



## Disposal of MSWI fly ash through a combined washing-immobilisation process

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### Abstract

The objective of this work was to investigate the feasibility of a combined washing-immobilisation process as a means of optimising the disposal of fly ash resulting from municipal solid waste incineration (MSWI) in cementitious matrices. Two different types of Italian MSWI fly ash and an ordinary Portland cement (ASTM Type I) were used. Washing pre-treatment of fly ash with water always produces a wastewater that can be successfully treated by reducing the pH to values of 6.5–7.5. This treatment is capable of removing the detected contaminants (Al, Cd, Pb, Zn) through two different mechanisms: precipitation of aluminium hydroxide and adsorption of cadmium, lead and zinc ions onto floc particles of  $\text{Al}(\text{OH})_3$ . Setting and leaching tests on cementitious mixes prove that the hazardous sludge produced from wastewater treatment can be completely mixed with washed fly ash and this mixture can be incorporated into cementitious matrices to a great extent (75 wt.% of total solid) without the risks of an unacceptable delay of cement setting and an excessive heavy metals leachability from solidified products. The better performance of the combined washing-immobilisation process as compared to the immobilisation process of unwashed fly ash may be ascribed primarily to the ability of the washing step in promoting the formation of hydrate phases that incorporate and/or convert heavy metal compounds into less reactive forms and, secondarily, to its ability of removing significant amounts of alkali chlorides and sulphates from fly ash. As a result, MSWI fly ash is transformed into a material that adversely affects cement hydration to a much lower extent than unwashed fly ash.

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## 1. Introduction

Fly ash resulting from municipal solid waste incineration (MSWI) is classified as a hazardous waste by the Italian legislation on solid waste disposal [1], owing to its heavy metals and, in some cases, toxic chlorinated organics content.

Disposal of MSWI fly ash into ordinary landfill sites poses serious environmental problems, principally because this material contains high concentrations of leachable heavy metals.

Various technologies have been investigated in order to reduce the hazardous characteristics of MSWI fly ash.

Thermal immobilisation processes such as sintering [2,3] or vitrification [4–6] have been proposed to convert MSWI fly ash into ceramic- or glass-type materials, respectively. However, these processes are not yet fully developed and seem to be very expensive. Moreover, difficulties encountered in the application of these techniques arise from the presence of alkali chlorides and sulphates and of other volatile metallic compounds in raw fly ash.

The transformation of MSWI fly ash into a non-hazardous material through a combination of chemical and thermal processes has also been proposed. This is the case of the so-called 3R-process [7] which is aimed at destroying chlorinated organic pollutants and recovering heavy metals from MSWI fly ash. This process basically consists of the following four steps of treatment: (1) washing of fly ash with hydrochloric acid solution at pH 0–1 to leach as much of heavy metal as possible, (2) recovery of heavy metals from the leachate by ion exchange, (3) combination and compaction of washed fly ash with neutral sludge resulting from neutralisation of the ion exchanger effluent, and (4) recycle of this mixture to the combustion chamber of municipal solid wastes in order to mineralise the 3R-residues and combine them with bottom ash.

At present, the most widely applied technique consists of immobilising MSWI fly ash through a process of solidification/stabilisation (S/S), using cement or another inorganic binding agent (powdered blast furnace slag, calcium sulphate) [8,9].

The major drawback of the S/S process lies in the necessity of using a high binder/ash ratio that multiplies the mass to be disposed of by a factor of two or more. Moreover, some metallic species such as cadmium, chromium(VI), molybdenum and zinc cannot be sufficiently bound or encapsulated to meet the leaching standards [10].

To overcome these difficulties, a number of preliminary treatments of MSWI fly ash have been proposed to transform this material into a waste that may be incorporated into cementitious matrices without the risk of an excessive release of contaminants. Such pre-treatments include a washing step with nitric acid solution at pH 4 [10], a washing step with water followed by moderate phosphoric acid addition and calcination [11], or a washing step with ferrous sulphate solution followed by ferrous sulphate oxidation [12].

As reported in a previous paper [13], a relevant reduction of the binder/ash ratio in the S/S process can be attained through a preliminary washing treatment of MSWI fly ash with water. For certain types of fly ash, this pre-treatment was found to reduce the consumption of cement by 60–85% without the risk of heavy metal leachability from solidified products. In that paper no explanation was given about the beneficial effect of the ash washing pre-treatment on the setting of ash–cement mixtures.

Similarly to what was found in the development of the 3R-process [7] and the other aforementioned pre-treatments [10–12], the washing pre-treatment of MSWI fly ash with water generates a wastewater that needs treatment in order to reduce the pH and the concentrations of certain heavy metals below the standard limits established by the local regulations on wastewater disposal.

Furthermore, the wastewater treatment will generate a hazardous sludge, i.e. an additional solid waste stream that needs to be managed. In this context, the possibility of immobilising this sludge in combination with washed fly ash without detrimental effects on the efficacy of the S/S process would represent an important advantageous element in determining the economical feasibility of the combined washing-immobilisation process.

