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# Optimization of the solidification/stabilization process of MSW fly ash in cementitious matrices

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## Abstract

The solidification/stabilization (S/S) process of municipal solid waste (MSW) fly ash in cementitious matrices was investigated in order to ascertain the feasibility of a washing pretreatment of fly ash with water as a means of maximizing the ash content of cementitious mixtures. Four types of fly ash resulting from different Italian MSW incineration plants and ASTM Type III Portland cement were used in this study. Ash–cement mixtures with different fly ash/cement (FA/C) ratios were made using untreated and washed fly ash. Washing of fly ash with water was realized by a two-stage treatment (liquid/solid = 25; mixing time = 15 min for each stage). The cementitious mixtures were characterized for water demand, setting time, mechanical strength, and heavy metals leachability. Comparison between the above properties of mixtures incorporating untreated and washed fly ash (particularly, setting characteristics), coupled with economical evaluation of the S/S process when applied to untreated and washed fly ash, proved the feasibility of washing pretreatment as a means of maximizing the incorporation of MSW fly ash in cementitious matrices (ash content up to 75%–90% by weight of total solid). © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* MSW fly ash; Solidification/stabilization process; Washing pretreatment

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## 1. Introduction

The disposal of fly ash resulting from municipal solid waste incineration (MSW fly ash) into landfill sites generally poses serious environmental problems, due to the high heavy metals content of this material and the high leachability of these metals, which may cause strong contamination of groundwater.

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At present, MSW fly ash is commonly disposed after a solidification/stabilization (S/S) process which immobilizes the heavy metals in cementitious matrices by physical encapsulation and/or chemical stabilization [1–4].

However, the adverse characteristics of most MSW fly ashes in terms of chemical composition — in particular, the high content of sulfates, chlorides, alkalies, and heavy metals — often limit their dosage to less than 15%–20% by weight of ash–cement mixtures, since higher ash dosages would result in delaying the final setting time of the cementitious mixtures to an unacceptable level [5,6].

Our previous work [6], although limited to the study of ash–cement mixtures with ash dosages not higher than 35% by weight, proved the suitability of a washing pretreatment of MSW fly ash with water as a means of improving the characteristics of ash–cement mixtures in terms of setting time, early hardening, and mechanical strength.

The practical inference of this finding is that much higher fly ash/cement (FA/C) ratios could be used when inertizing washed fly ash and, consequently, considerable economical benefits would be attained as a result of a lesser consumption of cement and a reduced volume of the final product to be disposed.

However, it must be considered that increasing FA/C ratio of ash–cement mixtures greatly enhances the risks of heavy metals leachability. Also, washing pretreatment results in an additional cost which basically includes the treatment cost for the wastewater resulting from such a process. Washing pretreatment also produces a heavy metals enrichment of fly ash, thus increasing the risks of heavy metals leachability. It follows that inertization of washed fly ash in cementitious matrices may be an advantageous S/S process only if considerable amounts of washed fly ash may be incorporated in cementitious matrices without the risk of heavy metals release from solidified products.

On the basis of the above considerations, the present study was undertaken to investigate the feasibility of such a treatment for a number of fly ashes coming from different Italian MSW incineration plants.

For this purpose, ash–cement mixtures with different FA/C ratios were made using untreated or washed fly ash, and these mixtures were characterized for water demand, setting time, mechanical strength, and leaching properties.

This paper presents the results of these experiments together with an economical evaluation of the S/S process when applied to untreated or washed fly ash.

## **2. Materials and methods**

Four types of fly ash coming from MSW incineration plants located at four different Italian cities (Bologna, Forlì, Modena, and Rimini) were tested in this study. These fly ashes were designated by notations indicating the respective places of origin (BO, FO, MO, and RI).

Each fly ash was preliminarily dried in an oven at 105°C and then analyzed for its chemical composition, loss on ignition (L.O.I.), particle size distribution, and leaching properties.

The chemical composition was determined by X-ray fluorescence, flame atomic absorption spectrometry, gravimetric and volumetric analyses. L.O.I. was determined by heating to constant weight at 750°C. Particle size distribution was evaluated by a laser diffraction technique. Heavy metals leachability was evaluated by the Italian standard acetic acid leaching test [7]. This test consists of contacting a given amount of solid material with distilled water (liquid/solid weight ratio = 16) and keeping the pH of the leaching medium at  $5 \pm 0.2$  units throughout the test by addition of a 0.5-N acetic acid solution; the maximum amount of acetic acid solution to be added is 4 ml/g solid sample. After 24 h, solid–liquid separation is carried out through vacuum filtration on a 0.45- $\mu\text{m}$  membrane filter, and the resulting leachate is diluted with distilled water to a volume which is 20 times the weight (g) of solid material tested. Finally, the leachate is analyzed for heavy metals concentrations.

An aliquot of untreated fly ash was also subjected to a two-stage washing treatment with distilled water (liquid/solid weight ratio = 25; mixing time = 15 min for each stage of treatment). After each mixing step, the fly ash was filtered through a 0.45- $\mu\text{m}$  Millipore membrane and then dried in an oven at 105°C.

Untreated and washed fly ashes were also analyzed by X-ray diffraction (XRD) technique using Ni-filtered Cu K $\alpha$  radiation (copper tube operated at 40 kV and 30 mA) on a diffractometer at 1°/min, 5°–80° 2 $\theta$ . In some cases, infrared (IR) spectrometry was also used to detect some constituents that were not identified by XRD analysis.

The wastewater resulting from the two-stage ash washing process was analyzed for pH and chemical composition.

The ash–cement mixtures were made using untreated or washed fly ash, both preliminarily dried at 105°C, distilled water (specific conductance less than 2  $\mu\Omega^{-1}/\text{cm}$ ), and ASTM Type III Portland cement. Table 1 gives the physical and chemical characteristics of the Portland cement used, along with its mineralogical composition calculated by the Bogue method.

The ash content of the mixtures was varied over the range from 35% to 90% by weight of total (ash plus cement) solid, corresponding to FA/C ratios from 0.54 to 9.0.

