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Properties of Portland cement — stabilised MSWI fly ashes

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Abstract

In the present paper, the properties of Portland cement mixtures containing fly ashes (FA) collected at four different Italian municipal solid waste incineration (MSWI) plants were investigated.

In particular, physical/mechanical characteristics (setting time, unconfined compressive strength (UCS) and shrinkage/expansion), as well as the acid neutralisation behaviour of the solidified products were considered.

The FA composition, revealing enrichment in heavy metals, chlorides and sulphates, significantly altered the hydration behaviour of Portland cement. Consequently, for some of the investigated FA the maximum allowable content for the mixtures to achieve appreciable mechanical strength was 20 wt.%. Even at low FA dosages setting of cement was strongly delayed. In order to improve the properties of FA/cement mixtures, the use of additives was tested.

Moreover, the acid neutralisation capacity (ANC) of the solidified products was evaluated in order to assess the ability of the matrix to resist acidification, and also to provide information on hydration progression, as well as on heavy metal release under different pH conditions.

Comparison of the results from the present work with previous studies carried out on spiked mixtures lead to the conclusion that the mechanical properties of the stabilised FA could not be predicted based on the effect exerted by heavy metals and anions only, even when the dilution effect exerted on cement was taken into account. It was likely that a major role was also played by alkalis, which were present in the FA at much higher concentrations than in cement. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Solidification/stabilisation; MSWI fly ash; Acid neutralisation capacity; Specific strength; Additives

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1. Introduction

It is well known that several advantages arise from waste incineration, including volume and weight reduction of the original waste, waste detoxification, as well as the possibility of energy recovery. Nonetheless, the hazardous nature of residues resulting from waste combustion must be carefully considered.

The amount of solid residues generated by waste combustion generally accounts for 30–35 wt.% of the burnt waste. Bottom ash typically constitutes 25–30% of the original waste, the remaining amount being ascribed to air pollution control (APC) ashes.

The recent European regulation on solid waste management establishes that priority must be given to reuse, recycle and recovery of materials from waste rather than to energy recovery. For this reason, incineration of commingled waste is not expected to be as widely adopted in the near future as it has been so far in many European countries. Nonetheless, it is predictable that the combustible fraction resulting from waste selection will be increasingly used as a refuse derived fuel (RDF) in waste-to-energy combustion. Variations in both the amounts and the composition of solid residues from waste combustion are, therefore, likely to occur in the next future.

Bottom ash, which is classified as a non-hazardous waste according to the European Waste Catalogue, is typically composed of aluminosilicate phases and contains relatively small amounts of heavy metals, particularly volatile metals such as mercury, cadmium, zinc and lead; higher concentrations of lithophilic metals, like Ni, Cr and Cu are observed [10].

On the contrary, APC fly ash (FA) is classified as a hazardous waste. FA resulting from flue gas treatment is usually concentrated in heavy metals and chlorinated organic compounds, as well as soluble salts, and is also composed of very fine particles. Moreover, inorganic pollutants are typically associated with soluble compounds, which are, therefore, highly leachable from FA. APC FA resulting from dry or semi-dry processes is also highly alkaline, owing to the excess of basic agents injected for acid gas removal; the high pH promotes leaching of some strongly amphoteric heavy metals, including lead and zinc, when FA is contacted by a liquid medium.

The composition of APC FA is not as well defined as it is for bottom ash, as it strongly relies upon the technologies adopted for off-gas treatment.

Proper stabilisation of FA in order to reduce its environmental impact in the final disposal site has been claimed over the past years. Various technologies have been proposed, the most widely adopted consisting of solidification with a variety of hydraulic binders (such as cement and/or lime, blast furnace slag, etc.) [1,2,6,12,14,22].

Stabilising agents other than hydraulic binders have also been tested, including soluble phosphates [9,23] or ferrous sulphate [13,18], which are able to promote formation of chemically stable, insoluble mineral compounds with heavy metals and anions, thus, providing an immobilisation environment for the contaminants.

Thermal treatments such as vitrification or sintering have also been proposed [11,16] as a reliable and efficient way to immobilise inorganic contaminants within the amorphous structure of the resulting products. The major drawback of such treatments still lies on the occurrence of partial volatilisation of some heavy metals at the high temperatures of the process, which can, thus, escape the intended treatment.

Among the different available hazardous waste solidification and/or stabilisation technologies, cement-based processes still deserve major attention due to the relatively low treatment costs and ease of application. Yet the adverse effects exerted by FA on the normal hydration process of cement usually requires high cement dosages in the mixtures. Such adverse effects are commonly thought to be caused by heavy metals and soluble salts (such as chlorides and sulphates). In the present paper, an attempt to relate the chemical composition of municipal solid waste incineration (MSWI) FA to the effect exerted on cement hydration was made.

2. Materials and methods

The experimental campaign was carried out on four MSWI FA collected from the flue gas treatment unit of different Italian plants. The FAs that will be referred to as FA1 and FA2 were collected from the electrostatic precipitator (ESP) of two different incineration plants; the acid gas removal unit is located downstream of the ESP and consists of a wet treatment unit. Two additional FA samples were withdrawn from a third incineration plant, which is equipped with an ESP for particulate matter abatement, followed by a fabric filter (FF) downstream of the semi-dry acid gas treatment unit. Neutralisation of acid gases is accomplished using a sodium carbonate, Na_2CO_3 , solution. These two ashes will be indicated as FA3(ESP) and FA3(FF) in the following.