Based on the hypothesis that the sludge would not interfere with the solidification process of washed fly ash, it was estimated [13] that the global costs of the combined process would be much lower (about 47–50%) than the costs of solidification/stabilisation of unwashed fly ash. However, such a hypothesis has to be verified experimentally bearing in mind that: (1) the sludge resulting from wastewater treatment is commonly composed of heavy metals such as zinc and lead, which are known to greatly interfere with the hydration of cementitious materials [14–23], (2) the metallic species contained in the sludge should be expected to be more dangerous for cement hydration than the same metallic species contained within fly ash grains, and (3) little is yet known about the critical concentrations at which a given metallic species or its combination with other metallic species are able to inhibit the setting and hardening of cementitious materials.

Therefore, the present study was undertaken to investigate the feasibility of the combined washing-immobilisation process when applied to the treatment of two different types of fly ash that are representative of the wide variety of Italian MSWI fly ashes. In this context, particular attention was devoted to the wastewater treatment in order to minimise the production of sludge.

An interpretation of the different performance of the S/S process when applied to unwashed or washed fly ash was also attempted.

## 2. Materials and methods

The two types of MSWI fly ash used in this study were collected from the electrostatic precipitators of two different Italian incineration plants that were equipped with wet treatment units for acid gas removal, the later being located downstream of the electrostatic precipitators.

These two fly ashes were selected on the basis of their different contents of alkali chlorides and sulphates and were designated as low-alkali (LA) and high-alkali (HA) fly ash.

The main mineralogical constituents of each fly ash were halite (NaCl), sylvite (KCl) and  $\gamma$ -anhydrite ( $\text{CaSO}_4$ ), accompanied by lesser amounts of other minerals such as quartz ( $\alpha$ - $\text{SiO}_2$ ), calcium silicates, calcium aluminates and aluminosilicates, feldspars ( $\text{NaAlSi}_3\text{O}_8$  and  $\text{KAlSi}_3\text{O}_8$ ), and complex alkali sulphates such as apthitalite ( $(\text{Na}, \text{K})_3\text{Na}(\text{SO}_4)_2$ ). The predominant heavy metals in both fly ashes were zinc and lead, accompanied by lesser amounts of Cd, Cr, Cu and Ni. The heavy metals were present in the form of compounds not detectable by X-ray diffraction (XRD) (amorphous phases, crystalline phases at

Table 1  
Elemental analysis and particle size distribution of MSWI fly ashes

Element (g/kg fly ash)	LA fly ash	HA fly ash
Ca	182	152
Si	106	101
K	36	62
Na	28	44
Al	59	46
Fe	10	12
Mg	14	12
S <sup>a</sup>	43	67
Cl	56	87
Zn	6.4	18
Pb	4.0	7.0
Cu	0.90	1.4
Cr	0.20	0.40
Ni	0.09	0.11
Cd	0.02	0.03
Hg	$<2.5 \times 10^{-5}$	$<2.5 \times 10^{-5}$
As	$<5.3 \times 10^{-5}$	$<5.3 \times 10^{-5}$
Particle size distribution ( $\mu\text{m}$ )	Undersize (%)	
150	96	98
100	90	95
75	78	89
50	65	76
40	54	65
20	34	41
10	18	21

<sup>a</sup> Water-soluble sulphates expressed as sulphur.

concentration levels below XRD detection limit, or impure, complex crystalline compounds). Table 1 gives the elemental analysis and the particle size distribution of the two fly ashes.

### 2.1. Washing process

An aliquot of each fly ash was preliminarily dried in an oven at 105 °C and then divided into five samples that were subjected to the washing treatment, using distilled water as a leachant.

As reported in a previous paper [13], a two-stage washing pre-treatment with water (ambient temperature, water/solid (w/s) weight ratio = 25, mixing time = 15 min, for each stage of treatment) is enough to maximise the incorporation of fly ash into cementitious matrices.

Following this procedure, after the first washing step of a given ash sample, the aqueous suspension was filtered through a 45- $\mu\text{m}$  membrane filter and the filtered liquid was collected. The solid residue was dried for 10 h in a vacuum over calcium chloride and then subjected to the second washing step. The two portions of filtered liquid were combined

and the resulting wastewater was mixed with those arising from the washing of the other four samples of fly ash in order to equalise the wastewater composition. The combined wastewater was analysed for pH and the concentrations of chloride, sulphate, alkaline and heavy metal ions. The ionic strength of the wastewater was also calculated on the basis of its chemical composition.

Chloride ion concentration was determined by a volumetric method using a 0.1N silver nitrate solution and  $K_2CrO_4$  as an indicator. Sulphates were analysed by a turbidimetric method with a spectrophotometer operating at a wavelength of 420 nm. The concentrations of alkaline and heavy metal ions were measured by an atomic absorption spectrophotometer equipped with a graphite furnace.

