons waste materials was burnt in the 13 existing facilities of waste incineration in the Netherlands [1]. More than half of this waste originated from the municipal and household waste. Incineration of the waste reduces the initial volume by 90% [2] in addition to the recovery of energy in the form of electricity and heat [3]. Large amounts of Municipal Solid Waste Incineration (MSWI) by-products are produced during this process [4]. The main by-product is Bottom Ash (BA), and fly ashes in terms of generated volumes. BA residues are generating increased interest from the scientific community because of their amounts and challenges faced in their end disposal. Currently, these residues are used in a number of applications such as road construction [5] and acoustic barriers [6]. However, utilization of the BA as a secondary raw material in concrete faces challenges due to the environmental impact of heavy metals and ability of the chlorides to accelerate the corrosion mechanism of the steel in reinforced concrete [7].

BA is a highly inhomogeneous by-product of the incineration process and mainly consist of ceramics, metals, unburnt organics, slag and glass [8]. Speciation of mineralogical phases and chemical forms is a challenging task because of their ever changing nature and the complexity of the system. The composition of the BA residues can vary greatly due to seasonal changes in the generated waste in a particular area. To make these residues environmentally safe, different strategies to remove heavy metals and chlorides are used which include thermal treatment, stabilization and washing [9]. Many researchers employed washing with water to extract the soluble salts containing chlorides, sulfates and heavy metals [10–12]. Furthermore, enhanced leaching of these heavy metals from BA under the influence of acidic and alkaline media is also employed [13]. Tang et al. [14] have reported the use of different mineral acids (nitric, sulfuric and hydrochloric acid) for the extraction of heavy metals from MSWI incineration residues. However, the application of acidic and alkaline reagents can produce high amounts of waste water which needs to be treated afterwards. So, the application of plain water for the removal of these contaminants is usually a preferred option.

In this study BA (0 – 4 mm) was characterized in terms of its chemical composition. Preliminary investigations on this BA regarding the washing and distribution of contaminants with respect to particle size is reported by Florea et al. [15, 16]. Based on these results three different fractions, large (1 – 4 mm), medium (0.125 – 1 mm) and small (≤ 0.125 mm) were obtained from the complete BA fraction and investigated for the distribution of heavy metals (Pb, Zn, Cu, Mn, Sb, Mo, Cr, Ni and Cd) and chloride content. In order to bring the content of heavy metals and chlorides under the acceptable limit established by Soil Quality Decree [17], a two steps washing treatment was designed. During the washing treatment, soluble salts were extracted and fine particles were removed from the large and medium fractions. These fine particles were found to be rich in heavy metals and chlorides. In addition to that, the main objective of this study was to use a minimum amount of water for the cleaning of residues. Furthermore, the influence of different washing parameters, such as washing duration, liquid to solid ratio and liberation of fine particles during washing was investigated for the extraction of these components.

2 Materials and methods

The BA 0–4 mm used in this study was provided by Heros Sluiskil B.V. located in the Netherlands. BA is produced by the incineration of the municipal solid waste at the temperature of 800-900 °C, which is then either treated for application in building materials or landfilled. The BA fraction below 4 mm was collected for this investigation as this fraction is considered to be the most contaminated with respect to rest of BA [18].
2.1 Physical characteristics of BA

40 kg of initial material was sieved into three different fractions and named as large (1 – 4 mm), medium (0.125 – 1 mm) and small (≤ 0.125 mm) fraction with respect to their particle size distribution (PSD). Fig. 1a represents the distribution of the original BA in different categories. The small fraction accounted for 4% of the total material and its PSD is provided in Fig. 1b.

![Fractionation of initial BA into three fractions named as small (≤ 0.125 mm), medium (0.125 – 1 mm) and large (1 – 4 mm) fractions.](image)

In order to investigate a treatment for the removal of heavy metals and chlorides these fractions were studied for their physical and elemental composition. Table 1 provides the moisture content and Loss on Ignition (LOI) measured at 1000 °C for all fractions. The smallest fraction of BA contained the highest amount of moisture and has shown the highest LOI compared to the medium and large fractions.

