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Effect of incorporating ferroalloy industry wastes as complementary cementing materials on the properties of blended cement matrices

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Abstract

The main purpose of this study is to evaluate the characteristics of two by-products obtained during ferroalloys production, SiMn slag and Mn oxide filter cakes, and their possible use as complementary cementing materials for commercial Portland cement manufacturing, considering 5% and 15% additions.

The results obtained have revealed that by-product characteristics make them suitable to be added to blended cement production processes since they fulfill the European regulations for the chemical, physical and mechanical requirements. Regarding the Mn oxide filter cakes use, a strength loss has been detected in blended cement mortars after a 90 days curing, although pore size distribution in this case is similar to that of a control mortar.

Keywords: Ferroalloys production wastes; Pozzolanic activity; New blended cements; Physicomechanical properties

1. Introduction

During the last several decades, pozzolanic additions have been used as complementary cementing materials in construction because of their positive influence on blended cement matrix properties, especially on their microstructure, durability and strength [1–5].

Ferroalloys production involves the generation of different industrial by-products that nowadays are often transported to landfills and for which recycling alternatives must therefore be found. Cement industry is a sector that may be one of such alternatives. In Spain, nearly 200.000 tons of these by-products are obtained every year, a quantity that is big enough to consider their recycling in construction.

This study has considered two different by-products obtained during ferroalloys production:

(a) SiMn slag, obtained during SiMn production, as an agglutination of the non-profitable part of the raw materials and additives that are added to ferroalloys production furnaces in order to make the casting achieve certain physical properties (fluxes as quartz or lime). During the casting, this slag is separated from the ferroalloy (SiMn) using differences in density, is then poured to a slag bed, and once a day is transported from its bed to be classified, if necessary, and stored. Granulated slag is quickly cooled with water in order to increase of glassy material content (a higher reactive silica) than slag when cooled slowly just for being outside and for this reason every time that samples for cement purposes are prepared, they are quickly cooled.

(b) Manganese oxides filter cakes, the final product from the ferromanganese and silicomanganese furnaces

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> fumes treatment. These fumes are cleaned with wet systems that collect all particles that they contain into water, obtaining dirty water that is conducted to a water treatment plant, where coagulation and flocculation are used in order to form bigger particles able to be separated in a circular thickener. Once separated, clean water is recycled into the cleaning water closed circuit (it is used to clean furnaces fumes again), and the mud obtained is filtered in a press filter, becoming filter cakes.

According to literature there is a lack of experimental results about both by-products recycling as complementary cementing materials in blended cements manufacturing, most of them only focused on SiMn slag. Pioneer works with these materials have shown contradictory results about the influence of high amounts of manganese on the materials mechanical properties [6,7]. This fact would be related to the presence the high MnO content in this kind of industrial wastes. It is well known than the incorporation of minor or traces elements in the different stages of the cement manufacture process (starting materials, combustibles, and mainly from active additions) can affect the hydration reaction of Portland cement [8–25].

Later, Pera et al. [26] studied five granulated blast-furnace slags containing high Mn contents (between 5.4% and 21%) characteristics, concluding that they could be used in concrete production. Recently, Frías et al. [27,28] have published the first research carried on in Spain about SiMn slag recycling as cement addition viability.

Due to the paucity of experimental studies completed to evaluate the use of both wastes in construction (not possible for Mn oxide filter cakes), the current paper investigates the characteristics of these wastes and its influence on new Portland cement matrixes characteristics using different additions of these two wastes that have been introduced.

2. Experimental

In order to study the characteristics and behaviour of Mn oxide filter cakes and SiMn slag, the following materials and mixtures were used:

2.1. Materials

The wastes tested have been obtained from the plant that Ferroatlantica owns at Bóo de Guarnizo, Cantabria, Spain, after its reduction to a particle size below 90 μm. The specific surface values obtained with the Blaine permeability method were of 4569 cm^2/g for the SiMn slag and 11,671 cm^2/g for the Mn oxides. Macroscopically, both wastes present different morphologies as can clearly be seen in Fig. 1. SiMn slag shows different morphologies, colours from light green to nearly black and different particle sizes. These differences are caused by the cooling process of the slag and its management and storage conditions. On the other hand, manganese oxides are filter cakes obtained from very small size particles agglomerated in a filter-press, have a much more homogeneous colour, being grey, and it is normally storage in very regular size pieces in which they are easily broken when they loss humidity and became dry.