The wastewater treatment was performed by reducing the pH to values over the range from 5.5 to 9.5 through addition of concentrated hydrochloric acid. This pH range corresponded to the lower and upper limits established for this parameter by the Italian legislation on wastewater disposal.

After pH correction, an aliquot of wastewater (1 l) was subjected to agitation in a jar tester under established operating conditions (paddle rotational speed = 30 rpm; mean velocity gradient =  $15\text{ s}^{-1}$ ; mixing time = 10–30 min). In some tests, flocculation of solid particles was enhanced by adding an anionic, polyamide-type polyelectrolyte at a dosage of 2 mg/l.

At the end of the established mixing time, the wastewater was subjected to sedimentation in an Imhoff cone and the volume of sludge was measured at different settling times. After 2 h of sedimentation, an aliquot of treated wastewater was analysed for the residual concentrations of metal ions.

For every operating condition investigated, the wastewater treatment was performed in triplicate and the residual concentrations of metal ions were determined as the average of three measurements. The coefficient of variation for average metal ion concentration was always less than 4%.

In some tests, an aliquot of sludge was dried for 10 h in a vacuum over calcium chloride and then analysed for its chemical and mineralogical composition by using X-ray diffraction and fluorescence techniques.

## 2.2. Solidification/stabilisation process

The sludge in its slurry form was combined with washed fly ash (which had first been dried in a vacuum over calcium chloride) in a solid weight ratio of approximately 1/170, and this mixture was then subjected to the solidification/stabilisation process with cement. This mix proportioning was established on the basis of the amount of sludge produced per unit weight of washed fly ash.

An ordinary Portland cement (ASTM Type I) was used to prepare cementitious mixes with a water/solid (w/s) weight ratio of 0.40 and an ash + sludge/cement ratio of 3.0 on a solids basis. Similar mixes were also made using cement and unwashed fly ash or washed fly ash without addition of sludge. A cement mortar (w/s = 0.40) made with 25% (w/w) Portland cement and 75% (w/w) quartzite sand having a particle size distribution similar to that of the tested fly ashes (Table 1) was used as a control specimen.

All the mixes were tested for initial and final setting times according to ASTM C191-92 (Vicat apparatus).

For the cementitious mixes incorporating unwashed fly ash or washed fly ash and sludge, cubic specimens (40 mm side) were also prepared and cured for 7 days in air at 20 °C and 100% relative humidity (RH). After curing, these specimens were crushed and characterised for heavy metals leachability according to the standard US EPA TCLP (Toxicity Characteristic Leaching Procedure) extraction test. For the specimens incorporating washed fly ash and sludge, unconfined compressive strength was also measured.

All the tests were carried out in triplicate and the results were determined as the average of three measurements. The coefficients of variation for measurements of compressive strength, setting time, and leaching (concentrations of metal ions in the leachate below 300 µg/l) within a set of specimens were always less than 4, 4.5, and 10%, respectively.

### 3. Results and discussion

#### 3.1. Wastewater characterisation and treatment

Table 2 gives the chemical composition of the two wastewaters resulting from the washing treatment of five samples of LA or HA fly ash (LA or HA wastewater). In this table the calculated values of the ionic strength along with the standard limits established for the various chemical species by the Italian legislation for effluents discharged to surface waters are also reported.

Table 2  
Chemical characteristics of wastewaters

Ionic species (mg/l)	LA wastewater	HA wastewater	Standard limit <sup>a</sup> (mg/l)
Na	500	788	–
K	610	978	–
Ca	500	400	–
Fe	0.23	0.16	2.0
Mg	0.65	0.95	–
Al	31.4	27.9	1.0
Si	1.51	1.51	–
Zn	0.71	0.87	0.5
Pb	0.25	0.34	0.2
Cr(VI)	0.11	0.16	2.0
Cu	0.08	0.09	0.1
Ni	0.08	0.10	2.0
Cd	0.026	0.036	0.02
Chloride	896	1089	1200 <sup>b</sup>
Sulphate	1625	2464	1200 <sup>b</sup>
pH	11.4	10.8	5.5–9.5
Ionic strength (mol/l)	0.09 <sup>c</sup>	0.12 <sup>c</sup>	

<sup>a</sup> D.L. 11/5/1999, no. 152, Gazz. Uff. Rep. It. N. 11, 29/5/1999.

<sup>b</sup> These limits do not apply to disposal of effluents into marine waters. If effluents are to be discharged into surface waters, a dilution with cooling and/or power plant water is allowed after heavy metals removal.

<sup>c</sup> Calculated values.

