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Electric arc furnace slag and its use in hydraulic concrete

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HIGHLIGHTS

- EAF slag is a rocky material of use in construction and civil engineering.
- EAF slag shows some chemical changes and slight expansiveness over time.
- Collaboration producers-consumers of EAF slag is essential to efficient re-use.
- EAF slag is a suitable aggregate for hydraulic cement concrete.
- EAF slag forms a particular type of microstructure in the interfacial transition zone.

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ABSTRACT

Electric arc furnace oxidizing slag (EAFS) is a by-product of the steelmaking industry, generated after the melting and the preliminary acid refining of liquid steel. It is a stony material that is easy to crush for use as aggregate in concrete mixes.

This study examines the long-term aging reactions of EAFS and its volumetric stability, to gain further knowledge of this by-product, its behaviour as a construction material, and its inherent risk of swelling. Additionally, the good compressive strength of hydraulic mixes that incorporate this slag can be analyzed and explained on the basis of its steady and expansive compounds and its chemical evolution over time in the interfacial transition zone (ITZ); the appearance of calcium carbonate enhances the cohesiveness, stiffness and strength of this zone and, as a consequence, of the hydraulic concrete.

1. Introduction

The sustainability of human activity has become a key issue in the last decade of the 20th century and the first decade of the 21st century. The search for sustainability has driven the reuse of suitable industrial by-products with the right properties, thereby reducing the consumption of natural resources. Since the pioneering papers of Motz, Geiseler and Koros [1–3], almost all kinds of iron and steelmaking (as well as other metal) slags have been proposed for use in construction and civil engineering. Researchers now face the task of finding the most efficient and appropriate techniques for their reuse [4–20]. Several investigations on the re-use of steelmaking slags have been published over the last decades; some of them concerning mortar and concrete (rigid-stiff matrices) [21–43], and mixtures with granular soils (compliant-flexible and porous matrices) [44–58].

Electric arc furnace oxidizing slag (EAFS) is a by-product of the steelmaking industry, generated after the melting and the primary acid refining of liquid steel. Its chemical composition is based on its content of calcium, iron and silicon oxides in a global amount of over 80%; aluminium, magnesium, manganese and phosphorus oxides are also present. Variations in the proportion of these oxides are due to the kind of steel, the refractory materials of the furnace and some technological advances. In standard oxidizing electric arc furnace slag (EAFS), the proportion of acid oxides (silica, alumina, iron oxide ...) is predominant on the proportion of basic oxides (lime, magnesia and alkalis).

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The similarity between the oxides, which may even be present in similar proportions in both EAFS and LD converter slag (Linz-Donawitz converter slag) or BOF-slag, (Basic Oxygen Furnace slag) and their common stony-gravel presentation, might lead to the erroneous impression that they are the same material. However, these products differ slightly, due the lower amount of free calcium oxide, CaO, also called free lime [59–68] in the EAFS, which also explains its lower expansiveness. Nowadays, the use of EAFS as a coarse aggregate in hydraulic concrete is widely accepted, while LD-slag is mainly applied in roadbeds. Maximum levels of volumetric expansion in materials used as concrete aggregates and as roadbedding are set at around 1% and 5%, respectively, in current standards.

Pioneering papers that detailed rigorous, systematic and global studies of the use of EAFS in mortar and concrete were published in Japan between 1991 and 1999 by K. Morino et al. [69–71]; other publications in the same field over the same decade were less systematic. At the start of the 21st century, their work and those of other Japanese authors [72–74] were published in English, and several new research teams begin to work on this subject. Our team began its research in this field in 1997, beginning with the PhD Thesis of Prof. Manso; an initiative now exists among several EU research groups to establish pre-normative standards in this field.

The present study deals with EAFS expansion following spontaneous (weathering) and accelerated testing and, subsequently, its particular application as a coarse aggregate in hydraulic concrete. The composition and characteristics of EAFS are studied by means of standard analytical techniques: X-ray diffraction, thermogravimetric and differential calorimetric scanning analysis, low-vacuum SEM microscopy and EDX analysis. This article, based on the PhD Thesis of Ms Idoia Arribas, extends the results and adds subsequent findings from the research team. The long-term evolution of EAFS is studied, especially in terms of CaO migration, which is related to the characteristics of the Interfacial Transition Zone (ITZ) observed in the concrete mixes, leading to interesting results and relevant conclusions.