<table>
<thead>
<tr>
<th>BA Fractions</th>
<th>Moisture Content (wt-%)</th>
<th>LOI 1000 °C (wt-%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small (≤ 0.125 mm)</td>
<td>15.8</td>
<td>27.5</td>
</tr>
<tr>
<td>Medium (0.125 – 1 mm)</td>
<td>14</td>
<td>24.2</td>
</tr>
<tr>
<td>Large (1 – 4 mm)</td>
<td>13</td>
<td>18.5</td>
</tr>
</tbody>
</table>

2.2 Chemical analysis

The chemical composition of the BA fractions was determined by X-ray fluorescence spectroscopy (PANalytical Epsilon 3 range). Table 2 gives the oxide composition of the BA fractions. The major oxides present in the BA fractions were Si, Ca, Fe and Al. The content of the SiO₂ decreased with the reduction in the particle size of the BA fraction and the inverse is true for the CaO and Fe₂O₃ content. Furthermore, most of the heavy metals have shown a tendency to accumulate in the smallest fraction. These heavy metals comprise Zn, Cu, Ni, Cr, Mn, Pb, Ti, Sb and Mo.

![Chemical composition (wt-%) of the BA fractions, large (1 – 4 mm), medium (0.125 – 1 mm) and small (≤ 0.125 mm) in the form of oxides. R.O.(Remaining Oxides) and LOI 1000 °C.](image)
2.3 Characteristics of leachates from BA

The high content of the heavy metals and chlorides in the BA fractions restricts their application as non-shaped materials in the construction industry. The maximum emission values provided by the Soil Quality Decree [17] given in Table 3. In order to assess leachability of heavy metals from the BA fractions, a rigorous washing procedure was applied to the incineration residue. All fractions were washed with distilled water with liquid to solid ratio (L/S) of 12 for the duration of 72 h followed by filtration. These leachates were analyzed with Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES).

Table 3. Emission limit for the heavy metals established by Dutch Legislation (Soil Quality Decree) and maximum leachable amount of heavy metals obtained from complete BA fraction (0 – 4 mm), large (1 – 4 mm), medium (0.125 – 1 mm) and small (≤0.125 mm) fractions.

<table>
<thead>
<tr>
<th>Contaminants</th>
<th>1 Non-Shaped Building materials [mg/Kg d.m.]</th>
<th>2 0-4 mm BA [mg/Kg d.m.]</th>
<th>3 Large fraction [mg/Kg of d.m.]</th>
<th>4 Medium fraction [mg/Kg of d.m.]</th>
<th>5 Small fraction [mg/Kg d.m.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>22</td>
<td>0.69</td>
<td>0.724</td>
<td>0.663</td>
<td>0.821</td>
</tr>
<tr>
<td>Cr</td>
<td>0.63</td>
<td>0.12</td>
<td>0.414</td>
<td>0.651</td>
<td>1.786</td>
</tr>
<tr>
<td>Cu</td>
<td>0.9</td>
<td>14</td>
<td>1.954</td>
<td>2.558</td>
<td>9.643</td>
</tr>
<tr>
<td>Mo</td>
<td>1</td>
<td>1.1</td>
<td>1.011</td>
<td>1.023</td>
<td>2.024</td>
</tr>
<tr>
<td>Sb</td>
<td>0.32</td>
<td>0.22</td>
<td>0.724</td>
<td>0.663</td>
<td>0.821</td>
</tr>
<tr>
<td>As</td>
<td>0.9</td>
<td>&lt;0.05</td>
<td>0.057</td>
<td>0.058</td>
<td>0.060</td>
</tr>
<tr>
<td>Cd</td>
<td>0.04</td>
<td>&lt;0.001</td>
<td>&lt; L.D.</td>
<td>&lt; L.D.</td>
<td>&lt; L.D.</td>
</tr>
<tr>
<td>Co</td>
<td>0.54</td>
<td>&lt;0.030</td>
<td>0.034</td>
<td>0.035</td>
<td>0.036</td>
</tr>
<tr>
<td>Pb</td>
<td>2.3</td>
<td>&lt;0.1</td>
<td>0.115</td>
<td>0.116</td>
<td>0.119</td>
</tr>
<tr>
<td>Ni</td>
<td>0.44</td>
<td>0.24</td>
<td>0.057</td>
<td>0.058</td>
<td>0.077</td>
</tr>
<tr>
<td>Se</td>
<td>0.15</td>
<td>&lt;0.007</td>
<td>&lt; L.D.</td>
<td>&lt; L.D.</td>
<td>&lt; L.D.</td>
</tr>
<tr>
<td>Sn</td>
<td>0.4</td>
<td>&lt;0.02</td>
<td>&lt; L.D.</td>
<td>&lt; L.D.</td>
<td>&lt; L.D.</td>
</tr>
<tr>
<td>V</td>
<td>1.8</td>
<td>&lt;0.1</td>
<td>&lt; L.D.</td>
<td>&lt; L.D.</td>
<td>&lt; L.D.</td>
</tr>
<tr>
<td>Zn</td>
<td>4.5</td>
<td>0.48</td>
<td>&lt; L.D.</td>
<td>&lt; L.D.</td>
<td>&lt; L.D.</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>616</td>
<td>6200</td>
<td>6354</td>
<td>7516</td>
<td>11013</td>
</tr>
<tr>
<td>Br⁻</td>
<td>20</td>
<td>-</td>
<td>9.3</td>
<td>11.4</td>
<td>21.4</td>
</tr>
<tr>
<td>F⁻</td>
<td>55</td>
<td>2.4</td>
<td>3.2</td>
<td>3.9</td>
<td>6.5</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>1730</td>
<td>1700</td>
<td>3120</td>
<td>2558</td>
<td>9404</td>
</tr>
</tbody>
</table>