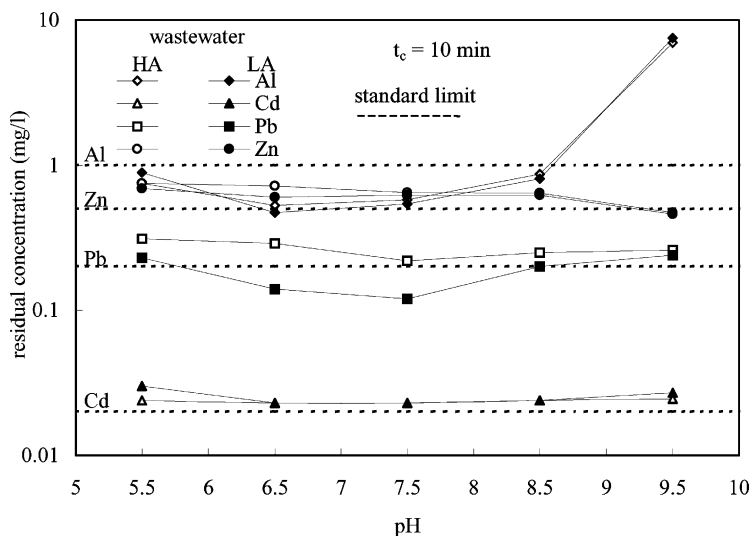


Fig. 1. Effect of pH upon residual concentration of metal ions in wastewater (10 min of treatment).

The two wastewaters were always characterised by high pH values (10.8–11.4) and high concentrations of alkali chlorides and sulphates. Significant were also the concentrations of calcium and aluminium ions. Heavy metals such as Cd, Cr, Cu, Ni, Pb, and Zn were also present at much lower concentrations.

As can be calculated from the data in Tables 1 and 2, in terms of percentage release of heavy metals, cadmium was the element leached to the greatest extent (5.4–6.0%) from each fly ash after the two-stage washing treatment, while lead was the element released to the lowest extent (0.24–0.31%).

According to the Italian effluent limits, neither wastewater met the standard limits for pH and the concentrations of aluminium, cadmium, lead, and zinc ions. Therefore, the wastewater treatment was focused on the removal of these metallic species.

Fig. 1 shows the effect of reducing the pH of wastewater on the residual concentrations of aluminium, cadmium, lead, and zinc ions, when a mixing time,  $t_c$ , of 10 min and a settling time of 2 h were adopted for wastewater treatment.

Under these operating conditions, the wastewater treatment was inadequate over the whole range of pH examined (5.5–9.5), because the residual concentration of cadmium ion was always above its standard limit (0.02 mg/l).

Irrespective of the type of wastewater tested, the greatest removals of aluminium, cadmium and lead ions were always achieved within the pH range of 6.5–7.5. In this pH range, the removal of aluminium ion was virtually complete (98.0–98.5%) and the percentage removals of lead (15–52%) and cadmium (12–40%) ions were comparable. For both wastewaters, the greatest removal of zinc ion (35–46%) was achieved at a pH of 9.5.

As shown in Fig. 2, prolonging the duration of wastewater treatment from 10 to 30 min did not significantly improve the removal of aluminium ion but always produced a significant increase in the removal of cadmium, lead, and zinc ions. In particular, over the pH range

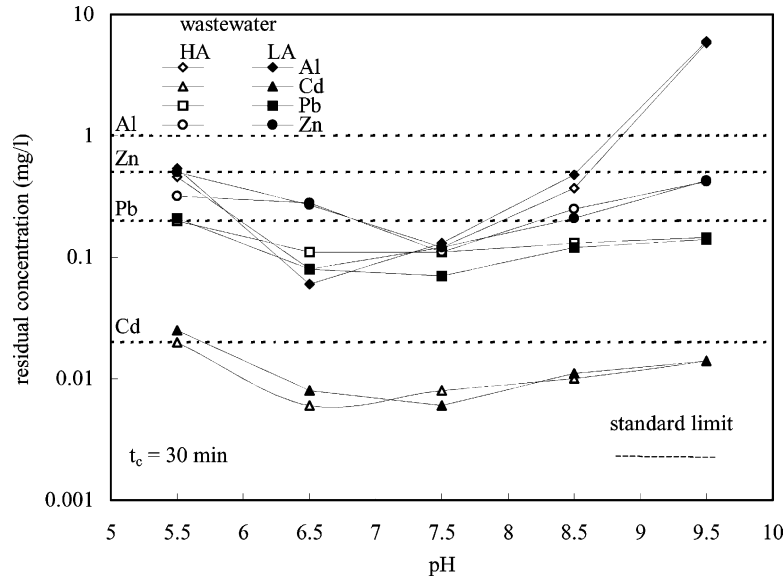


Fig. 2. Effect of pH upon residual concentration of metal ions in wastewater (30 min of treatment).

from about 5.8 to 8.6 the residual concentrations of all the examined metallic species were always found to be below the respective standard limits and, therefore, the wastewater treatment proved to be effective. Even in this case, the greatest removals of the various species (Al = 99.6–99.8%; Cd = 69–83%; Pb = 67–72%; Zn = 62–87%) were achieved within the pH range of 6.5–7.5.

