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Waste Materials in Construction: Putting Theory into Practice

PROPERTIES OF PORTLAND CEMENT MORTARS INCORPORATING HIGH AMOUNTS OF OIL-FUEL ASHES.

J. Payá, M.V. Borrachero, J. Monzó, M.J. Blanquer and E.González-López.
Grupo de Investigación en Química de los Materiales de Construcción (GIQUIMA)
Departamento de Ingeniería de la Construcción
Universidad Politécnica de Valencia
c/ Camino de Vera s/n
46071 Valencia (Spain)

Abstract

The residue of oil-fuel burned at the electrical power plant of Grao de Castellón (Spain) has been incorporated in Portland cement mortar and concrete. The used oil-fuel ash presented a high percentage of magnesium compounds because of magnesium oxide addition for removing slag and ashes into boiler and pipes.

Several researches had been carried out on stabilization of toxic metals also occurring in oil-fuel ashes (specially vanadium and nickel), by mixture with coal fly ashes and cement. In our case, the presence of magnesium compounds in the composition of the studied oil-fuel ashes could alter the mechanical and chemical properties of cement matrix in fresh and hardened mortar and concrete.

We present here the chemical, physical and mineralogical characterisation of oil-fuel ashes and the behaviour of Portland cement mortars incorporating high amounts of these oil-fuel ashes: workability, water demand, setting time, expansion and and compressive strength developments.

Preliminary results demonstrated a high absorption of water on oil-fuel ash particles, which promotes an increasing of water/cement ratio for a given workability; a setting acceleration of Portland cement/oil-fuel ash pastes was observed, due to the presence of carbonates. On the other hand, no significant expansions in specimens due to the presence of magnesium compounds were detected and, consequently, mechanical properties of hardened mortars containing oil-fuel ashes did not drop with curing time, but compressive strength for mortars containing OFA were very lower than control mortar ones.

Introduction

The combustion of oil-fuel at electric power plants yields oil ashes as a solid residue. Oil-fuel ash (OFA) composition depends on, logically, the nature of the oil fuel burned and the additives used for removing them from the boiler and pipes. Oil fuel ashes produced by combustion of oil-fuel are enriched in heavy metals, specially in vanadium, which would be recovered by the steel industry [1]. However, in many cases, the residue is simply stabilised for avoiding leaching processes which could release toxic elements to the environment. Stabilization of oil ash wastes has been carried out within fly ash/cement/lime matrix; the stability of the solid blocks prepared also has been investigated from structural and chemical aspects [2], as soon as fouling community development when materials were used as concrete reefs [3].

Composition of OFA will be altered by the use of additives for removing ashes and slag from the boiler and pipes, as for example, using magnesium compounds (magnesium oxide and magnesium hydroxide); in addition to changes in chemical composition, new compounds will be synthesised by reactions between additives and oil fuel ash residue. These compounds could play an important role on the final properties of the stabilising matrix in mixtures within cement and other materials (for fresh and hardened materials).

Finally, if OFA has been exposed to atmospheric agents, several reactions (carbonation, hydration, dissolution, selective dissolution, ion exchange,...) would be promoted and the nature of OFA compounds substantially altered.

Experimental section

Oil fuel ashes were obtained from the electric power plant of Iberdrola in Grao de Castellón (Spain). A representative sample of OFA was chosen and dried at 105 °C for 24 hours. Part of the sample was ground using a laboratory ball-mill within alumina balls [4]. Cement was an ASTM type I Portland cement; a natural sand was used for preparing mortars (3.56 modulus fineness). Sikatard was used as setting retarder (phosphate-based additive) and Sikanol-M as plasticizer. OFA samples were studied by several techniques: Thermogravimetric analysis (TGA850 Themogravimetric Measuring Module, Mettler-Toledo), Scanning electron microscopy (JEOL JSM-6300, equipped with microanalysis based on energy dispersive X-ray), X-ray diffraction (PW1710 Based Diffractometer) . Preparation of mortars, setting determination, and mechanical strength measurements were carried out according to the corresponding ASTM procedures. Workability of mortars was determined using a flow table, measuring the spreading of mortar cones [5] (FTS values).