1 Leaching limit imposed by the Soil Quality Decree for the non-shaped building materials
2 Column leaching test was performed in accordance with NEN-EN 12457-4
3 Amount of the elements in the leachates extracted by rigorous washing with L/S 12 for 72 h.
< L.D. Concentration of the element was below the detection limit.
d.m. dry mass

The small fraction of the BA was found to be rich in most of the contaminants such as Cr, Cu, Mo, Cl, and Sb, which is in accordance with the results obtained by XRF analysis. In the case of Sb and sulphates, a higher amounts were extracted when all three fractions were subjected to washing treatment with L/S=12 for 72 h as compared to the column leaching test in accordance with NEN-EN 12457-4. This indicates the washing treatment applied for the assessment of leachability of contaminants from BA was more aggressive than the column leaching proposed by the Soil Quality Decree [17]. Due to the higher concentration of the contaminants and lower mass of small fraction with respect to initial mass of complete BA, washing treatment was not applied on this fraction.
2.4 Washing treatment

The large and medium fractions of the BA were investigated under different washing conditions. The washing of these fractions was carried out with the different L/S ratios and durations. Reciprocating shaker was used for the washing of samples containing the BA fraction and distilled water. Subsequently, this mixture was wet sieved for the liberation of fine particles (≤ 0.125 mm) from the main fraction. The resulting mixture of water and fines was filtered and the contents of liberated fines were determined. The contents of soluble chlorides in water was measured argentometrically. The motivation of applying this two steps washing treatment was to extract contaminants and fine particles from the large and medium fractions. A higher content of the contaminants is expected to concentrate in these liberated fines and their removal from the main fraction would result in a relatively cleaner fraction of BA.

3 Results and discussion

Due to the presence of highly soluble chlorides in the large and medium fraction, the washing treatment was optimized on the basis of chlorides removed from the incineration ashes. The leachability of chlorides under different washing parameters was investigated. Different chloride-containing phases such as Friedel’s salt were identified in inhomogeneous matrix of MSWI BA from different sources [19]. However, this study only focuses on the removal of soluble chlorides and heavy metals.