The FAs were characterised for their physical properties (including bulk density, water content and loss on ignition (LOI)), as well as chemical composition (including phase oxide composition, elemental composition and anion content). Measurements were taken in triplicate and followed ASTM C29 for bulk density, ASTM D2216 for water content, and ASTM C25 for LOI. The oxide composition was determined through total X-ray fluorescence (TXRF). Analysis of elements was performed by means of acetylene flame-operated atomic absorption spectrometry (Perkin-Elmer model 3030 B) after sample digestion according to the APHA 3030H procedure. Anion measurements were taken using ion chromatography (Metrohm model 761 Compact IC) after solubilisation according to the Italian UNI 8520 methods.

The microstructural composition of the FAs was also investigated by means of powder X-ray diffraction analysis (XRD). The XRD technique used $\text{Cu K}\alpha$ radiation (copper tube operated at 30 kV and 40 mA) on a Scintag model X1 diffractometer operated at $0.05^\circ/2\theta$ (count time: 3 s).

The four FAs were also characterised for their acid neutralisation behaviour according to the acid neutralisation capacity (ANC) test developed at the Wastewater Technology Centre [19]. Prior to the test, the materials were ball-milled to less than 150 μm and dried at 105°C until a constant weight was obtained.

The test was carried out over a 48 h period by contacting 11 sub-samples of the material with nitric acid solutions ($\text{L/S} = 6 \text{ ml/g}$ dry weight) having increasing acid concentrations. Agitation was accomplished through tumbling. The acid addition schedule was arranged so as to cover pHs in the final eluate ranging from the material-controlled value to approximately three units. The equivalents of acid added were, therefore, dependent on the ANC of the individual FA tested. After 48 h, the pH, redox potential and electrical conductivity

were measured in the suspension, and the liquid phase was extracted through centrifugation followed by 0.45 μm filtration for subsequent chemical analyses. Five eluate samples were taken for the chemical analyses, namely, those at 0 acid addition and $\text{pH} = \pm 5$ and ± 10 . Metals were analysed by means of atomic absorption spectrometry (Perkin-Elmer model 3030B operated in acetylene flame configuration with background correction using a deuterium lamp).

The four FAs were treated with class 42.5R ordinary Portland cement (OPC).

Prior to mixing with cement, the FAs were oven-dried at 105°C and, when necessary, subsequently ball-milled to less than 150 μm . Different mix formulations were prepared by varying the FA/(FA + OPC) ratio, as well as the water (W)/total solids ratio, the latter depending on workability of the pastes. Distilled water was used as mixing water. The mixing procedure followed the ASTM C305 protocol.

Addition of accelerating admixtures or activators (which will be referred to as ADM in the following), including calcium chloride, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, and sodium methasilicate, $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, was also tested at various percentages. The details of the mix designs adopted throughout the study are provided in Table 1; the mixture components proportions are expressed as percent of total dry weight (i.e. excluding the mixing water).

The mixtures were cast in 50 mm \times 50 mm \times 50 mm moulds and allowed to cure at ambient temperature under controlled humidity conditions ($\text{RH} > 90\%$) for 24 h. Afterwards, the

Table 1
Mixture formulations

Waste	Weight ratio (%)			ADM type	Composition (% dry weight)			
	FA/ (FA+OPC)	W/ (FA+OPC)	ADM/ (FA+OPC)		OPC	FA	ADM	W
–	0	30	0	–	100	0	–	30
–	0	35	0	–	100	0	–	35
–	0	40	0	–	100	0	–	40
FA1	10	30	0	–	90	10	–	30
FA1	20	30	0	–	80	20	–	30
FA1	30	30	0	–	70	30	–	30
FA1	50	30	0	–	50	50	–	30
FA1	80	30	0	–	20	80	–	30
FA1	10	35	0	–	90	10	–	35
FA2	10	30	0	–	90	10	–	30
FA3(FF)	10	30	0	–	90	10	–	30
FA3(FF)	20	30	0	–	80	20	–	30
FA3(ESP)	10	30	0	–	90	10	–	30
FA3(ESP)	10	30	1.5	Na_2SiO_3	88.7	9.8	1.5	29.6
FA3(ESP)	10	30	2.5	Na_2SiO_3	87.8	9.8	2.4	29.3
FA3(ESP)	10	30	3.5	Na_2SiO_3	87.0	9.7	3.4	29.0
FA3(ESP)	20	40	1.5	Na_2SiO_3	78.8	19.7	1.5	39.4
FA3(ESP)	20	40	3.5	Na_2SiO_3	77.3	19.3	3.4	38.6
FA3(ESP)	30	40	1.5	Na_2SiO_3	69.0	29.6	1.5	39.4
FA3(ESP)	30	40	3.5	Na_2SiO_3	67.6	29.0	3.4	38.6
FA3(ESP)	10	30	2	CaCl_2	87.7	9.7	2.6	29.2
FA3(ESP)	20	30	2	CaCl_2	77.9	19.5	2.6	29.2
FA3(ESP)	30	30	2	CaCl_2	68.2	29.2	2.6	29.2

specimens were demoulded and kept at ambient temperature and RH > 90% until the time of testing. Different curing times were selected, namely, 1, 7, 28, 56 and 90 days.

Initial and final setting time measurements were also taken according to the ASTM C191 method (Vicat apparatus). The solidified wastes were tested for unconfined compressive strength (UCS) and bulk density at the above specified curing times. The testing methods were the ASTM C109 procedure for UCS and an internal method consisting of measurement of volume and weight for bulk density. All the measurements were taken in triplicate. In some cases, testing at early ages was not feasible due to the strong delay in hydration produced for some formulations.