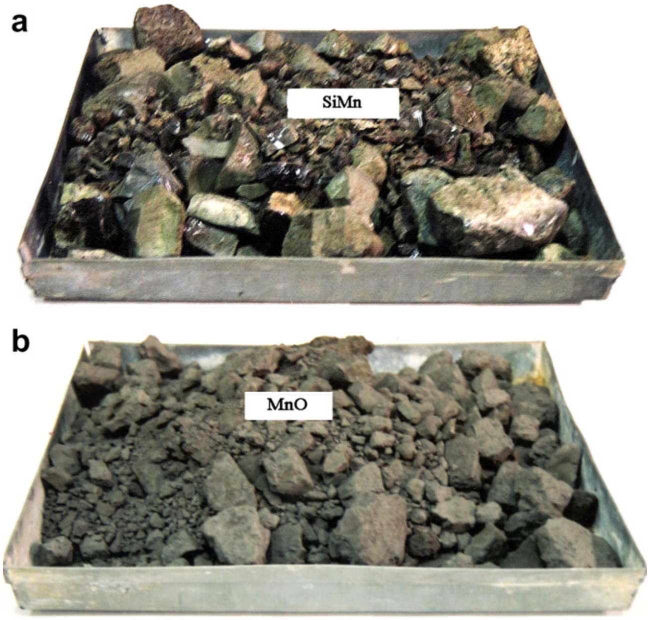

Fig. 1. Morphological aspect of the raw wastes.

Chemical and mineralogical compositions of these materials have been determined by inductively coupled plasma emission (ICP) and X-ray diffraction (XRD) techniques, respectively.

Analytical grade calcium hydroxide (min. 95%) was used for the pozzolanic activity test.

Commercial Portland cement designated as CEM I-42.5R, according to the European standard EN 197-1 [29] was used as control cement.

Blended cements were prepared in a high-speed powder mixer to guarantee their perfect homogeneity. Mixtures were calculated by weight, and different proportions were used: cement/SiMn slag: 100/0, 95/5 and 85/15. These additions have been chosen because they represent the quantities allowed for cement manufacturing (max. 5%), and for type II/A cement (between 6% and 20%) [29].

2.2. Analytical procedures

2.2.1. Pozzolanic activity

The pozzolanic activity of these by-products was evaluated by means of an accelerated method used by the "Recycled Materials" research group of Eduardo Torroja Institute. The test consisted on putting the pozzolanic material (1 g) in contact with a saturated lime solution (75 ml) in individual double cap polyethylene flasks with 100 ml capacity and maintaining them in an oven at 40 ± 1 °C for 1, 7, 28 and 90 days (two flasks per period). At the end of each period, the solution was filtered and CaO concentration in the remaining solution was quantified. The fixed lime (mM/l) was obtained by the difference between CaO concentration in the saturated lime solution and in the solution in contact with the sample, at the end of a fixed period. This method is a result of modifying a European standard pozzolanicity test for pozzolanic cement [30].

2.2.2. Setting test

The evaluation of the rehological behaviour of the new blended cement pastes, the methodology described in the standard EN 196-3 was used [31]. According to the standard procedure the Vicat apparatus is used for the determination of normal consistency and setting times in cements.

2.2.3. Expansion test

The soundness determination of the blended cement pastes was carried out with Le Chatelier apparatus, according the current European standard [31].

2.2.4. Compressive strengths

The influence of these additions on the mechanical behaviour of new cements was carried out according the current standard. The standard EN 196-1 [32] describes the methodology used for testing the mortar manufacture (components, preparation, cured and strength tests). Blended cement mortars of 4 × 4 × 16 cm were prepared with a sand/binder ratio was 3/1 and water/binder ratio was 0.5.

