Cement-based immobilisation of municipal incinerator fly ash and reuse of solidified products as a construction material

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Abstract

A solidification/stabilisation (S/S) process of washed municipal incinerator fly ash with Portland cement was used to manufacture solidified products with high ash content (55 and 70 wt.% of solids) and good performance characteristics in terms of setting, dimensional stability, compressive strength, and environmental quality. The S/S product containing 70 wt.% fly ash aged for 180 days at 20°C and 100% RH was used as an artificial aggregate for the production of Portland cement mortars at four replacement levels of natural sand (0, 10, 50, and 100% by mass), and a water-to-cement weight ratio (w/c) of 0.62. Control mortars were also made at a w/c ratio of 0.50. All mortars were cured at 20°C and 100% RH up to 120 days. No substantial difference in the compressive strength between superplasticised artificial aggregate-bearing mortars and non-superplasticised control mortars was found only if the replacement level of natural sand was not greater than 50% by mass and a w/c ratio of 0.62 was used. All mortars were able to meet the Dutch regulatory limits for selected heavy metals (Cd, Cr, Cu, Ni, Pb, and Zn) when subject to the monolith leach test. Portland cement played an important part in the release of such heavy metals from mortar specimens. Keywords: municipal incinerator fly ash, solidification/stabilisation, reuse, cement mortar, compressive strength, leaching behaviour.

1 Introduction

In many industrialised countries, incineration is an increasingly alternative technology to landfill for the disposal of Municipal Solid Waste (MSW).
In the European Community, about 20% of MSW produced annually (approximately 150 million tons) is currently incinerated. In Italy, the annual production of MSW is about 29 million tons, of which only 7% is incinerated.

Generally, about one third of the mass of MSW incinerated remains as solid residue, whilst the rest is converted into gaseous compounds and is released into the atmosphere. The solid residues are bottom ash, fly ash, and scrubber residue, the major residue portion (about 85% wt. %) being constituted of bottom ash.

Both fly ash and scrubber residue generally behave as hazardous wastes, due mainly to their high concentration of leachable heavy metals and, in some cases, to the presence of toxic chlorinated organics. Bottom ash commonly behaves as a less hazardous waste as compared to fly ash and scrubber residue [1].

Disposal of MSW incinerator fly ash in landfill requires preliminary treatment to reduce the hazardous characteristics of this material. Preliminary treatments include advanced separation processes, solidification, chemical stabilisation, and encapsulation [1], [2].

At present, the most widely applied technique consists of immobilising MSW incinerator fly ash through a process of solidification/stabilisation (S/S) using cement or another inorganic binder. However, avoiding landfill disposal of such a waste by developing reuse applications is clearly the preferred option.

Use of cement-stabilised MSW incinerator fly ash as a concrete aggregate in the building industry could represent a sensible method of safe reuse of such a waste as it would greatly reduce the environmental problems and costs associated with land disposal and would also provide an alternative aggregate source, thus limiting the use of irreplaceable natural resources and still satisfying the growing demand for concrete aggregates.

As reported in our previous work aimed at maximising the incorporation of MSW incinerator fly ash into cementitious mixes for landfill disposal purposes [3], a preliminary washing treatment of raw fly ash with deionised water is needed to suppress the adverse effects of this material on cement hydration.

In the present study, a solidification/stabilisation process of washed MSW incinerator fly ash with Portland cement was first investigated in order to manufacture solidified products with high fly ash content, to be reused as artificial aggregates in cementitious mixes. Based on the physical and mechanical characteristics of the S/S products, Portland cement mortars at different replacement levels of natural sand by S/S product were then formulated and tested for physico-mechanical properties and leaching behaviour.

This paper reports the most significant results of such an investigation.

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.

This material had a complex structure and consisted of a mixture of phases. Chemically, it contained mainly Ca, Al, and Si compounds, partly in amorphous form, together with alkali metal chlorides, soluble sulphates, and heavy metal
salts. The characterisation data (physical, chemical and mineralogical) and properties of the raw fly ash were reported previously [3], [4].

A four-stage washing treatment of raw fly ash with deionised water (liquid-to-solid weight ratio = 12.5; mixing time = 30 min for each washing step) was performed using an agitation apparatus that was capable of rotating the extraction vessel in an end-over-end fashion at 30 rpm. After this treatment, the washed fly ash (WFA) was dried for 24 hours in a vacuum over calcium chloride, and then analysed for its chemical composition and physical properties.

