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Chemical assessment of the electric arc furnace slag as construction material: Expansive compounds

Moisés Frías Rojas*, M.I. Sánchez de Rojas

Eduardo Torroja Institute (CSIC), c/ Serrano Galvache n.4, 28033 Madrid, Spain

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Abstract

To carry out a correct management of electric arc furnace slags (EAS) requires a detailed knowledge of their properties. From a chemical point of view, the EAS are surrounded by some chemical problems related to its volume instability when they are used as construction materials, due to the presence of potentially expansive compounds such as free lime and mainly free MgO. The current work focuses on the chemical assessment of the black slags coming from an electric arc furnace in order to know the possible chemical disadvantages as construction materials. A complete study of chemical and mineralogical compositions, pozzolanic activity and the quantification of main expansive compounds in EAS were realised. The results show that the nature of these slags has a very high crystallinity; total absence of pozzolanic activity and the presence of expansive compounds in slags (Cl^-, SO_3, free CaO and free MgO) were very low, if not null concentrations.

Keywords: Electric arc furnace slag; Characterisation; Pozzolanic activity; Expansive compounds

1. Introduction

In 2000, the Spanish steel industries manufactured below 16 mT of steel in their different varieties. This process have associated the generation of large amounts of slag by-products whose management is not resolved yet from technical and environmental points of view. Thus, in Europe, nearly 12 mT of steel slags, mainly black ones, are produced every year. A high percentage of which is used in different applications but the 35% remaining slags are still dumped [1].

In industrialised countries, the slags from blast furnace have been recycled as active additions in the manufacture of commercial blended Portland cements either by their hydraulic or pozzolanic properties [2,3].

However, the electric arc furnace technology is widely used at present, permitting the manufacture of steel from scrap. These furnaces are more competitive in the present society than blast furnaces, but the industrial by-products, like black slags (EAF) and dusts, have a major problem for its recycling and reuse. According to data published by Malcolm et al. [4], 72% of EAF dusts have been disposed of in the past in landfills, and to a lesser degree, used for zinc recovery (14.5%) and for fertiliser manufacture (8.9%).

The estimable annual production of EAF is below 2 mT in Spain, which are dumped in landfills belonging to the own steel industries as well as public administrations. However, the landfills are not the sole solution in the medium and long term due to different technical, social and environmental aspects [5]. For this reason, one of the greatest preoccupations of the researchers of the present time is to establish a correct management of this kind of slags.

In order to reduce or minimise the great volume of slags produced, different alternatives are studied, the main alternative being recycled aggregate in road constructions [1,6–9]. Sakata and Ayano [10] reported that this alternative can be an effective idea to solve serious problems because of the requirement to protect the natural environmental is increasing and the supply capacity of good quality sand or gravel is decreasing.

In Spain, there is an important experience, either in laboratory tests or experimental sections, regarding the

* Corresponding author. Tel.: +34-91-30-20-440x220; fax: +34-91-30-20-700.

E-mail address: mfrias@ietcc.csic.es (M. Frías Rojas).

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usage of EAF slags in roads. In a previous paper, San José and Uría [11] reported the good qualities of these by-products as recycled aggregates in bituminous mixes used for asphaltic layers. Following this working line, studies carried out by Bollati and Solis [12] also manifested the possibility of using the EAF in porous pavements and high-performance concretes in the very near future.

According to the existing bibliography about the recycling of EAF slags in the construction sector, most of which are focused on physical and mechanical properties, behaviour in blended mixes, etc., values are obtained through its technical contribution. Depending on its application, the technical properties have a prioritizing role in the recycling process, but in other cases (bituminous layers, concretes, etc.), the volume stability is predominant. For this reason, there is a lack of basic investigation from a chemical point of view, which is necessary for users to have a better understanding about the advantages and disadvantages of EAF slags as recycled aggregates.

In a previous paper, Frías et al. [13] reported that despite good qualities of EAF slags as recycled aggregates, they are involved in some problematic aspects about their possible volume instability, due to the presence of some expansive compounds like free lime, free MgO, sulphurs, sulphates, high iron oxide contents, chlorides, etc. Depending on their concentration, they can cause a disintegration process and therefore loss of performance and durability of the slag blended mix. Moreover, Mozt and Geiseler [1] reported that the content of free lime, and mainly, free MgO, is the most important component for the utilisation of steel slags for civil engineering purposes with respect to their volume stability.

