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Characteristics of the slags produced in the fusion of scrap steel by electric arc furnace

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Abstract

The use of industrial by-products requires knowledge of the characteristics of the materials. This work presents characterization data on slags produced in the fusion of scrap steel by electric arc furnace. It includes the chemical, mineralogical, and microstructural analysis and physical characteristics. Mineralogically, scrap steel from electric arc furnace are a mix of anhydrous calcium silicates and iron composites and manganese oxides. No dimensional instability was detected. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Electric arc furnace slag; X-ray diffraction; Characterization

1. Introduction

The slags produced in Spanish electric arc furnace (EAF) steel manufacture are of two types. To ensure good quality steel, it is necessary to physically remove the slag. The slag is allowed to cool spontaneously in the open until it reaches temperatures lower than 50°C; it hardens as granular material of very different sizes.

This process generates two kinds of slags: (1) black basic slags, with a lime content lower than 40%, resulting from the cold loading of scrap, and (2) white basic slags, with a lime content higher than 40%, generated during fining, when more lime is added to remove sulphur and phosphorus.

This study was carried out on the black Spanish slag and is the first research on this by-product. Studies on the use of the EAF slags as granular materials had been made previously in Germany [1].

2. Methods

Each sample was ground in an agate mill to avoid contamination to a fineness less than 45 μm before chemical and mineralogical analysis. An extreme hardness and grinding resistance was verified, which is an indicator of its resistance to erosion and fragmentation.

The study was carried out using optical microscopy, chemical analysis by means of inductively coupled plasma (ICP) spectroscopy and solubilization of the samples by acid attack, mineralogical analysis [X-ray diffraction (XRD) and infrared (IR) absorption spectroscopy], and morphological and microstructural analysis by scanning electron microscopy with X-ray-dispersive energy analytical system.

Tests on the soundness of the slags for their use as aggregates were developed in accordance with RILEM TC 26-GM "Granular Materials" and with European standard prEN 1744-1 "Test for Chemical Properties of Aggregates. Chemical Analysis" and the testing methods described in standard NF P 18302 "Concretes — Crushed Slag." The physical characteristics were obtained on the granulometric range of 4.75 to 25 mm, applying the UNE 83134 "Aggregates for Concrete: Determination of Densities, Porosity, Absorption Coefficient and Water Content in Coarse Aggregate."

The European standards (EN 196-2 "Chemical Analysis of Cement" and prEN 1744-1) were used in the determination of compounds that can generate instability in slags (sulphides, sulphates, and free CaO).

3. Results and discussion

Samples of slags from two plants were similar and dark in colour. In sample EAFS-2, occasional small white agglomerates with a greater content of calcium carbonate

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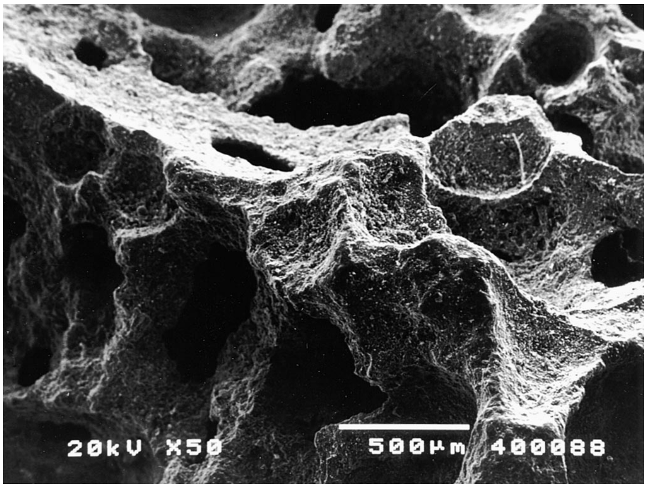

Fig. 1. SEM micrograph of the EAF slag-2.

(calcite and dolomite), due to contamination by white slags during storage, were identified by IR spectroscopy.