2. Background on EAFS

After cooling from 1580 °C, the EAFS by-product becomes a stony, cohesive, slightly porous, heavy, hard and tough material, the initial colour of which is almost black, due to the presence of iron oxides. Long-term outdoor weathering causes its colour to change to clear-grey shades. It is easily crushed, its residual metallic iron must be mostly separated, and it can then be employed as coarse and fine aggregate in hydraulic mortars and hydraulic or bituminous concrete. Its other possible uses include bedding material for roads and railways, and water depuration, as well as soil stabilization and correction.

All aggregate materials to be applied in concrete have to be analysed in depth before their use can be standardized. Problems of alkali-aggregate reactions and intrinsic chemical instability are examples of the risks associated with the use of certain natural minerals as aggregates. In the case of EAFS, an artificial material, there is a general consensus that its chief problem is volumetric expansiveness or swelling of pieces, lumps and particles, due to the chemical activity of expansive compounds such as free-CaO and, sometimes, free MgO-periclase, an expansive compound that has scarcely been reported in the literature [75]. Their presence is detrimental and should be carefully monitored when the concrete is prepared and throughout its in-service life.

The main physical and chemical characteristics of EAFS for use as mortar and concrete aggregate, which influence its weight and integrity, are its high density and its free calcium oxide content. Further relevant characteristics have to be analysed and evaluated in its application, which require a wide range of scientific analyses [76,77]. The immediate effects of the addition of large amounts of EAFS aggregate (on fresh and hard concrete) are loss of workability and an increase in the short-term mechanical properties (strength at 7 and 28 days). These and other important questions (i.e. durability tests) have been studied by the authors over the past decade and their results and opinions form part of the scientific literature.

The main compounds of EAFS, according to the scientific literature, are single and complex calcium silicates (containing aluminium or magnesium) and single and complex iron-based oxides (containing calcium, magnesium, chromium, manganese, among others) which are in a liquid state above 1500 °C, aided by fluxes such as CaF_2, which solidify at under 1200 °C. Silicates (dicalcium silicate β or γ belite-larnite, ackermanite, gehlenite, wollastonite, calcium-olivine, kirschsteinite, melilite, and others) and iron-based oxides (wustite, magnetite, hematite, dicalcium ferrite, R-O phase...) can be considered to add to short-term stability, although their long-term chemical stability is not evident and has to be verified. The undesirable presence of metallic iron in the slag must be eliminated through efficient magnetic separation. Additionally, fresh EAFS slag (unweathered, after cooling) often contains small amounts of free-CaO (also called free-lime) dispersed in its microstructure. Despite its presence, some of the analytical procedures to quantify its amount in the slag are unreliable. A more precise method of quantifying free-CaO content in EAFS is accelerated aging until total hydro-carbonation is achieved, followed by thermo-gravimetric heating analysis up to 900 °C.

Several reasons explain the volumetric instability of generic metallurgical slags. Firstly, the evolution of silicate β to γ is accompanied by an increase in volume, although this reaction is less likely in EAFS, due to the presence of P_2O_5 and other β-phase stabilizers. Secondly, the long-term oxidation of metallic iron from iron +2 to iron +3, although infrequent, has also been observed in metallurgical slags. Thirdly, it has been observed a low-temperature hydroxylation of free-CaO and subsequent carbonation, in the presence of moisture, and even of free-MgO, although the latter is uncommon in EAFS. These reactions are associated with a significant increase in volume, sometimes with short-term and at other times with long-term effects.

According to the scientific literature [61,66], the free lime found in LD-slag can be divided into two groups. The first group is residual free lime (not completely dissolved in a liquid state) that is grainy or spongy with particle sizes of between 2 and 40 microns. The second group, precipitated free lime, is smaller than 4 μm and may be found in the grain boundaries of some iron-oxide-based compounds (dicalcium ferrite or R-O phase), either dispersed in the calcium silicates, in SC_3 crystals or in SC_2 crystals. Both are found in EAFS, although the latter are by far the most common.

Despite the fact that EAFS is an "oxidizing" slag, in which the predominant acid oxides are capable of dissolving all of the basic oxides, it is not uncommon to find some types of EAFS that contain undissolved particles of free-CaO. These particles are a consequence of the electric arc furnace procedure; partial addition of lime is sometimes made near the end of the "acid" refining process, without sufficient time for the other acid slag components to dissolve this lime. Finally, this free-CaO remains undissolved in the mass of the slag as it cools.

Furthermore, other operations such as the "foaming" of the slag in the electric arc furnace, the pouring process, and slag cooling method to room temperature all form part of the steelmaking process. There are at least two methods for cooling EAFS, from furnace temperatures to room temperature. One method is cooling in continuous mode, dousing a small flow of slag with water and obtaining particles, lumps and pieces of a size under 40 mm; these particles may be used as gravel after metallic iron separation. The other method involves pouring the liquid slag into a large pit