In this light, it is important to take into account the words stated by Galván [14] in a previous paper. He reported that the correct management of industrial by-products requires an in-depth knowledge of its composition and physicochemical properties. Therefore, with the characterisation of the by-product, one can get a double objective: to supply the necessary information for its cataloguing and codification according to the current standards and to provide data which determine the most suitable processing system.

Taking account all things mentioned above, the current work presents the results of an experimental study about two black slags of different steel industries, paying special attention to the chemical viability of these slags as recycled aggregates. A detailed study of chemical and mineralogical compositions, pozzolanic activity and the quantification of main expansive compounds were realised.

2. Experimental

Two electric arc furnace black slags (EAS 1 and EAS 2) from different Spanish steel industries were sifted in order to obtain four granulometric intervals related to granulometric fractions used normally in the elaboration of concretes. Then, they were ground in order to get particle sizes below 100 μm. Chemical and mineralogical compositions of granulometric intervals were carried out by inductive couple plasma (ICP) and XRD, respectively.

The evaluation of the pozzolanic activity of slags was determined by means of an accelerated method. The test consisted of putting the material in contact with a saturated lime solution at 40 °C. The fixed lime (mM/l) was obtained by 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 a given period.

The methodology used for the chemical quantification of expansive compounds (free CaO, sulphates and chlorides) is described in the corresponding Spanish standard [15]. This fact is not true for the case of free MgO. Up to now, there is no specific standard for its quantification; there is a total absence of research in this line. The existing standards only limit the total magnesium oxide content with the aim of avoiding important amounts of free MgO as periclase, making an alternative but not a solution.

As a first approach to getting the first data of free MgO content present in slags and due to the importance this expansive compound has on the correct management of EAF slags, the authors of the present work took as starting point for its determination the methodology suggested by Taylor and Bogue [16], which is based on the leaching of MgO out of the clinker in a nonaqueous solution.

3. Results and discussion

3.1. Chemical composition of EAS

Fig. 1 shows the chemical compositions of EAS for the different granulometric intervals. The chemical results reported that the most abundant oxides corresponded to SiO_2, Fe_2O_3 and CaO (the sum of these oxides exceeds 73%), followed by MgO, Al_2O_3 and MnO.

The oxide percentages varied from slag to slag depending on its origin. Thus, EAS 1 showed a more basic composition than that obtained for EAS 2. The indices $[(CaO + MgO)/(SiO_2 + Al_2O_3)]$ for EAS 1 and EAS 2 were 2.06 and 1.2, respectively. The chemical composition of these EAS was very different to that found for blastfurnace slags [13], which are used normally in the manufacture of commercial cements.

The chemical composition was not affected by aggregate size. In all cases, the granulometric intervals showed very similar chemical compositions.

3.2. Mineralogical composition of EAS

The mineralogical composition for these EAS is illustrated in Fig. 2. Slags showed a very high crystalline nature, detecting the presence of the following: iron oxides, such as w/plustite (W), magnesioferrite/magnetite (M) and hematite

