Executive Summary
Bottom ash (BA) is the residue produced in greatest amount from incineration of municipal solid wastes. Several countries allow reuse of BA for civil engineering applications; however, potential leaching of heavy metals from BA is one of the main constraints to this opportunity. Therefore, usually BA need to be processed (e.g. by inertization) before landfilling or reuse, in order to avoid pollution arising from heavy metals leaching (Sabbas et al., 2003; Reijnders, 2005, Ferraris et al., 2009). This requirement increases the costs of the entire combustion treatment process (Ferraris et al., 2009).

This paper presents the first results of a wider research activity which aims to investigate the characteristics of BA from two municipal Refuse Derived Fuel (RDF) gasification plants. For instance, both technical and environmental parameters were determined, including: grain size distribution, water content and major anions contents, elemental composition. Besides, leaching characteristics were also determined by means of the EN 12457-2 batch leaching test, the TS 14429 acid neutralization capacity (ANC) test and the Availability test (NEN 7371).

Data obtained from the analysis of chemical composition, EN 12457-2 batch leaching test and the percentage by weight of each particle size were used to predict a mean metals content of the raw bottom ash, by means of the Monte Carlo statistical method. A great number of hypothetical samples were generated considering 5% of uncertainty for each grain size class fraction by weight; the minimum and maximum concentration of each metal was determined for every sample. The lowest and the highest concentration values obtained for each element represent the limits of the expected ranges.

Results from EN-12457 batch leaching test were compared with the Italian law limits for either landfilling (as inert or not hazardous waste) or reuse. One of the two analyzed BA samples (named A) showed levels of heavy metals always below the Italian regulatory limits for reuse (except for Cu in the fraction >1mm), the other BA sample (named B) displayed concentrations of Pb (only for the grain size in the range 1÷2 mm), Cu, Cr and Ni above the limits for reuse and of Pb, Cu and Cr above the limits for inert waste landfill. The different behaviour of these residues was attributed to the characteristics of the RDFs delivered to the gasification plants; also the wear of the furnace refractories might have exerted some influence (Ecke et al., 2001, Kwak et al., 2006).

The vitrified structure of the tested residues, as a consequence of the high operating temperature of the gasification plants, reduced availability of metals for leaching. The formation of a glassy material decreases the surface area and reduces the mobility of metals, which are entrapped within the amorphous matrix (Ferraris et al., 2009).

Results from ANC test confirmed the glassy structure of the residues: a sharped decrease of pH with the addition of acid indicated that the tested BA were made up of a larger proportion of glassy materials with hydrophobic characteristics (Johnson et al., 1995).
Tests results demonstrated that some kind of pre-treatment could be necessary for the residues to fulfill heavy metals leaching law limits. The utilization of size separation as pre-treatment was also discussed.

**Introduction**

Incineration of Municipal Solid Waste (MSW) offers many advantages as compared to the other waste treatment alternatives: above all, volume reduction is of much interest since can reach up to 90% of feed waste. Nevertheless, it must be taken into account production of residues, such as Bottom Ash (BA) and Fly Ash (FA), in amount of about 30% by weight of the incinerated waste. Several countries allow the use of BA for civil engineering applications, as road construction, embankment, pavement, aggregate, filler for concrete, asphalt, or low-cost tiles (Ferraris et al., 2009). However, leaching of heavy metals is one of the main constraints to these reuse options. The use of vitrified bottom ash is expected to eliminate the above mentioned drawbacks: recent works demonstrated that heavy metals are immobilized within the vitrified matrix. For instance, melting of MSW at high temperature reduces the availability of Cr, Cu, Zn and Pb for leaching as formation of glassy material decreases the surface area and entraps the metals within the amorphous glassy matrix (Ecke et al., 2009). However, vitrification of BA is a very energy-consuming process due to the high temperatures required; therefore, related costs can be significant and impair its advantages.

The vitrification treatment can be avoided by adopting modern incineration plants which operate at temperatures above 1600°C and use waste as a fuel. Different studies demonstrated that BA arising from standard MSW combustion plants exhibit chemical and morphological characteristics depending upon their particle size distribution (Chimenos et al., 1998, Chimenos et al., 2003). For instance, bulk composition of samples collected from many facilities indicated that the finest particle fraction has a relative high content of heavy metals (Chimenos et al., 1998, Stagemann et al., 1995, Chimenos et al. 2003).

