Development of alkaline activation materials from metallurgical slags: ferrosilicon and steel slags

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Abstract

The goal of this work is obtaining new alkali activated cements at room temperature by using ferrosilicon slags. Ferrosilicon slag were used as precursors. The addition of steel slags in differente proportions (10-50 wt %) were studied. A sodium silicate solution and a 6 M solution of sodium hydroxide were used as an alkaline activator. Physical, mechanical and thermal properties of alkali activated cements have been determined. Experimental investigation revealed that the addition of steel slag in the ferrosilicon based alkali activated cements improved their reactivity reaching a compressive strength of 13 MPa, with the addition of 50 wt % of steel slag. The improvement of mechanical strength can be attributed to the better reaction of geopolymerization and the better structure in the geopolymeric gel. Therefore, the use of these new and more sustainable conglomerates may reduce CO_2 emissions and relieve one of the causes of global warming, as well as making good use of metal slags which are considered industrial debris.

Introduction

In recent years, geopolymer and alkali-activated materials technology have gained much attention as a sustainable alternative to conventional Portland cement due to their higher strength, durability and ecological characteristics [1, 2]. Compared to conventional cement, CO_2 emissions and energy consumption can be significantly reduced during its synthesis [3]. Alkali activated materials are low-carbon binders that are prepared by mixing the appropriate amount of an alkaline solution with solid material rich in silica, aluminium and/or calcium (mostly from waste). These binders are therefore based solely on natural minerals (kaolin), industrial waste or by-products (blast furnace slag, fly ash) and an alkaline activator [4] .

Alkali-activated materials are considered to be the materials of the future due to their low environmental impact and high performance in terms of raw material consumption, low energy consumption, as well as a significant reduction of approximately 85% in CO_2 emissions in their production [5]. Consequently, the production of these new substitute materials for traditional materials that have a lower environmental impact is one of the main strategies to combat climate change that can contribute very effectively to a future more sustainable and eco-efficient "revolution" in the sector of inorganic non-metallic building materials (cement, concrete and ceramics).

Ferrosilicon slag is a by-product of the silicon and ferrosilicon industries after reducing quartz using carbon in an electric arc furnace. The amount of by-product obtained can vary between 3-5 % of the alloy mass [6]. The average production of ferrosilicon in 2014-2018 was 6.91 million tonnes, so 0.276 million tonnes of slag was produced [7]. Given its low cost, a portion is used in the iron and steel and Portland cement industries [8], although part of the production is stored in landfills, so there is a need to develop new ways of valorization.

Black slag from electric arc steel is a by-product produced in steelmaking when molten steel and impurities are separated [9]. This by-product has been used as a raw material in the manufacture of alkali activated cements [10].

This study focuses on the development of alkaline activated cements cured at room temperature using ferrosilicon slag (FSS) and electric arc furnace slag (EAFS). The experimental programme includes the characterisation of the precursors and the evaluation of the binders as a function of the amount of electric arc furnace slag added (10-50 wt%) through the determination of physical, mechanical and thermal properties.

Materials and methods

Two types of metallurgical slag have been used as raw materials. Ferrosilicon slag (FSS) from the Ferroatlántica group, specifically from its factory located in Boo de Guarnizo (Cantabria, Spain) and electric arc slag (EAFS) supplied by Siderúrgica Balboa S.A. located in Jerez de los Caballeros (Badajoz, Spain). The slags were crushed in a jaw mill prior to grinding in a ball mill. The chemical composition of the precursor FSS and EAFS is shown in Table 1.