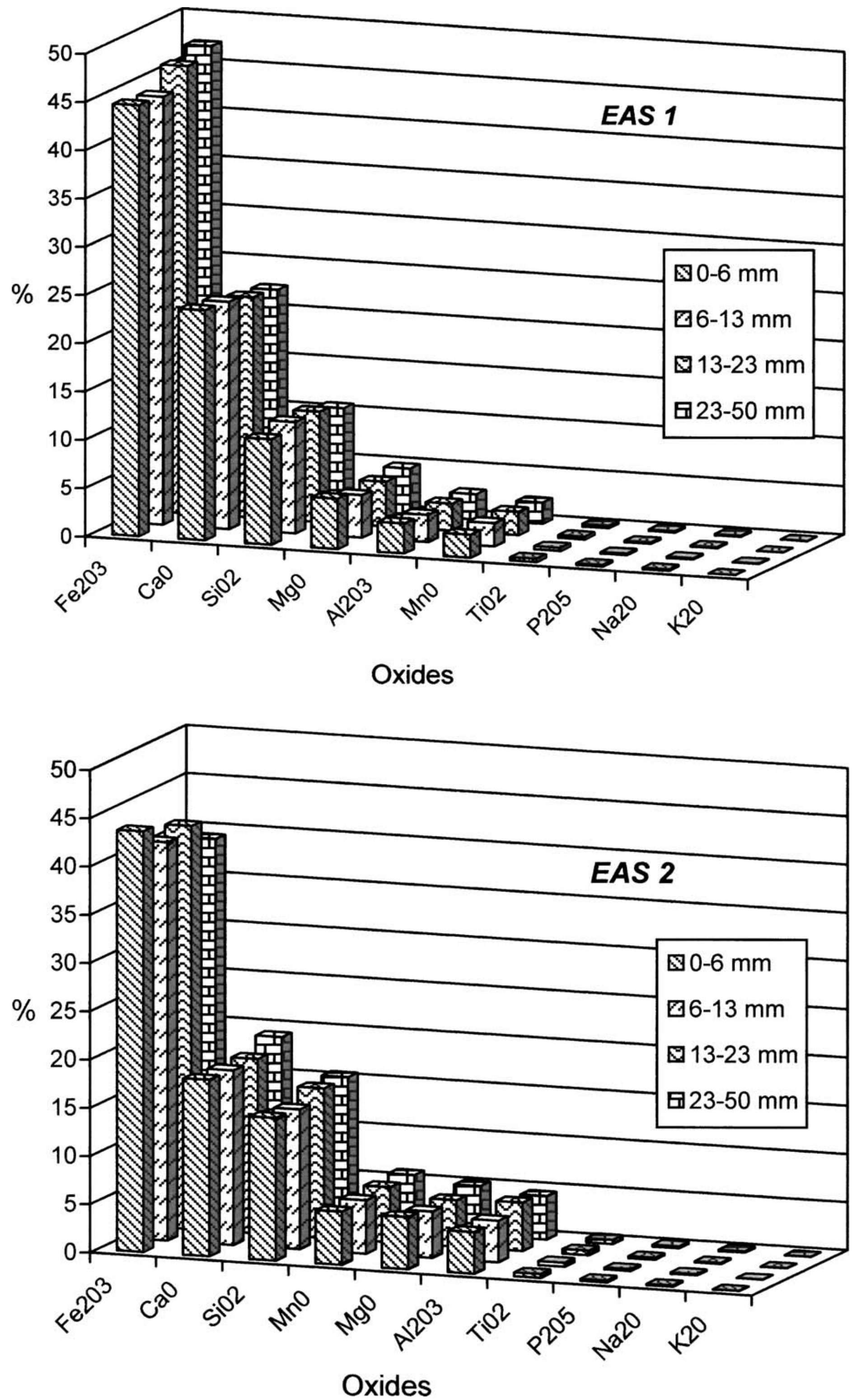

Fig.1. Chemical composition for EAS 1 and EAS 2.

(H); silicates, such as larnite (L), bredigite/merwinite (B) and gehlenite (G); and finally, oxides, such as birnessite/groutellite (manganese oxides, Mn).

With respect to peak intensity of some crystalline compounds, it is possible to observe important differences between EAS 1 and EAS 2. EAS 1 showed the presence of a higher amount of L and M while EAS 2 showed the presence of a higher amount of W and G.

Moreover, it was also detected that some of these peak intensities varied with the granulometric interval, for exam-

