Effect of addition of spent oil filtering earths on electric arc furnace slag alkaline activated cements

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Abstract

The effects of the substitution of electric arc furnace slag (EAFS) by oil spent filter earths from the manufacture of oils and fats (SOFE) (10-50 wt %) on the technological properties of alkaline activated cements cured at room temperature were evaluated. As a control, a binder containing only EAFS was manufactured. Physical properties such as bulk density, water absorption, total porosity, mechanical properties such as flexural strength and compressive strength and thermal properties such as thermal conductivity of alkaline activated cements with different SOFE contents were investigated. The results indicate that the addition of SOFE resulted in a delay of precursor activation, which resulted in a decrease in mechanical properties at low curing times, 7 days. However, substitution of EAFS can improve physical, mechanical and thermal properties after 28 days of curing. Optimum substitution ratios are 30 wt % or higher. At the optimum substitution rates, the bulk densities of alkaline activated cements decrease, water absorption and total porosity increase, but conversely, flexural and compressive strengths increase from 8.3 MPa and 19.3 MPa, respectively for control cements to 11.3-11.8 MPa and 24.5-25.7 MPa with the incorporation of 30-50 wt % SFE. This increase in flexural strength and compression strength could be related to the higher formation of geopolymeric gel N-(A)-S-H with respect to C-(A)-S-H gel due to the higher amount of silica in the SOFE residue. The insulating capacity of the cements increases as increasing amounts of SOFE residue are incorporated, according to bulk density and total porosity data, with values ranging from 0.68 W/mK for control binders to 0.34-0.15 W/mK for cements incorporating 30-50 wt % SOFE. The results of this study may help to promote the application of SOFE in the production of environmentally friendly based alkaline-activated EAFS binders.

Keywords: spent oil filtering earths, electric arc furnace slag, alkaline activated cements, mechanical properties.

Introduction

The development of alternative cementitious materials to conventional cement has been gaining interest in the construction field in the last decades. The use of aluminosilicate-rich wastes, such as fly ash and slag, for the replacement of Portland cement is limited in quantities of 15-50 wt % of the total mass due to the low hydration rate and higher drying shrinkage of the wastes, resulting in pozzolanic cements [1]. The reactivity of these industrial by-products is enhanced in an alkaline environment giving rise to alkaline activated cements or geopolymers. Alkaline activated cements are the most eco-efficient and promising green cements or hydraulic binders, due to their low environmental impact, therefore, they are materials that considerably reduce CO_2 emissions without compromising economic costs [2]. Two models of alkali-activated joining systems have been established [3]. The first is the activation of silicon- and calcium-rich raw materials (electric arc steel slag) with an alkaline solution whose main reaction product is calcium silicate gel (C-S-H). In the second alkaline activation model, silicon- and aluminium-rich precursors (metakaolin or F-class fly ash) are used with alkaline solutions, and the reaction products are 3D Si-O-Al polymer chains. Davidovits named the second group as ”Geopolymer”, as they have a polymeric structure [4].

Alkali activation cements synthesis is influenced by a number of factors, such as physicochemical nature of the precursor, kind and amount of activator used and curing conditions [5-8]. In this sense it could be assumed that parameters like setting time, workability, mechanical strength, microstructure or durability of the synthetized products can be modified by varying the physicochemical properties of the industrial wastes used as precursors [9].

Partial replacement of slags by other silicon-rich wastes in raw material has been previously studied by other authors. Chi and Huang [10] studied the properties of alkali activated mortars made from fly ash and slag combined in different proportions and found that 50-50 wt% mixtures led to optimum results when 6 % Na_2O concentration was used in the activator.