Table 1. Composition of precursors: Escorias de ferrosilicio (FSS) y escorias de arco eléctrico (EAFS)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	Na_2O	K_2O	TiO_2	BaO	P_2O_5	LOI
FSS	38.91	11.94	0.63	28.06	4.12	9.53	0.07	1.22	0.26	2.87	-	0.00
EAFS	18.59	9.44	28.61	29.45	4.56	4.18	0.20	0.04	0.95	-	0.38	1.39

For both slags, the modulus of hydration was determined, which represents the hydraulic activity and is given by the ratio of (Al_2O_3+MgO+CaO)/SiO2 and the basicity coefficient, which relates the basic oxides (MgO+CaO) to the acidic ones (Al_2O_3 +SiO_2). The modulus of hydration was 1.13 and 2.34 and the basicity coefficient was 0.63 and 1.21 for the FSS and EAFS precursors respectively. These data indicated a lower reactivity of the by-product FSS, so the addition of EAFS will allow hardening on curing at room temperature and possibly improve the technological properties of the alkali activated cements. Different percentages of electric arc slag (EAFS) (20-50 wt %) have been added to ferrosilicon slag (FSS). As a control, specimens containing only FSS were prepared. As activating solution, a solution of sodium silicate and sodium hydroxide (35% silicate and 65% NaOH with a concentration of 6 M) was used. The l/s ratio was kept constant and equal to 0.4. For the manufacture of the binders, the slag was mixed for 90 seconds in a planetary mixer. The activating solution was then added and stirred for 90 seconds. The paste adhering to the walls of the container is peeled off and finally mixed for another 30 seconds. The paste is then poured into the 60x10x10 mm steel moulds, which are subjected to 60 blows on the shaking table to remove any air pockets. The moulds are covered with cling film and left to set and cure at room temperature. After 48 hours, the test specimens are demoulded and cured at room temperature until the age of the test, 7 or 28 days. The cements shall be designated according to the following nomenclature: xFSS-yEAFS where 'x' indicates the ferrosilicon slag content and 'y' is the electric arc slag content.

The bulk density and water absorption were determined according to ASTM 642-13 [11]. Flexural and compressive strength was determined according to UNE-EN105-11standard [12] y thermal according to the ISO 8302 standard [13].

Results and discussion

The bulk density of the binders is shown in Figure 1. It can be seen that the control specimen with 100% FSS have a bulk density of 1.78 and 1.81 g/cm^3 for curing times of 7 and 28 days respectively. The addition of EAFS resulted in an increase in bulk density as increasing amounts of by-product were incorporated. Thus, at 28 days of curing, the 80FSS-20EAFS alkali activated cements had a bulk density of 1.94 g/cm^3 increasing the bulk density to 2.12 g/cm^3 for the 50FSS-50EAFS specimens where 50 wt% EAFS were added. The increase in bulk density may be due to the higher real density of EAFS (3.58 g/cm^3) compared to FSS (3.12 g/cm^3). The evolution of bulk density with curing time indicates an increase indicating that the geopolymerisation and/or alkaline activation reaction continues after 7 days of curing.

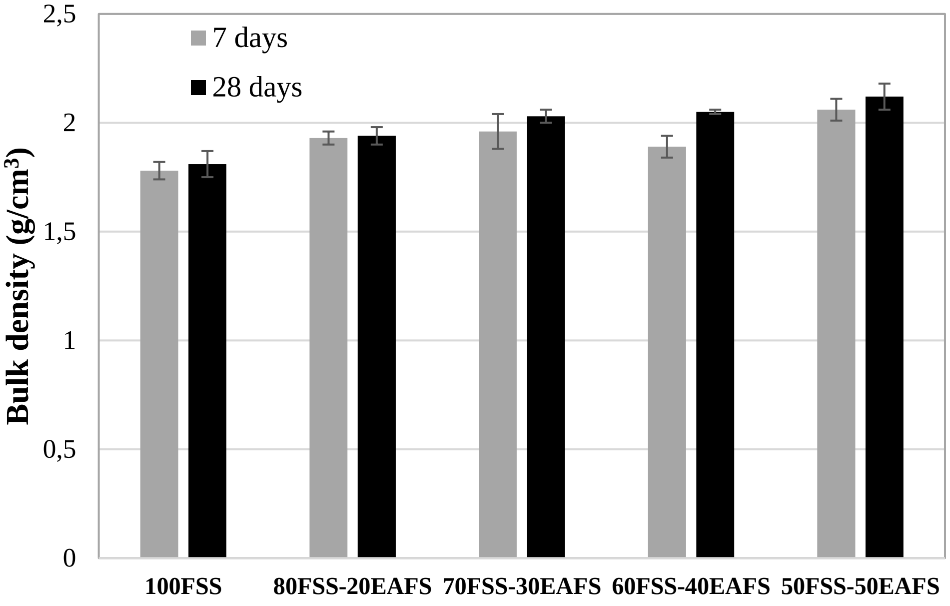

Figure 1. Bulk density of the alkali activated cements after 7 and 28 days of curing as a function of the EAFS content added.