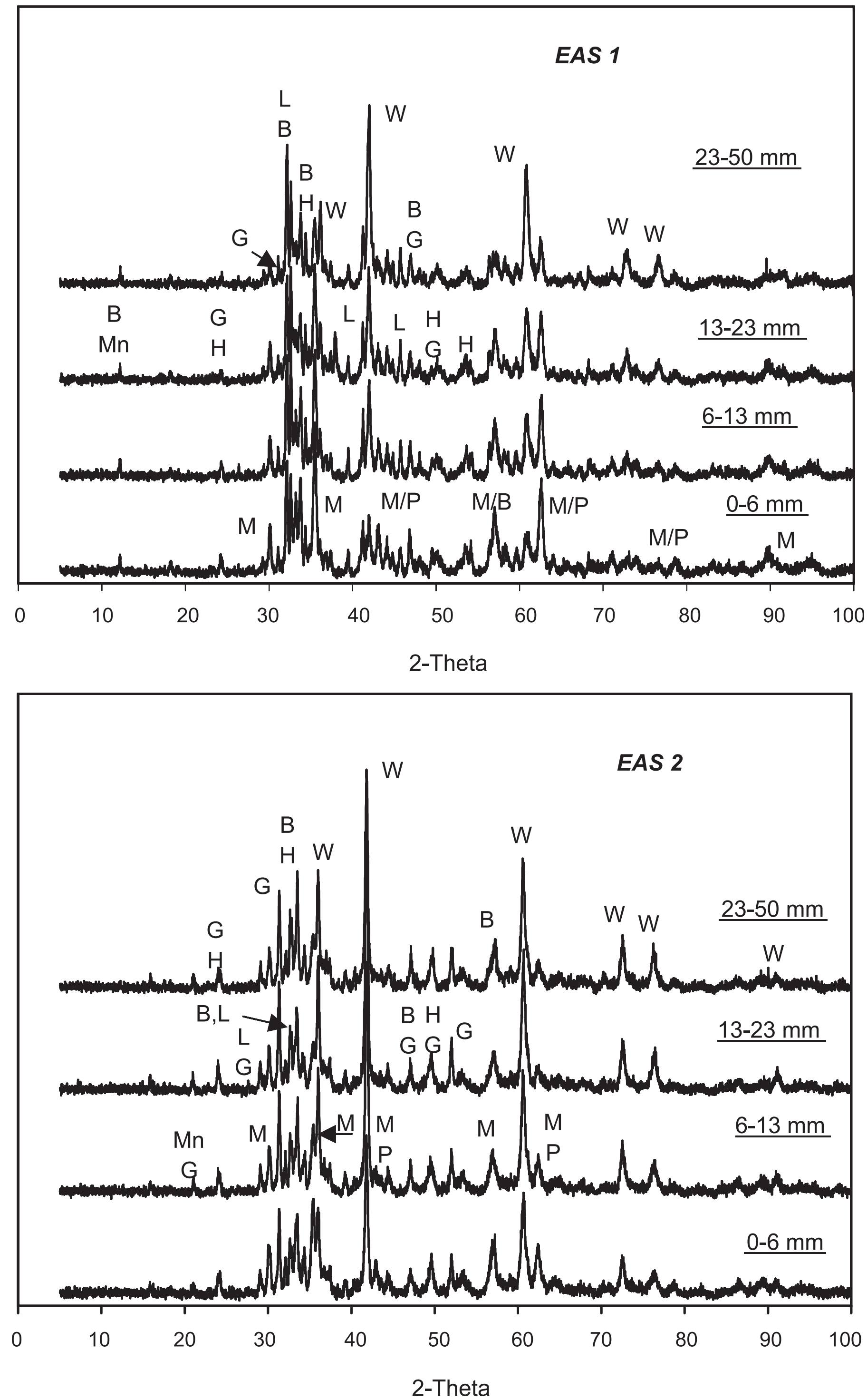

Fig. 2. XRD patterns for EAS 1 and EAS 2.

ple, W and M. Thus, the intensity of compound W increased with the increasing particle size while the intensity of M varied in the other direction. Taking into account the peak intensities localised at 60.77 and 62.5 (2θ) for this compound, this evolution was clearly observed for the case of EAS 1. However, this tendency was not so remarkable for EAS 2 wherein their intensities were similar in all intervals, a fact that might be related to a higher content of FeO in this slag.

In the study of the EAS as a possible component of cement and concrete, an important aspect to highlight is the presence of magnesium oxide (MgO) as periclase, crystalline and as a very insoluble compound related to expansive phenomena in the long term.

When this kind of slag is studied by XRD, an overlapping of periclase peaks [42.91, 62.31 and 78.6 (2θ)] was detected with the predominant crystalline compounds present in slag, mainly with the reflection peaks of M [43.06, 62.49 and 78.9 (2θ)]. Moreover, the peak of MgO situated at 36.95 (2θ) is hidden with the L peak. Therefore, it is not possible to get suitable information regarding the presence of periclase from XRD data.