Results and discussion

Morphological, chemical and mineralogical characterization.

OFA sample before grinding was made up of particles between 10 μm and 3 cm in diameter. After grinding, fineness of the OFA sample was similar to ordinary Portland cement one; electron microscopy studies on ground OFA samples showed that crushed particles were very irregular in shape, with diameter from 1 to 40 μm and particles showed rough surfaces (see Figures 1 and 2), and surface chemical composition was determined by means X-ray dispersive energy: sample showed a high content in magnesium; nickel, vanadium, iron, silicon and calcium were also present; and sulphur also was detected. Figure 3 shows X-ray dispersive energy surface elemental analysis pattern of ground OFA.

X-ray diffraction analysis of OFA demonstrated that the sample was a complex mixture of compounds; several crystalline substances were identified[6]: olivine-like compounds (forsterite Mg_2SiO_4, $Mg_xFe_{2-x}SiO_4$, fayalite Fe_2SiO_4), periclase-like compounds (periclase MgO, $Mg_xNi_{1-x}O$), bunsenite NiO), magnetite-like compounds (magnetite Fe_3O_4, magnesioferrite $MgFe_2O_4$, trevonite $NiFeO_4$), vanadates (magnesium vanadium oxide $Mg_3(VO_4)_2$, nickel vanadium oxide $Ni_3(VO_4)_2$), hydrated halloisite ($Al_2Si_2O_5(OH)_4 \cdot nH_2O$) and magnesium hidroxide sulphate hydrate ($Mg_4(OH)_6SO_4 \cdot 8H_2O$). X- ray diffractogramm for OFA was showed in Figure 4.

Thermal analysis of OFA permitted to determine the presence of other important substances; Figure 5 shows the thermogravimetric TG and DTG curves for OFA. Weight loss near 110 °C was attributable to moisture and loss between 100 and 250 °C was due to hydration water; weight loss in 250-400 °C range was attributed to water loss due to hydroxide groups, and weight loss in 400-600 °C range was attributed to CO_2 evolution due to carbonate anion decomposition. Probably, as thermogravimetric analysis suggests, OFA contains several substances, which were not detected by X-ray diffraction analysis, as magnesium carbonate-hydroxide hydrates $(MgCO_3)_x(Mg(OH)_2)_y{\cdot}nH_2O$. The study of thermogravimetric analysis of substances as $(MgCO_3)_4(Mg(OH)_2){\cdot}5H_2O$ permitted to assign the corresponding losses.