Table 1  
Chemical and physical characteristics of the Portland cement used

	%		%
SiO <sub>2</sub>	21.20	Na <sub>2</sub> O	0.27
Fe <sub>2</sub> O <sub>3</sub>	3.40	K <sub>2</sub> O	0.43
Al <sub>2</sub> O <sub>3</sub>	4.40	Na <sub>2</sub> O equiv.	0.55
CaO	63.10	Cl	0.01
Free CaO	0.14	L.O.I.	0.98
MgO	1.20	Density (kg/m <sup>3</sup> )	3155
SO <sub>3</sub>	3.30	Blaine specific surface area (m <sup>2</sup> /kg)	400
Mn <sub>2</sub> O <sub>3</sub>	0.04	C <sub>3</sub> S	51.50
TiO <sub>2</sub>	0.09	C <sub>2</sub> S	22.10
P <sub>2</sub> O <sub>5</sub>	0.10	C <sub>3</sub> A	5.90
SrO	0.06	C <sub>4</sub> AF	10.50

Table 2  
W/S and W/C ratios for ash–cement mixtures at normal consistency

Fly ash content of mixtures	35%		50%		75%		90%	
	W/S	W/C	W/S	W/C	W/S	W/C	W/S	W/C
Untreated FO	0.435	0.669	0.515	1.030	0.655	2.62	0.825	8.25
Washed FO	0.525	0.807	0.650	1.300	0.925	3.70	1.150	11.50
Untreated BO	0.360	0.554	0.385	0.770	0.395	1.58	0.470	4.70
Washed BO	0.445	0.685	0.485	0.970	0.600	2.40	0.725	7.25
Untreated MO	0.350	0.538	0.370	0.740	0.410	1.64	0.460	4.60
Washed MO	0.500	0.770	0.585	1.170	0.710	2.84	0.800	8.00
Untreated RI	0.360	0.554	0.385	0.770	0.410	1.64	0.430	4.30
Washed RI	0.430	0.660	0.510	1.020	0.640	2.56	0.875	8.75

The water content of each mixture was adjusted so as to obtain the same consistency (normal consistency) as that established by the ASTM C187-86 test method [8] for setting time measurements by Vicat needle. Table 2 gives the water/solid (W/S) ratios and the corresponding water/cement (W/C) ratios for all the mixtures investigated.

All the mixtures were tested for initial and final setting times, according to the ASTM C191-92 test method [9]. On the basis of these results, some ash–cement mixtures were selected and successively tested for strength and leaching properties.

Unconfined compressive strength was measured on cubic specimens (40 mm side) after their storage in molds for 2 days in air at 20°C and R.H. > 90% and their subsequent immersion in water at 20°C for 5 days. The average compressive strength was calculated from three replicates; the coefficient of variation for compressive strength measurements was 4.5%.

Standard acetic acid leaching tests were performed on cubic specimens (40 mm side) after their storage for 7 days in air at 20°C and 100% R.H. The concentrations of heavy metals in the leachate were determined by an atomic absorption spectrophotometer equipped with a graphite furnace.

### 3. Results and discussion

#### 3.1. Characterization of untreated fly ash

The elemental and particle size analyses of the untreated fly ashes are reported in Table 3 and Fig. 1, respectively.

All the fly ashes were characterized by particle sizes lower than 150  $\mu\text{m}$  and did not greatly differ for the grain size distribution. However, the highest content of fine particles was found for MO fly ash.

All the fly ashes exhibited high contents of alkalis (6.6%–16.6% as  $\text{Na}_2\text{O}$  equivalent), chlorides (5.6%–11.9% as Cl) and water-soluble sulfates (10.8%–18.0% as  $\text{SO}_3$ ), and these species were particularly abundant in MO and RI fly ashes (Table 3).

The predominant heavy metals were always nickel (2.2%–2.8%), zinc (0.37%–1.8%), lead (0.22%–0.70%) and copper (0.06%–0.14%), accompanied by lesser amount of

Table 3  
Elemental analyses of untreated fly ashes

Element	BO	FO	MO	RI
Ca (%)	18.2	20.2	15.2	14.2
Si (%)	10.6	10.1	10.1	7.7
K (%)	3.6	5.4	6.2	6.6
Al (%)	5.9	4.4	4.6	2.9
Na (%)	2.8	2.0	4.4	8.4
Fe (%)	1.0	1.0	1.2	0.91
Mg (%)	1.4	1.7	1.2	0.97
S <sup>a</sup> (%)	4.3	4.3	6.7	7.2
Cl (%)	5.6	7.2	8.7	11.9
Ni (%)	2.8	2.7	2.6	2.2
Zn (%)	0.64	0.37	1.8	1.7
Pb (%)	0.40	0.22	0.70	0.46
Cu (ppm)	900	600	1400	700
Cd (ppm)	30	< 0.25	240	150
Cr (ppm)	200	500	400	300
Hg (ppm)	< 0.025	< 0.025	< 0.025	< 0.025
As (ppm)	< 0.053	200	< 0.053	< 0.053
L.O.I. (%)	19.3	14.8	12.0	13.5

<sup>a</sup>Water-soluble sulfates expressed as sulfur.

chromium, cadmium, mercury, and arsenic. In terms of total amount of heavy metals, these species were more abundant in MO and RI fly ashes (Table 3).

The XRD patterns of untreated fly ashes, shown in Fig. 2, revealed that the main crystalline phases of all the fly ashes were  $\gamma$ -anhydrite, halite and sylvite. Also, calcite was detected in BO, FO, and MO fly ashes, and apthitalite ((Na,K)<sub>3</sub>Na(SO<sub>4</sub>)<sub>2</sub>) was identified in FO and RI fly ashes. The inability to match XRD peaks with known heavy metal phases or with calcium silicates and aluminosilicates suggested that the detectable metals were present as impure, complex compounds and that the calcium silicates and aluminates were present as amorphous and/or complex crystalline phases (solid solutions with alkalis and/or alkaline sulfates). On the other hand, the presence of silicates and aluminosilicates in the untreated fly ashes was confirmed by the IR spectra showing the broadened peak of SiO<sub>4</sub> groups over the range of wave numbers of 900–1300 cm<sup>-1</sup>.

Table 4 gives the results of the standard acetic acid leaching tests, along with the limit concentrations of the heavy metals established by the Italian law for solid waste disposal [10,11].

These results revealed that, for all the fly ashes investigated, the concentrations of some heavy metals (Cd, Cr, Cu or Pb) in the leachate were higher than the corresponding limit values as established by the Italian regulation. Furthermore, for FO, MO, and RI fly ashes, the concentrations of some heavy metals in the leachate (Pb for all the fly ashes, Cd for MO and RI, and Cu for MO) were as high as more than 10 times the corresponding limit values.

