Production of artificial aggregates from ceramic processing of municipal incinerator fly ash

G. De Casa, T. Mangialardi & L. Piga
Facoltà di Ingegneria, Università di Roma “La Sapienza”, Italy

Abstract

Municipal Solid Waste (MSW) incinerator fly ash was processed to form new ceramic materials using conventional ceramic processing technology (dry milling, powder compaction and sintering). A preliminary washing step of raw fly ash with water was used to improve the chemical composition of this material. The effects of particle size distribution, powder compaction pressure, and sintering temperature and time on the physical and mechanical properties and leaching behaviour of sintered products were investigated. It was found that a washing step followed by a milling step is able to transform raw fly ash into a material with consistent chemical and physical characteristics for its thermal processing. With such a pretreatment it is possible to reduce the power input of the sintering process (temperature reduction from 1210 to 1140°C) and to manufacture sintered products that are characterised by high density (2.65-2.80 g/cm³), high compressive strength (260-450 N/mm²), very low water absorption capacity (0.1-0.2%), and reduced heavy metals leachability. Such materials are able to meet the requirements for normal-weight aggregates for use in concrete.

Keywords: incinerator fly ash, washing step, ceramic processing, sintering, waste reuse, artificial aggregates, heavy metals, leaching behaviour.

1 Introduction

Although landfill remains the primary disposal method for Municipal Solid Waste (MSW), poor availability of new landfill sites combined with increasing MSW production and landfilling costs, and potential long-term adverse environmental effects of landfilling have hastened efforts in many industrialised countries to adopt incineration as a viable alternative for MSW management.
Among the mineral residues generated from MSW incineration, fly ash is regarded as a very toxic material owing to its high content of leachable heavy metals and, in some cases, to the presence of chlorinated organic compounds.

At present, landfilling is a common practice for MSW incinerator fly ash disposal, although a preliminary treatment of this material is needed to reduce its hazardous characteristics [1], [2]. Avoiding landfill disposal of such a waste by developing reuse applications is clearly the preferred option.

In recent years, thermal treatments such as melting and sintering have been proposed to convert MSW incinerator fly ash into glass- and ceramic-type materials, respectively [3], [4].

The melting technology generally involves the heating of fly ash at high temperatures (> 1300°C) to produce physical and chemical state changes. This technology appears to be too expensive and also needs to be improved in certain areas, e.g., reducing the rate of repairing refractory materials and improving control techniques to ensure stable operation of high-temperature melting [3].

Comparatively, the sintering technology appears to be less expensive but it requires several improvements, also in consideration of a number of adverse chemical characteristics exhibited by MSW incinerator fly ash (high concentrations of alkali metal chlorides and sulphates, and relatively low content of vitrifying oxides) [4], [5].

As reported in a previous work [5], the sintering process of MSW incinerator fly ash proves to be effective for manufacturing ceramic materials with good characteristics in terms of mechanical strength and chemical water-stability only if the raw fly ash is preliminarily subject to a washing treatment with water, which greatly improves the chemical composition of this material.

In the present study, a new pretreatment of raw MSW incinerator fly ash was investigated in order to reduce the power input of the sintering process and/or to improve the properties of the sintered products, in view of their utilisation as artificial aggregates in concrete formulations. This pretreatment consisted of a washing step of raw fly ash with water followed by a milling step of washed ash. The latter step was included bearing in mind that the particle size and the particle size distribution of powders are two very important factors in affecting the sintering process [6]. The effects of particle size distribution, powder compaction pressure, and firing time and temperature on the physical and mechanical properties, and leaching behaviour of the sintered products were studied.

2 Materials and methods

The MSW incinerator fly ash used in this study came from an Italian MSW incineration plant equipped with an electrostatic precipitator and a wet treatment unit for acid gas removal.

Grab samples of raw fly ash (UFA) were collected from the electrostatic precipitator at three time intervals on a daily basis over a one-week period, in order to obtain a representative ash sample to be used for all experiments.

An aliquot of this sample was subject to a four-stage washing treatment with deionised water (liquid-to-solid weight ratio = 12.5; mixing time = 30 min for
each washing step) using an agitation apparatus that was capable of rotating the extraction vessel in an end-over-end fashion at 30 rpm. After the washing treatment, the cumulative percentage weight loss of ash (LOS) was evaluated and taken as a measure of the content of water-soluble compounds in the raw fly ash.