The water absorption results are in agreement with the bulk density data. The control specimens (100FSS) showed water absorption values of 11.82 and 11.30 % for curing times of 7 and 28 days respectively. The addition of increasing amounts of electric arc slag (20-50 wt % EAFS) resulted in a slight decrease in open porosity, with the specimens having water absorption values between 9.42% and 9.68% (80FSS-20EFAS) and 8.62 and 9.12% for the binders incorporating 50 wt% EFAS (50FSS-50EFAS) after 7 and 28 days of curing respectively (Figure 2).

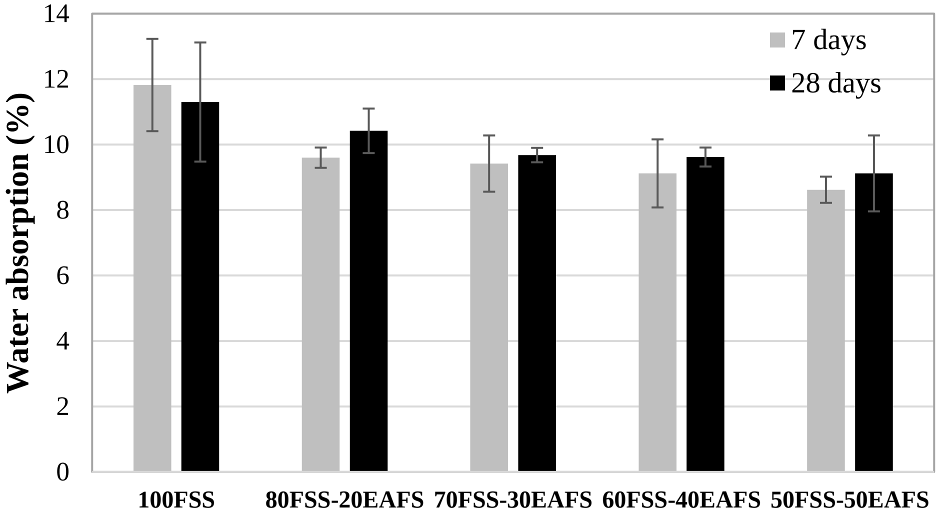

Figure 2. Water absorption of alkali activated binders as a function of EFAS content and curing time 7 and 28 days.

The mechanical properties of the alkali activated cements as a function of the percentage of EAFS added are presented in figures 3 and 4. The single flexural strength of the control specimens was 2.16 and 2.20 MPa after 7 and 28 days of curing. The incorporation of increasing amounts of electric arc slag (EFAS) produced a very slight increase up to the incorporation of 40 wt % by-product, obtaining values of 2.41 and 2.73 MPa for the 60FSS-40EFAS specimens after 7 and 28 days of curing. On the contrary, it is observed that the alkaline activated cements specimens containing 50 wt % of EAFS have a high flexural strength value of 5.03 MPa after 28 days of curing. Compared to the 28-day strength of the concrete, which is 25MPa in compression and according to ASTM C293/ C293M-16 [15], the concrete has a flexural modulus of rupture close to 20 % of the compressive strength; which is 5 MPa. The flexural strength properties for the alkali activated cement 50FSS-50EAFS at 5.03 MPa are similar to those of concrete.