Two formulations of washed fly ash, Portland cement (CEM I 42.5), and deionised water were used to manufacture solidified products through a S/S process. A sulphonated naphthalene-based superplasticiser (SNF) at a dose level of 2 wt. % of cement was also used. Table 1 gives the chemical and physical characteristics of the Portland cement together with those of the washed fly ash.

Table 1: Chemical and physical characteristics of Portland cement (CEM I 42.5) and washed fly ash.

<table>
<thead>
<tr>
<th>Component (%)</th>
<th>Portland cement*</th>
<th>Washed fly ash</th>
<th>Component (mg/kg)</th>
<th>Portland cement*</th>
<th>Washed fly ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>63.10</td>
<td>27.44</td>
<td>Cd</td>
<td>3</td>
<td>115</td>
</tr>
<tr>
<td>SiO₂</td>
<td>21.20</td>
<td>31.29</td>
<td>Cr</td>
<td>5</td>
<td>252</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.40</td>
<td>2.00</td>
<td>Cu</td>
<td>22</td>
<td>1230</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>4.40</td>
<td>15.30</td>
<td>Ni</td>
<td>7</td>
<td>110</td>
</tr>
<tr>
<td>MgO</td>
<td>1.20</td>
<td>3.22</td>
<td>Pb</td>
<td>110</td>
<td>5220</td>
</tr>
<tr>
<td>SO₃</td>
<td>3.30</td>
<td>2.96</td>
<td>Zn</td>
<td>135</td>
<td>9430</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.27</td>
<td>0.05</td>
<td>L.O.I. at 950°C (%)</td>
<td>0.98</td>
<td>15.90</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.43</td>
<td>0.04</td>
<td>Bulk Specific Gravity</td>
<td>3.15</td>
<td>2.43</td>
</tr>
<tr>
<td>Cl</td>
<td>0.01</td>
<td>0.13</td>
<td>Specific surface area (m²/kg)</td>
<td>400 Blaine</td>
<td>10800 BET</td>
</tr>
</tbody>
</table>

* Bogue potential constituents: C₃S=51.5% ; C₂S=22.1 %; C₃A=5.9%; C₄AF=10.5%.

The ash contents of the two formulations were 55% and 70% by weight of total solids (ash+cement) and the water-to-cement (w/c) weight ratios were 0.94 and 1.56, respectively. These w/c values corresponded to the minimum w/c ratios needed to achieve sufficient workability for the two ash-cement mixtures.

An aliquot of each mixture was tested for the initial and final setting times through the use of the Vicat apparatus [5], while the remaining mix portion was used to prepare prismatic specimens for measurements of unconfined compressive strength (UCS), dimensional change, and heavy metals leachability. After two days of storage of the specimens in the moulds at ambient temperature and RH>90%, they were demoulded and transferred to the moist-curing room at 20°C and 100% RH, until required for testing.

UCS and dimensional change measurements were periodically made up to 180 days on three replicate 40x40x160 mm specimens.

Aafter 180 days of curing, the two S/S products were characterised for the leachability of selected heavy metals (Cd, Cr, Cu, Ni, Pb, and Zn) through the use of the Italian monolith leach test [6]. This test was performed using ten
replicate 10x10x40 mm specimens of each S/S product that were contacted with deionised water at a leachant-to-solid volume ratio ($V_L/V_S$) of 5.0. The leachate was periodically replaced with deionised water after cumulative times of 2, 8, 24, 48, 72, 102, 168, and 384 hours. Each leachate was filtered through a 0.45-μm membrane filter and, after pH measurement, acidified with 1 M HNO$_3$ to pH 2.0 and analysed for selected heavy metals by using an atomic absorption spectrophotometer equipped with a graphite furnace.

On the basis of the results of UCS and leaching tests, the worse S/S product (ash content =70 wt.% of total solids) aged for 180 days at 20°C and 100% RH was selected and tested as an artificial aggregate for the production of Portland cement mortars. This S/S product (also referred to as artificial aggregate) was ground to a size grading closely resembling that of a natural sand, and was then analysed for its chemical composition and physical properties.