According to the Italian regulation [10,11], the examined fly ashes have to be disposed in II Category, class C, landfills. The only exception is represented by BO fly

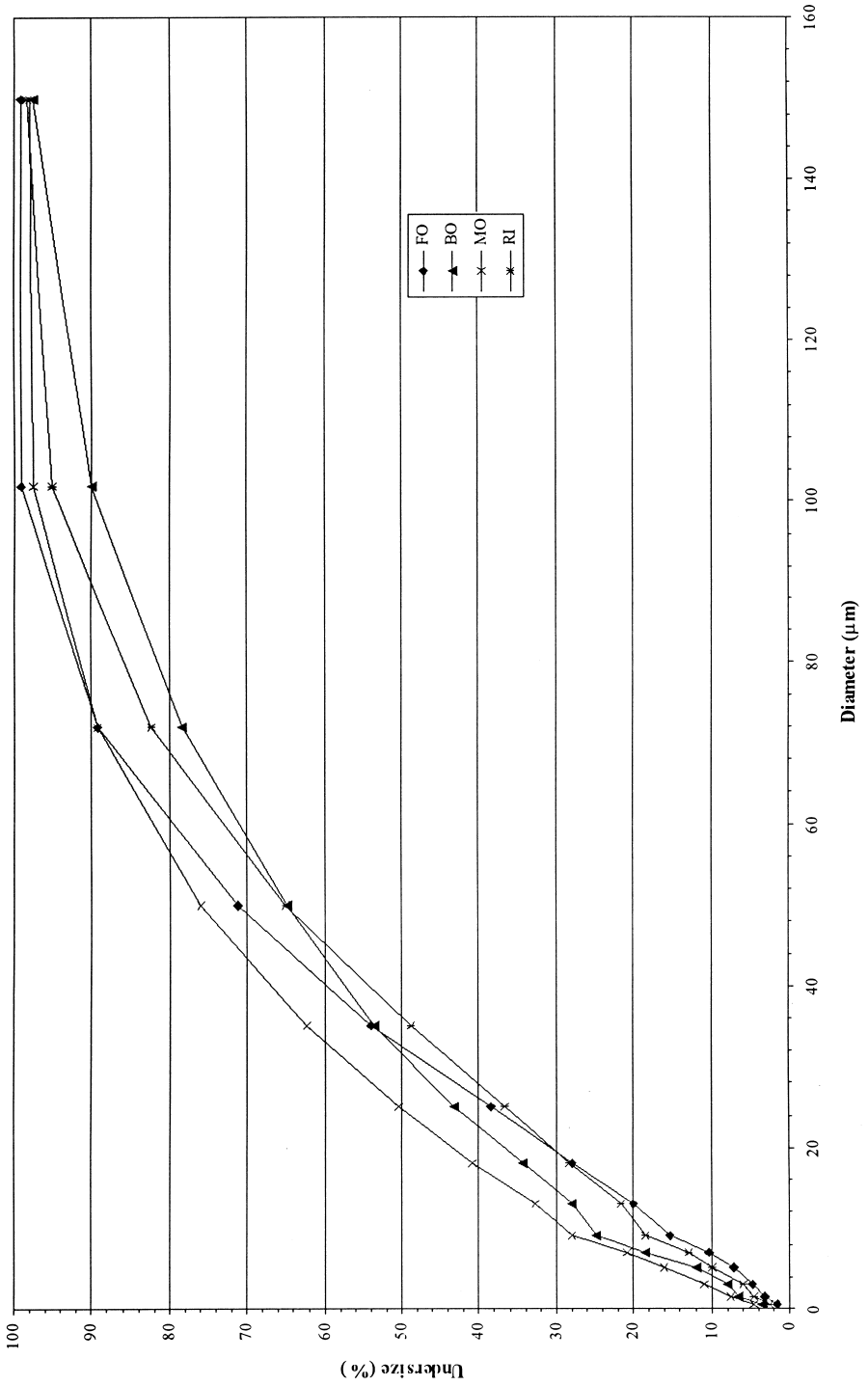


Fig. 1. Particle size distribution of fly ashes.

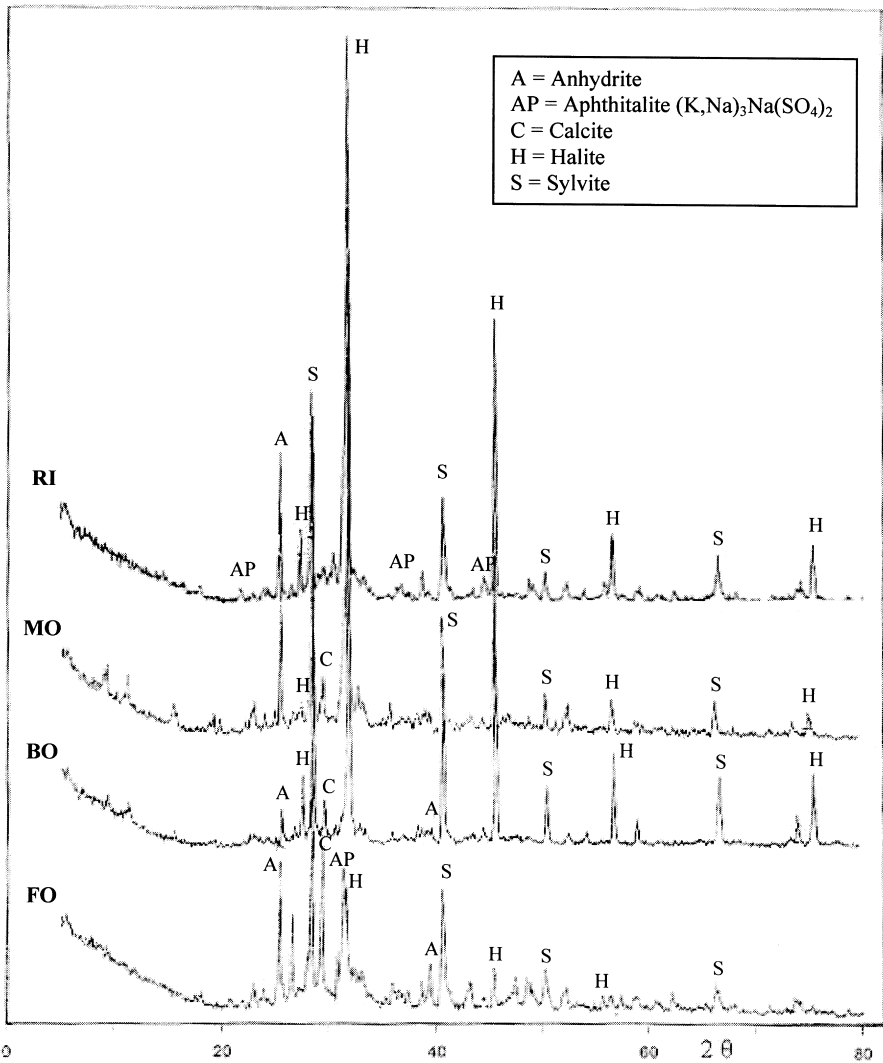


Fig. 2. XRD patterns of untreated fly ashes.

ash, which could be disposed in II Category, class B', landfills if there are particular hydraulic, geological and hydrogeological conditions that may reduce site vulnerability.