The present study shows the results obtained through an experimental study carried out to investigate the characteristics of BA from two municipal RDF gasification plants. Much concern was devoted to evaluate behaviour of the different particle size fractions with the aim of assessing suitability to be reused.

**Materials and Methods**

Characterization was carried out on two representative samples of BA (referred to as sample A and sample B, respectively) collected from two RDF fixed-bed gasification facilities. These plants are operated at atmospheric pressure, with a maximum temperature of about 2000°C, as asserted by the operators.

Sampling was performed through quartering and additional quartering steps so as to ensure collection of homogeneous and representative samples to undergo the laboratory analyses. The general physical and chemical characterization of bottom ash involved determination of both technical and environmental parameters, including grain size distribution, water and major anions contents, elemental composition.

The size distribution curves were built from the weight fraction of the samples passing through stainless steel sieves of decreasing size. The chemical composition of each sieved fraction of bottom ash was obtained after pre-digestion with HNO₃, according to the APHA 3030H procedure. The samples were then analysed with Atomic Absorption Spectrophotometry (AAS) or Graphite Furnace (GF) to determine concentrations of the following metals: Pb, Cu, Zn, Cd, Cr, Ni, Mn, Fe, As. All measurements were conducted in triplicate. According to the Italian law in force, the EN 12457-2 batch leaching test was chosen to evaluate the different heavy metals leaching behaviour of each grain size class. The test was performed on the following sieved fractions: 0-0.105, 0.105-0.25, 0.25-0.5, 0.5-1, 1-2 and >2mm (>1 mm for sample A). These batch tests were performed under the following operative conditions: a liquid/solid ratio
of 10 by using deionised water, continuous stirring, room temperature, duration of 24h. Then, the pH was recorded and the suspensions filtered with 0.45µm membrane filters. A part of the filtrates was acidified with concentrated HNO₃ for the analysis of metals with AAS or GF, while the other part of the filtrates was left untreated and used to determine anion concentrations by ion chromatography (IC). All tests were conducted at least in double.

The Acid Neutralization Capacity (ANC) test was performed on both BA samples and on three different grain size classes for sample B. For this purpose, 15g of material was dried at 40°C and then reduced dimensionally by ball mill to less than 1mm. It was then put into contact with 150 ml of nitric acid solutions, at increasing acid concentrations, and shacked for 48 h, according to the TS 14429. The acid addition schedule was based on the buffering capacity of the material, which was estimated through a 48 h preliminary test. For every sample, 15 sub-samples with different acid concentration solutions were considered. After 48 h, the pH values were measured in the leachates and then plotted against the relative amount of acid added.

The Availability Test was also carried out, according to the NEN 7371:2004 procedure, in order to estimate the fraction which can be long-term leached under natural conditions. The test consists of a pH-controlled extraction procedure which works at subsequent pH of 7 and 4. The availability test was performed on the following samples: 40°C dried, <0.105mm ball-milled samples and the same materials considered for the ANC trials.

Results and Discussion

The particle size distribution was determined for both samples A and B. The results obtained, shown in Figure 1, highlight that for both samples dimensions fall within the range between sand and gravel.

Chemical compositions determined on three grain size fractions of sample B are reported in Figure 2. It can be observed that a correlation between metals content and grain size is lacking. For Cr and Cu only, concentrations are higher in the fraction below 1mm; by contrast, concentrations of Fe, Pb, Zn, Ni and Cd are almost constant, while Mn is more abundant in the coarse fraction. Error bars were also included to indicate the standard deviation of experimental data.

These results are in contrast with the data commonly observed on BA from standard combustion plants: in these cases, metal contents of each BA particle size fraction differ and higher concentrations are usually found in the finest fractions (Chimentos et al., 1998; Chimentos et al., 2003; Stegemann et al., 1995).

Data obtained from the chemical composition analysis and the percentage by weight of each particle size class were used to predict a mean metal content in the BA, by means of a Monte Carlo statistical method. A great number of hypothetical samples were generated considering 5% of uncertainty for each grain size classes (>2mm, 1-2 mm and <1mm); for each sample, minimum and
maximum concentration of each metal were determined. The lowest and the highest concentration values obtained for each element represent the limits of the expected ranges reported in Table 1.