A natural quartzitic sand from an Italian quarry (SiO$_2$=91.24%; bulk specific gravity=2.65; water absorption=2.0%; size gradation= 0.08-2.00 mm) was used to prepare blends with artificial aggregate at four replacement levels of natural sand (0, 10, 50, and 100% by mass). Chemical analysis of natural sand revealed no detectable presence of heavy metals such as Cd, Cr, Cu, Ni, Pb, and Zn.

A Portland cement, Class CEM I 52.5, was used to prepare mortar samples. Table 2 gives the chemical and physical characteristics of this cement together with those of the artificial aggregate.

<table>
<thead>
<tr>
<th>Component (%)</th>
<th>Portland cement*</th>
<th>Artificial aggregate</th>
<th>Component (mg/kg)</th>
<th>Portland cement*</th>
<th>Artificial aggregate</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>61.97</td>
<td>25.96</td>
<td>Cd</td>
<td>4</td>
<td>53</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>20.02</td>
<td>18.71</td>
<td>Cr</td>
<td>38</td>
<td>118</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>2.94</td>
<td>1.65</td>
<td>Cu</td>
<td>30</td>
<td>590</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>4.26</td>
<td>8.20</td>
<td>Ni</td>
<td>8</td>
<td>49</td>
</tr>
<tr>
<td>MgO</td>
<td>1.36</td>
<td>1.78</td>
<td>Pb</td>
<td>120</td>
<td>2500</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>2.99</td>
<td>2.09</td>
<td>Zn</td>
<td>160</td>
<td>4500</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.23</td>
<td>0.08</td>
<td>Bulk Specific Gravity</td>
<td>3.15</td>
<td>1.73</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>1.40</td>
<td>0.11</td>
<td>Water absorption (%)</td>
<td>-</td>
<td>29.2</td>
</tr>
<tr>
<td>Cl</td>
<td>0.01</td>
<td>0.02</td>
<td>Specific surface area (m$^2$/kg)</td>
<td>500</td>
<td>27300 mercury porosimetry</td>
</tr>
<tr>
<td>L.O.I. (950°C)</td>
<td>1.20</td>
<td>37.51</td>
<td>Blaine</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Bogue potential constituents: C$_3$S=49.4% ; C$_2$S=26.5 %; C$_3$A=7.0%; C$_4$AF=9.9%.

The choice of such a cement in place of the binder (CEM I 42.5) used for the S/S process of washed fly ash was made with the purpose of testing the behaviour of the artificial aggregate in cement mortars characterised by a higher mechanical strength development.

Mortar samples were prepared by mixing Portland cement, dry aggregate (natural sand and/or artificial aggregate), and deionised water at a w/c ratio of
0.62 and an aggregate-to-cement weight ratio of 3.0. A control mortar (0% sand replacement level) at a w/c ratio of 0.50 was also made. All artificial aggregate-bearing mortars were made using SNF superplasticiser at a dose level of 2 wt.% of cement. The w/c ratio of 0.62 corresponded to the minimum w/c ratio needed to achieve sufficient mix workability, especially for the superplasticised mortars incorporating higher amounts of artificial aggregate. After the 1-day storage of the mortar specimens in the moulds, they were demoulded and transferred to the moist-curing room at 20°C and 100% RH, until required for testing.

UCS measurements were periodically made up to 120 days on three replicate 40x40x160 mm specimens. After 28 days of curing, all types of mortar were characterised for their porosity and heavy metals leachability. The porosity was measured using a mercury intrusion porosimeter. The heavy metals leachability was evaluated through the use of the monolith leach test developed by Van der Sloot et al. [7]. According to this leaching protocol, three replicate 40-mm cubic specimens of each mortar were contacted with deionised water at a liquid-to-surface area ratio of 10 cm³ of water for every cm² of exposed solid surface area, corresponding to a \( V_L/V_S \) ratio of 15.0. The leachate was replaced with deionised water at cumulative times of 2, 5, 8, 24, 48, 96, and 192 hours and then analysed for heavy metals. In order to achieve more information about longer term release, this schedule was extended up to 64 days of testing, with three intermediate leachate renewals after cumulative times of 14, 21, and 34 days.

3 Results and discussion

3.1 Solidification/stabilisation of washed fly ash

The two tested ash-cement mixtures showed initial and final setting times (initial time = 2.5-3.0 hours; final time = 5.5-7.0 hours) that were comparable to those measured on natural sand-Portland cement mixture (initial time = 3.6 hours; final time = 7.5 hours). These data confirmed that the incorporation of high amounts of washed MSW incinerator fly ash into cementitious mixes does not adversely affect the cement setting, differently from what is commonly observed in the case of raw fly ash-cement mixtures (strong set retardation) [3], [8].