### 3.2. Characterization of wastewater and washed fly ash

Table 5 gives the chemical composition of the wastewater resulting from the two-stage washing pretreatment of each fly ash tested, together with the limit concentrations of the ionic species established by the Italian law for wastewater disposal into

Table 4

Results of standard acetic acid leaching tests on untreated fly ashes

Element	BO	MO	RI	FO	Limit value <sup>a</sup>
Hg (mg/l)	< 0.001	< 0.001	0.004	< 0.001	0.005
As (mg/l)	< 0.01	< 0.01	< 0.01	< 0.01	0.5
Pb (mg/l)	0.44	78.95	3.30	12.60	0.2
Cu (mg/l)	0.012	18.32	0.38	0.27	0.1
Cr(VI) (mg/l)	1.04	0.51	0.14	0.63	0.2
Cd (mg/l)	0.014	15.30	5.12	< 0.001	0.02
Ni (mg/l)	0.33	0.47	0.25	0.31	–
Zn (mg/l)	7.70	195.50	180.20	5.75	–

<sup>a</sup>Limit concentrations for Zn and Ni are not given by Italian regulation [10,11].

surface waters [12]. This table also gives the cumulative weight loss of each fly ash and the solubilities of heavy metals hydroxides calculated on the basis of the solubility product constants, the pH and ionic strength of wastewater and the complex-forming reactions between the heavy metals and OH<sup>-</sup>, Cl<sup>-</sup> or SO<sub>4</sub><sup>2-</sup> ions.

As expected, the water-soluble species such as alkalis, sulfates and chlorides were greatly leached out of each fly ash (75%–84% for potassium, 85%–89% for sodium, 63%–70% for sulfates, and 50%–80% for chlorides). The concentration of sulfates in

Table 5

Chemical composition of wastewater resulting from ash washing process

n.d.: not detectable.

Ionic species concentration <sup>a</sup> (mg/l)	Wastewater resulting from washing of fly ash				Limit values (mg/l)
	BO	FO	MO	RI	
Na	500	358	788	1428	–
K	610	864	978	990	–
Ca	375	424	480	284	–
Mg	0.65	1.02	0.95	0.58	–
Al	31.4	25.5	27.9	17.4	1.0
Fe	0.23	0.18	0.16	0.16	2.0
Si	1.51	1.52	1.51	1.16	–
Zn	0.71 (0.78)	0.61 (0.53)	0.87 (0.47)	1.19 (0.79)	0.5
Pb	0.25 (191)	0.12 (66)	0.34 (48)	0.25 (197)	0.2
Cd	0.036 (0.18)	n.d. (0.30)	0.026 (0.53)	0.025 (0.20)	0.02
Ni	0.096 (5.71)	0.086 (3.39)	0.081 (2.84)	0.070 (5.75)	2.0
Cu	0.089 (0.59)	0.048 (0.58)	0.099 (0.58)	0.056 (0.59)	0.1
Cr	0.11 (0.009)	0.18 (0.004)	0.16 (0.003)	0.12 (0.010)	2.0 Cr, 0.2 Cr(VI)
Chlorides	896	1080	1089	1185	1200 <sup>b</sup>
Sulfates as SO <sub>4</sub> <sup>2-</sup>	1625	1625	2656	2968	1200 <sup>b</sup>
pH	11.4	11.0	10.8	11.4	5.5–9.5
Cumulative weight loss of fly ash (%)	19.7	21.4	30.8	35.4	

<sup>a</sup>Numbers within brackets correspond to metal hydroxide solubilities.

<sup>b</sup>These limits do not apply to marine waters.



the wastewater was always above the limit value established for wastewater disposal into surface waters [12].

The release of heavy metals was always very low, the highest percentage of release being found for chromium (1.8%–2.8%) and cadmium (0.5%–6%). The concentrations of Cd, Cu, Ni, and Pb ions in the wastewaters were always well below the solubilities of the respective metal hydroxides, while the concentrations of Zn and Cr ions were near and well above the equilibrium concentrations of the respective metal hydroxides. Furthermore, the ionic concentration of zinc was always above the limit value established by the Italian law [12], while the ionic concentrations of cadmium and lead exceeded the respective limit values for the wastewaters resulting from the washing pretreatment of BO, MO, and RI fly ashes.

Due to the release of significant amounts of calcium hydroxide by hydrolysis of calcium silicates and aluminosilicates, all the wastewaters exhibited pH values (10.8–11.4) which were well above the limit values (5.5–9.5). Also, the ionic concentration of aluminum always exceeded the established limit value (Table 5).

As a consequence of the high release of water-soluble compounds and the low release of heavy metals, all the fly ashes resulted to be enriched in heavy metals after the washing process. Table 6 gives the elemental analyses of the washed fly ashes calculated on the basis of the results in Tables 3 and 5.

Fig. 3 shows the XRD patterns of washed fly ashes. A comparison between the XRD spectra of untreated and washed fly ashes (Figs. 2 and 3) revealed that the washing pretreatment did not substantially modify the nature of the crystalline phases of the fly ashes, except for the occurrence of two new crystalline phases such as gypsum (MO fly ash) and syngenite (MO and BO fly ashes). Obviously, the intensities of the XRD peaks corresponding to very water-soluble compounds such as halite and sylvite were significantly reduced in the XRD spectra of washed fly ashes.

### 3.3. Water demand of ash–cement mixtures

Figs. 4 and 5 show how the W/S ratio of ash–cement mixtures varies as a function of ash content, when these mixtures were made at normal consistency by using untreated or washed fly ash, respectively. For mixtures not containing fly ash (Portland cement pastes), normal consistency was achieved using a W/C ratio of 0.415.

As can be seen from Fig. 4, the partial replacement of Portland cement with untreated fly ash influenced the W/S ratio of the mixtures in a different way, depending on the type of fly ash used.