The observed high removals of different metallic species at the same pH range raised doubts about the mechanism governing their removal from wastewater. In particular, precipitation of heavy metals as hydroxides could not be invoked as the unique removal mechanism.

To elucidate this question, the theoretical solubility of aluminium, cadmium, lead, and zinc hydroxide in terms of total soluble metal ion concentration (mg/l) was calculated at different pH values, taking into account the ionic strength of the wastewater [24] and the formation reactions of hydroxocomplexes, chlorocomplexes and sulphate complexes [25].

Based on these theoretical calculations and the results in Fig. 2 and Table 2, the following observations can be made:

- the theoretical pH of minimum solubility of Al hydroxide was about 6.5 for both the wastewaters and the corresponding equilibrium concentration of aluminium ion was always 0.02 mg/l. This theoretical concentration was only slightly lower than those obtained (0.06–0.08 mg/l) from wastewater treatment at a pH of 6.5–7.5 (Fig. 2), thus indicating that, after 30 min of treatment, equilibrium conditions for Al hydroxide precipitation were virtually reached;
- the theoretical pH of minimum solubility of cadmium, lead, and zinc hydroxide (12.0 for Cd, 10.1 for Pb, and 9.9 for Zn) greatly differed from the pH values (6.5–7.5) at which the maximum removal of these metallic species was observed (Fig. 2);



- (c) the initial concentrations of cadmium (0.026–0.036 mg/l) and lead (0.25–0.34 mg/l) ions in both the wastewaters (Table 2) were always much lower than the theoretical concentrations of minimum solubility of the respective metal hydroxides (0.13 mg/l as Cd and 29 mg/l as Pb);
- (d) the initial concentration of zinc ion in the LA wastewater (0.71 mg/l) was similar to the theoretical equilibrium concentration of zinc hydroxide (0.73 mg/l as Zn) at the initial pH of this wastewater (11.4). Conversely, the initial concentration of zinc ion in the HA wastewater (0.87 mg/l) was higher than the theoretical equilibrium concentration of zinc hydroxide (0.47 mg/l as Zn) at the initial pH of this wastewater (10.8). This indicated that the LA wastewater was virtually saturated in zinc hydroxide while the HA wastewater was oversaturated. Also, at pH values less than 9.0, the initial concentration of zinc ion in both wastewaters was lower than the respective theoretical equilibrium concentrations of zinc hydroxide. Conversely, within the pH range from 9.1 to 10.9, the theoretical equilibrium concentrations of zinc hydroxide were always lower than both the initial zinc ion concentration and its standard limit (0.5 mg/l).

These observations clearly indicated that the removal of aluminium ion from the tested wastewaters was always due to its precipitation as metal hydroxide. Conversely, the removal of cadmium and lead ions could not be ascribed to a precipitation process of the respective metal hydroxides. This was also true for zinc ion over the pH range from 5.5 to 9.0. At a pH value of 9.5, precipitation of zinc hydroxide was possible and residual concentrations of zinc ion less than its standard limit could be achieved.

Considering that: (1) the removal of aluminium ion at a pH of 6.5–7.5 was virtually complete after 10 min of treatment, and (2) the maximum removal of cadmium, lead, and zinc ions always occurred within this pH range, it was concluded that the removal of these heavy metals from the tested wastewaters was essentially due to an adsorption process onto the floc particles of aluminium hydroxide. Obviously, this adsorption process required a certain contact time to effectively remove the examined heavy metals.

As shown in Fig. 3, a contact time of 20 min was enough to reduce the concentrations of all the examined metallic species below the respective standard limits, when the wastewater treatment was carried out at a pH of 7.0. This pH value was selected on a conservative basis bearing in mind the removal mechanisms of heavy metals from both wastewaters.

As is well known, aluminium hydroxide precipitates in form of voluminous flocs that are characterised by a relatively high specific surface area and a negative electric charge. Therefore, these flocs have a high capacity for adsorbing various metallic species, as also demonstrated in this study, but they exhibit poor settling characteristics. The addition of a polyelectrolyte greatly improves the settling characteristics of these flocs but greatly reduces their specific surface area, thus reducing their adsorption capacity.

In order to simultaneously achieve effective removal of metallic species and good sedimentation of aluminium hydroxide flocs, the following operating conditions were adopted for the treatment of each wastewater: pH = 7.0; mixing time without polyelectrolyte = 20 min; mixing time in the presence of 2 mg/l of anionic polyelectrolyte = 10 min; settling time = 2 h.