Figure 1. Micrograph of ground OFA sample

Figure 2. Surface of an OFA particle

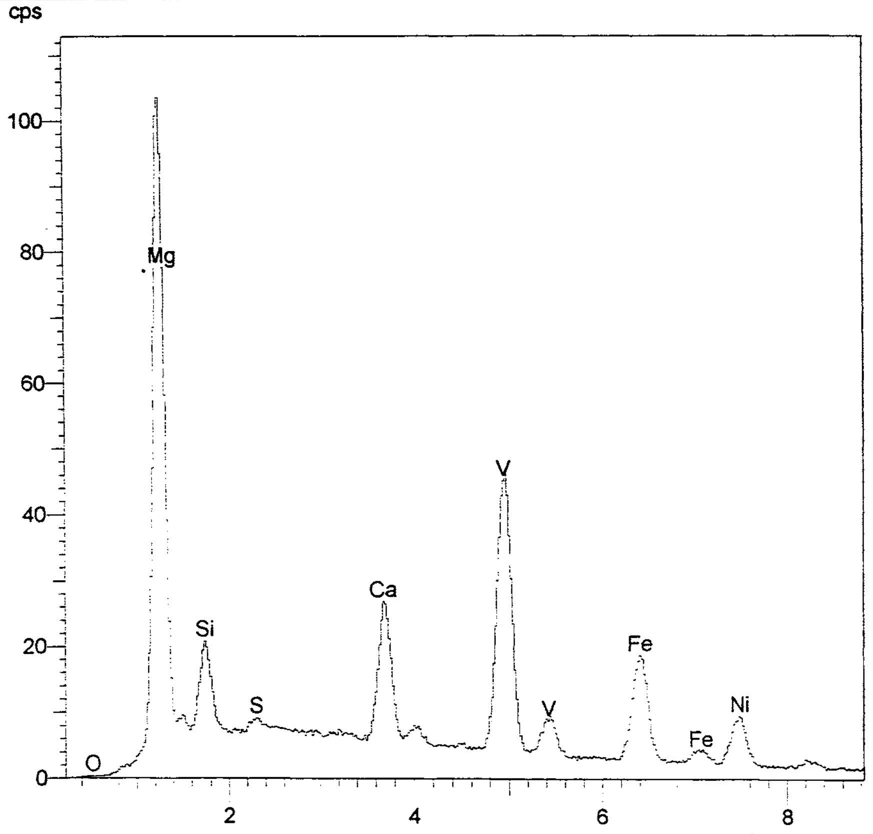

Figure 3. Energy dispersive X-ray pattern of OFA sample

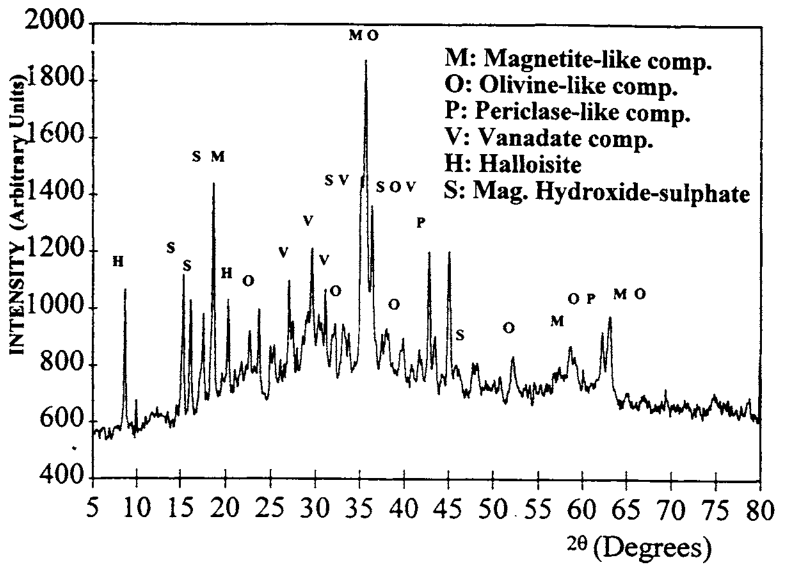

Figure 4. X-ray diffractogramm of OFA sample

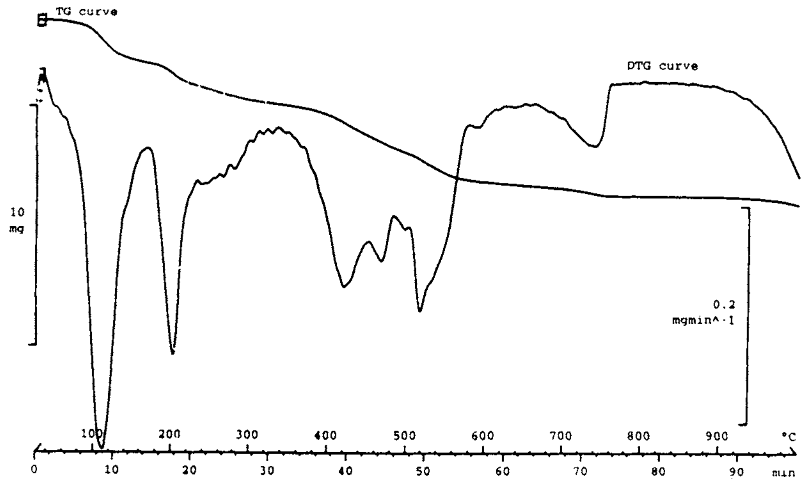

Figure 5. TG and DTG curves of OFA sample

Constancy of volume for Portland cement/OFA pastes

The presence in OFA samples of magnesium oxide and sulphate compounds could produce dangerous expansion processes of cement paste due to hydration of MgO to form brucite:

$$MgO + H_2O \Rightarrow Mg(OH)_2$$

or due to reaction of sulphates with calcium aluminate hydrates to yield ettringite [7].