With respect to the Portland cement pastes, mixtures incorporating FO fly ash always exhibited higher W/S ratios than the other fly ashes and this ratio greatly increased with increasing ash content. Conversely, mixtures incorporating BO, MO, or RI fly ash always exhibited lower W/S ratios than the FO fly ash when the ash content was varied over the range of 35%–75% by weight. Also, the W/S ratio was much less affected by ash content.

This different rheological behavior of the examined fly ashes cannot be explained on the basis of their particle size distribution shown in Fig. 1.

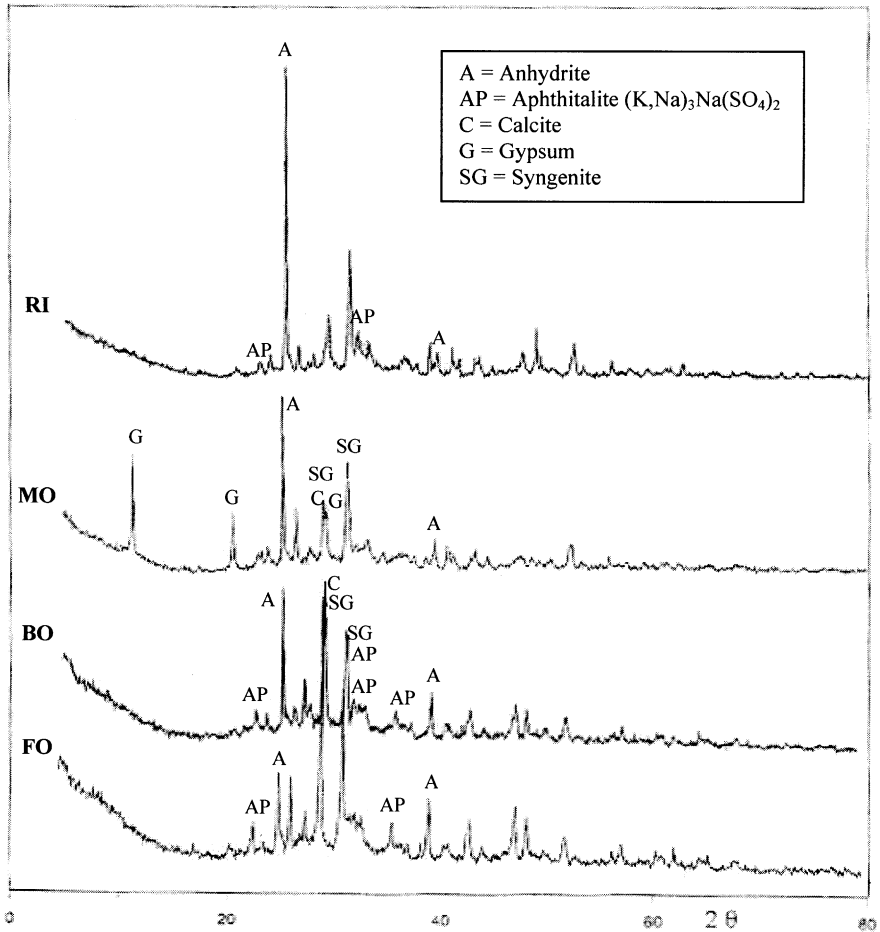


Fig. 3. XRD patterns of washed fly ashes.

Regardless of the type of fly ash tested, the use of washed fly ash always resulted in a marked increase of the W/S ratio of ash–cement mixtures (Fig. 5), when compared both to Portland cement pastes and untreated fly ash–cement mixtures. In all cases, the W/S ratio was found to significantly increase with increasing ash content. At a given ash content, the highest W/S values were always monitored for mixtures incorporating FO fly ash, similarly to what was observed for untreated fly ash (Fig. 4).

It is undoubted that the increased water demand of the mixtures incorporating washed fly ash represents a relevant drawback for the inertization of washed fly ash in cementitious matrices, because higher W/S ratios will reduce the compressive strength of solidified products, will enhance the risks of heavy metals leachability from solidified products, and will also increase the final volume of solidified products.

However, it is well-known that the W/S ratio of cementitious mixtures can significantly be reduced by using superplasticizing agents [13]. Thus, for example, in the case