Depending on their origin, the slags showed differences in texture and morphology that affect their behaviour: EAFS-2 had a high porosity (Fig. 1), while EASF-1 was more dense and compact (Fig. 2) and at its surface, small particles with high iron content were detected through scanning electron microscopy (SEM)/energy dispersive spectrometry (EDS). These microstructural characteristics are directly related to the densities, higher in EAFS-1 than in EAFS-2, and in their different capacities for absorbing water, highest in EAFS-2 (Table 1; UNE 83134).

If the values obtained are compared with the specifications of the standard DIN 40 301 "Ferrous and Non-Ferrous blast Furnace Slags for Building Uses" (water absorption <6% and specific gravity >2.8 kg/dm^3), it appears that both the slags fulfill the requirements, although they differ in porosity (Fig. 2) and water absorption.

Fig. 2. SEM micrograph of the EAF slag-1. This sample has lower porosity and water absorption than EAFS-2.

Table 1
Characteristics of EAF slags

EAF slag	Unit weight (kg/dm^3)	Water absorption (%)
1	3.37	1.56
2	3.13	4.21

The most abundant elements in the EAF slags, determined by ICP, are shown as oxides in Table 2. Magnesium, expressed as MgO, is less than the detection limit by XRD (Table 3).

The stability (no disintegration or expansive compounds) of the slags is a requirement that permits their possible use as aggregate or, by fine grinding, incorporation in binders. The potential to hydrate expansively was evaluated. The presence of free CaO, MgO, or sulphides in slags could create problems. In Table 3 the values obtained through these determinations are shown (crystallized MgO was obtained by XRD), and the conclusion is that EAF slags samples tested do not contain potentially expansive components.

The mineralogical compositions differ slightly between the two EAF slags: The most important compounds, identified through XRD (Fig. 3), are: gehlenite [Ca_2 $Al(Al,Si)_2$ O_7], identified by two different reference patterns (25-0123 and 35-0755); larnite (Ca_2SiO_4) (reference pattern 33-0302); and other compounds presented in low-intensity peaks, which could be attributed to bredigite syn [$Ca_{14}Mg_2(SiO_4)_8$] (reference pattern 36-0399). Variable amounts of manganese oxides (Mn_3O_4, MnO_2), magnesioferrite ($MgFe_2O_4$), and magnetite (Fe_3O_4) were detected.

In the various chemical moduli used to verify quality of slags, three included the MnO component in the denominator, which means that MnO is an activity reductor [2]. However, the main components of the EAF slags (studied by XRD) are anhydrous calcium silicates (gehlenite, larnite, and bredigite), which may be poten-

Table 2
Chemical analysis of the EAF slags

Compound (%)	EAFS-1	EAFS-2
SiO_2	6.04	15.35
Al_2O_3	14.07	12.21
FeO	27.41	34.36
CaO	29.11	24.40
MnO	15.58	5.57
MgO	3.35	2.91
Na_2O	0.13	0.19
K_2O	1.08	1.52
Cr_2O_5	0.70	0.99
P_2O_5	1.24	1.19
PbO	0.22	0.32
NiO	<0.10 ppm	<0.09 ppm
V_2O_5	0.06	<0.26 ppm
TiO_2	0.54	0.56
BaO	0.40	0.32
Li_2O	0.07	0.09

Table 3
Composition of EAF slags in relation to stability

Sample	Free CaO (%)	Periclase (%) (XRD)	S^{2-} (%)	SO_3 (%)
EAFS-1	0	Below detection limit	0.04	0.15
EAFS-2	0	Below detection limit	0.08	0.15

tially reactive mineralogical phases, depending on the conditions such as temperature.

IR spectroscopy allows identification of silicates as the most abundant compounds [the absorptions are typically centered at around 520 (υ_4), 1,000 (υ_3), and 450 (υ_2) cm^{-1}] (Fig. 4) and corroborate XRD results. Thus, absorptions of higher intensity are found in the zone between 900 and 1,020 cm^{-1} [3] due to the Si-O valence vibrations of SiO_4, with different absorptions that correspond to the different compounds of silicates present in the sample, and absorptions in 520 and 470 cm^{-1}.