2.2.5. Microporosity

Total porosity and pore size distribution measurements were carried out using mercury intrusion porosimeter (MIP), with a Micromeritic Autopore Model 9200 instrument. The mercury porosimetry is able to measure pore size diameter up to 60 Å.

3. Results and discussion

3.1. Chemical and mineralogical composition of ferroalloys production wastes

3.1.1. Chemical composition of ferroalloys production wastes

Table 1 shows both by-products chemical composition. It can be seen that both materials contain the same oxides but in different proportions. Therefore, SiMn slag shows a silico-calcium nature mean while Mn oxide filter cakes present a silico-manganese one. The main oxides in these by-products are SiO_2, followed by CaO, MnO and Al_2O_3 (Al_2O_3 appears only in SiMn slag). Other oxides such as Fe_2O_3, MgO, TiO_2 and alkaline ones are present in smaller amounts. It is also important to note the presence of sulphates (expressed as SO_3) in Mn oxide filter cakes and a weight gain of the LOI. was recorded for SiMn slag (represented as negative value according the standard), as a result of the low percentages of oxidizable compounds (probably by the presence of magnesium and potassium sulphides, according to the XRD data). However, this negative effect was not detected for the case of Mn oxide. The difference between LOI in SiMn slag and Mn oxide is caused by the fact that Mn oxide has a C content that represents approximately 7% of this composition. This C comes from coke that is one of the raw materials used to produce SiMn: some coke particles go out of the furnace with the furnace fumes that are the origin of the Mn oxides. With a minor importance, there can be another aspect to consider, as is the fact that when the furnace fumes are depurated using a wet system, some water becomes part of the final product composition, then even if Mn oxides are dried, this water remains as composition water, and when testing LOI it is lost.

In general, the replacement of cement by these wastes (5% and 15%) does modify substantially the chemical composition of the control cement, only for the case of calcium and manganese oxides (Table 2). The Table also includes some minor elements (in ppm) by their possible influence on the blended cement properties. It is important to note that Zn content increases substantially with the addition of Mn oxides while the Ba content increases with the incorporation of SiMn slag to the cementing matrix.

3.1.2. Mineralogical composition of ferroalloys production by-products

From a mineralogical point of view, both by-products are qualitatively quite similar (Fig. 2), as the detection of

Table 2
Chemical composition for the blended cements

Blended cements	Ref. cement	5% Mn oxide	15% Mn oxide	5% SiMn	15 % SiMn
SiO_2 (%)	19.07	19.21	18.91	20.28	22.21
Al_2O_3 (%)	6.00	5.92	5.66	6.41	7.12
Fe_2O_3 (%)	2.28	2.27	2.20	2.23	2.12
CaO (%)	60.74	58.53	52.56	59.46	55.68
MgO (%)	1.51	1.65	1.86	1.71	2.00
SO_3 (%)	2.77	2.75	2.58	2.69	2.47
K_2O (%)	1.21	1.34	1.59	1.23	1.27
Na_2O (%)	0.17	0.23	0.36	0.18	0.19
TiO_2 (%)	0.31	0.30	0.27	0.32	0.32
P_2O_3 (%)	0.11	0.11	0.11	0.11	0.10
Mn_2O_3 (%)	0.07	2.10	5.70	0.70	1.92
LOI (%)	5.34	4.98	7.34	4.25	4.22
V (ppm)	169	165	146	161	147
Zn (ppm)	52	1740	4770	54	61
Sr (ppm)	718	738	742	750	764
Ba (ppm)	215	306	455	568	1250

Table 1
Chemical composition for the starting wastes

%	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	MnO	TiO_2	SO_3	LOI
SiMn	42.6	12.2	1.0	25.2	4.2	0.4	2.2	9.9	0.4	0.1	−0.9
MnO	33.8	3.1	1.7	7.4	3.5	1.1	4.0	23.0	0.1	2.2	18.7