Main hydration products are alkali amorphous aluminosilicate and low-crystallinity calcium silicate hydrate gel. Puertas et al. [11] studied the mechanical strength and hydration products of fly ash/slag materials activated with sodium hydroxide, concluding that best results were found when 50-50 mixtures were activated with 10 M NaOH solution and cured at 25 ºC. Fly ash – slag proportion turned out to be one of the main factors influencing the mechanical properties development. Mehta y Siddique [12] studied the influence of the use of Rice husk ash (RHA) as partial substitution of ground granulated blast furnace slag (GGBS) for the development of sustainable geopolymer concrete. Their findings showed that denser microstructure and best mechanical properties for the geopolymeric concrete manufactured where obtained with the addition of 15 % of RHA owing to the coexistence of polymerization products and calcium based hydration products. This study is focused on the partial substitution of electric arc furnace slags (EAFS) with spent oil filtering earths (SOFE) from agrifood industry for the development of alkali activated cements. Both residues were selected for having relatively high calcium and silica content, respectively.

Electric arc furnace slag (EAFS) and spent oil filtering earths (SOFE) are industrial wastes or byproducts obtained from steel manufacture industry and oil and fat filtering processes. EAFS is mainly composed of calcium oxide, silica and alumina while SOFE main components are silica. Filtering earhs are generally bentonites, or clays of small particle size and large specific surface area, containing low percentages of crystalline silica and high percentages of amorphous silica. These wastes contain 20-40 wt % of residual oil, metallic impurities and other organic compounds [13]. Spent filtration earths is a type of waste that is difficult to handle and manage, both because of its nature and the volume generated, as well as the lack of real alternatives for its recovery. Therefore, the most feasible solution at the moment focuses on the collection and disposal of these wastes by authorized agents.

In view of this background, the aim of this study is to use spent filter soils as a secondary raw material for the manufacture of alkaline activated cements based on electric arc furnace slag studying its effect on physical, mechanical and thermal properties.

2. Materials and Methods

2.1. Raw materials

Electric arc furnace slag (EAFS) was supplied by “Siderurgica Sevilla” company located in Seville (Spain) and Spent oil filtering earths (SOFE) was provided by Aceites del Sur Coosur, S.A, company located in Vilches (Jaén, Spain). Filtering earths were subjected to a heat treatment to remove the organic fraction. In order to determine the proper temperature of this treatment, a thermogravimetric analysis (TGA) Thermodifferencial analysis (DTA) of the dry residue was carried out (Figure 1). The equipment used was a Mettler Toledo thermal analyser model TGA/DSC 1. The air flow was set at 50 mL/min, with a heating rate of 10ºC/min from 30 ºC to 900 ºC. The temperature of the heat treatment was set at 700 ºC (constant weight).

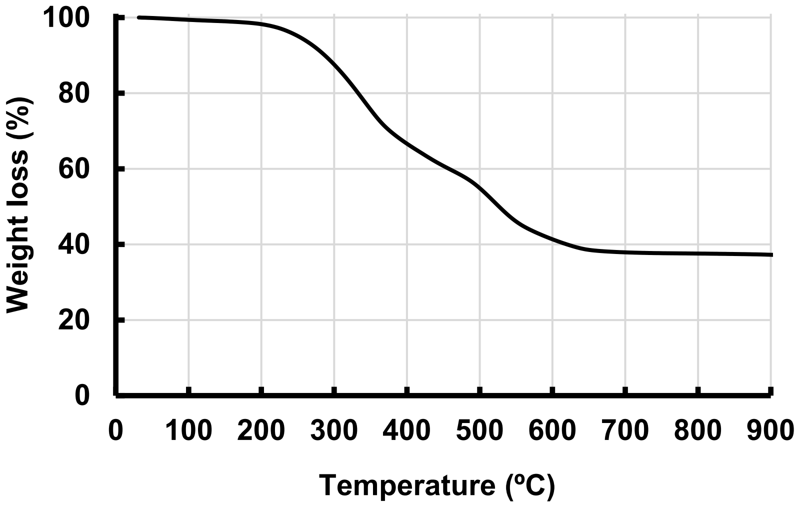

Figure 1. TGA study of spent oil filtering earths (SOFE)

The chemical composition of the residues was determined by X-ray fluorescence (XRF) (Table 1) with a Zetium Malvern Panalytical apparatus (United Stated).