Expansive processes in cement/OFA pastes were monitored using Le Chatelier needles, measuring the distance between the indicator needles after a thermal treatment in water. Expansion values found for pastes with different cement/OFA ratios are summarized in Table 1. In all cases, the distance between indicator needles did not exceed 10 mm, suggesting that expansive reactions did not affect appreciably the volume of the pastes. Consequently, cracks due to expansion processes will not occur when using OFA in mortar and concrete, and structural stability is guaranteed in relation to internal attack processes.

Table 1. Distances between indicator needles (Le Chatelier needles) for different Portland cement/OFA pastes.

Portland cement (%)	OFA (%)	cement/OFA ratio	Distance between needles (mm)
85	15	5.67	2.3
70	30	2.33	3.5
55	45	1.22	1.6
40	60	0.67	2.1

Setting time of cement/OFA pastes

Usually, ordinary Portland cement contains gypsum as retarder; so, setting time is controlled by chemical interaction between calcium aluminate hydrates and calcium sulphate dihydrate. The presence of other compounds in cement could affect its setting, since these substances can act as retarders or accelerators. In the setting process of cement, two periods are distinguished, the initial set and the final set [8], and the Vicat needle is used almost universally.

When OFA is added to Portland cement, an acceleration of setting was observed; so, if the percentage of OFA is equal or greater than 30 %, a flash set is caused. Setting times for cement/OFA pastes are summarized in Table 2. Setting acceleration observed when OFA is mixed with Portland cement could be attributed to the presence in OFA of magnesium hydroxide carbonates $(MgCO_3)_x(Mg(OH)_2)y{\cdot}nH_2O$; these compounds would interact with tricalcium aluminates forming carboaluminate compounds [9]. So, an intense crystal formation accompanied by crystal bonding, yielding an strong three-dimensional network is achieved.

Table2. Setting time for cement/OFA pastes

OFA (%)	Water for defined consistence (%)	Initial set (minutes)	Final set (minutes)	Setting time (minutes)
0	28	82	113	31
15	31	30	122	88
30	33	10	39	29
45	38	12	25	13
60	44	13	17	4

The addition of a phosphate-based retarder (Sikatard) in cement/OFA pastes (0.1 % of cement+OFA weight) increased notably initial and final sets. Probably, the precipitation of calcium-phosphate salts [10] hinder carboaluminate network crystallization. Table 3 summarizes setting time values for cement/OFA pastes using this retarder.

Table3. Setting time for cement/OFA pastes using a setting retarder

OFA (%)	Water for defined consistence (%)	Initial set (minutes)	Final set (minutes)	Setting time (minutes)
15	31	165	265	100
30	33	120	165	45
45	38	60	125	65
60	44	60	120	60

Workability of cement/OFA mortars

Control mortar was prepared mixing 450 g of Portland cement, 225 mL of water and 1350 g of natural sand, whereas OFA replacing mortars were prepared replacing part of the cement by ground OFA, with variable water/(cement+OFA) ratios. For studying the influence of OFA on workability of cement mortars, flow table spread (FTS) of mortar cones was measured according to the already reported method[5]. OFA replacing mortars (15-60 % replacement of cement by OFA) were prepared with 0.5 w/(c+OFA) ratio and FTS values are depicted in Figure 6. FTS values for mortars prepared by the same way and using plasticizer (Sikanol-M, 0.1% in weight of the total amount c+OFA) also are represented in Figure 6. It can be noticed that the presence of OFA decreases strongly the workability of mortars. When plasticizer was not used, replacing percentages greater than 15 % producen poorly workable mixtures; the addition of plasticizer enhances workability only for 15 and 30 % OFA replacing mortars. For enhancing workability of mortars containing high volumes of OFA, greater w/(c+OFA) ratios were necessary. So, in Figure 7, FTS values for mortars containing 45 and 60 % of OFA are represented (using plasticizer and increasing w/(c+OFA) ratio). Morphology and roughness of ground OFA particles and, probably, adsorption of water on particle's surface, are responsible for decreasing workability of mortars.