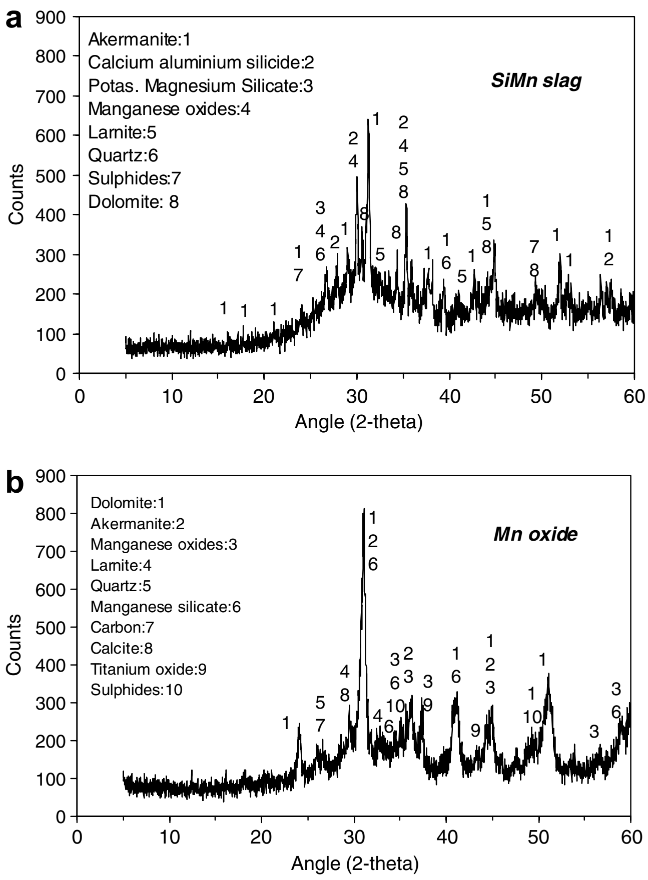

Fig. 2. Mineralogical composition of the wastes.

akermanite (main crystalline compound in SiMn slag), dolomite (main crystalline compound in Mn oxide filter cakes), manganese oxides, larnite, quartz and sulphides (manganese sulphides mainly) shows in both of them. Other crystalline compounds such as calcium aluminium silicide and potassium magnesium silicate in SiMn slag and others like manganese silicate, carbon and titanium oxides are identified in Mn oxide filter cakes could be present in wastes but their identification is doubtful by XRD due to the over lapping of their characteristic peaks by the main compounds peaks. In the case of SiMn slag, the XRD pattern showed a diffuse wide band from a glassy phase located at approximately 30° (2-θ) and extended approximately from 20° to 40°.

3.2. Pozzolanic behaviour of ferroalloys production by-products

Fig. 3 shows fixed lime content fluctuations for both wastes versus the reaction time. The figure also presents the same data for silica fume (SF) and fly ash (FA), pozzolanic materials that are commonly used in commercial cement manufacturing.

Ferroalloys production by-products (SiMn slag and Mn oxide filter cakes) have pozzolanic activities intermediate between FA and SF ones during the first 28 days of curing; however, Mn oxide filter cakes are closer to SF than to FA.

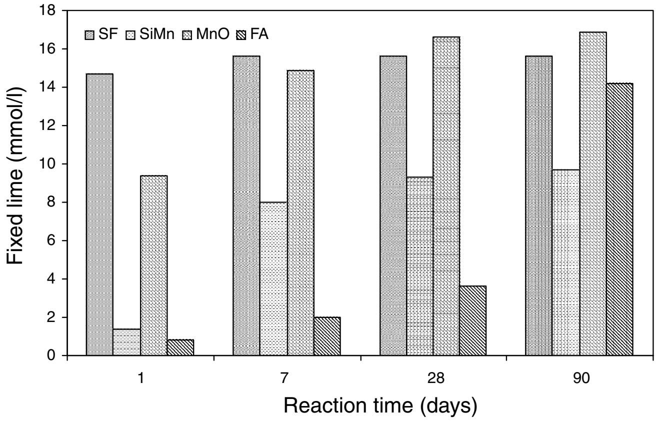

Fig. 3. Pozzolanic activity evolution.