The solidified samples were subjected to the ANC test, similar to what was done for the untreated FAs. Prior to the test, the specimens were ball-milled to less than 150 μm , and care was taken to carry out grinding in an inert environment (N_2 atmosphere) in order to prevent carbonation. The material was then dried at 60°C until the weight was constant.

The results from the ANC test were reported as titration curves showing the final pH of the eluate as a function of the amount of acid added. The so-called differential acid neutralisation analysis [7] was thereafter carried out by calculating the inverse of the titration curve slope, so as to visually identify the pH ranges corresponding to occurrence of pH plateaus. The differential acid neutralisation analysis resulted in a spectrum of peaks, each peak being associated with a pH plateau, which in turn could be related to the presence of particular solid phases responsible for a resistance to acidification.

It has been shown [8] that the pH value at which the individual plateaus occur is related to the nature of the pH-controlling solid phases and not to their quantity, the latter being inferred from the amount of acid required for the corresponding pH variation to be induced [7].

When dealing with cementitious systems, if the assumption is made that the pore solution is in a steady-state condition close to thermodynamic equilibrium with the hydration products, the pH values at which the individual plateaus occur are determined by the solubility of the associated hydration phase(s).

The values of the pH plateaus distinctive of the hydration products of Portland cement have been identified by various researchers for pure systems. Most of the data available in the literature refers to the $\text{CaO-SiO}_2\text{-H}_2\text{O}$ system, in that it largely dictates the chemical behaviour of hydrated cements. For this system, the equilibrium pH was shown to be approximately 12.5 either in the presence of portlandite or in the presence of portlandite coexistent with Ca-rich C-S-H. The stability pH also decreases as the Ca/Si ratio of C-S-H decreases (three different C-S-H phases are generally considered, spanning the Ca/Si range of persistence: Ca/Si = 1.8, 1.1 and 0.8), but always remains above 10 [20]. This is particularly noteworthy when dealing with hazardous waste solidification/stabilisation, since most contaminants form sparingly soluble complexes at high pHs. The pH values corresponding to the different pH-controlling phases for the $\text{CaO-SiO}_2\text{-H}_2\text{O}$ system are listed in column (2) of Table 2 [20]. Also, the influence of alkalis must be taken into account, in that they can strongly affect both pH and solubility. In particular, the effect of alkalis is to decrease the solubility of both portlandite and C-S-H and to increase that of silica gel; furthermore, alkalis produce a raise in pH, as the Na^+OH^- (or K^+OH^-) ion pair replaces the less alkaline $(\text{Ca}^{2+}\text{OH}^-)^+$ in solution [20]. The pH stability values for the different controlling phases in the $\text{CaO-SiO}_2\text{-H}_2\text{O}$ system in the presence of alkalis are listed in columns (3) and (4) of Table 2.

Table 2
pH stability values for pure CaO–SiO₂–H₂O systems with or without alkalis (after Stronach and Glasser [20])

Solids in equilibrium	pH without Na ⁺	pH with Na ⁺ (50 mmol/kg)	pH with Na ⁺ (250 mmol/kg)
CH	12.52	12.71	13.24
CH + C–S–H (1.8)	12.53	12.71	13.24
C–S–H (1.8)			13.24
C–S–H (1.1) + C–S–H (1.8)	12.43	12.69	13.24
C–S–H (1.1)	11.03	12.61	13.24
C–S–H (0.8) + C–S–H (1.1)	10.91	11.72	12.04
C–S–H (0.8)	10.88		
Silica gel + C–S–H (0.8)	10.17	11.09	11.45
Silica gel	6.38	11.09	11.45

From Table 2, a stepwise decrease in pH can be observed, each step corresponding to destabilisation of a particular hydration phase. Therefore, in a continuous titration curve the observed pH plateaus will be relevant to those steps and will, therefore, be ascribed to the presence of one or more hydration phases.

The theoretical pH plateau values obtained for pure systems can be significantly different from those distinctive of real systems, especially in the presence of impurities. The influence of chlorides and sulphates on the solubility of the main hydration phases has been studied by a number of investigators [4,5,20]. Chlorides can alter the solubility of both portlandite and C–S–H through formation of oxychlorides (3CaO·CaCl₂·15H₂O and CaO·CaCl₂·2H₂O) and chemisorption onto C–S–H. The latter is also influenced by the Ca/Si ratio of C–S–H. Various pH stability values have been proposed in the presence of chlorides, corresponding to the coexistence of different phases (portlandite, C–S–H and chloride salts), as reported in Table 3 [20].

When sulphates are present, the three additional hydrates, ettringite, monosulphoaluminate and gypsum, can control solution pH. Depending on the sulphate concentration, the system can be in equilibrium with these hydrates as well as with gibbsite, hydrogarnet or portlandite [4,5].

Table 3
pH stability values for pure CaO–SiO₂–CaCl₂–H₂O (after Stronach and Glasser [20])

Solids in equilibrium	pH
CH + C–S–H (1.8) + 3CaO·CaCl ₂ ·15H ₂ O	11.83
CaO·CaCl ₂ ·2H ₂ O + 3CaO·CaCl ₂ ·15H ₂ O + C–S–H (1.1)	11.34
CaCl ₂ ·6H ₂ O + C–S–H (0.8) + silica gel	8.76
CaCl ₂ ·6H ₂ O + C–S–H (0.8) + CaO·CaCl ₂ ·2H ₂ O	10.73
Silica gel + CaCl ₂ ·6H ₂ O	5.77
CaO·CaCl ₂ ·2H ₂ O + CaCl ₂ ·6H ₂ O	10.73
CaO·CaCl ₂ ·2H ₂ O + 3CaO·CaCl ₂ ·15H ₂ O	11.34
CH + 3CaO·CaCl ₂ ·15H ₂ O	11.82
CaCl ₂ ·6H ₂ O	5.78

3. Results and discussion

Table 4 shows the physical properties of the FAs and their phase oxide composition along with that of OPC, while Table 5 gives the elements and anion concentrations. The values are given as the average of the three replicates.

