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Recycling of silicomanganese slag as pozzolanic material in Portland cements: Basic and engineering properties

Moisés Frias [a,*], M. Isabel Sánchez de Rojas [a], Jesús Santamaría [b], Cristina Rodríguez [b]

[a] Eduardo Torroja Institute (CSIC), Serrano Galvache, n.4, 28033 Madrid, Spain
[b] Ferroatlántica, División de Ferroaleaciones, Fábrica de Bóo de Guarnizo, Cantabria, Spain

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Abstract

Correct use of SiMn slags requires a detailed knowledge of their properties, as chemical and mineralogical composition, pozzolanic activity, reaction kinetics, setting time, volume expansion and strength play important role in the final valorisation of SiMn slag as pozzolanic material. This kind of slag is formed mainly of SiO2 and CaO, followed by Al2O3 and MnO which sum is nearly 90%. Sulphites content of 0.42% was detected. The main crystalline compound identified in SiMn slag is akermanite.

The results obtained show that SiMn slag blended cements do not show volume instability, the strength values are very close to the control mortar and they have a denser matrix. SiMn blended matrices fulfil standard specification requirements (chemical, physical and mechanical ones) and show that SiMn slag is suitable for blended cements manufacture.

Keywords: SiMn slag; Characterisation; Pozzolan; Setting times; Strength

1. Introduction

During the last decades, the use of granulated blastfurnace slag has been of interest because of its good behaviour in blended matrices, due to its hydraulic properties. This product has been recycled as an active compound in commercial blended Portland cements, in order to make use of its hydraulic and pozzolanic properties [1–3].

Nowadays, new slags are being produced by steel industries using electric arc furnace technology. These furnaces are more competitive than blast furnaces, but the industrial by-products (slag) produced show important problems for their recycling and reuse. One of the possible ways for recycling these slags is to use them as aggregates. Frías et al. [4,5] have shown results based on a Spanish electric arc furnace slag produced by an electric arc furnace, which present very high crystallinity, total absence of pozzolanic activity and a very low or nil concentration of typical expansive compounds (Cl^-, SO_3, free CaO and free MgO); suggesting that it is viable to use it as a recycled aggregate.

However, the ferroalloy industries produce another kind of slag. One of these by-products is the slag coming from the silico–manganese industry. In Spain, the amount of SiMn slag represents annually about 150,000 t.

SiMn slag is characterized by its high manganese content, compared with traditional (blastfurnace) slags. The first work done with SiMN slag showed two different results: some researchers considered that the presence of high amounts of manganese were responsible for the loss of slag hydraulic activity [6,7]; while others, for example Taneja et al. [8], did not find any relationship between strength loss and the MnO content.

Recently, Pera et al. [9,10] have studied five ground granulated blast-furnace slags possessing high Mn contents (between 5.4% and 21%). The results obtained, have shown that the use of this slag in concrete is possible.

These contradictory results motivated the current research into the basic and engineering aspects of the use of SiMn slag as pozzolanic material in blended cements. A detailed study of the SiMn slag as well as its behaviour in a cementitious matrix was carried out in order to identify its chemical and technical viability as an active addition to cements.

* Corresponding author. Fax: +34 91 3020700.
E-mail address: mfrias@ietcc.csic.es (M. Frias).

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2. Experimental

In order to study the basic and engineering properties of matrices containing SiMn slag, the following materials and mixtures were used:

* Materials
  - A Spanish SiMn slag as pozzolan with a Blaine fineness of 456.9 m^2/kg.
  - Commercial Portland cement designated as CEM I-42.5R, according to the European standard EN 197-1:2000 [11].
* Mixes
  - The blended cements were prepared in a high-speed powder mixer to guarantee their homogeneity. Mixtures were prepared by weight in the following proportions: cement/ SiMn slag: 100/0; 95/5 and 85/15. These slag additions are those permitted for minor components in cement (max. 5%), and the normal percentage used for type II/A cement (between 6–20%), according to European standards [11].
  - These blended cements were used for the manufacture of pastes for setting time and volume stability tests. The manufacture of pastes was carried out according to the existing European standard [12].
  - Blended cements with a standard [13] were used for the manufacture of mortars for strength test. Sand/binder ratio was 3/1 and water/binder ratio was 0.5. Manufacturing and curing of specimens (4 × 4 × 16 cm prisms) was carried out according to the existing European standard [13].
* Pozzolanic activity.