![Graph showing concentration of metals for each particle fraction (sample B)](image)

**Figure 2: Concentration of metals for each particle fraction (sample B)**

<table>
<thead>
<tr>
<th>Bulk composition</th>
<th>Element</th>
<th>mg/kg</th>
<th>Element</th>
<th>mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pb</td>
<td>32÷52</td>
<td>Cr</td>
<td>1089÷1191</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>1445÷1051</td>
<td>Ni</td>
<td>27÷31</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>31÷40</td>
<td>Mn</td>
<td>550÷585</td>
</tr>
<tr>
<td></td>
<td>Cd</td>
<td>0.8÷1.8</td>
<td>Fe</td>
<td>5054÷5941</td>
</tr>
</tbody>
</table>

**Table 1: Calculated concentrations of metals for the total bottom ash (sample B)**

Behaviour of each particle size fraction was then evaluated in terms of leaching characteristics. Figure 4 shows pH value and metal and anion concentrations determined in the leachate. The value obtained for each parameter was compared with the limit posed by the Italian law in force for
landfilling or reuse. Error bars were included to indicate standard deviation of the experimental data.

Figure 4 shows that for both the samples pH values did not differ appreciably with the grain size. For sample B only, there is a one-point reduction of pH with the decrease of grain size. For sample A, Pb was always found below the instrumental detection limit of 5 µg/l. For sample B, the 50 µg/l limit for disposal in inert waste landfill or reuse was not accomplished only for the 1-2 mm fraction; for the other portions, Pb concentrations were always below 10 µg/l.

Copper was found to exhibit a very different behaviour in the two considered samples. In sample A, Cu concentration showed a decreasing trend from the coarse to the finest fraction: this would allow BA to be disposed in a sanitary landfill for inert waste. Fraction above 1mm exceeded the reuse limits. In sample B, Cu concentration in the leachate was always higher and exceeded the limits for disposal in inert waste sanitary landfill. The main contribution to leaching was attributed to the fractions between 1 and 0.105mm, which represented about 26% of total BA. It is interesting to note that the different concentrations of Cu are not so relevant in the results from the chemical composition, especially for the classes below 1 and between 1 and 2mm (Figure 2). Furthermore, the results from the Availability Test for Cu shown in Figure 3, compared with the results of Figure 2, confirms that its leaching behaviour is directly related to the grain size distribution. For instance, Cu percentage available for leaching is about 10% and less than 3.5% of the total Cu for the fractions below 1mm and for the 1:2 mm fraction, respectively.

Sample A exhibited Cr content always below the limit for reuse and inert waste landfilling, with a slight increase in the size fraction above 1mm. Sample B showed concentrations always above the same limits, except for the finest fraction.

Concentration of Ni in leachate from sample A was always below 5 µg/l, with quite a constant trend among the different grain size classes. Sample B showed higher concentrations, particularly in the fractions between 0.5 and 0.105mm. For Fe and Mn, the higher concentrations were associated to the fractions between 1 and 0.105mm. The law in force in Italy does not pose any limit to these metals. Concentrations of chlorides, nitrates and sulphates increased with material size decreasing; however, for all these elements, the detected values were very far below the law limit (at least ten times lower).

For both samples and all grain size classes Zn, As and Cd were always below the detection limits of 0.1 mg/l, 25 µg/l and 1 µg/l, respectively.

As well as for the chemical composition, the statistical Monte Carlo method was applied to find out the probable range of concentrations of each element in the leachate from total raw BA samples.
Figure 4: Results of EN 12457-2 leaching test for each grain size class and Italian law limits for not hazardous and inert landfilling (Ministerial Order 03/08/05) and reuse (Ministerial Order 05/02/98)
The results obtained are listed in Table 2. The Italian law limits for reuse and not hazardous and inert waste landfilling are also reported.