Samples of raw or washed (WFA) fly ash were oven-dried overnight at 105°C and then analysed for their chemical composition and particle size distribution.

The chemical composition was determined by X-ray fluorescence, thermal analysis (TG/DTA), lithium metaborate fusion or acid digestion, with digests analysed by using gravimetric and volumetric methods, and flame or graphite furnace atomic absorption spectrophotometry.

The particle size distribution was evaluated using a laser diffraction technique. Dodecane was used as a suspending medium to avoid chemical interaction between fly ash and water.

Samples of washed fly ash were dry-milled for 5 min in a vibrating cup mill consisting of two agate elements (one disk and one ring) for comminution without metallic contamination (rotation speed=1000 rpm). An aliquot of milled and washed fly ash (MWFA) was then analysed for its particle size distribution.

Dried powder of UFA, WFA, or MWFA was uniaxially pressed in a stainless steel die, to form 15 mm diameter and approximately 15 mm high cylindrical “green” specimens. These specimens were characterised for their density (green density) and then sintered at an established temperature (T) by using a ramp rate of 6°C/min and an established dwell time (t_d). Three sets of specimens were formed. The first set was made at different compact pressures (14-166 N/mm²) and sintered at 1140°C for a dwell time of 1 h. The second set was formed at a compact pressure of 28 N/mm² and sintered at temperatures between 950°C and 1210°C for a dwell time of 1 h. The third set (not including UFA powder) was pressed at 28 N/mm² and sintered at an established temperature (1140°C for MWFA and 1210°C for WFA) for dwell times ranging from 0.25 to 1 h.

All sintered products were characterised for their density (fired density) and unconfined compressive strength (UCS) using five replicate specimens and standard test procedures. Some sintered products were also tested for their water absorption capacity, and the sintered product with the best performance characteristics (sintered MWFA) was also analysed for its acid neutralisation capacity (ANC) and heavy metals leachability.

Water absorption capacity was determined from the increase in weight of “surface dry” samples after immersion in deionised water for 24 h.

The acid neutralisation capacity test, combined with leachate analysis, was performed on crushed samples of sintered product (particle sizes < 2.0 mm) [7]. 5-g dried samples were mixed with 50 ml of aqueous solutions having different concentrations of nitric acid. The slurries obtained were mixed for 48 h in a rotary extractor and then centrifuged at 4000 rpm for 10 min. Each leachate was extracted and, after pH measurement, was filtered through a 0.45-µm membrane filter and then analysed for selected heavy metals (Cd, Cr, Cu, Pb, and Zn). For comparative purposes, the ANC tests and leachate analyses were also performed using dried samples of raw and washed fly ash.
3 Results and discussion

3.1 Ash characterisation

Table 1 gives the elemental analyses of raw and washed fly ash.

<table>
<thead>
<tr>
<th>Element (g/kg)</th>
<th>Raw fly ash</th>
<th>Washed fly ash</th>
<th>Element (g/kg)</th>
<th>Raw fly ash</th>
<th>Washed fly ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>176.10</td>
<td>235.10</td>
<td>P</td>
<td>7.60</td>
<td>10.80</td>
</tr>
<tr>
<td>Si</td>
<td>91.20</td>
<td>132.70</td>
<td>C**</td>
<td>4.64</td>
<td>5.50</td>
</tr>
<tr>
<td>Al</td>
<td>51.00</td>
<td>70.20</td>
<td>Cd</td>
<td>0.30</td>
<td>0.42</td>
</tr>
<tr>
<td>Fe</td>
<td>14.80</td>
<td>22.40</td>
<td>Cr</td>
<td>0.22</td>
<td>0.28</td>
</tr>
<tr>
<td>Mg</td>
<td>17.60</td>
<td>25.50</td>
<td>Cu</td>
<td>1.75</td>
<td>2.42</td>
</tr>
<tr>
<td>Na</td>
<td>52.70</td>
<td>8.30</td>
<td>Ni</td>
<td>0.09</td>
<td>0.11</td>
</tr>
<tr>
<td>K</td>
<td>67.40</td>
<td>10.60</td>
<td>Pb</td>
<td>9.67</td>
<td>13.42</td>
</tr>
<tr>
<td>Mn</td>
<td>0.70</td>
<td>1.10</td>
<td>Zn</td>
<td>18.33</td>
<td>26.67</td>
</tr>
<tr>
<td>Ti</td>
<td>12.90</td>
<td>19.50</td>
<td>L.O.I. at 1000°C (%)</td>
<td>21.20</td>
<td>10.55</td>
</tr>
<tr>
<td>S*</td>
<td>20.60</td>
<td>7.60</td>
<td>Density (g/cm³)</td>
<td>2.54</td>
<td>2.84</td>
</tr>
<tr>
<td>Cl</td>
<td>132.40</td>
<td>3.20</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*acid-soluble sulphates; ** total carbonates

