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Manufacture of hybrid cements with fly ash and bottom ash from a municipal solid waste incinerator

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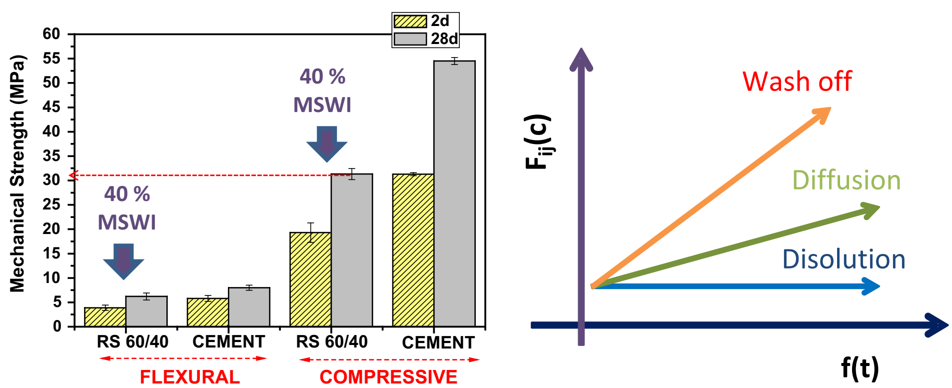
HIGHLIGHTS

- Valorization of high proportions of incinerator fly ash and bottom ash via geopolymerization process.
- Development of a hybrid cement with useful technical properties.
- Immobilization of metal species present un MSW incinerator ashes in the material and hence reduction in their toxicity.

GRAPHICAL ABSTRACT



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ABSTRACT

Concerns about the large volume of fly ash and bottom ash generated by the incineration of municipal solid waste (MSW) have induced the scientific community to seek ways to reduce their environmental impact. One of the proposals that has been researched most intensely is their valorisation as supplementary cementitious materials and aggregates in Portland cement-based pastes, mortars and concretes. The present paper proposes an alternative use for this waste: as a raw material in alkali-activated hybrid cements. A hybrid cement developed for that purpose by blending 60 wt% clinker and 40 wt% incinerator bottom ash and fly ash exhibited good 28-day mechanical strength (upward of 32.5 MPa). The leaching of potentially toxic metals present in the hybrid cement as a result of the inclusion of MSW fly ash and bottom ash was tested with different leaching procedures. The findings and the results of the analysis of the leaching parameters measured (*Li*, *Fij*...) showed that the hybrid cement proposed can effectively immobilise the potentially hazardous metals present in MSW fly ash and bottom ash.

1. Introduction

Incineration is one of the alternatives for managing municipal solid waste (MSW). Given the steep rise in MSW generation, the number of incinerators in developed countries is expected to grow steadily, with a concomitant increase in the amount of bottom and fly ash. Although some 46% of MSW incinerator ashes in Europe is re-used, billions of tonnes remain which must be treated to prevent subsequent environmental problems [1].

There is some potential for using MSW incinerator ashes in construction materials such as concrete fillers, aggregate or admixtures [1–13]. Other industrial by-products, including coal fly ash and blast furnace slags, are routinely used in cement manufacture. Due to its

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significant lime content (24–47%) and the silicates and aluminosilicates in its composition, MSW incinerator fly ash holds promise as a component in cement production. One of the applications for this waste that has been researched with particular interest is the manufacture of calcium sulfoaluminate cements (obtained at relatively kiln temperatures [1–3]. To be so used, however, the ash must be pre-treated to eliminate or control its heavy metal content to avert undesirably high concentrations of such elements [1,2].