From inspection of Tables 4 and 5 it is clear that very different compositions were measured for the ESP ash compared with the FF ash. The FF ash had a very high alkali content, due to the sodium carbonate used for acid gas removal. Since alkalis are known to affect cement set and hydration, such high alkali concentrations were expected to influence

Table 4
Physical properties and phase oxide composition of FAs and OPC

	FA1	FA2	FA3(ESP)	FA3(FF)	OPC
Physical property					
Bulk density (kg/m ³)	1013	660	614	465	
Specific gravity	2.64	3.44	2.90	2.94	
Water content (% dry weight)	15.53	0.23	0.46	2.16	
Loss on ignition (% wet weight)	28.51	9.26	19.07	80.16	
Oxide composition (% dry weight)					
SiO ₂	30.40	22.82	27.01	4.29	25.94
TiO ₂	2.09	1.53	2.31	0.12	0.33
Al ₂ O ₃	13.09	8.01	11.73	1.36	5.01
Fe ₂ O ₃	3.10	2.92	2.33	0.19	4.85
MnO	0.12	0.14	0.10	0.01	0.07
MgO	3.76	2.54	3.73	0.19	2.27
CaO	29.74	22.57	23.28	1.25	52.23
Na ₂ O	5.81	15.73	11.96	72.35	0.32
K ₂ O	5.25	17.02	7.56	1.37	1.98
P ₂ O ₅	1.33	1.24	1.74	0.18	0.12

Table 5
Elemental composition and anions content of FAs

Element	Concentration			
	FA1	FA2	FA3(ESP)	FA3(FF)
Cd (mg/kg dry weight)	151	301	176	89
Cr (mg/kg dry weight)	405	493	529	84
Cu (mg/kg dry weight)	867	379	1312	490
Ni (mg/kg dry weight)	80	125	86	<40
Pb (mg/kg dry weight)	4415	4579	4666	2201
Zn (mg/kg dry weight)	8627	9970	15440	5874
Chloride (% dry weight)	6.0	2.9	8.8	33.7
Fluoride (% dry weight)	<0.2	<0.2	<0.2	<0.2
Nitrate (% dry weight)	<0.2	<0.2	<0.2	<0.2
Phosphate (% dry weight)	<0.2	<0.2	<0.2	<0.2
Sulphate (% dry weight)	8.0	10.5	7.9	4.0

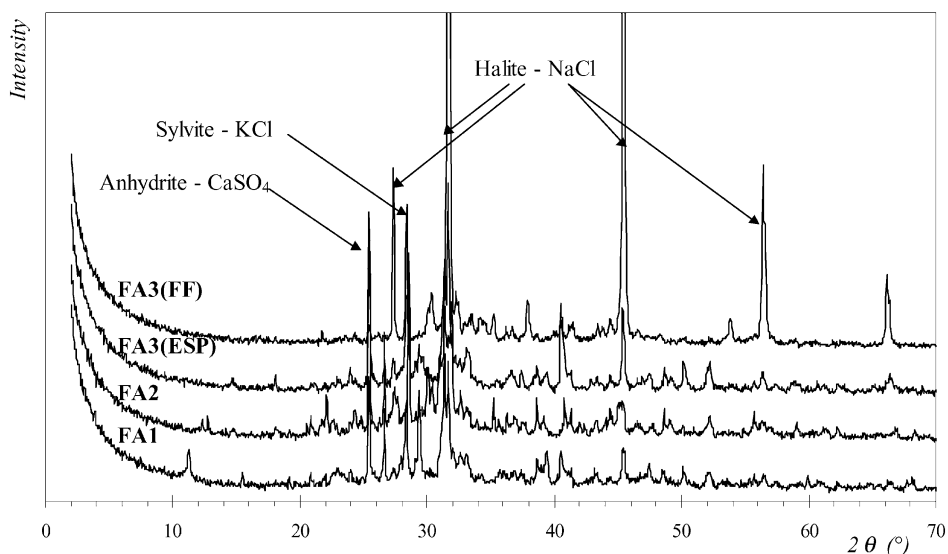


Fig. 1. XRD analysis of FAs.

the final properties of the solidified products. Moreover, high anion concentrations were detected; inspection of the XRD spectra (see Fig. 1) revealed that the major crystalline phases consisted of chlorides (mainly halite, NaCl).

From XRD analysis it was found that for the ESP ashes the crystalline species were mainly chlorides (sylvite, KCl, and halite, NaCl) and sulphates (anhydrite, CaSO₄). Minor amounts of quartz (SiO₂), syngenite (K₂Ca(SO₄)₂·H₂O), as well as Na or K feldspars (NaAlSi₃O₈ or KAlSi₃O₈) were also detected.

The relative amount of crystalline species in the ashes was obtained by calculating the so-called crystallinity index I_c , given by the ratio between the peaks area (A_p) and total area (A_t) of the XRD spectrum. The quantity $(1 - I_c)$ provides an indication on the amorphous content of FA. The amorphous content was approximately found to be 30% for FA1, 27% for FA2, 38% for FA3(ESP) and 13% for FA3(FF).