Pozzolanic activity evolution relationship with reaction time is quite different for these two by-products. In 1 day, Mn oxide filter cakes fix 54% of total available lime and in the same time SiMn slag fixes only 8%. In 28 days, lime consumption increased up to 96% and 53%, respectively. After 28 days of curing, lime consumption for both by-products becomes practically insignificant. These results conclude that industrial by-products show pozzolanic activity but it varies substantially. The Mn oxide filter cakes lime consumption is higher than SiMn slag one.

However, this better pozzolanic behaviour of the Mn oxides is not totally true if two fundamental aspects are considered: (1) its high fineness (11,671 cm^2/g versus 4569 cm^2/g for the SiMn slag) and; (2) a higher manganese oxide content (23.0% versus 9.0% for SiMn slag), which caused an increase in lime consumption during pozzolanic reaction to form calcium manganese oxide hydrates, according the findings carried out by Frías et al. [28] in a previous paper about reaction kinetics in SiMn slag-calcium hydroxide system. These aspects mask the real pozzolanic reaction between the acid components (SiO_2, Al_2O_3 and CaO) present in Mn oxide waste and calcium hydroxide and therefore its total lime consumption cannot be comparable with that shown by SiMn slag. This additional consumption of lime plus its high fineness of Mn oxides could also explain the similar reactivity even more than silica fume. However, this pozzolanic behaviour for the Mn oxides has not a chemical and mineralogical explanation since the acid component amounts present in SiMn slag are higher than those ones in Mn oxides (Table 1), which indicates a higher potential for pozzolanic reactions. Furthermore, the difractograms show a more pronounced amorphous halo in SiMn slag between 20° and 40° (2-θ) than that Mn oxides (Fig. 2).

3.3. Blended mortar behaviour

3.3.1. Chemical requirements

Table 3 shows for each of the studied wastes their loss of ignition (LOI), insoluble residue (IR), soluble sulphates (expressed as SO_3) and chloride (Cl^-) contents in percentage

Table 3
Chemical requirements for the blended cement analyzed

Cements	LOI (%)	SO_3 (%)	IR (%)	Cl^- (%)
Standardised requirements	*⩽5.0*	*⩽4.0*	*⩽5.0*	*⩽0.10*
5% SiMn slag	3.4	2.5	1.9	0.01
15% SiMn slag	2.9	2.3	2.6	0.01
5% Mn oxide	4.2	2.6	1.5	0.01
15% Mn oxide	5.0	2.7	1.6	0.03

of cement mass (or binder), according to European standards [29]. All the results obtained for the different blended cements are under the standardised requirements.

3.3.2. Setting times

Table 4 shows the results obtained for initial and final setting time for the blended cement pastes prepared, determined using the methodology described in the standard UNE-EN 196-3 [31]. It is clearly detected that the incorporation of these wastes in cement pastes does not modify setting times substantially. Compared to the control paste, a slight delay of initial and final setting time values was detected when by-products were incorporated into the cementing matrixes, although this requirement is not specified in standard. The same tendency was only observed in initial setting when Mn oxides incorporated to the cement matrix. In this case, the delay would be related to the Zn content in Mn oxide blended cements, according a previous work [33]. No variation of the initial setting was observed with the incorporation of 5% and 15% SiMn slag.

3.3.3. Volume stability

Expansion tests were carried out according to EN 196-3 [31]. Table 5 shows the results obtained for each of the three different cements prepared, that indicate that SiMn slag blended cements do not show volume instability.