Alkaline cements are binders available today whose performance can match or even exceed ordinary Portland cements thanks to their physical–chemical properties, although mineralogically they differ from OPC. They are obtained by alkali-activating amorphous or vitreous aluminosiliceous materials. When added to a highly alkaline medium (normally containing a NaOH or Na_2SiO_3 solution or certain inorganic salts), such materials undergo an intense structural transformation, ultimately generating compact cementitious skeletons [14–20]. Alkaline cements have also shown good potential in the field of stabilisation and 53 solidification of wastes containing soluble heavy metals [21–23]. Alkaline activation is a technique that has been successfully applied to coal-fired steam power plant fly ash [19,24] and blast furnace slag [25–27]. Moreover, research is presently underway to formulate hybrid cements (or blended alkaline cements) by alkali-activating blends of 20–30% Portland clinker and 70–80% natural pozzolan- or industrial by-product-based supplementary cementitious materials (SCMs) [28–30].

The present research aimed to assess the application of alkaline activation technology to incinerator bottom ash and fly ash and moderate amounts of Portland clinker to develop a hybrid cement compliant with the quality requirements set out in European standard EN-197 (EN 196-1) [31] and the leaching thresholds laid down by the United States Environmental Protection Agency (USEPA) [32,33].

2. Experimental

2.1. Starting materials

A Portland cement clinker (CK) supplied by a European Union manufacturer and MSW incineration fly ash (R1) and bottom ash (R2) from a facility also in the EU were used in this study. The reference system consisted of a type IV pozzolanic cement (CEM IV) consisting of a blend of 65% clinker and 35% pozzolanic coal fly ash sourced from the same manufacture as the clinker.

The clinker (CK) and MSW bottom ash (R2) were dry milled separately until 100% of their particles passed through a 45-μm sieve. The MSW fly ash (R1) was used as produced in the incinerator with no prior grinding, since 85% of the particles in ex-plant sample were already smaller than 45 μm.

The ground raw materials were blended to prepare a hybrid cement consisting of 60 wt% clinker (CK) and 40 wt% incinerator waste (R). The incinerator waste (R), in turn, consisted of a blend of 17% fly ash (R1) and 83% bottom ash (R2). Five per cent sulphate (a mix of $CaSO_4$ and Na_2SO_4) was added to the aforementioned blend to regulate setting and introduce alkalis in the system. The resulting blend was dry milled to obtain a material in which 96% of the particles passed the 45-μm sieve and over 90% the 30-μm sieve.

The chemical composition of all these materials is given in Table 1. Elemental composition was determined by X-ray fluorescence, using radiation at an acceleration voltage of 100 kV and an 800-mA current (Philips PW 1404/00/01). The silicocalcareous incinerator fly ash (R1) was high in CaO and low in SiO_2 and Al_2O_3. It also exhibited fairly high Cl and alkali contents. The incinerator bottom ash (R2) was CaO-rich as well but had higher percentages of SiO_2, Fe_2O_3 and Al_2O_3 than observed in the ash. CaO was the most prominent constituent of the hybrid cement, which had lower silica and alumina contents than found in the CEM IV used as a reference.

The trace elements present in the various materials are listed in Table 2. The elements of particular interest, given their toxic and hazardous potential, bear an asterisk (*).

Other toxic and hazardous elements normally detected in this type of waste [1], such as silver, mercury and cadmium, proved to be below the instrument's detection threshold and lower than the ceiling concentrations defined by the EPA to constitute toxic and hazardous waste [32,33]. Furthermore, the trace metal content was considerably lower in the hybrid cement (in particular Ba, Cr and Zn) than in the incinerator waste used as a raw material due to the obvious dilution of the latter (Table 2).

X-ray diffractograms of powdered samples were recorded with a Phillips PW 1730 CuKa radiation diffractometer. Specimens were step-scanned at $2°\,min^{-1}$, with a 2θ angle of 2–60°, a 1° divergence slit, a 1° anti-scatter slit and a 0.1-mm receiving slit.

The diffractograms for the clinker and commercial cement CEM IV are reproduced in Fig. 1. The clinker comprised a mix of crystalline phases, with alite (C_3S) and belite (C_2S) as the majority minerals. It also contained other characteristic phases such as tricalcium aluminate (C_3A) and C_4AF, a ferrite. In addition to the characteristic clinker phases, the reference cement diffraction pattern contained a series of lines attributed to crystalline minerals such as quartz (SiO_2) and mullite ($3Al_2O_3{\cdot}2SiO_2$), normally present in the coal combustion fly ash additioned to this cement [24].