The major elements of the raw fly ash were Ca, Cl, and Si accompanied by lesser amounts of K, Na, Al, S, Mg, and Fe. The predominant heavy metals of particular environmental concern were zinc and lead accompanied by lesser amounts of Cu, Cd, Cr, and Ni. The raw fly ash was characterised by a very high content of water-soluble compounds such as alkali metal chlorides and sulphates (LOS = 33.9 %) and by a very high loss on ignition (LOI=21.2%), the latter being mostly due to the presence of volatile salts (mainly, alkali metal chlorides), carbonates, and coal (2.21% as measured by thermogravimetry).

The main crystalline phases identified by X-ray powder diffraction analysis (XRPD) (not reported here) were halite (NaCl), sylvite (KCl) and complex alkali metal and alkali metal earth sulphates, accompanied by lesser amounts of calcium silicates, aluminates and aluminosilicates. No heavy metal compound was detectable by XRPD. Light-microscopic observations revealed the presence of platy coal particles and high amounts of spheroidal glass particles.

Due to a high release of water-soluble compounds and a low release of heavy metals from the raw fly ash during washing steps, the washed fly ash was found to be richer in heavy metals and much less rich in chlorides and sulphates than raw fly ash. A significant increase in Ca, Si, Al, Mg, and Fe content was also observed. The total content of these elements in terms of metal oxides was 82.2% against 58.9% for UFA. The washed fly ash also exhibited a higher coal content (3.51%) and a much lower loss on ignition (10.55%).

Figure 1 shows the particle size distributions of raw, washed, and milled-washed fly ash.
These curves revealed that both the raw and washed fly ash were finely grained, with about 95% of particles having sizes ($d_{95}$) of less than 100 $\mu$m. The washed fly ash was characterised by a somewhat finer size grading with a $d_{50}$ value of 21 $\mu$m against 25 $\mu$m for UFA. The milled-washed fly ash was a very fine material with $d_{95}$ and $d_{50}$ values of 25 and 3.7 $\mu$m, respectively. It had a slightly higher loss on ignition (12.0%) and a similar coal content (3.47%) as compared to WFA.

### 3.2 Physical and mechanical properties of sintered products

Figure 2 depicts the effect of compact pressure on the density and porosity of “green” specimens (a) and the compressive strength and density of sintered products (b), when these products were manufactured under identical firing conditions ($T=1140^\circ$C; $t_d=1$ h).

Increasing compact pressure ($P_c$) always resulted in increased density ($\rho$) and reduced porosity ($\alpha$) of the green specimens (Figure 2a). This effect was more pronounced over the range of $P_c$ values from 14 to 83 N/mm$^2$ ($\alpha$ decreased from...
about 0.56 to 0.35 and ρ increased from 1.12-1.36 to 1.66-1.82, depending on the type of powder used). At a fixed compact pressure, the green porosity was little affected by the type of powder, so higher green densities were always measured on the compacts made with WFA and MWFA, in virtue of their higher powder density as compared to UFA (Table 1).

As shown in Figure 2b, the compressive strength and fired density of the sintered products were primarily affected by the type of powder and, to a minor extent, by the compact pressure.

The sintered UFA specimens were always characterised by very low UCS values (1.3-7.4 N/mm²) and also exhibited lower densities (0.91-1.27 g/cm³) than the respective green specimens (1.12-1.80 g/cm³) (Figure 2a).