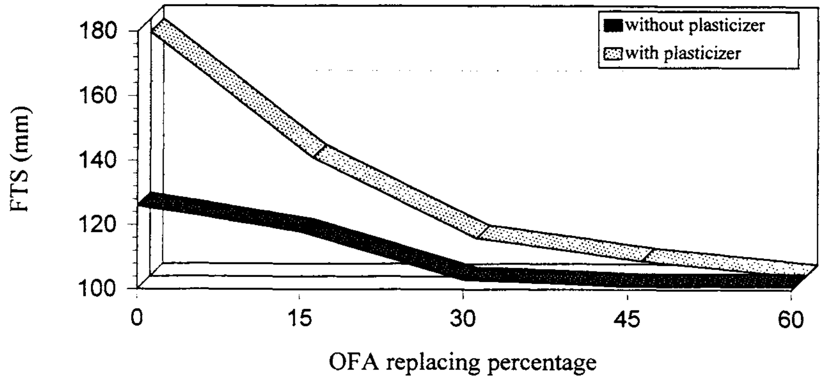

Figure 6. FTS values for mortars containing OFA (w/(c+OFA)=0.5)

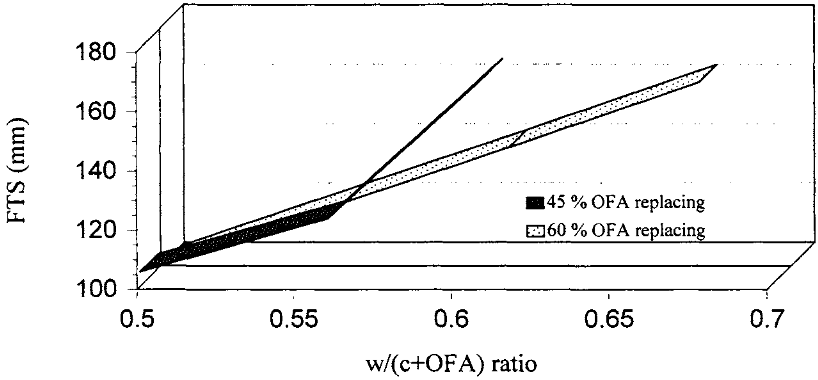

Figure 7. FTS values for mortars containing 45 and 60 % replacing percentages

Strength development of cement/OFA mortars

Prismatic mortar specimens (16x4x4 cm) were prepared and, after 24 hours at 20 °C in a moisture room, were cured at 40 °C until test age. Mortars were prepared using retarder and plasticizer. Figure 8 shows compressive strength development of mortars containing ground OFA; w/(c+OFA) ratios are indicated for each replacing percentage. It can be noticed that values for mortars containing OFA showed very lower compressive strengths than control mortar one. This fact could be attributed to three factors: firstly, the increase on w/(c+OFA) ratio specially for mortars containing high amount of OFA; secondly, the presence of some compounds found in OFA may hinder the adequate development of the cementitious matrix; and, thirdly, the use of plasticizer could increase the air content with an irregular distribution. However, no decreasing on compressive strength was observed in any case with curing time, suggesting that dangerous expansive reactions in the cementitious matrix were not occur.