Furthermore, when comparing the ESP ashes compositions, it was found that FA3(ESP) had higher contents of heavy metals (Cr, Cu, Pb and Zn) and chlorides. The chloride content of ESP ashes can be ascribed to volatile metal chloride condensation due to the flue gas temperature decrease downstream of the furnace. Furthermore, since chlorides are generally highly soluble, the presence of metal chlorides in FA is expected to result in high metal leachability from the material. By the way, the highest chloride concentration was obviously exhibited by FA3(FF), which was the solid residue from acid gas neutralisation. This fact is also mirrored by the LOI, which represents an indirect measure of the amount of chlorides, carbonates, as well as organic matter in the material [15].

The XRD patterns did not allow peaks relevant to known heavy metal phases to be matched, thus, suggesting that the detectable metals were present either as impure, complex compounds or as amorphous species.

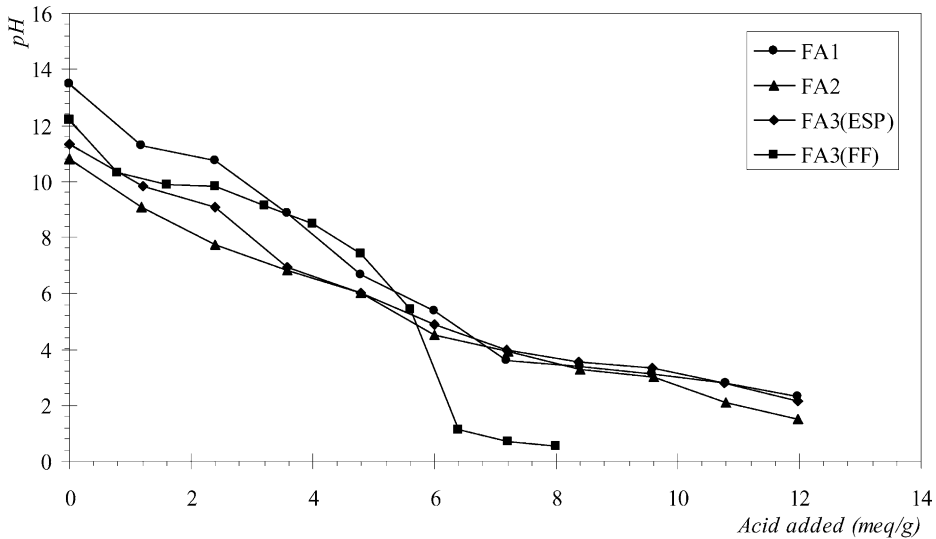


Fig. 2. Acid neutralisation behaviour of the four FAs.

As far as the ANC of the four ashes is concerned, the results from the ANC test are compared in Fig. 2.

The material-controlled pH, as calculated by the pH value in the eluates at 0 acid addition, were 13.45 for FA1, 10.82 for FA2, 11.32 for FA3(ESP) and 12.17 for FA3(FF). The resistance of the material to acidification was calculated from Fig. 2 at pH = 7. The corresponding values were 4.60 meq/g for FA1, 3.35 meq/g for FA2, 3.56 meq/g for FA3(ESP) and 4.96 meq/g for FA3(FF). The highest ANC down to pH = 7 was, therefore, exhibited by FA3(FF), owing to its high alkaline metals content. Furthermore, it was found that FA1 exerted a high buffering capacity, as well, which was probably related to its higher calcium content if compared with the other ESP ashes.

Fig. 3a–d depict the heavy metal concentrations in the eluate from the ANC test as a function of the final pH. It can be noticed that the measured metal concentrations were always higher than would be predicted based on the corresponding hydroxide solubility, probably owing to the increase in solubility caused by complexation effects.

Furthermore, with the exception of Cr, the heavy metal release under strongly acidic conditions was very close to the corresponding total content in FA.

When looking at the properties of the solidified FAs, in Table 6 the initial and final setting times are shown for the different mixtures tested. The control samples at 30 and 40% water content showed initial setting times of 255 and 323 min, while the final setting times were 360 and 435 min, respectively.

From inspection of Table 6, it is apparent that with up to 30% FA dosages the mixtures incorporating FA1 exhibited a similar setting behaviour if compared with the control mixture, the initial and final setting times being close to those measured for Portland cement. At 50 and 80% FA dosages, cement dilution effects delayed both initial and final set, even