  The evaluation of the pozzolanic activity of slags was carried out by means of an accelerated method used by the research group. The test consisted in putting the material in contact with a saturated lime solution at 40 °C (analytical grade Ca(OH)2). The fixed lime (mM/L) was obtained as the difference between the concentration in the saturated lime solution and the CaO found in the solution in contact with the sample at the end of each fixed period. This method is based upon a pozzolanicity test for pozzolanic cement [14], but substituting saturated calcium hydroxide solution for the Portland cement. This method allows the pozzolanic activity of a cement with pozzolan (type CEM- II/ A–B) to be evaluated whereas the standard test is not applicable to this type of cement.

3. Results and discussion

3.1. SiMn slag chemical composition

Table 1 shows the chemical composition of SiMn slag. The main oxides are SiO_2 and CaO (the sum of these oxides exceeds 67%), followed by Al_2O_3 and MnO (12.2% and 9.9%, respectively). The remaining compounds amounts to less than 5%. It is important to also note the presence of sulphides (0.42%) and a L.O.I value of −0.91%.

Table 1
SiMn slag chemical composition

Oxides	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	MnO	TiO_2	SO_3
(%)	42.6	12.2	1.0	25.2	4.2	0.36	2.2	9.9	0.36	0.12

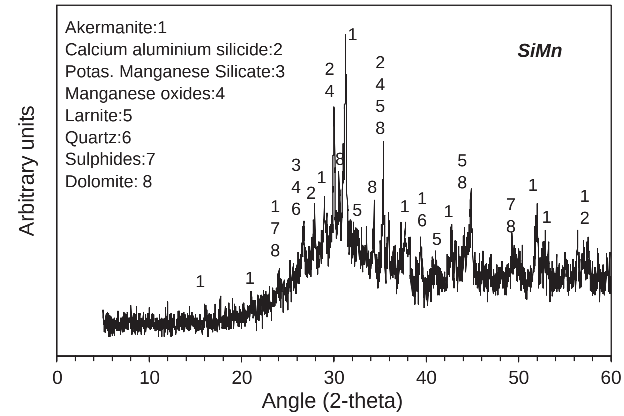

Fig. 1. SiMn slag mineralogical composition.

According to Pera et al. [9] slags with chemical modulus C/S < 1 are acid; while modulus C/S > 1 are basic. With a C/S value of 0.59, the SiMn slag used in this study would therefore be classified as acidic.

3.2. SiMn slag mineralogical composition

XRD analysis of SiMn slag identified the following crystalline components: akermanite (calcium magnesium silicate) as the main compound (1), calcium aluminum silicide (2), potassium magnesium silicate (3), manganese oxides (4), larnite (5), quartz (6) and sulphides (manganese sulphides mainly) (7) are identified in the slag (Fig. 1). Other compounds such as titanium and iron oxides can be present in this kind of slag but their identification by XRD is doubtful due to the overlapping of their characteristic peaks with the manganese oxides peaks. The slag sample XRD pattern showed a diffuse wide band from a glassy phase localising at approximately 30° (2-theta) that extended from about 20° to 40°.

3.3. SiMn slag pozzolanic activity

Fig. 2 shows the fixed lime content variation as a function of SiMn slag reaction time. The figure also shows results for fly

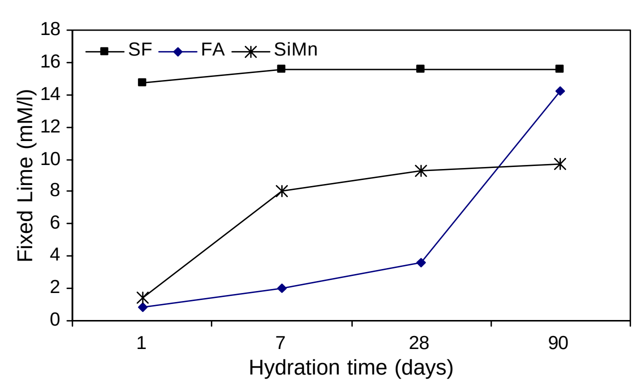

Fig. 2. SiMn slag pozzolanic activity.

ash (FA) and silica fume (SF); pozzolanic materials that are commonly used in commercial cements manufacture.