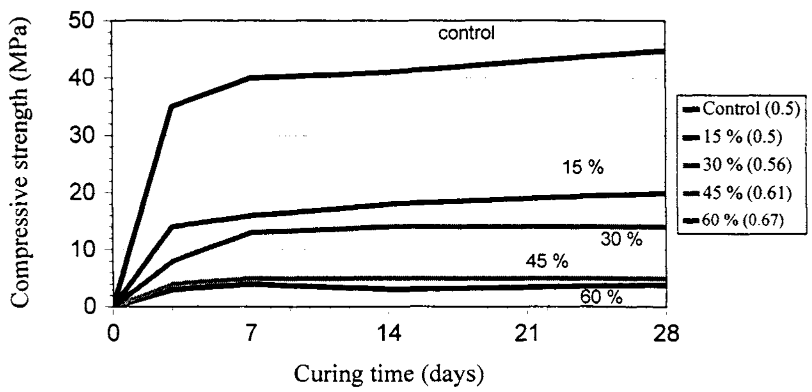

Figure 8. Compressive strength development for cement/OFA mortars. For each mixture w/(c+OFA) ratios are given in parentheses

Better mechanical properties were obtained when OFA was used without grinding and after sieving (for obtaining a material with particles less than 5 mm in diameter, coarse particles were crushed and sieved; retained material on sieve was finally discarded). This sieved OFA was used for replacing part of the sand (10-30 % in weight). So, mortars were prepared as follows: 450 g of cement, 0.5 water/cement ratio and 1350 g of sand+OFA. Specimens were molded and cured in the same conditions than above, and compressive strength measured at 28 days curing time. Figure 9 shows the relationship between compressive strength and the replacing percentage of sand by sieved OFA. Despite w/c ratio and the total amount of cement are maintained constant for all prepared mortars, also compressive strength value decreased with increasing replacing percentage; this fact suggest that OFA altered the cementitious matrix, and, consequently, mechanical properties of cured mortar worsen.

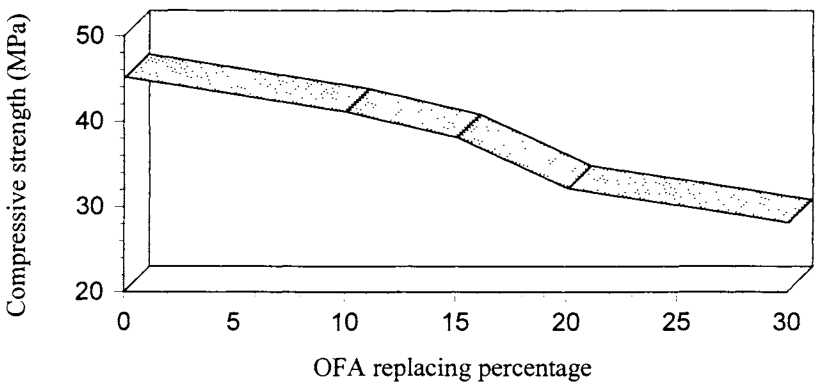

Figure 9. Compressive strength values for mortars containing sieved OFA replacing sand (40 °C curing temperature, 28 days).

Conclusions

Based on the experimental reported in this paper about the incorporation of oil-fuel ashes (OFA) in cement mixtures, the following conclusions are made:

1- Ground OFA showed irregular particles with rough surfaces; magnesium is the main metallic element, and nickel, vanadium, iron, silicon, calcium and sulphur also were detected. Different compounds were identified by X-ray diffraction and thermogravimetric analysis: olivine-like compounds, periclase-like compounds, vanadates, magnetite-like compounds and magnesium hydroxide-carbonate compounds.

2.- No expansive processes were detected in OFA/cement pastes, and structural stability due to internal attack is guaranteed.

3.- An acceleration of setting is produced due to the presence of OFA in cement pastes, and when high percentages of OFA are used a flash set is caused; the use of setting retarder permitted increasing initial and final sets of OFA/cement pastes.

4.- Morphology and surface roughness of OFA particles are responsible to decreasing workability of mortars containing OFA. Workability was enhanced using a plasticizer, but an increasing of w/(c+OFA) ratio is necessary for mortars containing high OFA replacing percentages.

5.- Mortars containing ground OFA showed very lower compressive strengths than control mortar ones, although no drop in compressive strength was observed with curing time.

6.- The substitution of sand by sieved OFA permitted to obtaining mortars with better mechanical properties, but compressive strength decreased with the increase of replacing percentage of sand by sieved OFA.

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