Figure 1 shows the dimensional changes and the compressive strengths of the two S/S products plotted against time over a curing period of 180 days. The recorded dimensional changes do not include those occurring after the final set of the specimens within the moulds.

No significant expansion was monitored for both types of S/S product. These products only showed a slight swelling (0.04-0.05% at 180 days) which was mostly attributable to water absorption, as evidenced by weight measurements. Such a behaviour may be explained taking in mind that the preliminary washing treatment of raw fly ash with deionised water was able to greatly reduce the content of alkali metal and alkali metal earth chlorides (98% removal as Cl) and sulphates (54% removal as \( SO_3 \)) of this material, thus reducing/preventing the formation of expansive compounds such as ettringite (\( C_3A \cdot 3CaSO_4 \cdot 32H_2O \)) and calcium monochloroaluminate (\( C_3A \cdot CaCl_2 \cdot 10H_2O \)) during hydration of ash-cement mixtures.
In spite of the high w/c ratios used, both types of S/S product were able to develop relatively high compressive strengths after 28 days of curing, and a further significant increase in UCS was monitored after 180 days. As expected, at a fixed curing time, the higher UCS values were always measured on the S/S product incorporating 55 wt.% fly ash (UCS = 44 N/mm² at 180 days against 27 N/mm² for the S/S product containing 70 wt.% fly ash).

Figure 2 shows the results of the Italian monolith leach test for both types of S/S product after 180 days of curing.

In this figure, for each heavy metal examined, the sum of the metal ion concentrations (Σci) in the eight leachates collected throughout the test (test duration = 16 days; leachate pH=12.0-12.5) is compared to the respective regulatory limit (Cd = 5 µg/l; Cr = 50 µg/l; Cu = 50 µg/l; Ni = 10 µg/l; Pb = 50 µg/l; Zn = 3000 µg/l). As can be seen, both types of S/S product were able to meet the regulatory limits for all selected heavy metals.
Although the S/S product containing 55 wt.% fly ash showed better characteristics in terms of both compressive strength and environmental quality, the S/S product incorporating 70 wt.% fly ash was selected and tested as an artificial aggregate for the production of Portland cement mortars. In this way, it was possible to better evaluate the limitations to reuse of solidified/stabilised MSW incinerator fly ash as an artificial aggregate in the building industry.

3.2 Reuse of S/S product in cement mortars

Figure 3 shows the compressive strengths of Portland cement mortars incorporating different amounts of artificial aggregate after 28 and 120 days of curing at 20°C and 100% RH.

At a w/c ratio of 0.62, a marked reduction in the compressive strength between superplasticised artificial aggregate-bearing mortars and not superplasticised control mortars was observed only if natural sand was totally replaced by artificial aggregate. At sand replacement levels of 10% and 50% by mass, only a slight reduction of UCS (about 10%) was monitored.

If the UCS values obtained for the mortars incorporating 10% and 50% artificial aggregate were compared to those exhibited by the control mortar having a w/c ratio of 0.50, a marked UCS reduction for the former specimens was observed (about 44% after 120 days of curing).

These UCS values were consistent with the mercury intrusion porosities measured on the various types of mortar after 28 days of curing. In particular, the control mortar (w/c=0.50) was characterised by the lowest porosity (9.8 %) while the highest porosity (25.9%) was measured on the mortar containing 100% artificial aggregate. The mortars incorporating 0, 10, and 50% artificial aggregate (w/c=0.62) showed similar porosities (13.0-14.8), despite the high porosity (29.2%) exhibited by the artificial aggregate (Table 2).

The results in Figure 3 also evidenced the impossibility of achieving compressive strengths above 33 N/mm² for the artificial aggregate-bearing mortars. However, it was noteworthy that, with the use of the S/S product having an initial UCS of 27 N/mm², it was possible to manufacture mortar specimens with UCS values up to 33 N/mm² after 120 days of curing. This was attributable
to an improved mechanical strength of the artificial aggregate as a result of its chemical interaction with Portland cement during hydration of mortar specimens and, secondarily, of its longer curing time (10 months) (Figure 2).