Much higher UCS values were measured on sintered WFA specimens. A compact pressure of 28 N/mm² was enough to yield sintered products with good strength characteristics (UCS=53 N/mm²). As the compact pressure was increased from 28 to 55 N/mm², a remarkable increase in strength (UCS = 110 N/mm²) was obtained. At higher Pc values, no further significant increase in UCS was monitored. At a fixed compact pressure, the densities of the sintered specimens (1.53-2.61 g/cm³) were always higher than those of the respective green specimens (1.31-1.97 g/cm³) (Figure 2a).

Irrespective of the compact pressure used, the highest values of UCS and density were always measured on sintered MWFA samples. A compact pressure of 14 N/mm² was enough to yield sintered products with UCS and density of 385 N/mm² and 2.61 g/cm³, respectively. At higher compact pressures, UCS values of 400 to 450 N/mm² and fired densities of 2.78 to 2.84 g/cm³ were measured.

Figure 3a shows the effect of sintering temperature on the UCS and density of sintered products, when these products were manufactured at an established compact pressure (28 N/mm²) and a fixed dwell time (1 h).

At temperatures between 950° and 1100°C, poor consolidation was achieved especially for UFA and WFA samples. At 1100°C, only the MWFA samples showed significant strength development (UCS=34 N/mm²). At higher temperatures, consolidation of UFA and WFA samples was also observed. However, even at 1210°C the sintered UFA samples exhibited poor strength (UCS=7.4 N/mm²) and reduced fired density (1.22 g/cm³ ) as compared to green specimens (ρ = 1.38 g/cm³). Conversely, the sintered WFA samples showed a progressive, remarkable increase in strength and density with increasing temperature (UCS = 266 N/mm² and ρ = 2.54 g/cm³ at 1210°C). In the case of MWFA samples, firing above 1140°C resulted in a remarkable decrease in strength and fired density. However, only above 1180°C sintered MWFA products exhibited lower strength and fired density than sintered WFA samples.

Figure 3b shows the effect of dwell time on the UCS and fired density of sintered products, when these products were made with WFA or MWFA powder (Pc = 28 N/mm²) and sintered at their optimal sintering temperatures (1140°C for MWFA and 1210°C for WFA).

In the case of WFA samples, no significant change in UCS and fired density with dwell time was observed over the whole range of td values investigated (15-60 min). Conversely, in the case of MWFA samples, a remarkable increase in
UCS and fired density with dwell time was monitored. Thus, at a $t_d$ value of 15 min, the two types of sintered products showed similar UCS and densities. At higher dwell times, the sintered MWFA samples always exhibited higher densities and much higher UCS.

Figure 3: Effect of sintering temperature (a) and dwell time (b) on the UCS and fired density of sintered products.

The data in Figures 2 and 3 confirmed that raw MSW incinerator fly ash was an unsuitable material for manufacturing sintered products with good performance characteristics.

Although the washing treatment of raw fly ash with water produced a heavy metals enrichment of this material (Table 1), it was capable of transforming raw fly ash into a material with consistent chemical composition for its subsequent thermal processing. However, high firing temperature ($1210^\circ C$) was needed to form high-strength ceramic materials (UCS=$260-275$ N/mm$^2$).

Combining the washing treatment with a milling step resulted in a marked reduction of the power input of the sintering process (firing temperature reduction from $1210^\circ C$ to $1140^\circ C$). With this pretreatment, it was also possible to manufacture sintered products with much higher compressive strengths (UCS up to 450 N/mm$^2$).

The high strength development in the MWFA samples sintered at $1140^\circ C$ was ascribed to a significant formation of new crystalline phases, mainly gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$), as evidenced by XRPD analysis. The development of a dense, well-sintered microstructure was also confirmed by the very low values of water absorption capacity (0.10-0.20%). Very low water absorption (0.06-0.10%) was also exhibited by the WFA samples sintered at $1210^\circ C$. Conversely, the UFA samples sintered at $1210^\circ C$ showed very high water absorption (31.5%).

With reference to the density and UCS characteristics, both the MWFA samples sintered at $1140^\circ C$ and the WFA samples sintered at $1210^\circ C$ were able to meet the requirements for normal-weight aggregates ($2.0 \leq \rho \leq 3.0$ g/cm$^3$) for use in concrete (Category A: specified compressive strength $\geq 100$ N/mm$^2$) [8].
3.3 ANC and leaching behaviour of sintered products

Figure 4a shows the results of the acid neutralisation capacity test (final leachate pH vs. acid addition) for the raw and washed fly ash, and the sintered MWFA product ($P_c=28$ N/mm$^2$; $T=1140^\circ$C; $t_d=1$ h). The releases of heavy metals in terms of mass of metal released per unit mass of dry waste (mg/kg) are shown plotted as a function of final leachate pH in Figure 4 b-f.