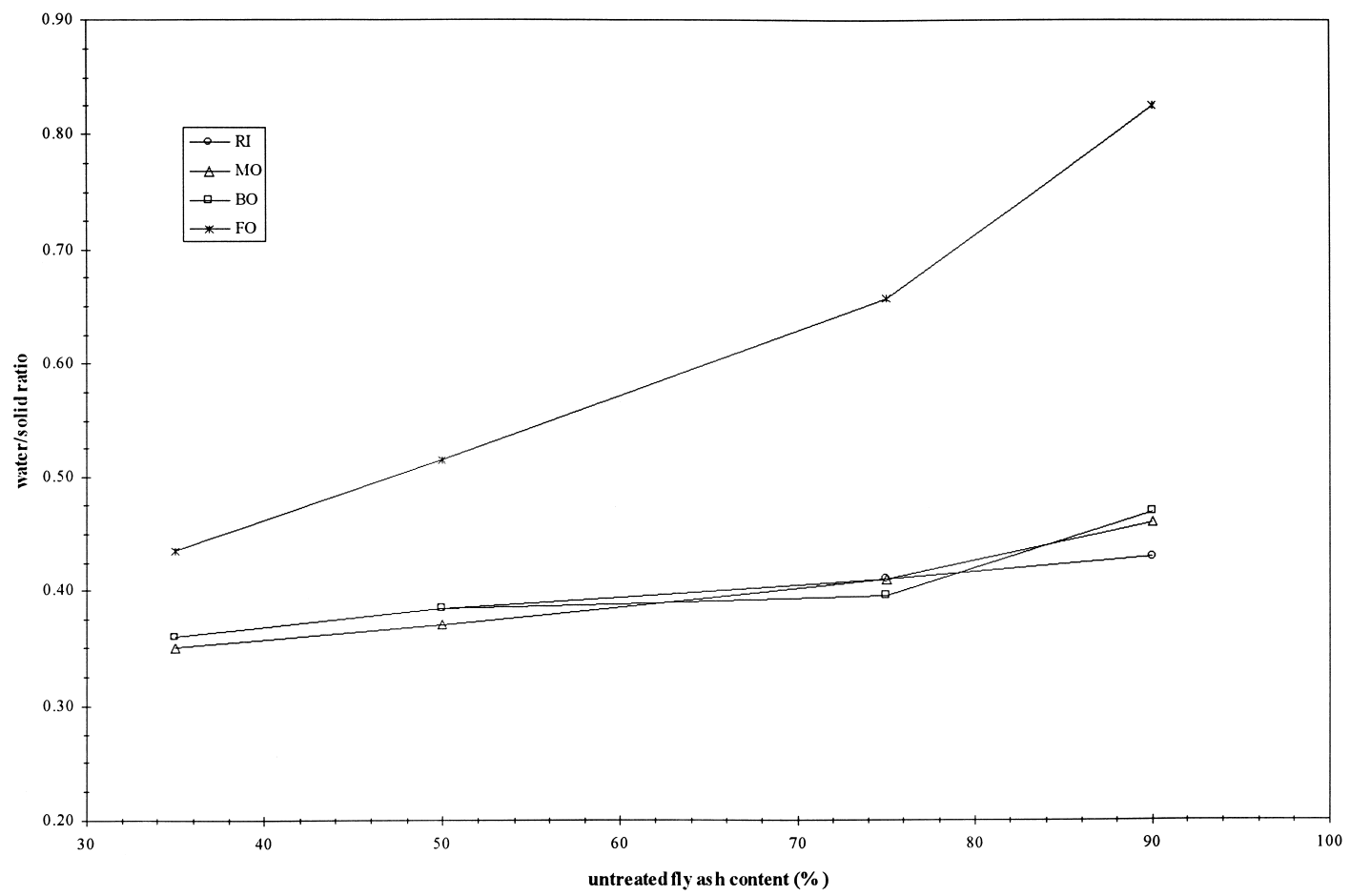


Fig. 4. Effect of ash content on W/S ratio of ash–cement mixtures at normal consistency (untreated fly ash).

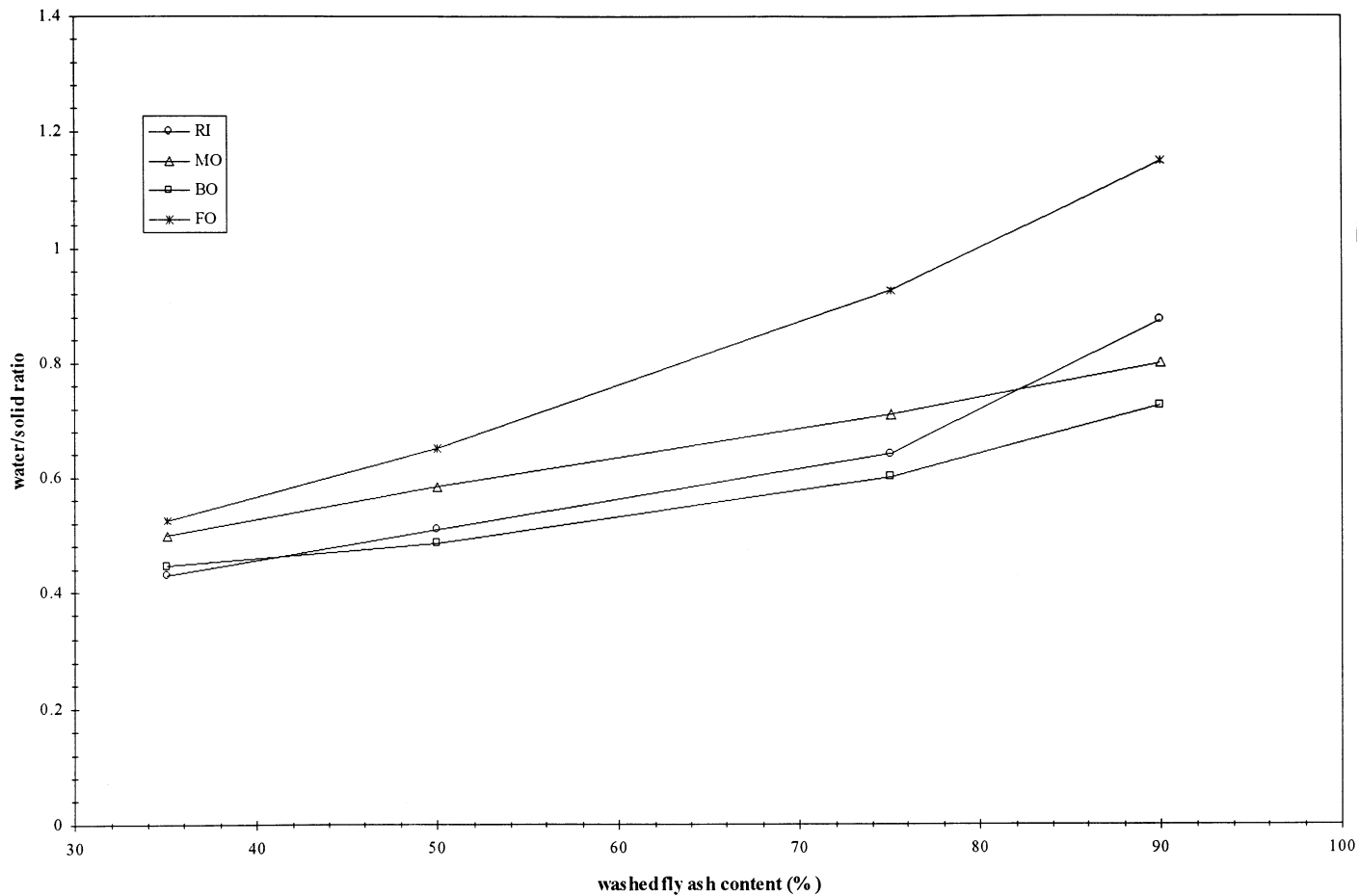


Fig. 5. Effect of ash content on W/S ratio of ash–cement mixtures at normal consistency (washed fly ash).

of mixtures incorporating 90% RI fly ash, the normal consistency of these mixtures was achieved using W/S ratios of 0.43 or 0.875 when untreated or washed fly ash were used, respectively (Table 2). If the mixture incorporating 90% washed fly ash was added with 2% w/w sulfonated naphthalene-based superplasticizing agent, it was then possible to achieve the normal consistency by reducing the W/S ratio from 0.875 to 0.57.

### 3.4. Setting times of ash–cement mixtures

Fig. 6a–d shows the initial and final setting times of mixtures incorporating untreated or washed fly ash as a function of ash content. For Portland cement pastes, the initial and final setting times were found to be 3.3 and 5.3 h, respectively.

The partial replacement of Portland cement with untreated fly ash always resulted in delaying both the initial and final setting of the cementitious mixtures.