Table 1. Chemical composition of escorias de acero de arco eléctrico (EAFS) and Spent Oil Filtering Earths (SOFE).

Raw material	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	MnO (%)	Na_2O (%)	K_2O (%)	TiO_2 (%)	P_2O_5 (%)	SO_3 (%)	LOI (%)
EAFS	17.29	10.71	24.16	30.89	2.63	5.68	0.16	0.03	0.79	0.41	0.28	5.39
SOFE	84.30	5.87	2.41	0.96	0.38	0.02	3.47	1.50	0.57	0.33	0.05	0.14

The residue EAFS is mainly composed by CaO (30.9 %), Fe_2O3 (24,2 %), SiO_2 (17.3 %) and Al_2O3 (10.7 %) and to a lesser extent MnO (5.7 %) and MgO (2.6 %). SOFE is mainly composed of SiO_2 (84.3 %) and in smaller proportions of Al_2O_3 (5.9 %), Fe_2O_3 (2.4 %) and K_2O (1.5 %). SOFE represents a potential source of silica in the manufacture of alkaline activated cements.

X-ray diffraction (XRD) tests were conducted at 2θ degree from 10° to 60° with Cu-Kα radiation ($\lambda = 1.54$ Å) to investigate the mineralogical composition of the precursors. The XRD reveal that wuestite, larnite, gehlenite and Mn_3O_4 are the main crystals phases in EAFS, while the main observed phase in SOFE was cristobalite, whose presence can be attributable to the calcination process of this raw material and illite, albite and anorthite were also detected as minor components.

2.2. Test plan

SFE was used to partially replace EAFS as raw material in the alkali activated binders with the aim of studying the influence of the replacement percentage on the technological properties of the alkali activated slag cements. Table 1 shows the composition of the mixtures. Samples were named as EAFS-xSFE, where "x" is the percentage of SOFE used as replacement of EAFS. Alkali activating solution was made by mixing in equal weight ratio commercial sodium silicate solution and 8 M NaOH solution prepared in the lab.

Table 2. Mix formulations of alkali activated cement in weight proportion.

Nomenclature	EAFS (g)	SOFE (g)	Relation (water/binder)	NaOH/NaSiO3(g)
EAFS	300	0	0,30	90
EAFS-10SOFE	270	30	0,45	135
EAFS-20SOFE	240	60	0,55	165
EAFS-30SOFE	210	90	0,65	195
EAFS-40SOFE	180	120	0,75	225
EAFS-50SOFE	150	150	0,90	270

The amount of activating solution added to the mixture was increased as the percentage of SOFE is higher in order to maintain constant workability in the pastes. As expected, the amount of solution needed by SOFE to become a paste is higher owing to the fineness of the material and its greater specific surface [14].

2.3. Sample preparation

In a first stage, EAFS and SOFE were blended in a planetary mixer for 90 s. Then, the previously prepared and cool down to room temperature activating solution was added and the whole mix was homogenized for 90 s more. The paste was at that moment pour into steel moulds to create prismatic samples of 60 x 10 x 10 mm size. The moulds with the paste were subjected to 60 strokes in a punching table and covered with plastic film for the first 24 hours to avoid evaporation. Afterwards, the samples were demoulded and placed in laboratory conditions (23 ºC and 60 % relative humidity) until the age of test, 7 and 28 days.

2.4. Test methods

Bulk density and water absorption of binders were measured according to the UNE-EN 1015 standard [15]. The real density was determined by pycnometry using ethanol as solvent. The total porosity was obtained from the ratio between the bulk density and the real density. The flexural and compressive strengths of alkaline activated cements were determined according to UNE-EN 1015-11:2000/A1:2007 [16]. An MTS Insight 5 machine (5 kN capacity) with a travel speed of 1.0 mm/min was used to determine the flexural strength. A universal testing machine, MTS 8101 (100 kN capacity), with a travel speed of 2 mm/min, was used to determine the compressive strength. The thermal conductivity of the binders at 20 ºC was performed with a FOX 50 TA Instruments thermal flow meter according to ISO 8302: 1991 [17].