Fig. 1 also shows the diffractograms for the incinerator fly ash (R1) and bottom ash (R2). The fly ash consisted primarily of quartz (SiO_2), anhydrite ($CaSO_4$), halite (NaCl), periclase (MgO), sylvite (KCl), portlandite ($Ca(OH)_2$), calcite ($CaCO_3$) and calcium hydrochloride (CaClOH). Calcite ($CaCO_3$), portlandite ($Ca(OH)_2$), akermanite ($Ca_2MgSi_2O_7$), quartz (SiO_2), magnetite (Fe_2O_3), gehlenite ($Ca_2Al(AlSi)$), halite (NaCl), calcium sulphate and an aluminium and magnesium hydroxide hydrate ($Mg_6Al_2(OH)_{18}{\cdot}4.5H_2O$) were identified on the diffractogram for bottom ash. In both cases a hump at 2θ 25–40° was observed, normally associated with the presence of vitreous material [21]. It was more visible in the bottom ash, perhaps an indication of a higher percentage of vitreous material than in the ash.

2.2. Hybrid cement mortar and paste preparation

As recommended in European standard EN-196-1, the bending and compressive strength values of hybrid cement RS 60/40 were tested on $4 \times 4 \times 16\text{-cm}^3$ prismatic mortar specimens prepared with standardised siliceous sand aggregate at an aggregate/cement ratio of 3:1. De-ionised water was added during mixing at a L/S ratio of 0.5. These specimens were cured for 24 h in a chamber at 21 °C and 99% relative humidity. After removal from the moulds they were stored in the chamber for a further 1 day or 27 days, then tested on an IBERTEST Autotest-200/10-SW frame. The reference specimens consisted in commercial cement type IV mortars cured under the same conditions as the mortars made with hybrid cement RS 60/40.

Cement pastes were prepared and cured under the same conditions as the mortars in order to better identify the activation products generated in the hybrid cements. The hydration medium was de-ionised water here as well, at a w/c ratio of 0.4. The specimens were characterised on a JEOL JSM 5400 scanning electron microscope fitted with a LINKS-ISIS energy dispersive microanalysis system and on a PHILIPS diffractometer.

2.3. Leaching tests

Hybrid cement immobilisation of the heavy metals present in the incinerator waste (Table 2) was assessed with two test methods [34–39] the toxicity characteristic leaching procedure (TCLP) [37] and ANSI/ANS 16.1 [36]. Whereas the former merely classifies the material as hazardous or otherwise depending on the concentration of the leached element, the latter furnishes valuable information on the mechanisms governing element leaching in the sample analysed and its immobilisation by the matrix.

Table 1
Chemical composition of the raw materials (wt%), as per XRF analysis.

	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	P_2O_5	Na_2O_{eq} [a]	Cl	Br	Other [b]	LoI [c]
Clinker (CK)	67.96	20.49	4.68	1.12	1.12	1.12	0.12	0.72	–	–	3.25	0.46
CEM IV	43.67	26.78	12.59	3.19	2.29	3.56	0.24	1.56	0.04	–	1.06	4.96
Inc. fly ash (R1)	37.34	2.54	1.15	0.43	0.97	5.10	0.52	10.37	12.46	0.09	1.25	27.80
Inc. bottom ash (R2)	35.01	16.77	7.27	11.97	3.78	2.95	2.45	3.37	1.04	0.02	1.84	13.60
RS 60/40 [d]	47.74	15.20	4.08	7.34	2.06	5.37	0.91	5.27*	2.05	0.01	1.09	8.84

[a] Na_2O eq.: wt% Na_2O + wt% K_2O.
[b] Others: minority metal oxides.
[c] LoI: loss on ignition (1000 °C).
[d] Hybrid cement: 60 wt% clinker + 40 wt% MSW incinerator waste, where MSW = 17% ash (R1) + 83% slag (R2) (*Na_2O eq = 5.27% = 1.82% from MSIW + 3.45% from activator).