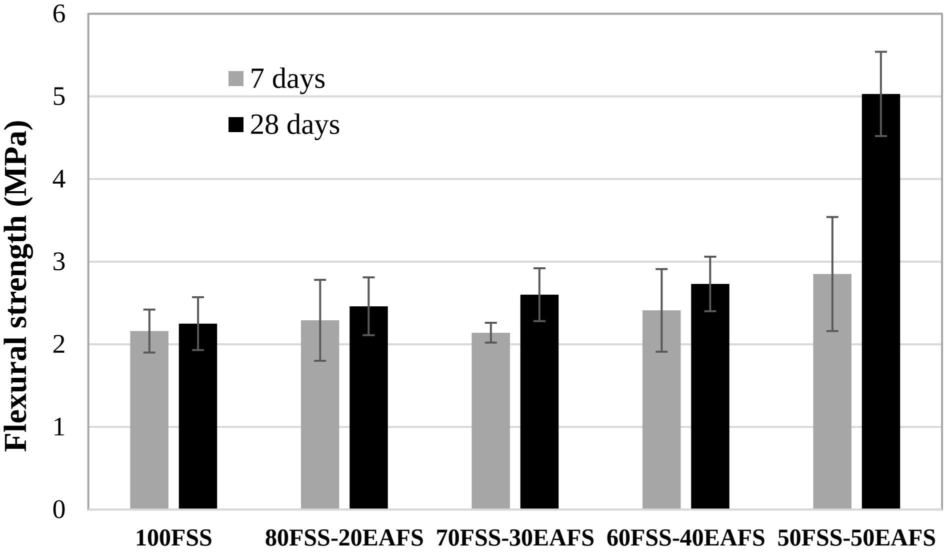

Figure 3. Flexural strength of alkali activated binders as a function of EFAS content and curing time 7 and 28 days.

For compressive strength, the trend is similar to the flexural strength, with compressive strength increasing as the incorporation of higher amounts of EAFS increases. The compressive strength of the control specimens was 2.4 and 3.6 MPa after 7 and 28 days of curing respectively. The addition of up to 40 wt % EFAS produced a slight increase up to 8.8 MPa which remains constant with curing time, reaching the maximum compressive strength after 7 days of curing. The highest compressive strengths are achieved with the addition of 50 wt % EAFS, obtaining values of 11.1 and 13.1 MPa after 7 and 28 days of curing respectively. The higher compressive strength values of these specimens may be related to the higher bulk density, lower water absorption and higher amount of hydrated calcium silicates (C-A-S-H) and geopolymer gel (N-A-H-S). The presence of Fe in the EAFS by-product (28.6 wt %) has also been reported to be beneficial for the development of mechanical strength of alkali activated materials due, like calcium, to its easy dissolution [15].

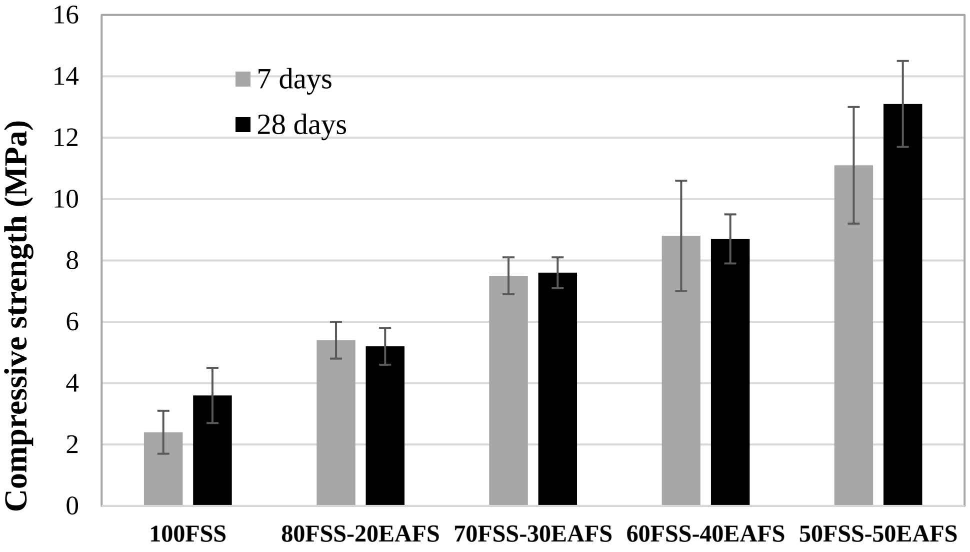

Figure 4. Compressive strength of alkali activated binders as a function of EAFS content and curing time 7 and 28 days..