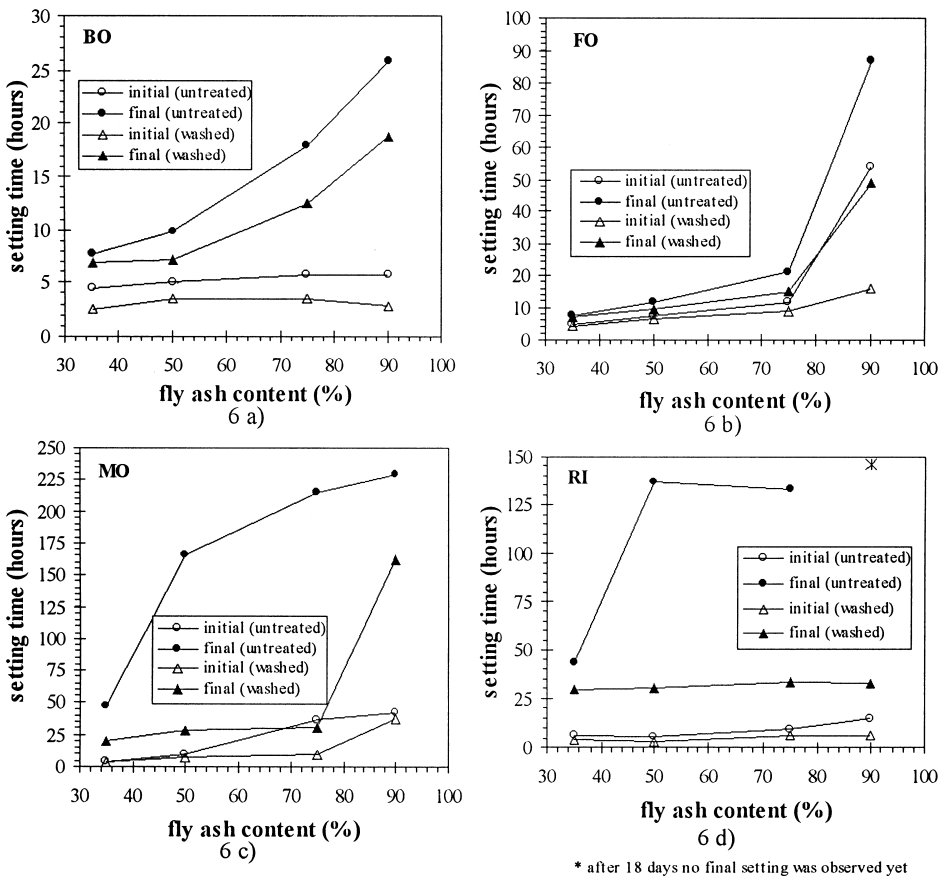


Fig. 6. (a–d) Effect of fly ash content on setting time of ash–cement mixtures made with untreated or washed fly ash.

Regardless of the type of fly ash used, the retarding effect became more and more pronounced as the ash content of the mixtures was increased. However, for some types of fly ash such as BO or FO fly ash (Fig. 6a and b), the final setting times of the cementitious mixtures did not exceed technologically acceptable limits (24–48 h) even when these mixtures were made with considerable amounts of fly ash (75% by weight for FO fly ash and 90% by weight for BO fly ash). Conversely, for other types of fly ash such as MO or RI fly ash (Fig. 6c and d), acceptable times for final setting were obtained only if the ash content of these mixtures was not higher than 35% by weight. For mixtures incorporating 90% MO or RI fly ash, final setting was observed after 230 h for the former mixtures, while no final setting was recorded for the latter mixtures even if the curing time was prolonged up to 18 days.

Regardless of the type of fly ash tested, the retarding effect of fly ash on setting was largely reduced when washed fly ash was used instead of untreated fly ash. Obviously, the major benefits resulting from washing pretreatment were observed for MO and RI fly ashes. As can be seen from Fig. 6c and d, even mixtures incorporating 75% MO or 90% RI fly ash exhibited acceptable times for final setting (31–33 h) when these mixtures were made with washed fly ash. Also, the final setting times of these mixtures were not virtually modified by the addition of 2% w/w sulfonated naphthalene-based superplasticizing agent. On the other hand, mixtures incorporating 90% MO washed fly ash exhibited unacceptable final setting times (about 160 h).

Considering that the presence of certain heavy metals such as Zn, Pb, and As in cementitious mixes could markedly delay the hydration of Portland cement [14] but the washing pretreatment produced a heavy metals enrichment of fly ashes (Table 6), the beneficial effect of ash washing process on setting of ash–cement mixtures was attributable to the elimination of significant amounts of water-soluble compounds from the fly ashes.

Table 6  
Elemental analyses of washed fly ashes

Element	BO	FO	MO	RI
Ca (%)	20.3	23.0	18.5	19.8
Si (%)	13.2	12.8	14.6	11.9
K (%)	0.68	1.38	1.89	2.55
Al (%)	7.10	5.43	6.45	4.35
Na (%)	0.37	0.26	0.66	1.95
Fe (%)	1.25	1.27	1.73	1.40
Mg (%)	1.74	2.15	1.73	1.50
S <sup>a</sup> (%)	1.98	2.03	3.28	3.49
Cl (%)	1.39	2.29	4.69	9.13
Ni (%)	3.49	3.43	3.76	3.41
Zn (%)	0.79	0.47	2.59	2.62
Pb (%)	0.50	0.27	1.01	0.71
Cu (ppm)	1100	750	2000	1100
Cd (ppm)	35	–	340	230
Cr (ppm)	240	600	540	440

<sup>a</sup>Water-soluble sulfates expressed as sulfur.

However, some preliminary tests on the hydration of Portland cement in mixtures made with 90% calcite (ground to particle sizes lower than 45  $\mu\text{m}$ ), 10% Portland cement and saturated sodium chloride solution or saturated potassium sulfate solution as mixing water, indicated that the setting of these mixtures was not delayed to an unacceptable level when compared with the setting of Portland cement pastes made with the same W/S ratio (the final setting time was increased from 5.3 to 12–14 h). Therefore, further work is needed to elucidate the beneficial effect of the ash washing pretreatment on the setting of ash–cement mixtures.

On the basis of the results in Fig. 6a–d and keeping in mind that increasing FA/C and/or W/S ratio generally reduces the compressive strength of ash–cement mixtures and, at the same time, enhances the risks of heavy metals leachability from solidified products, the characterization of the solidified products for mechanical strength and leaching properties was limited only to the mixtures made with 75% MO or 90% RI washed fly ash and no superplasticizer addition.