3.1 Effect of washing time on leaching of chlorides

In order to find out the optimum washing time for the removal of soluble chlorides from both fractions of the BA different washing times were studied at a constant L/S ratio of 10. The large and medium fraction were washed for 3 min, 60 min and 72 h. The amount of soluble chlorides released during these washing treatment is provided in Fig. 3. No significant difference in the leachability of the chlorides was noted under different washing durations. The contents of chlorides released during the washing treatment of 3 min and 72 h is very close. A very small difference in the amount of chlorides can be attributed to the inhomogeneous nature of the incineration residues. Most of the chlorides found in nature have very high solubility in the water, with the exception of silver chloride.

![Figure 3. Amount of chlorides released under the influence of different washing duration of 3 min, 60 min and 72 h at constant L/S 10 from the medium (0.125 – 1 mm) and large (1 – 4mm) fractions of BA.](image)

Due to the very high solubility of the chlorides found in the large and medium fraction, the presence of alkali and alkaline earth metal chlorides can be speculated. Furthermore, the extraction of chlorides in 3 min indicates that the majority of these soluble chlorides are present on the surface of these ash residue as reported by Schollbach et al., [20].
3.2 Influence of L/S on leachability of chlorides

The water amount required for the treatment is a crucial parameter because large volume of contaminated water render washing economically unfeasible. Several L/S ratios were studied to find out the optimum ratio of water for chlorides removal. Large and medium fractions of BA were washed with the L/S of 1, 2, 3, 5, and 10. The washing duration was kept at 3 and 60 minutes as it was found that higher washing time does not have any effect on the leachability of the soluble chlorides.

![Figure 4. Amount of soluble chlorides (mg/kg of BA) removed with washing treatments under the influence of different L/S ratios and a washing duration of 3 and 60 minutes. a) Large fraction (1 – 4 mm) b) Medium fraction (0.125 – 1 mm).](image)

The chloride leachability increased with the increase in the amount of water (Fig. 4) used for the treatment. The maximum amounts of the chlorides were extracted by using L/S ratio of 10. However, even the application of 10 times more water with respect to incineration ash was not adequate to completely remove the soluble chlorides. Relatively, a small increase was observed in the extracted amount of chloride above the L/S ratio of 3. Due to the high solubility of the majority of chlorides, the total amount of soluble chlorides present in these incineration ashes is not sufficient to saturate the washing solution in terms of chlorides. However, this leaching behavior of the soluble chlorides from incineration ashes is widely reported in the literature [10, 12, 21, 22]. The leaching mechanism of the soluble chlorides from incineration ashes remains uninvestigated.

![Figure 5. Soluble chloride content of the treated and untreated large (1 – 4 mm) and medium (0.125 – 1 mm) fraction of the BA. Solid line represents the permissible limit established by Soil Quality Decree for the chlorides content.](image)
The washing treatment with L/S 3 was repeated twice on the same sample to successfully bring chloride emission from both fractions under the limit. More than 95% of soluble chlorides were extracted from both fractions by applying this washing treatment. A comparison of the soluble chloride content of treated and untreated fractions of BA is shown in the Fig. 5. The total amount of soluble chlorides of the BA fractions was determined by applying number of washing cycles on the same residues.

3.3 Liberation of fines during washing treatment

Fine particles (≤ 0.125 mm) were liberated from the BA fractions to remove heavy metals from the ash residues. Fig. 6 provides the amount of fines removed from the large and medium fraction during the washing treatment.

![Figure 6. Amount of fine particles (≤ 0.125 mm) liberated from large (1 – 4 mm) and medium (0.125 – 1 mm) fraction of BA with different L/S ratio used for washing treatment. MF and LF represent the fine particles liberated from the large and medium fractions, respectively.](image)

The amount of the fines liberated increased significantly with increase in washing time because of more energy was applied in the form of shaking consequently leading to the liberation of fine particles. This small amount of liberated material was most contaminated because of the presence of heavy metals.

The medium fraction liberated a significant amount of fines under the influence of the shaking in absence of water followed by the large fraction. The washing with water increased the amount of fines liberated from both fractions. A gradual decrease in the amount of liberated fines was observed when L/S was increased above 2. Chemical composition (Table 4) of these fines have shown similarity with the small fraction of BA. High content of the contaminants were removed in the form of liberated fines. Particle size dependency for the distribution of the chlorides was reported by Yang et al., [23]. In this study, this dependency was found for the heavy metals as well.