SiMn slag has a pozzolanic activity intermediate between FA and SF during the first 28 days of curing. After 28 days, the lime consumption for SiMn slag is practically insignificant and at the end of the test (90 days of curing) the lime consumption was only 55% of the total available lime. From these results, it is possible to say that SiMn slag shows pozzolanic activity, mainly at earlier age (<28 days).

3.4. Reaction kinetics in a slag-lime system at 40 °C

The residues obtained from pozzolanic tests, once filtered and dried were analysed by XRD in order to identify the crystalline compounds formed during the pozzolanic reaction. Fig. 3 shows the XRD patterns for the SiMn slag-lime system as a function of curing time at 40 °C. At 7 days, only a decrease of the main starting crystalline compounds peak intensities was detected. There is no evidence of crystalline phases pozzolanic reaction products. There is a weak band located at 11.6 (2 theta) which could correspond to calcium aluminium oxide hydrate (C_4AH_{13}) and/or calcium aluminium oxide carbonate hydroxide hydrate (C_4ACcH_{11}).

At 28 days of curing, peaks located at 7.1°, 14.2° and 21.4° (2-theta) indicate the presence of stratlingite (C_2ASH_8). Peaks at 10.7° and 11.4° (2 theta) could correspond to C_4AH_{13} (a compound with a low degree of crystallinity) but carbonated phases also show peaks at these angles: $Ca_4Al_2O_7CO2\ 11H_2O$ (11.68°, 2-theta) and /or $Ca_4Al_2O_6(CO_3)0.5\ (OH)\ 11.5\ H_2O$ (10.78°, 2-theta). There is also a low intensity peak at 12.5° (2-theta) which could correspond to different calcium manganese oxide hydrates: $(Mn,Ca)_3Mn_{12}O_{27}\ 15H_2O$, $Ca(MnO_4)_2\ 4H_2O$, etc.

At 90 days of curing time, the reaction kinetics have not change a lot but C_4AH_{13} and/or $Ca_4Al_2O_7CO_2\ 11H_2O$ are the predominant crystalline phases obtained from the pozzolanic reaction at 40 °C. Peaks at 21.4° (plus stratlingite) and 22.6° (2 theta) can be attributed to carbonated phases. Comparing these results with previous publications about fly ashes placed in the same curing conditions [15], it can be stated that pozzolanic reaction kinetics between SiMn slag and lime bears some similarity to the fly ash/lime system.

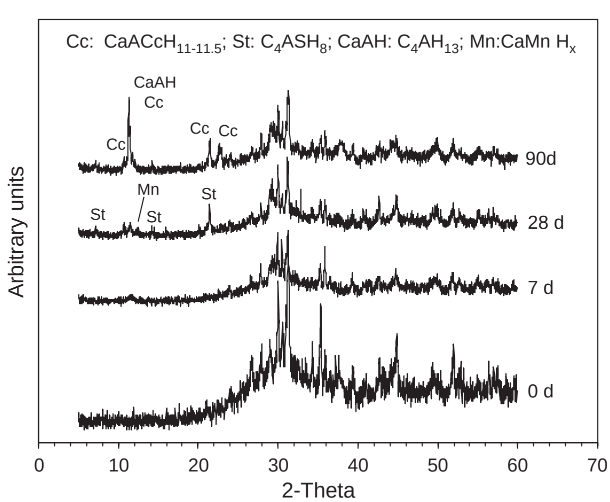

Fig. 3. Reaction kinetics from XRD patterns.

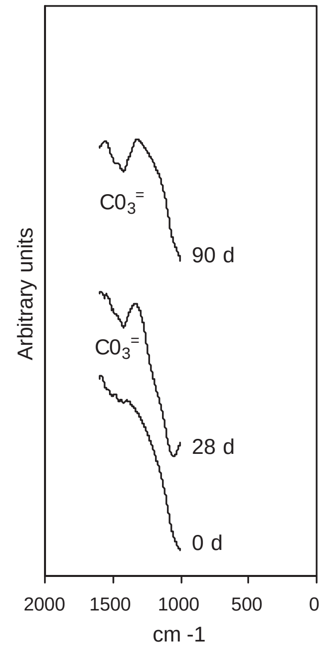

Fig. 4. IR spectrum for frequency interval in the range of 1.000 to 1.700 cm^{-1}.