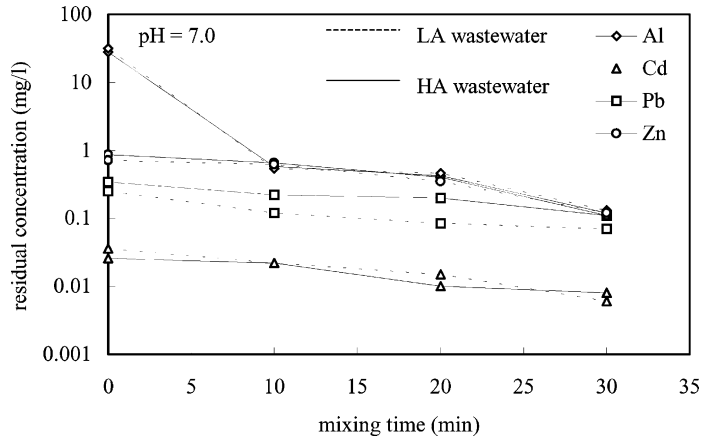


Fig. 3. Effect of mixing time upon removal of metal ions.

Under these operating conditions, the residual concentrations of aluminium, cadmium, lead, and zinc ions did not differ significantly from the values reported in Fig. 3 ( $t_c = 20$  min), while the settling rate of the Al hydroxide flocs was improved by a factor of about 4.

### 3.2. Sludge production and characterisation

After 2 h of sedimentation, the volume of sludge produced per litre of wastewater treated was 32–36 and 48–52 cm<sup>3</sup>/l in the presence or absence of polyelectrolyte, respectively.

On a dry weight basis, the production of sludge was 4.07 and 4.57 g solids/kg unwashed fly ash for HA and LA ash, respectively. Bearing in mind that the two-stage washing pre-treatment of MSWI fly ash with water caused a significant percentage weight loss

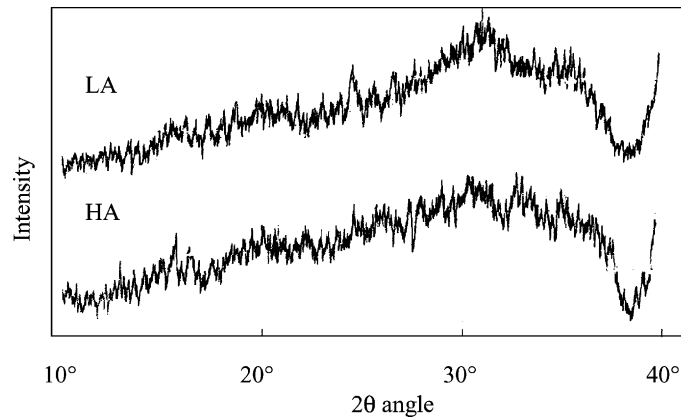


Fig. 4. XRD patterns of dried sludges.

Table 3  
Elemental analyses of dried sludges

Element (g/kg)	LA sludge	HA sludge
Al	343	342
Cd	0.2	0.3
Pb	1.6	3.0
Zn	6.6	8.3

of fly ash (19.7% for LA ash and 30.8% for HA ash), the production of sludge amounted to 5.69 and 5.88 g solids/kg washed fly ash for LA and HA ash, respectively.

Fig. 4 shows the X-ray diffraction patterns of the two sludges after their drying in a vacuum over calcium chloride.

These XRD patterns were always characterised by a large and intense band located over the  $2\theta$  range from 10 to  $40^\circ$  and by the absence of peaks corresponding to crystalline phases. This suggested that aluminium hydroxide was essentially precipitated from wastewater as an amorphous solid.

The elemental analyses of the two dried sludges, as given in Table 3, confirmed the hazardous characteristics of these wastes, due to their high heavy metals content.

### 3.3. Solidification/stabilisation of fly ash and sludge with cement

Table 4 gives the initial and final setting times of the cementitious mixes ( $w/s = 0.40$ ) without fly ash (cement–quartzite mixture) or with unwashed fly ash, washed fly ash, or washed fly ash + sludge. In all the mixes, the content of cement was 25 wt.% of total solid. The mixes incorporating sludge had a sludge to washed fly ash ratio of approximately 1/170 on a solids basis, corresponding to a complete combination of the two waste streams resulting from the ash washing and wastewater treatment.

From this table the following observations can be made:

- (a) the incorporation of unwashed fly ash into cementitious mixes always produced a delay in the cement setting that greatly depended on the fly ash composition. In particular, the final setting time of the mixes increased from 9.5 (control specimen) to 18 h or to

Table 4  
Setting data of cementitious mixtures

Mixture	Setting time (h)	
	Initial	Final
Control	5.8	9.5
LA unwashed ash–cement	5.5	18.0
HA unwashed ash–cement	30.2	210
LA washed ash–cement	4.9	10.0
HA washed ash–cement	8.1	25.0
LA washed ash–sludge–cement	5.6	11.0
HA washed ash–sludge–cement	9.3	26.0

Table 5  
Results of the TCLP extraction tests on solidified products (7 days curing in air at 20 °C and 100% RH)

Element (µg/l)	LA unwashed ash–cement	LA washed ash–sludge–cement	HA unwashed ash–cement	HA washed ash–sludge–cement	Standard limit (µg/l)
Cd	25	10	280	15	20
Cr(VI)	240	18	850	25	2000 Cr; 200 Cr(VI)
Cu	60	42	970	50	100
Pb	6270	52	32500	68	200

a practically unacceptable value (210 h) when LA or HA unwashed fly ash was used, respectively;

- (b) the retarding effect of fly ash on setting was markedly reduced when unwashed fly ash was replaced with washed fly ash. In the case of HA fly ash, the final setting time of the mixes reduced to an acceptable value (25 h) and, in the case of LA fly ash, to a value (10 h) denoting a negligible retarding effect of this ash on cement setting;
- (c) the cementitious mixes incorporating sludge and washed fly ash always exhibited setting times which were only slightly higher than the respective times measured for the mixes incorporating washed fly ash alone (final setting times of 11 h for LA washed ash–sludge and 26 h for HA washed ash–sludge mixture).