The thermal conductivity of the binders is presented in Figure 5. The thermal conductivity of the control specimens was 0.206 W/mK. The addition of increasing amounts of EAFS resulted in an increase in thermal conductivity according to the bulk density data, with values ranging from 0.247 W/mK for the 800FSS-20EAFS specimens to 0.338 W/mK for the 50FSS-50EAFS cements after 28 days of curing. These data indicated a decrease in insulation performance as increasing amounts of electric arc slag were incorporated. However, the insulation capacity of the manufactured alkaline activated cements is higher than that of concrete, with a thermal conductivity of 0.8 W/mK.

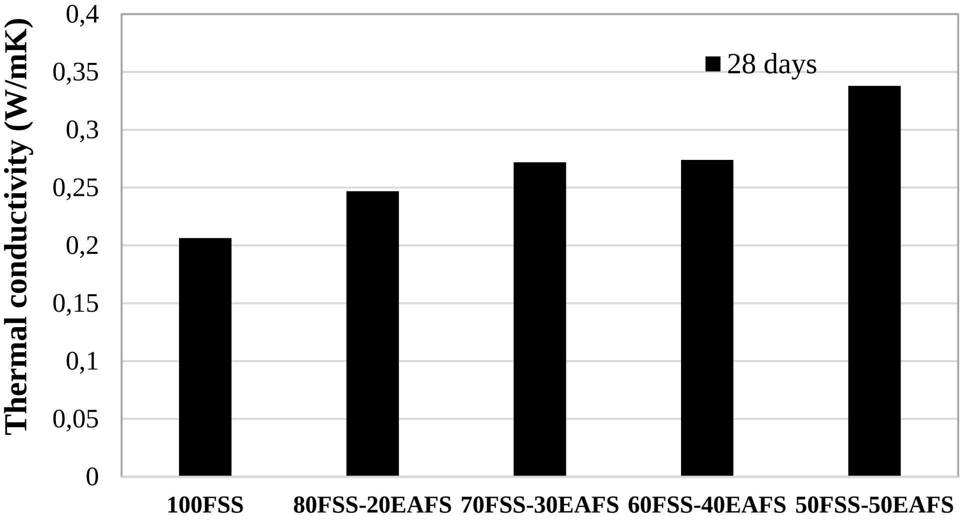

Figure 5. Thermal conductivity of alkali activated binders as a function of EAFS content after 28 days curing.

Conclusions

Alkali activated cements cured at room temperature have been developed using ferrosilicon slag as the main precursor. Steel electric arc slag has been added due to the higher hydraulic capacity of the residue, evaluating the physical, mechanical and thermal properties as a function of the amount of EAFS incorporated (20-50 wt %). The bulk density of the alkali activated binders increased, while the water absorption decreased as increasing amounts of EAFS were introduced. The mechanical properties flexural and compressive strength increased with the incorporation of the EAFS by-product obtaining values of 5.0 MPa and 13.1 MPa respectively for the 50FSS-50EAFS specimens. The incorporation of EAFS produced greater densification and favours the formation of a greater amount of hydrated calcium silicates C-A-S-H and geopolymer gel (N-A-S-H). The thermal conductivity of alkali activated cements increased as increasing amounts of EAFS were incorporated according to bulk density data. However, the compositions studied showed thermal conductivity values between 0.21 W/mK for the 100FSS specimens and 0.34 W/mK for the 50FSS-50EAFS specimens. Therefore, the experimental results reveal that ferrosilicon slag wastes can be partially employed in the synthesis of sustainable alkali activated cements cured at room temperature. The incorporation of up to 50 wt % EAFS produced binders with improved mechanical properties and suitable physical and thermal properties.

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