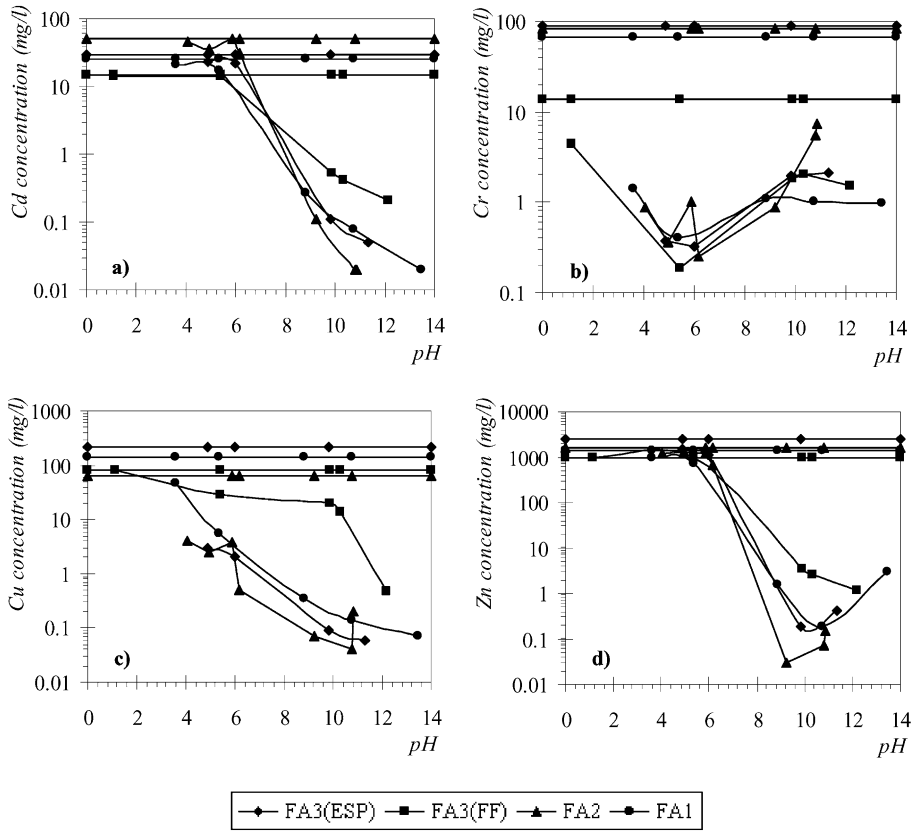


Fig. 3. Heavy metals leachability from FAs as a function of pH.

Table 6
Initial and final setting times (min) of the solidified FAs

Fly ash	FA/(FA+OPC)									
	10%		20%		30%		50%		80%	
	t_i	t_f	t_i	t_f	t_i	t_f	t_i	t_f	t_i	t_f
FA1	200	285	201	270	372	472	502	675	798	1225
FA2	390	1510	–	–	–	–	–	–	–	–
FA3(ESP)	836	945	–	–	–	–	–	–	–	–
FA3(ESP) + 1.5% Na ₂ SiO ₃	377	520	1145	1362	2280	2460	–	–	–	–
FA3(ESP) + 3.5% Na ₂ SiO ₃	169	387	299	524	657	1175	–	–	–	–
FA3(ESP) + 2% CaCl ₂	454	544	1230	1690	645	1711	–	–	–	–
FA3(FF)	39	218	1446	1755	–	–	–	–	–	–

though at 50% waste dosage the extent of set retardation still lay within technologically acceptable thresholds.

Unlike FA1, the other FAs adversely affected the setting process, so that adopting cement replacement levels higher than 20% always delayed the initial setting time beyond 24 h.

Out of the four FAs, FA1 and FA3(ESP) were chosen for the subsequent stages of the experimental work, the former allowing the solidification treatment with cement only, while the latter requiring use of chemical additives in order to improve the mechanical and leaching properties of the final products. For FA3(ESP) use of either an accelerator (CaCl_2) at 2 wt.% dosage or an activator (Na_2SiO_3) at 1.5 and 3.5 wt.% dosage was tested in order to enhance setting and hardening of the mixtures. The values of the initial and final setting times for the FA3(ESP)-incorporating mixtures in the presence of such additives are listed in Table 6; the values show that both CaCl_2 and Na_2SiO_3 were able to produce a significant reduction in the time required for setting to take place, even though CaCl_2 seemed to be more effective for high FA dosages (30%).

As far as the mechanical properties of the mixtures were concerned, analysis of the FA1 products (see Fig. 4a) showed UCS values higher than 30 MPa after 7 days of curing for FA dosages up to 30%.

An attempt was made to separate any contribution of cement to strength from that of FA. The UCS value of each mixture was divided by the corresponding cement content (%), and the value obtained was referred to as a specific UCS (SUCS) [17]. The SUCS calculated for the control mixture was regarded as the unit contribution of cement to strength. Any SUCS value higher than the SUCS calculated for the control mixture would, therefore, mean that FA itself also contributes to strength development. Fig. 4b depicts the SUCS values for the investigated FA1 mixtures (relative to the SUCS of the control sample at each age) as a function of the FA dosage. It is evident that, in addition to dilution effects, some other interference mechanisms produced a decrease in mechanical strength, especially at early ages. However, for long curing times (90 days) and high FA contents (80%), surprisingly the SUCS attained a value of 1.05, which would mean that the decrease in mechanical strength was to be ascribed to cement dilution only. This implies that the interferences on strength

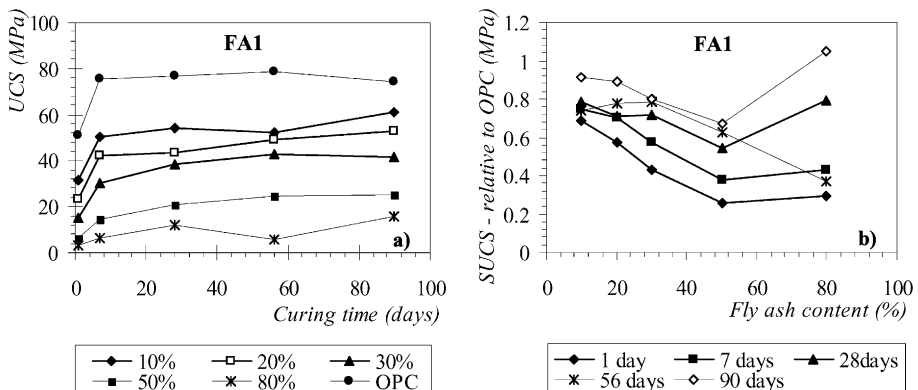


Fig. 4. UCS and SUCS (relative to cement) for FA1 mixtures.

development exerted by the contaminants introduced with FA1 were completely removed at long ages.