Table 2: Calculated concentrations of metals and anions in leachates for total raw BA samples and Italian law limits for not hazardous and inert landfilling (Ministerial Order 03/08/05) and reuse (Ministerial Order 05/02/98)

<table>
<thead>
<tr>
<th>Leaching Test</th>
<th>pH</th>
<th>Mn (µg/l)</th>
<th>Cu (µg/l)</th>
<th>Pb (µg/l)</th>
<th>Zn (µg/l)</th>
<th>As (µg/l)</th>
<th>Cd (µg/l)</th>
<th>Cr (µg/l)</th>
<th>Ni (µg/l)</th>
<th>Fe (µg/l)</th>
<th>Clorides (mg/l)</th>
<th>Nitrates (mg/l)</th>
<th>Sulphates (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td></td>
<td>9.3÷9.8</td>
<td>180÷197</td>
<td>18÷21</td>
<td>&lt;5</td>
<td>&lt;100</td>
<td>&lt;25</td>
<td>&lt;1</td>
<td>11÷13</td>
<td>1.5÷2.5</td>
<td>44÷88</td>
<td>0.2÷0.3</td>
<td>0.02÷0.05</td>
</tr>
<tr>
<td>Sample B</td>
<td></td>
<td>9.3÷9.5</td>
<td>30÷40</td>
<td>542÷673</td>
<td>20÷40</td>
<td>&lt;100</td>
<td>&lt;25</td>
<td>&lt;1</td>
<td>61÷74</td>
<td>8÷12</td>
<td>249÷314</td>
<td>0.2÷0.4</td>
<td>0.02÷0.03</td>
</tr>
<tr>
<td>Not hazardous</td>
<td>-</td>
<td>-</td>
<td>5000</td>
<td>1000</td>
<td>5000</td>
<td>200</td>
<td>20</td>
<td>1000</td>
<td>1000</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Inert landfill</td>
<td>-</td>
<td>-</td>
<td>50</td>
<td>50</td>
<td>400</td>
<td>50</td>
<td>40</td>
<td>10</td>
<td>100</td>
<td>-</td>
<td>80</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>Reuse</td>
<td>5.5&lt;pH&lt;12</td>
<td>50</td>
<td>50</td>
<td>3000</td>
<td>50</td>
<td>50</td>
<td>10</td>
<td>100</td>
<td>-</td>
<td>100</td>
<td>50</td>
<td>250</td>
<td></td>
</tr>
</tbody>
</table>

The ANC test was carried out on both BA samples and on the classes <1mm, 1-2mm and >2mm for sample B only. The results shown in Figure 5 and 6 are representative of a typical glass fraction-rich materials. The very fast decrease of pH with the addition of acid indicates that the material is made up of a larger proportion of glassy materials with hydrophobic characteristics (Johnson et al., 1995).
Conclusion
The results of the present study showed a marked difference in behaviour and quality for the two considered residues. Since the two gasification plants are very similar, these differences could be attributed to the characteristics of the RDFs delivered, but also the wear of the furnace refractories might have exerted some influence (Ecke et al., 2001, Kwak et al., 2006).
Metals and anions concentrations in leachates from sample A (total raw BA) were always below the limits for reuse and inert waste landfilling.
For sample B the release of heavy metals appears to be a limitation for reuse, but also for landfilling as inert waste. Italian law limits for not hazardous waste landfilling were always widely fulfilled. For this residue, even if a correlation between metals content and grain size, but also between metals leaching and grain size is lacking, a size separation pre-treatment could be considered, especially for Cu and Ni, by which the fractions between 0.5 and 0.105mm resulted to be more contaminated. For Cr, this kind of treatment would have no effect on the leaching characteristic, which appear to be almost the same for each grain size, even if the finest fraction (<1mm) was found to be the richest in this element.
For the most contaminated fractions other kind of pre-treatments, like inertization or washing, could be assumed.
After investigations concerning the mechanical behaviour of the residues (e.g. Proctor test, Triaxial test, Direct shear test, etc.) more specific hypothesis about reuse opportunities for civil engineering applications (road construction, embankment, pavement, aggregate, filler for concrete, asphalt, or low-cost tiles) may be evaluated.
Acknowledgments
Authors would like to thank Lucia Pifferi of the University of Florence, and the staff of Quadrifoglio Spa laboratory: Gianni Donnini, Tania Cianchi and Simone Nanni.

References