Despite this overlapping, a much more detailed observation of XRD pattern at 42.91 (2θ), the main reflection peak for this crystalline phase, observed indistinct traces of periclase for EAS 1 and no traces for EAS 2 (Fig. 3). This fact means the absence of or very low crystallinity of MgO compound in EAS.

As what happened with the MgO phase, the XRD technique was not appropriate for the identification of crystalline CaO phase because of the overlapping of its main reflection peaks with L peaks.

3.3. Pozzolanic activity of EAS

The results obtained from the pozzolanic activity test are shown in Fig. 4. The CaO content was kept practically constant during the test and its value was close to starting concentration. These by-products (EAS) did not show any reaction with the lime before 90 days; therefore, the results showed no presence of pozzolanic activity in EAS. For this reason, EAS 1 is only included in Fig. 4.

The figure also includes the pozzolanic behaviour of fly ash (FA), metakaolin (MK) and silica fume (SF). It is well known that these by-products show an important reaction with lime despite the fact that the pozzolanic reaction rates are different. Further information regarding this is found in Ref. [17].

The viability of using by-products in the manufacture of commercial blended cements and/or concretes depends on its pozzolanic behaviour. The absence of this activity

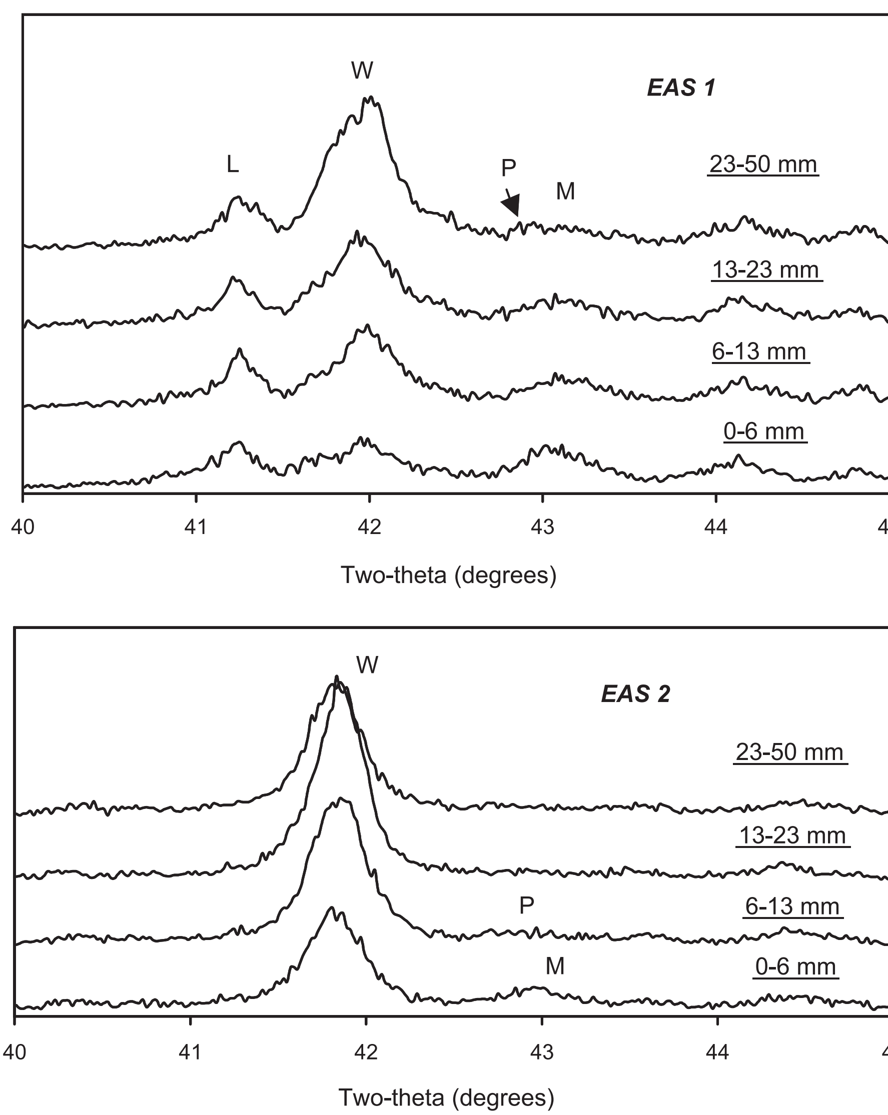

Fig. 3. XRD patterns for EAS 1 and EAS 2 in interval 40–45 (2θ).

