INITIAL APPROACH TO THE ALKALINE ACTIVATION OF GROUND GRANULATED SiMn SLAG

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Introduction

In this research, the waste material whose valorisation is proposed as raw material to design an ecological binder is a SiMn slag generated in the production of silico-manganese iron alloys. In the silico-manganese process, 0.9–2.2 tons of slags are discharged to produce 1 ton of silico-manganese. In Spain, near 200,000 ton/year of silico-manganese alloy are produced and the total production of SiMn slag is about 350,000 tons per year, so the amount is high enough to propose its reuse and valorisation. This SiMn slag presents a silico-calcic nature similar to blast furnace slag, but with a different chemical composition: lower content of CaO and a significantly high proportion of MnO.

At present, most published researches about this slag have been focused on its pozzolanic properties, and have proposed its valorisation as cementing material replacing different percentages of Portland cement[1]. Chemical, mineralogical and pozzolanic characteristics presented by the SiMn slag make possible its use as a substrate to obtain alkali activated materials. Kumar *et al.*[2] studied the effect of the mechanical activation of the slag in the activation process, and it was evidenced the potential of the SiMn slag to be activated with a sodium hydroxide. The conclusion was that the reactivity of the slag was improved by the mechanical activation and it depends on the type of milling used.

The aim of this research is to explore the viability of using ground-granulated SiMn slag as raw material for producing alkali-activated binders. For that reason, the slag has been characterised in terms of its chemical composition, mineralogy, physical properties and microstructure. The factors and interactions which affect compressive strength of pastes were studied by ad-hoc designs based on the d-optimal criterion. Four factors were studied at several levels: slag fineness, type of activator, %Na_2O and solution to slag ratio.

Experimental

The primary raw material used was a SiMn slag from the Ferroatlántica plant sited at Boo de Guarnizo (Cantabria, Spain). Table 1 shows the results of the chemical analysis obtained by X-ray fluorescence analysis. According to the slag basicity index (CaO/SiO_2 = 0.80 and $(CaO+MgO)/(SiO_2+Al_2O_3)$ = 0.73) and hydraulicity index ($(CaO+0.5MgO+Al_2O_3)/(SiO_2+MnO)$ = 0.85), this residue can be classified as an acid slag with moderate hydraulicity. The determination of crystalline phases and the vitreous phase content by X-ray diffraction have been determined by Rietveld method. Results showed 2% of alabandite (MnS), 2% of graphite (C) and 96% of vitreous phases. The slag also offered a 33.8% of reactive silica and 3.35% of insoluble residue.

Table 1: Composition of the SiMn slag determined by X-ray fluorescence analysis

Component	%	Component	%	Component	%	Component	%
SiO_2	36.53	MgO	4.69	SO_3	2.77	SrO	0.14
CaO	29.10	Fe_2O_3	0.92	Cl^-	0.16	TiO_2	0.19
MnO	12.23	K_2O	1.08	BaO	1.60	ZrO_2	0.04
Al_2O_3	9.86	Na_2O	0.34	P_2O_5	0.35	L.O.I.	-1.25

The slag was ground in dry conditions using a laboratory ball mill for 25 minutes and 40 minutes with the aim of obtaining two different degrees of fineness. The Blaine's fineness after the 25-minute grinding was 5500 cm^2/g and ground slag particle size distribution offered the following characteristic values: D_{50} = 9.2 µm and $D_{4,3}$ = 15.2 µm. Additionally, the Blaine's fineness after the 40-minute grinding was 6800 cm^2/g, and ground slag particle size distribution offered the following characteristic values: D_{50} = 6.9 µm and $D_{4,3}$ = 10.8 µm. Alkaline solutions used to activate the SiMn slag were waterglass (WG) prepared with a commercial sodium silicate (Na_2SiO_3 (neutral solution QP, Panreac): SiO_2/Na_2O molar ratio = 3.28) and sodium hydroxide (technical grade, Panreac). Alkali activation efficiency has been studied taking into account the influence of following four factors which were studied at several levels: slag fineness (A1: 5500 cm^2/g; A2: 6800 cm^2/g), type of activator (B1: NaOH; B2: WG), %Na_2O (C1: 3%; C2: 4%; C3: 5%) and solution to slag ratio (D1: 0.35; D2: 0.40; D3: 0.45). The $SiO^-{}_2/Na_2O$ ratio for the WG solution was set to 1.0. No additives have been used in this work and all specimens have been cured in a humid chamber with a 100% of relative humidity (RH) and 20 ±2 ºC. The analysis of main factors and their first order interactions have been made through the compressive strength (Sc) of samples, which were prepared and tested according standard EN 196-1. Samples were cured in 100% RH for 7, 14 and 28 days at 20 ± 2°C. Further details about the statistical procedure used can be found in the literature[3].

Results

Table 2 presents a selection of the three best compressive strength results obtained with each activator after 7, 14 and 28 days of curing time, in order to show the potentiality of this slag within the studied experimental conditions.