3.3.4. Compressive strength evolution

Fig. 4 (up) shows compressive strength evolution versus hydration time. During the first days (up to 28 days), mortars prepared with wastes additions (SiMn slag and Mn oxide filter cakes) show lower compressive strengths if compared with the reference mortar ones. After longer reaction times (90 days), compressive strength evolution varies depending on the waste used: SiMn slag addition to blended mortars make them obtain similar compressive strengths than the reference mortar ones; however Mn oxide filter cakes incorporation cause an important strength decrease. This compressive strength loss for blended cement mortars can be calculated taking as a reference the control mortar values at different curing periods. As can be clearly seen on Fig. 4 (down), the strength loss increased from 5.2% to 13.8% for the blended mortars with additions of 5% and 15% of Mn oxide filter cakes; in case of using SiMn slag, strength losses decreased with increasing curing time of blended mortars with 5% and 15% waste additions.

Table 4
Setting time evolution

Blended cement pastes	Initial set (min.)	Final set (min.)
Reference	132	254
5% Mn oxide	144	264
15% Mn oxide	142	262
5% SiMn slag	133	263
15% SiMn slag	132	262

Table 5
Volume stability

Blended cement pastes	Expansion (mm)	Standard (mm)
Reference	0	
5% Mn oxide	0	
15% Mn oxide	0	⩽10
5% SiMn slag	1	
15% SiMn slag	0	

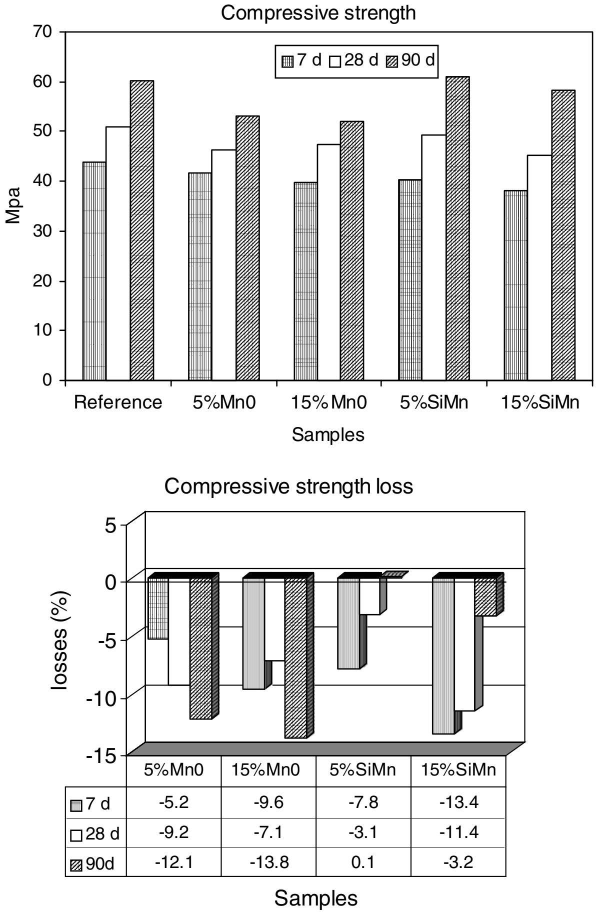

Fig. 4. Compressive strength evolution.

These results agree with those reported by Tenaje et al. [34] who reinforced that SiMn slag cement strengths at short term of curing are much lower than those of control Portland cement. Pera et al. [26] also reported that high levels of manganese seem to inhibit the early age activity of the slag.

In a later paper Frías et al. [28] reported the existance of different phenomena related to the decrease and delay of strengths at short terms when using SiMn slag: this ferroalloy waste acts as a filler during the first days of reaction, decreasing calcium hydroxide solubility in presence of alkalis, some activators presence and/or ions presence in either cement paste (i.e., sulphates) or in SiMn slag (sulphates, sulphures, Mn ions). These different phenomena in conjunction with the chemical analysis of the two wastes studied, could explain the difference between SiMn slag and Mn oxide filter cakes influence on strength evolution during the curing time. Apart from that, the Mn oxides need a special attention because they present two fundamental aspects with respect to SiMn how are the presence of a higher manganese content in Mn oxide filter cakes (23% MnO) than in SiMn slag waste (9.9% MnO) and a 7% C content which can have an additional negative influence on the resistances.