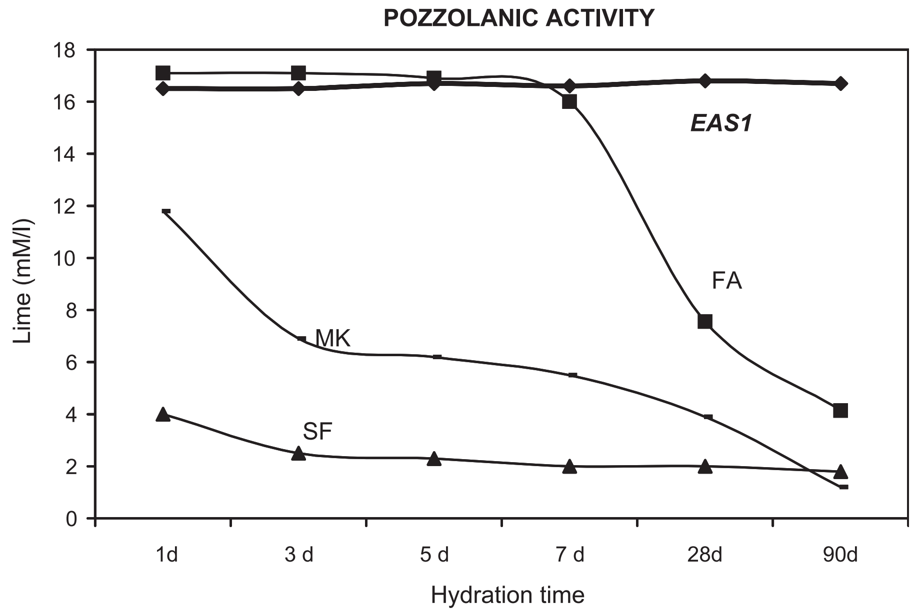

Fig. 4. Pozzolanic activity for EAS 1, SF, FA and MK.