![Figure 4: Acid neutralisation capacity (a) and heavy metals leaching (b-f) data for samples of UFA, WFA, and sintered MWFA.](image)

Raw fly ash was characterised by a significant acid neutralisation capacity (10.5 meq/g) as determined from the corresponding titration curve at pH = 7.0, this pH value being the titration end-point of the ANC test (Figure 4a).

As a result of the washing pretreatment, washed fly ash was found to have a slightly higher ANC value (12.0 meq/g). This was ascribed to an enrichment in
CaO, MgO, Al₂O₃, and Fe₂O₃ of fly ash and to the fact that most of the water-soluble compounds present in the raw fly ash were in the form of neutral salts (sodium and potassium chlorides and sulphates).

The titration curve of the sintered MWFA showed a rapid decline in pH with acid addition, corresponding to markedly reduced ANC (1.0 meq/g). This low ANC was attributable to the fact that, after sintering, most of the metal oxides responsible for buffer capacity of washed fly ash (mainly CaO, Al₂O₃) were bound into newly formed glassy and crystalline phases and, consequently, they were not available at pH 7.0. It was also noteworthy that, at a pH value of about 6.7, the titration curve of sintered MWFA showed a pH plateau over the range of acid addition from 1.1 to 2.3 meq/g, that was indicative of the presence of particular solid phases responsible for a resistance to acidification [9].

The leaching data in Figure 4b-f indicated that the leachate pH was the major parameter controlling the release of the selected heavy metals (Cd, Cr, Cu, Pb, and Zn) from both sintered and not sintered samples. However, differently from what was found for leaching of heavy metals from UFA and WFA samples (typical changes in metal release with leachate pH), sintered MWFA showed an abrupt change in leaching behaviour with leachate pH in correspondence of a narrow pH range. At pH values above 6.8, very low releases of all heavy metals were always measured irrespective of the leachate pH. Releases of 0.1 mg/kg were observed for Cd and Cr, corresponding to a metal concentration of 10 µg/l in the leachate. Copper, lead, and zinc were leached to a greater extent (0.2-0.5 mg/kg) but these releases were insignificant as compared to the concentrations of such metals in washed fly ash prior to sintering (Cu = 2420 mg/kg; Pb = 13420 mg/kg; Zn = 26670 mg/kg) (Table 1). Conversely, at pH values below about 4.8, the release of heavy metals from sintered MWFA greatly increased with decreasing leachate pH but these releases were always lower than those measured on UFA and WFA samples.

These results suggested that: 1) the great reduction in metal release caused by sintering was attributable to encapsulation and incorporation of metallic species into new glassy and crystalline phases formed during thermal processing, and 2) the chemical resistance of such solid phases greatly reduced under acid pH conditions. However, this deficiency should not reduce the possibility of using sintered MWFA products as artificial aggregates in concrete formulations, taking in mind the very high pH values (13.0-13.5) exhibited by the pore solutions within cementitious matrices.

4 Conclusions

Raw MSW incinerator fly ash proves to be an unsuitable material for manufacturing sintered products with good performance characteristics.

A preliminary washing treatment of raw fly ash with water followed by a milling step of washed ash is able to convert such a waste into a material with consistent chemical and physical characteristics for its thermal processing.

With such a pretreatment it is possible to significantly reduce the power input of the sintering process (the optimal sintering temperature reduces from 1210 to
1140°C if washed ash is also milled) and, at the same time, to manufacture sintered products with better performance characteristics in terms of density (2.65-2.80 g/cm$^3$) and compressive strength (260-450 N/mm$^2$).

Sintering reduces acid neutralisation capacity of fly ash but also greatly reduces leaching of heavy metals especially under neutral and basic pH conditions as a result of their encapsulation and incorporation into the glassy and crystalline phases formed during thermal processing. Sintered products also exhibit insignificant water absorption capacity (0.1-0.2%) due to their dense, well-sintered microstructure.

Such materials are able to meet the requirements for normal-weight aggregates for use in concrete.

References