From data and observations presented here, these wastes have a different behaviour since they are coming from the same industrial process but from totally different stages, giving to them special characteristics and properties. If, furthermore, there is an important absence of scientific and technical works on SiMn slag and there are no references for Mn oxides, it is logical to think that there is not still a scientific explanation about their influence on resistances and further investigation has to be carried out.

To sum up, the bad resistance of the Mn oxide blended mortars in comparison with SiMn slag blended ones is not as good as expected. This fact could be due to different factors: (1) The presence of a higher manganese content in Mn oxide filter cakes (23% MnO) than in SiMn slag (9.9% MnO) could affect and delay the strength development beyond 28–90 days of curing in Mn oxide blended mortars; (2) this strength loss and its relation with reaction time for this kind of blended mortar could also be related to the formation of an important amount of calcium manganese hydrate (CaMnHx), identified by XRD technique [28] that has not hydraulic properties.

3.4. *Waste-blended mortars microporosity*

Total porosity versus hydration time for all mortars prepared is shown in Fig. 5. After 7 days, the incorporation of Mn oxide filter cakes and SiMn slag produces a total porosity slight increase (16–16.2%) if compared to the reference mortar (14.8%). The nature and the addition of the waste does not seem to have an important influence on the total porosity.

Beyond 7 days, differences in the total porosity between control mortar and blended mortars can be observed. For Mn oxide filter cakes mortars, the porosities are always higher than the control mortar one: being the value porosity 12.5% for the control mortar, for these blended mortars at 90 days of curing achieves 15.4%. SiMn slag addition to cement mortars does not vary or varies slightly total porosities in reference to control mortar at 28 and 90 days of hydration.

From the results obtained, it can be concluded that total porosity evolution depends mainly on the waste nature and is not affected by the quantity of waste added. This porosity data are absolutely in agreement with the results obtained for the compressive strengths.

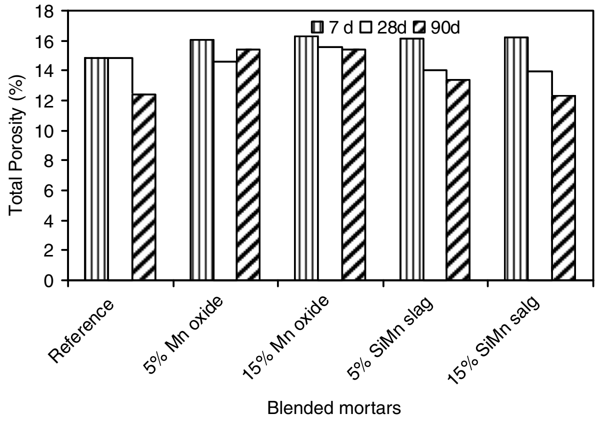

Fig. 5. Total porosity evolution.

A detailed study of pore size distribution frequency for all mortars does not show important differences between mortars with and without wastes. Fig. 6 shows the