In order to verify the possible presence of a carboaluminate phase, the samples were also studied by IR spectrometry. Fig. 4 shows the IR spectra of the samples at the frequency interval of 1.000–1.700 cm^{-1}. The double band situated at 1.423 and 1.479 cm^{-1} are attributed to carbonates. The total absence of this phase in the initial sample (0 d) confirms that the presence of carbonates during pozzolanic reaction is only caused by a saturated lime solution carbonation that occurs during the reaction time.

These findings are not totally in agreement with the results published by Pera et al. [9]. They also identified chloroaluminates as a reaction product, but this can be explained by halite in the slags which were cooled using sea-water. The chemical analysis carried out in the present paper shows no presence of chlorides in Spanish SiMn slag.

3.5. Setting times

Table 2 shows the results obtained for initial and final set for the blended cement pastes, according to the methodology described in the standard UNE-EN 196-3:1994 [12]. It is clearly detected that the incorporation of SiMn slag in cement pastes does not have any negative influence on setting. Both

Table 2
Setting times

Cement pastes	Initial set (min.)	Final set (min.)
Control	132	254
5% SiMn slag	133	263
10% SiMn slag	132	262

initial and final set values for SiMn cement pastes are very similar to the control cement paste.

3.6. Volume stability

The expansion tests were carried out according to the EN 196-3:1994 [12] (Le Chatelier expansion method). Table 3 shows the expansion results for the three cements. The values indicate that SiMn slag blended cements do not show volume instability.

3.7. Mechanical strengths

Fig. 5 (up) shows the evolution of flexural strength versus hydration time. During the first curing days, mortars with SiMn slag exhibit a lower flexural strength than the control mortar. The higher the SiMn content the lower strength. Above 7 days, the flexural strength values obtained for blended mortars increase substantially, and become similar to the control at 28 days of curing. At 90 days, there was no difference between the control mortar and the mortar with 5% SiMn slag, and the mortar with 15% slag was within 5% of the flexural strength of the control.

With respect to the compressive strength, Fig. 5 (down) shows the evolution of the compressive strength values versus curing time. The addition of the SiMn slag to the mixes leads to a slight decrease of the strength value when the SiMn content increases for the first 28 days of curing. At 90 days, the strength values were very similar to those of the control mortar.

At 7 days of curing, the strength loss, in both cases, corresponds approximately to the substitution grade of slag. For longer curing times (7–90 days), the reduction of the compressive strength loss falls from 7.8% and 13.4% to 0% and 3.2% for 5% and 15% mortars, respectively. At 90 days, the compressive strength values for the blended cement mortars are similar to the strength values obtained for the control mortar.

These results agree with those reported by Tenaje et al. [8] who reported that slag strengths at 3 and 7 days of curing are much lower than those of control Portland cement. Pera et al. [9,10] also reported that high levels of manganese seem to inhibit the early age activity of the slag. In both cases, no scientific explanation of this phenomenon is given.

With the available data in current paper, one possible explanation is based upon a number of different, but related, phenomena:

1) Up to 7 days of curing, the strength loss is proportional to level of SiMn slag in blended cements (7% and 14%, respectively). This fact means that the SiMn slag firstly acts as a filler. The calcium hydroxide liberated from cement is not enough to react with acid components of slag and to form hydrated phases from pozzolanic reaction (mainly CSH, C_2ASH_8, C_4AH_{13}, …). This fact could be caused by the reaction between some compounds of SiMn slag and lime, that involves hydrated calcium compounds formation, that do not have hydraulic properties. One of the possible compounds formed can be the calcium manganese hydrate, identified by XRD.
2) It well known that the solubility of calcium hydroxide decreases in presence of alkalis, which provokes an insufficient calcium ion amount to react with SiMn slag. This slag contains 2.8% of alkalis, a higher value than the Portland cement.
3) Also, it is important to note that the presence of some activators and /or ions in cement paste (i.e, sulphates) as well as SiMn slag (sulphates, sulphures and Mn ions) could alter the pozzolanic reaction kinetics, impeding or delaying the formation of hydrated phases in blended cement systems. Thus, in SiMn blended cements there are enough activators (from cement and slag) to influence reaction kinetics. The final balance is a decrease in pozzolanic reaction and therefore on earlier strength values in proportion to SiMn slag content. This fact would be in agreement with data from reaction kinetics from XRD patterns. The first hydrated crystalline compounds appear at 28 days of reaction in SiMn slag– calcium hydroxide system.