<table>
<thead>
<tr>
<th>Element</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>SO₃</th>
<th>TiO₂</th>
<th>MgO</th>
<th>P₂O₅</th>
<th>K₂O</th>
<th>ZnO</th>
<th>Cl</th>
<th>R.O.</th>
<th>Sum</th>
</tr>
</thead>
<tbody>
<tr>
<td>LF</td>
<td>46.6</td>
<td>14.3</td>
<td>13.5</td>
<td>8.6</td>
<td>6.3</td>
<td>2.3</td>
<td>1.8</td>
<td>1.9</td>
<td>1.1</td>
<td>1.5</td>
<td>0.2</td>
<td>2.0</td>
<td>100</td>
</tr>
<tr>
<td>MF</td>
<td>49.7</td>
<td>12.5</td>
<td>13.2</td>
<td>8.1</td>
<td>6.3</td>
<td>2.4</td>
<td>1.6</td>
<td>1.7</td>
<td>1.1</td>
<td>1.6</td>
<td>0.2</td>
<td>2.1</td>
<td>100</td>
</tr>
</tbody>
</table>
3.4 Effect of washing on heavy metals

By fractionating BA into three fractions most of the heavy metals were concentrated into the small fraction. This effect was most significant in case of Cu. The complete fraction of the BA (0 – 4 mm) leached of 14 mg Cu/kg of BA, when subjected to the column leaching test in accordance with NEN-EN 12457-4. By removing the small fraction from the complete BA more than 68 % of the Cu was removed from the large and medium fraction of BA (Fig. 7a). The similar trend was observed for Cr, Mo and Sb.

Figure 7. a) Amount of Cu present in the complete fraction of BA and its distribution across the three different fractions. b) Comparison between the content of heavy metals in the treated large (1 – 4 mm) and Medium (1 – 0.125 mm) fraction of BA (washed with L/S=3, 60 min) with their permissible emission limit established by Soil Quality Decree.

A washing treatment was applied to the large and medium fraction of BA to remove heavy metals from these incineration residues. In these two fractions, Cr, Mo, Sb and Cu exceed the permissible emission limit. By applying the washing treatment, the contents of Cr and Mo were brought under the emission limit established by Soil Quality Decree [17]. However, complete removal of the soluble Cu and Sb from the large and medium fraction was not possible in this treatment due to higher contents of these heavy metals in the complete BA (0 – 4 mm). Fig. 7b provides an overview of the permissible limit for the Cr, Cu, Mo and Sb emission and their content after the treatment. Further treatments are being investigated for the complete removal of heavy metals from these fractions of BA.

4 Conclusions

A physical and chemical characterization of large (1 – 4 mm), medium (0.125 – 1 mm) and small (≤ 0.125 mm) fraction of MSW1 bottom ash was performed. In order to remove chlorides and heavy metals, treatments comprising washing and fractionation of BA was applied.

- The distribution of contaminants with respect to the particle size of BA was investigated. It was observed that most of contaminants tend to concentrate in the smaller size particles. Thus, the sieving of the BA into three fractions was carried out to remove the small fraction which accounted for 4% of initial BA mass.
- A washing treatment was applied to liberate fine particles (≤ 125 µm) from the large and medium fraction of BA. These fine particles were found to be rich in chlorides and heavy metals and had a similar composition as the small fraction.
- Due to significantly higher content of chlorides in BA fractions, the washing treatment was optimized on the basis of leachability of soluble chlorides. It has been observed that a washing time above 3 minutes does not have any appreciable effect on chloride extraction, which indicates that the majority of chlorides are present on the outer surface of ash residues.
• The washing treatment with the L/S 3 for the duration of 60 minutes was repeated twice to bring the chlorides under 616 mg/kg of BA. Furthermore, the majority of heavy metals were removed with the exception of Cu and Sb. Significant amounts of copper and antimony were also extracted from BA by fractionation and the application of the washing treatment.

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References