3. Results and discussion

3.1. Bulk density, water absorption and total porosity

Table 3 shows the results of bulk density, water absorption and total porosity of every binder according to the replacement percentage of EAFS with SOFE at 7 and 28 days of curing. These results showed that water absorption and total porosity values trend is contrary to the bulk density variation. Reference sample (EAFS, 100 % slag) bulk density was determined to be 2499 and 2548 kg/m^3 while water absorption values observed were 7.3 and 6.9 %, with a total porosity of 26.5 and 22.2 %. All these results are given for 7 and 28 days respectively.

From those values, the addition of increasingly higher amounts of SOFE led to a progressive reduction of the bulk density with the subsequent rise of water absorption and total porosity. Test at 7 and 28 days showed minimum bulk density values (1549 and 1592 kg/m^3) and maximum water absorption (17.9 and 16.4 %) and total porosity percentages (39.5 and 36.2 %) were observed in the sample EAFS-50SOFE. Bulk density variation could be owing to the lower true density of the SOFE residue (2348 kg/m^3) in comparison with EAFS (3628 kg/m^3) and to the higher water/binder ratio used as SOFE percentage increases to maintain the workability of the paste. The later removal of the water used due to evaporation process during the curing could led to a higher porosity. However, the porosity rising trend observed could be considered lower than expected, probably owing to the further development of geopolymerization processes due to the higher reactivity of the binary mixtures which would produce a bigger amount of geopolymeric gel able to fill the porous produce by the evaporation of water.

As the curing time increases, it was found that apparent density rises while a reduction in the water absorption and total porosity takes place. These findings are consistent with the evolution of the geopolymerization and activation processes that, after some days of curing lead to compacter materials.

Table 3. Bulk density, water absoption and total porosity of alkali activated cements at 7 and 28 days of curing.

Sample	**Bulk density (kg/m^3)**		**Water absorption (%)**		**Total porosity (%)**	
Curing time	**7 days**	**28 days**	**7 days**	**28 days**	**7 days**	**28 days**
EAFS	2499 ± 3	2548 ± 9	7.33 ± 0.16	6.91 ± 0.17	26.5 ± 0.34	22.2 ± 0.46
EAFS-10SOFE	1950 ± 7	2223 ± 41	11.14 ± 0.34	10.23 ± 0.94	30.3 ± 0.86	28.5 ± 0.45
EAFS-20SOFE	1796 ± 19	1975 ± 26	15.23 ± 0.77	13.73 ± 0.58	34.8 ± 0.67	31.6 ± 0.96
EAFS-30SOFE	1689 ± 6	1833 ± 11	16.58 ± 0.50	14.81 ± 0.40	35.2 ± 0.79	32.8 ± 0.39
EAFS-40SOFE	1659 ± 6	1705 ± 16	17.08 ± 0.50	15.70 ± 0.72	38.2 ± 0.99	34.0 ± 0.77
EAFS-50SOFE	1557 ± 23	1592 ± 8	17.90 ± 0.53	16.35 ± 0.66	39.5 ± 0.76	36.2 ± 0.93

3.2. Flexural and compressive strength

Table 4 shows the results of flexural and compressive strength of every binder according to the replacement percentage of EAFS with SOFE at 7 and 28 days of curing. Flexural strength of reference sample (EAFS) at 7 and 28 days was determined to be 5.3 and 11.3 MPa, while compressive strength values observed were 10.0 and 16.3 MPa. SOFE addition reduces both flexural and compressive strength at 7 days owing to its slower mechanism of activation that provokes a later hardening of the sample. However, the results at 28 days showed that the addition of SOFE leads to superior materials in terms of mechanical properties, that can be comparable to flexural and compressive strength of cements with up to 20 wt % addition. Replacement percentages with SOFE of 30-50 % led to flexural strength values of 11.3 – 11.8 MPa and compressive strength values of 24.5 – 25.7 MPa. It is equivalent to percentual risings of 37 – 42 % for flexural strength and 27 – 33 % for compressive strength, at 7 and 28 days respectively.