Disintegration in slags may be due to conversion of unstable polymorphs dicalcium silicate to the low (γ) temperature form of Ca_2SiO_4, which is accompanied by an increase of 10% in volume and leads to disintegration of the slag. To avoid or to neutralize these defects, quick cooling of the slag is necessary.

Regarding the use of slags as aggregates, specific tests were carried out to verify their stability (RILEM TC 26-GM, prEN 1744-1, and NF P 18302). No trace indicating disintegration was observed in EAF slag samples by these tests.

The iron sulfide disintegration test (which consists of aging the samples in wet atmosphere or by water immersion) gave no disintegration. Moreover, the sulphur content combined as sulphide (less than 1%, see Table 3) supports these results.

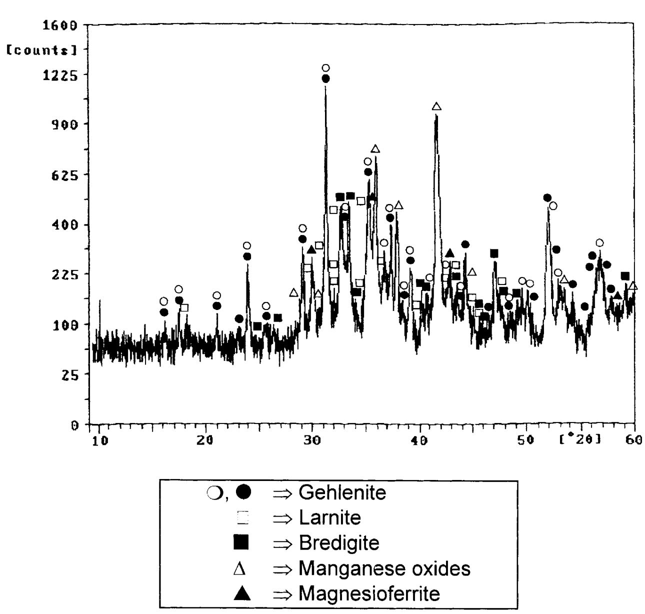

Fig. 3. X-ray diffractogram of the EAF slag (sample 1).

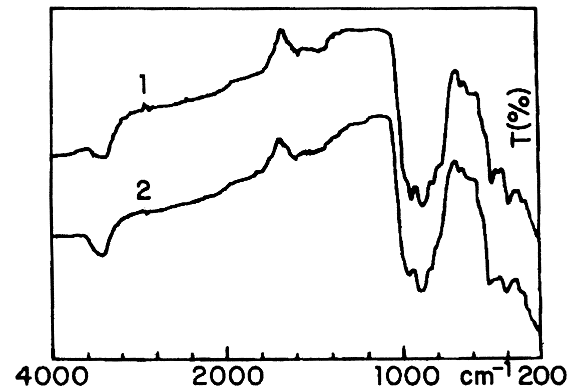

Fig. 4. IR spectra of EAF slags.

4. Conclusions

Studied EAF slags have similar characteristics and are resistant to grinding. The most abundant chemical elements in EAF slag composition are: Fe, Ca, Si, Mn, Al, and Mg. The mineralogical compounds are: anhydrous calcium silicates and silicoaluminates, gehlenite, larnite and bredigite, magnetite and magnesioferrite, and manganese oxides. The existence of anhydrous calcium silicates, especially larnite, in these slags may indicate a weak potential for hydraulic activity.

Quality control of these products must be carried out as is done in other residual products. A quick cooling of the EAF slags is recommended.

No adverse factors for the use of slags as building materials was detected through chemical and mineralogical analysis. According to the contents of MgO, free CaO, sulfides, and sulfates, the percentages are very low and point toward volumetric stability.

Behaviour in disintegration tests for free lime or iron sulfide does not induce unsoundness. No problems of disintegration, cracking, or dimensional instability appeared in aggregate tests for the EAF slags studied.

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