### 3.5. Compressive strength of ash–cement mixtures and heavy metals leachability

As expected, the 7-day compressive strengths ( $R_c$ ) of cubic specimens made with the mixtures incorporating 75% MO (W/S = 0.71; W/C = 2.84) or 90% RI (W/S = 0.875; W/C = 8.75) washed fly ash were found to be very low, namely, 1.4 and 0.6 MPa, respectively. The poor strength development of these mixtures was attributable to their very high W/C ratio and their low content of Portland cement. However, the above values of  $R_c$  were three to seven times higher than that needed (about 0.2 MPa) to support the dead-load of a dump in the case of a 10 m high column of S/S products having a density of 2000  $\text{kg}/\text{m}^3$ .

Also, the results of standard acetic acid leaching tests on cubic specimens preliminarily stored for 7 days in air at 20°C and 100% R.H. (Table 7) revealed that the mixtures incorporating 75% MO or 90% RI washed fly ash were effective in immobilizing the heavy metals examined (Cd, Cr, Cu, and Pb).

Therefore, these results coupled with setting data proved the technical feasibility of the washing pretreatment as a means of maximizing the incorporation of MSW fly ash in cementitious matrices.

### 3.6. Economical evaluation of S/S process

The washing pretreatment of fly ash with water represents a suitable process for maximizing the FA/C ratio of cementitious mixtures, but it involves additional costs

Table 7

Results of standard acetic acid leaching tests on solidified ash–cement mixtures after 7-day curing in air at 20°C and 100% R.H.

Mixture	Element ( $\mu\text{g}/\text{l}$ )			
	Cd	Cr	Cu	Pb
75% MO washed fly ash–25% Portland cement	10	30	40	50
90% RI washed fly ash–10% Portland cement	11	28	25	29
Limit value ( $\mu\text{g}/\text{l}$ )	20	2000 Cr, 200 Cr(VI)	100	200

related to construction and operation of the washing facility and wastewater treatment units.

As evidenced by the results in Table 5, the disposal of the wastewater resulting from the ash washing process requires a preliminary treatment to reduce the pH and the ionic concentrations of aluminum, cadmium, lead and zinc. A reduction of the sulfate concentration is also required in the case of wastewater disposal into surface waters.

If the sulfate removal is not required, the wastewater can successfully be treated by reducing the pH from 10.8–11.4 to 7.6, so as to cause the formation of Al hydroxide flocs which are able to reduce the concentrations of heavy metals below the limit values through adsorption mechanisms [15].

The production of sludge in the settling tank is 0.040–0.054 m<sup>3</sup>/m<sup>3</sup> of wastewater treated, corresponding to 0.002–0.0027 m<sup>3</sup>/kg of fly ash subjected to washing step. On a dry weight basis, the production of sludge is 6.5–7.4 g solids/kg untreated fly ash.

After sludge dewatering by a filter press, the heavy metals content of the sludge cake is about 0.07%–0.15% for zinc, 0.04%–0.06% for lead, and 35–45 ppm for cadmium; the amount of sludge cake is about 2.3%–3.0% by weight of washed fly ash. According to the Italian regulation on solid wastes [10,11], this sludge cake was classed as a hazardous waste and from the Italian standard acetic acid leaching test, it resulted that such a waste must be disposed in II Category, type C, landfills [7,10,12].

If the removal of sulfates from wastewater is also required and there is a great availability of cooling and/or power plant waters, the wastewater can firstly be subjected to a neutralization process for heavy metals removal and, successively, can be diluted with cooling and/or power plant water in accordance with the Italian legislation on wastewater disposal [12].

Table 8  
Capital, operational and total costs of the S/S process

	Scenario S1		Scenario S2		Scenario S3	
	\$	\$/year	\$	\$/year	\$	\$/year
<b>Capital costs</b>						
Mixing unit	47,058	7 658	29,411	1914	29,411	1914
Washing unit	–	–	117,647	19,146	117,647	19,146
Wastewater treatment plant	–	–	352,941	76,586	352,941	76,586
<b>Operational costs</b>						
	\$/t	\$/year	\$/t	\$/year	\$/t	\$/year
Fly ash	–	–	–	–	–	–
Portland cement	109	1,254,917	109	540,640	109	57,443
Water (mixing and washing)	0.29	2 054	0.29	90,859	0.29	90,696
Landfilling	235	5,827,295	235	2,383,605	235	1,986,690
	\$/kW h	\$/year	\$/kW h	\$/year	\$/kW h	\$/year
Energy	0.11	607,764	0.11	218,623	0.11	186,529
Total		6,570,295		3,331,373		2,419,004



In order to evaluate the economical feasibility of the S/S process when applied to washed fly ash, the incidence of the following items was considered:

- capital costs (mixing, washing, and wastewater treatment units);
- operational costs (energy and reagents);
- disposal costs.

The above mentioned costs were evaluated by taking into account the capital and operating costs of a fly ash washing treatment and a wastewater treatment plant consisting of neutralization and sedimentation units, as well as a dewatering treatment of the resulting sludge by means of filter presses.

The following scenarios were investigated:

- S1: 35% untreated fly ash/65% Portland cement;
- S2: 75% washed fly ash/25% Portland cement;
- S3: 90% washed fly ash/10% Portland cement.

Under the assumed scenarios, prior to the solidification/stabilization process, the sludge cake resulting from filter press dewatering should be mixed with washed fly ash.

Table 8 summarizes the capital, operational and total costs of the S/S process when applied to the above fly ash–cement mixtures, in the case of an inertization treatment of 20,000 kg fly ash/day.

#### 4. Conclusions

Washing pretreatment of MSW fly ash with water proves to be a suitable means of improving the setting characteristics of ash–cement mixtures, regardless of the type and amount of fly ash tested.

Moreover, for some varieties of MSW fly ash which exert a strong retarding effect on the setting of cementitious mixtures, washing pretreatment represents a suitable means of maximizing the incorporation of such fly ashes in cementitious matrices. In such cases, inertization of untreated fly ash should be limited to ash contents not higher than 35% by weight of total solid, while washed fly ash may be incorporated at ash contents up to 75%–90% by weight, without the risk of heavy metals leachability from solidified products.

As a result of a lesser consumption of cement and a reduced volume of solidified product, considerable economical benefits (reduction of the S/S treatment cost by about 50%–63%) can be attained from MSW fly ash washing pretreatment.

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