Table 3
Volume stability

Cements pastes	Expansion (mm)	Standard (mm)
Control	0	≤10
5% SiMn slag	1	
15% SiMn slag	0	

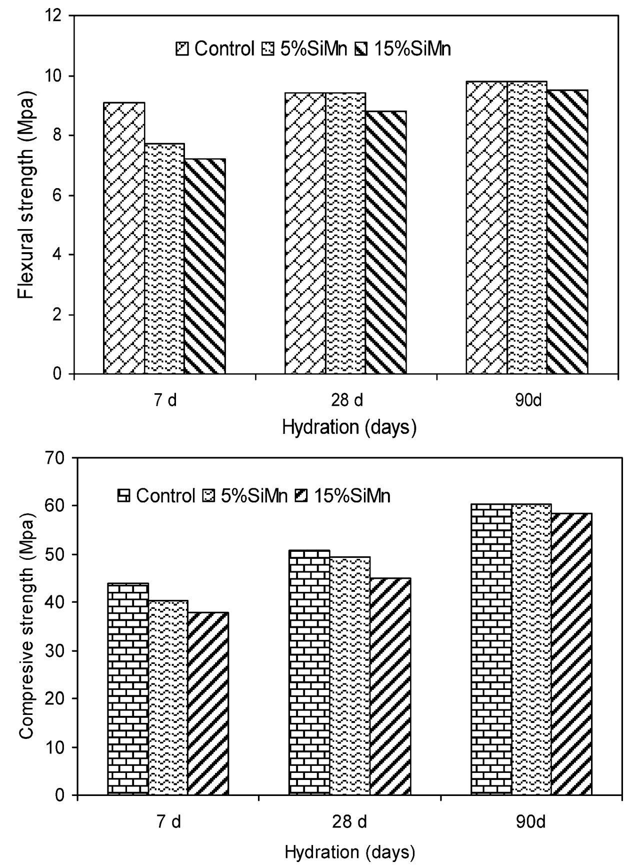

Fig. 5. Mechanical strength evolution.

As summary of all mentioned above, a possible process is proposed:

- 1st stage

$$\text{SiMn slag} + \text{lime (from cement hydration)}$$
$$-\text{Calcium manganese hydrate (CaMnHx)}$$

- 2nd stage

$$\text{SiMn slag} + \text{lime (from cement hydration)}$$
$$-\text{CSH}, C_2ASH_8, C_4AH_{13}, \text{CaACcH}_{11-11.5}.$$

4. Conclusions

From this research it can be concluded that:

1. SiMn slag used in this study shows that it has an acid composition. The main oxides present in it are SiO_2, CaO Al_2O_3 and MnO which sum to nearly 90%. The SiMn slag mineralogy is complex; the main crystalline compounds identified are: akermanite, potassium magnesium silicates, manganese oxides, larnite, quartz and sulphides.
2. SiMn slag shows a pozzolanic activity intermediate between silica fume and fly ash. According to the results obtained in the present work, the pozzolanic behaviour of SiMn slag is closer to fly ash than to silica fume.
3. The hydrated crystalline phases formed during the pozzolanic reaction are: stratlingite, carboaluminate hydrates and calcium aluminium hydrate. Calcium manganese oxide hydrates were identified in minor proportions, mainly at 28 days of curing.
4. The addition of an industrial by-product as SiMn slag (5% and 15%) in blended cements manufacture does not modify setting times cement. The Le Chatelier test shows that the blended pastes made with SiMn slag do not show volume instability.
5. Regarding mechanical strength, blended cements show two well defined behaviours: a) Up to 7 days of curing, the strength values are lower than those of control mortar, b) between 7 and 90 days, there is a clear gain of strength, reaching at the end of this period strength values equal to or very close to the control mortars.
6. According to the results obtained in the current research, it is possible to suggest the possible chemical and technical viability of using SiMn slag as pozzolanic material in blended cements.

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