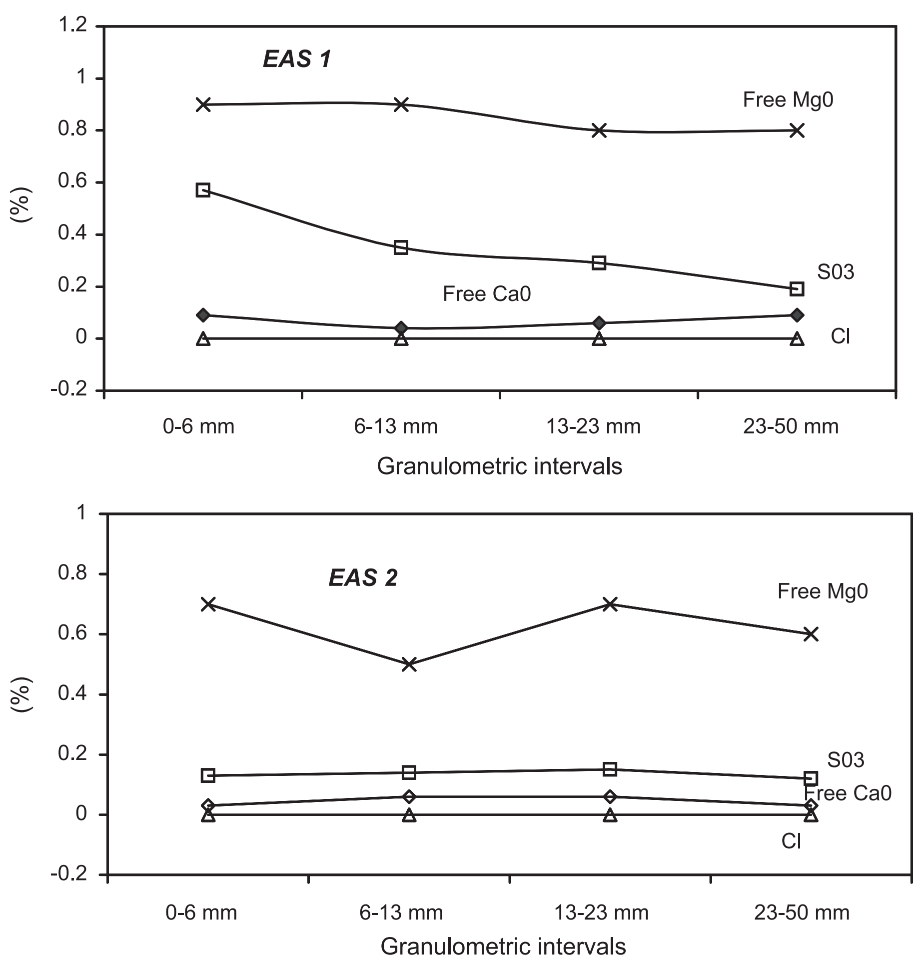

Fig. 5. Expansive compound contents versus granulometric intervals.

excludes its use as an active addition. The EAS is not a suitable material as pozzolan, and for this reason, the new alternatives of recycling are being guided to recycled aggregates.

3.4. Chemical quantification of expansive compounds

The aggregates (natural or recycled ones) used for the manufacture of concrete have to comply with specifications and limitations picked up in the International Standards [15].

The current research focuses on some problematic compounds that can be present in EAS, paying special attention to calcium oxide (free CaO), sulphates (SO_3), chlorides (Cl^-) and magnesium oxide (free MgO) as the main compounds responsible to the expansion phenomena.

Fig. 5 shows the expansive compound concentrations detected in two slags and its evolution versus granulometric intervals. The free lime concentrations present in all cases were very low (values below 0.1% were detected). The total sulphate content (expressed as SO_3) did not reach 0.6%; these are values below the limitations specified in EHE (maximum 1%). Moreover, these values were also lower than 0.8% specified in the instruction for soluble sulphates (maximum content of 0.8%). For this reason, it was not necessary to quantify the soluble sulphate content. EAS did not detect the presence of chlorides.

Free MgO contents in EAS were very low for the different granulometric intervals, values below 1% were detected in all cases. These concentrations of free MgO obtained from the chemical method fitted well with data obtained from XRD. As mentioned before, the periclase was not identified as a crystalline compound in slags. Therefore, it is possible to say that the noncombined magnesium oxide present in slag is of a vitreous or amorphous phase and not of a crystalline phase (periclase), which is responsible for the long-term expansion reaction.

These findings are totally in agreement with the investigations carried out by Taylor [18] in cements. He reported that quantities of this component in excess of about 2% could occur as periclase.

Considering the results obtained, it is possible to state that the concentrations of the these potentially expansive compounds in the two slags have null or very low content to produce expansive reactions with negative repercussions on the performance and durability of cementing matrices elaborated by these by-products.

4. Conclusions

The following conclusions are deduced from the above studies:

1. For both EAS, the chemical composition was similar and it was not affected by granulometric interval. The main oxides present in slags were Fe_2O_3, CaO and SiO_2, the sum of which is above 73%.
2. From a mineralogical point of view, the EAS are formed by highly crystalline compounds, such as w/plustite, magnesioferrite/magnetite, hematite, larnite, bridigite/merwinite, gehlenite and manganese oxides. The reflection peak intensities varied with the origin of the slag and granulometric interval (mainly in EAS 1).
3. Due to its high crystallinity, these by-products showed no presence of pozzolanic activity so that they cannot be used as active additions in the manufacture of cement and concrete.
4. Up to now, the use of EAS as aggregate in construction was limited due to the possibility of containing expansive compounds. The studies carried out in the current work show that these expansive compounds (quicklime, sulphates and chlorides) are present in very low or null concentrations (below limitations specified in standards). With respect to the free MgO, the concentrations detected in slags were under 1%. These amounts are not big enough to crystallise in the form of periclase.

In spite of the good chemical qualities of the EAS studied here for its use in construction, a much more experimental research is required to permit a better understanding regarding the nature and behaviour of EAS against water. On one hand, this study can be the basis for later researches because it is not possible to extrapolate these results to other steel industries due to its different manufacturing processes: starting materials, quality of scrap, etc. On the other hand, the presence of other oxides in the slag, such as iron oxide (FeO) and manganese oxide, can also have a direct influence on the expansive phenomena.

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