Analysis of the mechanical strength of FA3(ESP) mixtures revealed that, as predictable from setting time measurements, very low UCS values were attained in the absence of additives.

A previous work studied the interferences exerted by FA3(ESP) on cement hydration by means of spiking experiments [3]. Pure compounds containing five heavy metals (Cd, Cr, Cu, Pb and Zn) and two anions (Cl^- , SO_4^{2-}) were added in such concentrations as to simulate addition of 20% FA3(ESP) to Portland cement. Preliminary experiments showed that adopting the concentrations of Cd, Cr, Cu and Pb resulting from the FA content produced no appreciable effects on setting and hardening of cement, so that the dosages were increased in the final formulations. Conversely, the concentrations of Zn, Cl^- and SO_4^{2-} measured in the FA were maintained.

The results showed that significant effects on mechanical strength were exerted by zinc and the interaction between chlorides and sulphates. It was found that at 28- and 56-day curing the spiked mixture containing all the contaminants together exhibited UCS values of 36.40 and 44.71 MPa, respectively, which were significantly higher than those at the same curing times for the real mixtures. In particular, for the FA3(ESP) mixture containing 20% FA and 1.5% Na_2SiO_3 , UCS values of 17.60 and 24.71 MPa were measured at 28 and 56 days, respectively. Based on the contribution of OPC only to strength, i.e. considering the dilution effect, UCS values of 28.68 and 35.23 MPa would have been expected for those mixtures. Thus, even though Na_2SiO_3 itself is able to increase the mechanical strength of the solidified products, the UCS values were still below those predictable on the basis of the concomitant presence of the seven contaminants. This suggested that the adverse effect exerted by FA3(ESP) on strength development was not to be ascribed solely to the major heavy metals and anions in FA — as it is generally agreed upon in the literature — but other factors played a relevant role in affecting the properties of the solidified products. It is likely that in the case under examination a major role is played by alkalis, which, according to [21], are able to reduce the solubility of CaO and increase that of Al_2O_3 . The effect of alkalis can be also pointed out based on expansion observed for FA3(ESP) mixtures. Investigation of the joint effect exerted by heavy metals, anions and alkalis is, therefore, claimed in order to correctly predict the behaviour of cement-stabilised FA.

When looking at the results from the ANC test on the solidified products, which are depicted in Fig. 5a and b for the FA3(ESP) mixtures with 1.5% Na_2SiO_3 and 2% CaCl_2 added, it is clear that the ANC generally decreased with increasing FA content. This suggests that the amount of hydration phases produced was reduced in the presence of FA. This was confirmed by the results from the differential acid neutralisation analysis, which are reported in Table 7 for the FA3(ESP) mixtures in terms of pH of the detected plateaus and amount of acid added for each plateau.

The first plateau was detected for the investigated mixtures at pH varying between 12.68 and 13.49, while the corresponding value for the control mixture was 12.21. According to literature information [20], such pH values were tentatively related to the presence of portlandite and/or calcium-rich C–S–H in the presence of alkalis as well as chloride and sulphate species. This can also account for the rise in pH with respect to the control mixture;

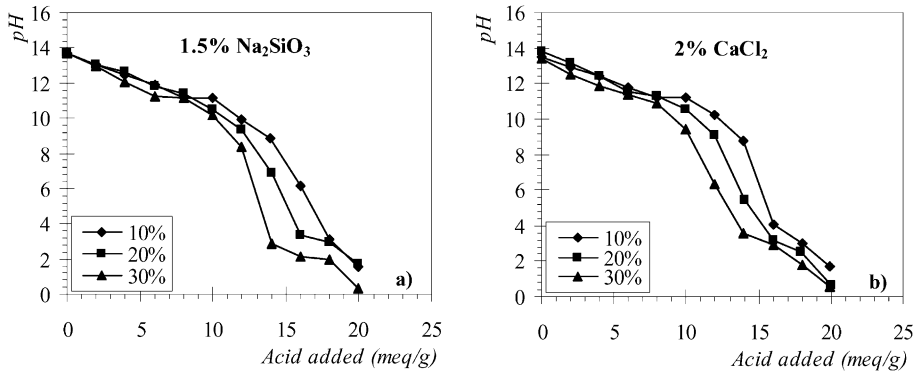


Fig. 5. Titration curves for the FA3(ESP) mixtures added with 1.5% Na_2SiO_3 and 2% CaCl_2 .

yet it appeared that chlorides produced a more pronounced rise in the pH plateau value than both alkalis and sulphates.

It was also noticed that the amount of acid added for the first plateau decreased when increasing the FA content, thus, indicating a decrease in the amount of those hydration phases. For the 2% CaCl_2 mixtures, at 30% FA content the first plateau was not recognisable at all, thus, indicating that the amount of the associated hydration phases was lower than the resolution of the method, corresponding to 3 meq H^+ per g of dry material.

A second pH plateau was recognised for all the examined FA3(ESP) mixtures at pH values ranging from 11.19 to 11.58, the corresponding value for the control mixture being 10.95. It can be hypothesised that the occurrence of the second plateau is related to the presence of C–S–H at various Ca/Si ratios (0.8 and/or 1.1) coexistent with impurities.