However, even when mechanical properties increase with the incorporation of SOFE, bulk density decreases and total porosity is higher. These phenomena can be attributed to the presence of a bigger amount of N-(A)-S-H gel owing to the increasingly higher amounts of silica-rich SOFE. This gel has been found to be stronger [].

Table 4. Mechanical properties of alkali activated cements at 7 and 28 days of curing.

Sample	**Flexural strength (MPa)**		**Compressive strength (MPa)**	
Curing time	**7 days**	**28 days**	**7 days**	**28 days**
EAFS	5.32 ± 0.79	8.27 ± 0.93	10.00 ± 1.4	16.3 ± 0.3
EAFS-10SOFE	3.12 ± 0.31	8.45± 1.01	6.5 ± 0.8	17.1 ± 0.5
EAFS-20SOFE	3.85 ± 0.58	8.95 ± 0.91	9.4 ± 0.9	18.4 ± 1.8
EAFS-30SOFE	3.32 ± 0.51	11.25 ± 0.63	9.6 ± 1.2	24.5 ± 1.3
EAFS-40SOFE	4.32 ± 0.31	11.40 ± 0.81	6.5 ± 0.8	25.1 ± 1.7
EAFS-50SOFE	2.43 ± 0.97	11.75 ± 0.30	2.2 ± 0.6	25.7 ± 1.5

3.3. Conductividad térmica

Table 5 shows the results of thermal conductivity of every binder according to the replacement percentage of EAFS with SOFE at 28 days of curing. It is observed how the increase in the replacement percentage leads to a reduction in the conductivity, which is consistent with the lower values of apparent density and the rise in the total porosity. In this sense, maximum value of 0.681 W/mK was obtained for the reference sample (EAFS) while the minimum thermal conductivity was observed in the sample EAFS-50SFE with a value of 0.136 W/mK, which is equivalent to a 80 % reduction in this magnitude.

Table 5. Thermal conductivity of alkali activated cements at 28 days of curing.

Sample	EAFS	EAFS-10SOFE	EAFS-20SOFE	EAFS-30SOFE	EAFS-40SOFE	EAFS-50SOFE
Thermal conductivity (W/mK)	0.681 ± 0.001	0.557 ± 0.001	0.506 ± 0.001	0.339 ± 0.001	0.150 ± 0.001	0.136 ± 0.001

4. Conclusions

In this work, the technological properties of alkaline activated cements based on electric arc furnace slags in which 0-50 wt % of the EAFS precursor is replaced by the spent oil filtering earths (SOBE) residue are studied.

The following conclusions can be drawn from the test results and analyses:

- Increasing the SOBE content decreases the bulk density and increases the water absorption and total porosity of the alkaline-activated mixers, which is mainly attributed to the lower real density of the SOBE residue and the higher water/binder ratio used to achieve adequate consistency and workability.
- The substitution of SOBE for EAFS increases the flexural and compressive strength of the binders, possibly because the incorporation of SOBE, silica-rich waste, favors the formation of N-(A)-S-H geopolymeric gel in combination with C-(A)-S-H gel formed in the more EAFS-rich binders.
- Substitution of SOBE for EAFS leads to cements with thermal insulation advantages

Therefore, the study demonstrates the positive effect of using a waste with basically no industrial application such as spent oil filtering earths as a substitute for the precursor electric arc steel slag in the manufacture of alkaline activation cements, giving rise to binders with improved physical, mechanical and thermal properties with respect to control cements.

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