Table 5 gives the results of the TCLP extraction tests on solidified products incorporating unwashed fly ash or washed fly ash and sludge, after 7 days curing in air at 20 °C and 100% RH. In this table the leaching standards established by the Italian legislation on solid wastes disposal are also reported. It can be seen that the cementitious matrices incorporating sludge and washed fly ash were always able to meet the leaching standards. No evaluation was made for Ni and Zn leaching since no standard limit for these metals is established by Italian legislation. Conversely, the cementitious matrices incorporating unwashed fly ash failed to meet the leaching standards and this was particularly evident for the mixture incorporating HA unwashed fly ash which exhibited a final setting time above 7 days (Table 4).

After 7 days curing, the unconfined compressive strengths of the solidified products incorporating sludge and washed fly ash were 2.4 N/mm<sup>2</sup> (HA fly ash) and 3.2 N/mm<sup>2</sup> (LA fly ash). These strength values were considered to be satisfactory in relation to the high water to cement weight ratio (1.6) of the mixes investigated and to the strength value of 0.2 N/mm<sup>2</sup> needed to support the dead-load of a 10 m-high column of S/S product having a density of 2000 kg/m<sup>3</sup>.

All these data proved the feasibility of the combined washing-immobilisation process as a suitable means of optimising the treatment of MSWI fly ash by cementitious stabilisation, especially when this process was applied to the treatment of fly ashes containing high amounts of heavy metals, alkali chlorides and sulphates.

Undoubtedly, the better performance of the combined washing-immobilisation process as compared with the simple S/S process arises from the ability of the washing step to transform MSWI fly ash into a material that adversely affects cement hydration to a much lower extent.

As evidenced by the elemental analyses of the two tested fly ashes (Table 1), HA unwashed fly ash was much richer in both water-soluble salts (alkali chlorides and sulphates) and heavy metals than LA unwashed fly ash.

Alkali chlorides are known to behave as set accelerators at low concentrations (e.g. less than 12 wt.% of cement) and to act as retarders at very high concentrations [26]. Typically, the final setting times of cement pastes containing 30% of NaCl by weight of cement may be two to three times those of pure cement pastes, depending on the composition and fineness of the cement [27].

Alkali sulphates commonly act as set accelerators by accelerating the hydration of tricalcium silicate ( $3\text{CaO}\cdot\text{SiO}_2$ ) phase [26]. At equivalent concentrations, alkali sulphates accelerate the cement setting to a lesser extent than alkali chlorides. Also, potassium sulphate can cause a false set of cement, due to the precipitation of syngenite ( $\text{CaSO}_4\cdot\text{K}_2\text{SO}_4\cdot\text{H}_2\text{O}$ ) and even produce a flash set, due to the removal of  $\text{CaSO}_4$  from the system.

Heavy metals such as chromium(III), cadmium, nickel, and mercury in the form of oxides or salts belong to inorganic compounds having slight or negligible inhibiting effect on cement hydration, probably because these metallic species are incorporated throughout the cement matrix (formation of reaction products, substitutional or interstitial solid solutions with hydrated cement phases) [15,23,28,29].

In contrast, lead and zinc compounds exert a strong retarding effect on cement hydration. Lead retards the setting of cement, due to the formation of colloidal gelatinous basic lead compounds that cover the silicate phase [17,19]. Zinc forms an amorphous layer of gel (zinc hydroxide or calcium zinc hydrate) around the cement grains, thus markedly retarding the hydration of tricalcium silicate phase and, to a minor extent, that of tricalcium aluminate ( $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ ) phase [16,18,20,22]. Due to a relevant absorption of water by the zinc hydrate gel, most of the water added to cement could even not be available for reaction with the silicate and aluminate phases [21]. Lieber [14] reported that, in the case of cement pastes (water to cement weight ratio = 0.35) doped with zinc oxide, the cement setting is markedly delayed by ZnO addition when this compound is added at concentration levels above about 0.2 wt.% of cement. At a 0.3% ZnO concentration, the initial setting time of the mixes was found to be prolonged up to 30–60 h, depending on the type of cement used. Tashiro et al. [15] and Olmo et al. [23] found that the retarding effect of zinc and lead compounds is particularly relevant (final setting retardation up to 170 h and more) when the concentrations of these metals exceed about 5 wt.% of cement.