Table 7

Results from the differential acid neutralisation analysis for the FA3(ESP) mixtures

FA/(FA + OPC)	10%		20%		30%	
	pH	Acid added (meq/g dry weight)	PH	Acid added (meq/g dry weight)	pH	Acid added (meq/g dry weight)
1.5% Na_2SiO_3						
Plateau 1	12.77	4	12.84	4	13.35	3
Plateau 2	11.18	4	11.58	10	11.19	10
Plateau 3	9.38	4	–	–	–	–
3.5% Na_2SiO_3						
Plateau 1	12.69	4	12.72	4	13.20	3
Plateau 2	11.24	6	11.43	4	11.20	10
Plateau 3	–	–	9.55	4	–	–
2% CaCl_2						
Plateau 1	12.68	4	13.49	5	–	–
Plateau 2	11.22	10	11.42	8	11.38	10

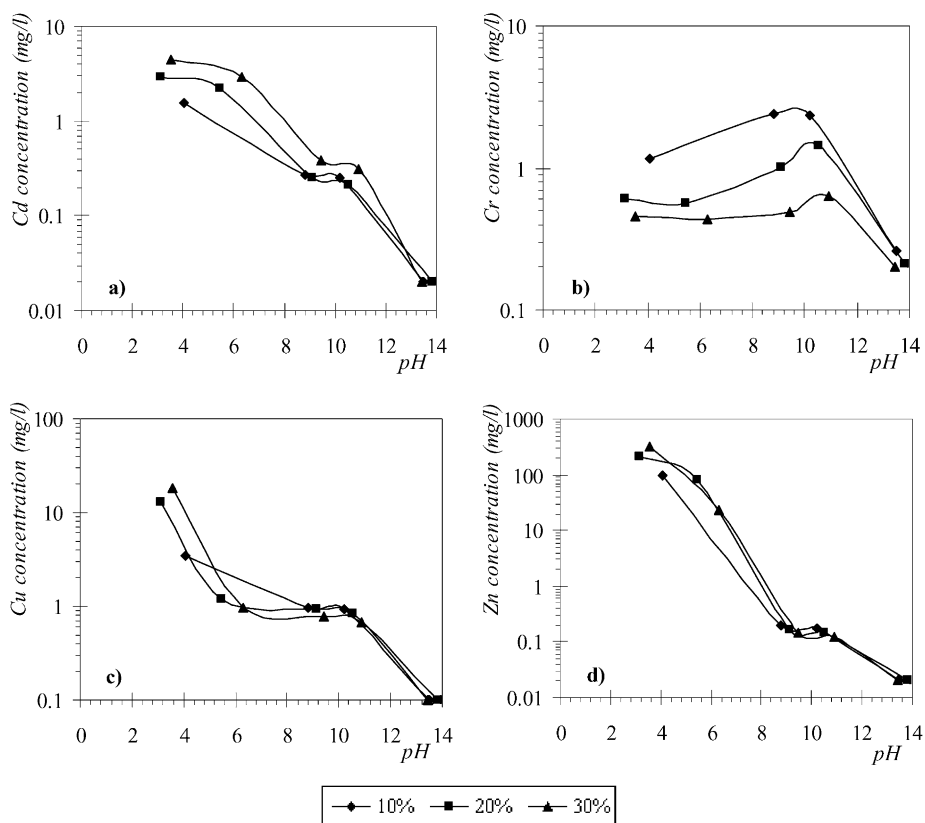


Fig. 6. Cd, Cr, Cu and Zn release from the FA3(ESP) mixtures at 2% CaCl₂ addition.

Similarly to what noticed above, the shift in pH with respect to the control mixture is to be ascribed to such impurities. The presence of a tail in the titration curves (probably due in part to inadequacy of glass electrodes at measuring very low pH values) did not allow for an accurate estimation of the amount of acid required for the second pH variation to be induced, thus, no comparison between the amount of C–S–H produced for the different mixtures could be made.

Fig. 6a–d show the release of Cd, Cr, Cu and Zn from the FA3(ESP) mixtures containing 2% CaCl₂. It was observed that for all the investigated mixtures the heavy metal concentrations in the eluate from the ANC test were considerably reduced at pH values below approximately 10 units, showing deviations from the theoretical curves resulting from metal hydroxides solubility. As it was previously addressed that C–S–H is stable for pH >10, the reduction in heavy metal leachability from the solidified samples if compared to the untreated FA can be partly ascribed to immobilisation within the structure of the hydration phases through either addition, substitution or sorption mechanisms. As a matter of fact, as the ANC test was carried out on finely ground samples, any physical immobilisation

effect due to reduction in the surface coming into contact with the leaching medium was completely removed.

In the case of chromium, it must be stressed that the contribution of cement may have been of relevance in determining the overall release from the solidified matrix, as the extent of chromium release decreased when the FA content was increased. Also, it was observed that the concentration versus pH curves can be explained based on the oxyanionic behaviour of chromium compounds.

4. Conclusions

The present experimental work showed that both the setting and hardening process of products incorporating different kinds of MSWI FA were strongly affected by the technology adopted for flue gas treatment downstream of the combustion chamber. For some FAs the chemical composition required addition of either accelerators or activators in order to allow mixtures with increased FA/OPC ratios to be formulated.

Furthermore, based on previous studies carried out on spiked mixtures, it appeared that the mechanical properties of the stabilised FAs could not be predicted based on the effect exerted by heavy metals and anions only, even when the interactions between them and the dilution effect were taken into account. Thus, it was likely that a major role was also played by alkalis, which were present in FAs at much higher concentrations than in cement.

Irrespective of the adverse effects exerted by FA on cement hydration, analysis of the eluate from the ANC test revealed that for the examined heavy metals some chemical immobilisation within the hydration phases occurred.

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