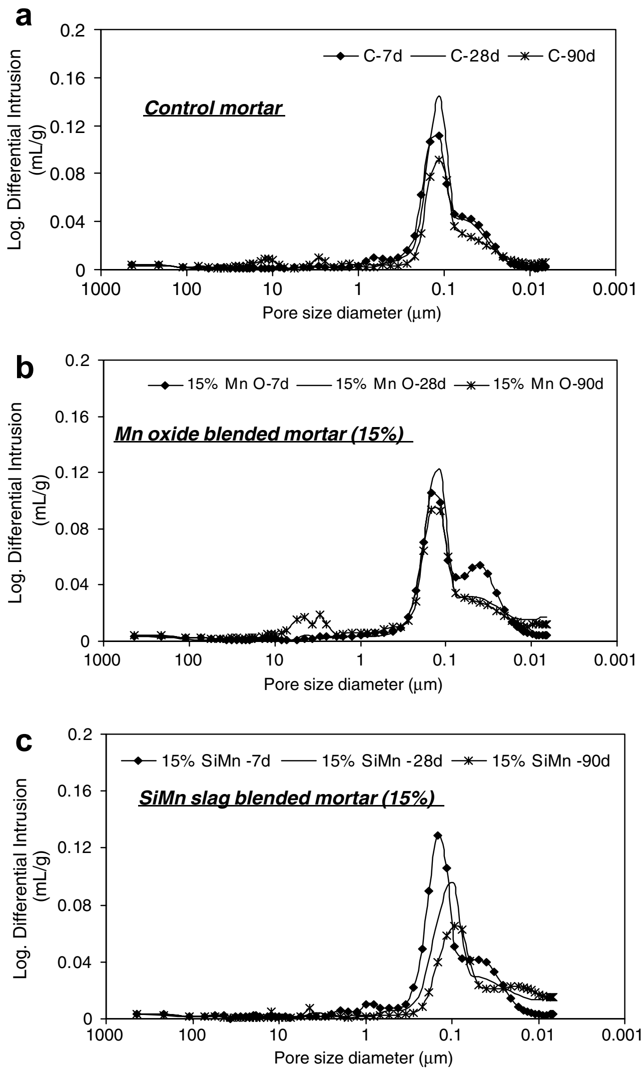

Fig. 6. Pore size distribution evolution.

frequency of pore sizes versus the hydration time for control and blended mortars, prepared with 15% additions of Mn oxide filter cakes and SiMn slag that are the quantities for which higher compressive strengths differences were detected.

Two modal distributions are showed for each of the mortars tested (prepared with 0%, 5% and 15% addition of waste). The main pore size distribution appears to be between 0.5 and 0.09 μm and the maximum is located at 0.1 μm, mean while a second distribution appears at lower pore size values.

Modal distributions for control and Mn oxide filter cakes blended mortars are quite similar with the exception of a little pore size distribution at 3–8 μm for the latest case. However, the incorporation of SiMn slag produces a pore size refinement that increase its importance with the curing time and the waste content. These tendencies can be seen clearly in Fig. 6 (down).

From the results obtained here, it can be concluded that Mn oxide filter cakes have a confused behaviour when are added to blended mortar matrixes since, on one hand, these mortars show a lower compressive strength than the control mortar one and, on the other hand, their pore size distribution is similar to the control cements ones, not justifying the strength loss. A possible explanation of this behaviour would be, as it was mentioned before, the formation of non-hydraulic compounds (calcium manganese hydrates mainly) during the pozzolanic reaction when Mn oxide filter cakes are incorporated to cementing matrixes, that would produce a strength decrease without varying the pore size distribution.

4. Conclusions

From this research it can be concluded that:

1. Wastes produced during manganese ferroalloys production have different chemical compositions. SiMn slag has a silico-calcium composition ($SiO_2 + CaO > 67\%$) and Mn oxide filter cakes have a silico–manganese composition ($SiO_2 + MnO \geqslant 56\%$ in weight).
2. Both wastes show similar mineralogical compositions but with quantitative differences, including different crystalline compounds. SiMn slag is mainly formed by akermanite ($Ca_2\ MgSi_2O_7$) mean while Mn oxide filter cakes is mainly formed by calcite. The wastes studied in the present work showed differences on their lime consumption rate during the reaction time due to its different nature.
3. Portland cements elaborated with these wastes (5% and 15%) comply with the chemical, physical and mechanical requirements, according to actual standards.
4. Regarding compressive strengths, blended cement mortars show two well defined behaviours:
   (a) When using Mn oxide filter cakes, the strength values are always lower than that of the control mortar during the first 90 days of curing.
   (b) Strength evolution for mortars with SiMn slag show two tendencies: up to 7 days of curing, strength values are below the control one and between 7 and 90 days, there is a clear gain of strength, reaching at 90 days of curing very similar values to the reference mortar.
5. The results obtained in the present work highlight that the use of SiMn slag and Mn oxide filter cakes as pozzolanic materials in blended cements is chemically and technically viable. For Mn oxide filter cakes use as secondary material even if the cements comply with current standards, further researches would be necessary in order to improve mortars compressive strengths.

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