Figure 4 shows the results of the monolith leach test ($V_L/V_S = 15$) for all types of mortar (test duration = 64 days; leachate $pH = 10.8-12.2$). In this figure, the measured cumulative mass of heavy metal released per unit exposed surface area of specimen ($mg/m^2$) is plotted vs. the square root of the cumulative leach time. No cumulative release plot is reported for Cd and Ni, because the concentrations of these two metals in several individual leachates were below their detection limits ($Cd<0.1 \mu g/l$; $Ni<0.5 \mu g/l$). However, the cumulative release of Cd ($0.13-0.34 mg/m^2$) and Ni ($0.22-0.65 mg/m^2$) within 64 days of leaching ($M_{c}$) were calculated from the analyses of the leachates yielding metal ion concentrations above the detection limits.

It was surprising to note that a significant amount of the selected heavy metals was released from the control mortars. On the other hand, the Portland cement used for the preparation of the mortar specimens (Table 2), as well as the Portland cement used for the S/S process of washed fly ash (Table 1) were both characterised by a significant presence of such heavy metals, despite these two cements were declared as binders manufactured from raw natural materials. Significant release of heavy metals from ordinary Portland cement mortars has also been reported by other researchers [9].

At a fixed $w/c$ ratio ($w/c = 0.62$), the mortars incorporating 10 and 50% artificial aggregate were found to release heavy metals to a lower extent than the
control mortar. This was in spite of the fact that such mortars exhibited similar mercury porosities and that Portland cement was much less rich in heavy metals than artificial aggregate (Table 2). These results suggested that the heavy metals contained in the Portland cement were by far more leachable than those present in the artificial aggregate, and that their leachability was greatly affected by the capillary porosity of the hydrated cement paste. In this regard, it was calculated that, at a w/c ratio of 0.62, an increase of the replacement level of natural sand from 0 to 50% resulted in a reduction of the capillary porosity of a completely hydrated cement paste from about 26 to 0%, as a consequence of a reduction of the actual w/c ratio (free water-to-cement ratio) of the mixture [10], the last being in turn due to water absorption by artificial aggregate.

If the w/c ratio of the control mortar was reduced from 0.62 to 0.50, this mortar was found to release the lowest amount of heavy metals in virtue of the reduced capillary porosity of the hydrated cement paste, the low heavy metal content, and the lowest mercury porosity (9.8%).

![Figure 5: 100-year estimated release of heavy metals.](image)

Elaboration of the results of Figure 4 in terms of arithmetical cumulative release of each metal, $M^*$ (mg/m$^2$) and cumulative leach time, $t_c$, [7] showed that, after the initial leaching path (leachates 1 to 3-5) largely controlled by dissolution and/or delayed diffusion of heavy metals from accessible surface (slopes $>$ 0.65 for the linear regressions of the plots log $M^*$=f (log $t_c$)), the further leaching of heavy metals was largely controlled by diffusion (slopes $<$ 0.65 and $>$ 0.35 for the linear regressions of the above plots). The mean effective diffusion coefficient of each heavy metal for the diffusion-controlled path was then calculated [7] and the cumulative diffusive releases of Cr, Cu, Pb, and Zn from a monolithic block with an exposed surface area of 1 m$^2$ during 100 years were estimated and added to initial surface releases. The total releases are compared in Figure 5 with the regulatory limits (Category I applications) as specified in the Dutch Building Materials Decree [11]. In this figure, are also reported the 100-year cumulative releases of Cd and Ni calculated from the leaching test data ($M'$) assuming that diffusion is the controlling leaching mechanism.

As can be seen, all mortars were able to meet such regulatory limits.
4 Conclusions

The solidification/stabilisation process of washed MSW incinerator fly ash with Portland cement yields solidified products with high ash contents (55 and 70 wt.% of total solids) that exhibit good performance characteristics in terms of setting, dimensional stability, compressive strength, and environmental quality.

The use of S/S products incorporating 70 wt.% fly ash as artificial aggregates in Portland cement mortars proves to be a promising method of safe reuse of cement-stabilised MSW incinerator fly ash. However, there exist some limitations to the development of high mechanical strengths that are essentially related to the high porosity of such S/S products. These limitations could be largely removed by reducing the ash content of the S/S products.

Despite a significant contribution of Portland cement to the release of heavy metals from mortar specimens, no environmental problem is encountered with the use of S/S products in Portland cement mortars.

References