Table 2: Compressive strength of pastes after 7, 14 and 28 days of curing time

Fineness (cm^2/g)	Activator	$\%Na_2O$	s/s	Sc 7 days (MPa)	Sc 14 days (MPa)	Sc 28 days (MPa)
6800	NaOH	4.0	0.35	21	35	43
6800	NaOH	3.0	0.35	9	28	33
6800	NaOH	4.0	0.40	18	21	31
6800	WG	4.0	0.35	18	31	41
5500	WG	5.5	0.40	17	19	33
6800	WG	5.5	0.35	23	31	29

Figure 1 shows the graphic analysis of the effects of the studied experimental factors on the response for Sc. The significant factors for Sc at any of the studied curing times are all the selected factors (A, B, C and D) since all of them have at least one level which affects this property. According to the sign of the effect of each particular level within each factor, it can be stated that Sc is increased when: fineness is higher; NaOH is used as activator up to 28 days of curing time; $\%Na_2O$ is increased; and s/s is reduced. With regards to the first order interactions, positive ones have been observed systematically for B2-C3 and C2-D1, and negative interactions were detected for B1-C3, so with the aim of obtaining the best performance it is recommended to use the combination of B2-C3 and C2-D1. Other interesting positive interactions can be B1-C1 and C1-D3.

Conclusions

1. The compressive strength developed by the alkali activation process of ground granulated SiMn slag significantly depends on: slag fineness, type of activator, $\%Na_2O$ and solution to slag ratio.
2. In order to enhance the compressive strength, it should increase slag fineness, use NaOH as activator, increase $\%Na_2O$ and decrease solution to slag ratio.

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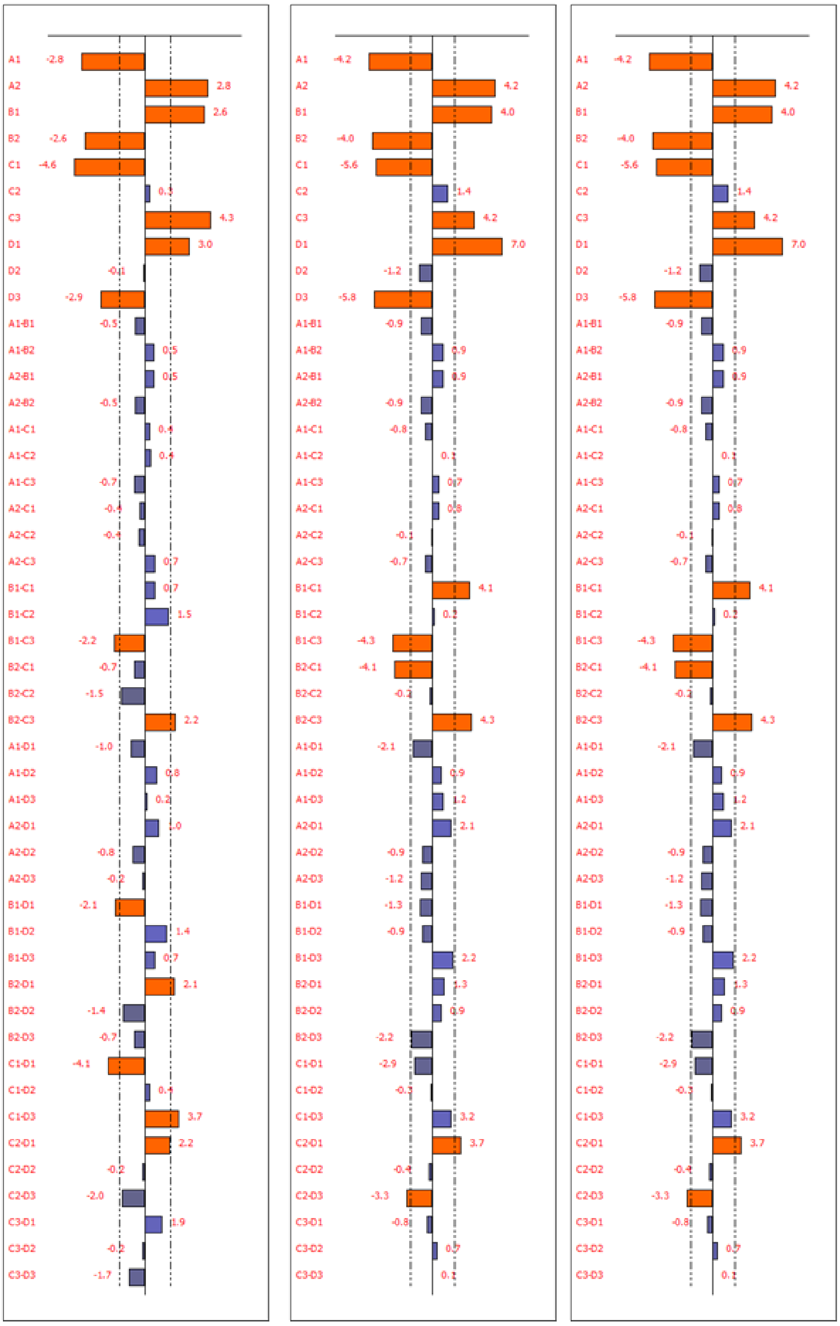

Figure 1: Graphic analysis of experimental factors effects on Sc at 7 (left), 14 (center) and 28 (right) days. Orange = significant; blue = non-significant

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