Therefore, these previous studies may explain why HA unwashed fly ash was found to adversely affect the setting of cement to a much greater extent than LA unwashed fly ash (Table 4).

However, as can be deduced from the data in Tables 1 and 2, washing pre-treatment always produced a significant heavy metal enrichment of fly ash, due to a great removal of chlorides (63–80%) and sulphates (63–66%) and to a low release of heavy metals. For example, the contents of Pb and Zn in HA washed ash were 1.01 and 2.59% against 0.70 and 1.80% in HA unwashed ash. Nevertheless, washed fly ash was always found to retard cement hydration to a much lower extent than unwashed fly ash (Table 4). This behaviour was particularly evident (reduction of final setting time from 210 to 25 h) for the HA fly ash–cement mixture containing heavy metals, in particular zinc, at concentration levels exceeding 5 wt.% of cement (5.4% Zn in unwashed ash–cement and 7.8% Zn in washed ash–cement mixture).

These observations suggested that the improved setting behaviour of washed fly ash–cement mixtures could not be ascribed to the only partial removal of alkali chlorides and sulphates from fly ash, but it should be related primarily to other types of interaction.

Previous studies [13,30] have shown that, during the washing step, the interaction of MSWI fly ash with water leads to a rapid formation of hydrate phases such as syngenite, gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), and ettringite ( $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$ ). A rapid formation of calcium hydroxyzincate ( $\text{CaZn}_2(\text{OH})_6 \cdot 2\text{H}_2\text{O}$ ) and laurionite ( $\text{Pb}(\text{OH})\text{Cl}$ ) have also been observed [30].

Thus, it was likely to think that such hydrate phases may form a protective surface layer around the grains of fly ash, thus markedly reducing the inhibiting action of this material and, in particular, of heavy metals on cement hydration.

Furthermore, Lieber [14] found that the retarding effect of zinc compounds on setting of cement pastes is extremely reduced when calcium hydroxyzincate is added instead of zinc oxide at an equivalent concentration.

The transformation of heavy metal compounds such as zinc oxide into less reactive forms, coupled with the formation of protective layers of hydrate phases over the grains of fly ash, may explain why the washing step was capable of converting MSWI fly ash into a material that adversely affected cement hydration to a much lower extent than unwashed fly ash.

As shown in Table 4, addition of the sludge to the washed fly ash prior to stabilisation process did not significantly modify the setting characteristics of washed fly ash–cement mixtures, in spite of the fact that zinc and lead were the predominant heavy metals in the sludge (Table 3) and the availability of these metals for cement interaction was much higher than that of the same metallic species within fly ash grains.

On the basis of the data in Table 3 and the composition of the cementitious mixes investigated, it was calculated that the concentrations of zinc and lead due to sludge addition, in terms of percentage of metal oxide by weight of cement, were 0.03% PbO and 0.14% ZnO for LA washed fly ash–cement mixture, and 0.06% PbO and 0.18% ZnO for HA washed fly ash–cement mixture. It can be seen that these concentrations of zinc were only slightly lower than 0.20% that is the concentration level above which zinc oxide was found to retard cement setting remarkably [14].

These calculations also suggested that a reduction of the cement content below 25 wt.% of total solid could create serious unfavourable effects on the setting and hardening of cementitious mixes incorporating sludge and washed fly ash.

#### 4. Conclusions

The combined washing-immobilisation process of MSWI fly ash proves to be a suitable means of optimising the disposal of this material in cementitious matrices, especially when this process is applied to the treatment of fly ashes containing high amounts of heavy metals, alkali chlorides and sulphates.

The use of this process does not create serious environmental problems related either to the treatment of wastewater resulting from fly ash washing step or to the disposal of sludge produced from wastewater treatment.

The wastewater treatment can be successfully realised through a simple reduction of pH to values of 6.5–7.5. This treatment is capable of removing the detected contaminants (Al, Cd, Pb, and Zn ions) through two different mechanisms: precipitation of aluminium ion

as metal hydroxide and adsorption of cadmium, lead, and zinc ions onto floc particles of aluminium hydroxide.

The sludge produced from wastewater treatment (about 5.8 g solids/kg washed fly ash) can be completely mixed with washed fly ash and this mixture can be incorporated into cementitious mixes to a great extent (75 wt.% of total solid) without the risks of an unacceptable delay of cement setting and an excessive heavy metals leachability from solidified products.

The improved performance of the combined washing-immobilisation process as compared with the immobilisation process of unwashed fly ash may be ascribed primarily to the ability of the washing step in promoting the formation of hydrate phases that incorporate and/or convert heavy metal compounds into less reactive forms and, secondarily, to its ability of removing significant amounts of alkali chlorides and sulphates from fly ash. As a result, MSWI fly ash is transformed into a material that adversely affects cement hydration to a much lower extent than unwashed fly ash.

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