



The long-term accelerated expansion of various ladle-furnace basic slags and their soil-stabilization applications



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HIGHLIGHTS

- Ladle furnace basic slag is a by-product of the steelmaking industry that interacts with the environment in a complex way.
- Ladle furnace basic slag is an appropriate material for use in construction and civil engineering.
- Ladle furnace basic slag reused as a material for the stabilization of clayey soils is highly effective.

ARTICLE INFO

Article history:

Received 30 January 2014

Received in revised form 3 July 2014

Accepted 5 July 2014

Available online 24 July 2014

Keywords:

Ladle furnace basic slag

Expansive compounds

Accelerated aging

Soil stabilization

Swelling

ABSTRACT

Ladle furnace basic slag (LFS) is a by-product of the steelmaking industry that can be used in civil works, especially for soil stabilization. This sustainable application is based on the reactivity of certain compounds at ambient temperatures such as calcium aluminates, free calcium oxide and free magnesium oxide. These compounds show hydraulic reactivity and subsequent interaction between each other and with the clayey fraction, resulting in improvements to the geotechnical properties of the soil such as its bearing capacity and free swelling.

This study looks at the long-term aging reactions of LFS and the properties of various soil–LFS mixes, to gain further knowledge of the behaviour of this by-product as a construction and building material and the inherent risk of volumetric instability associated with its use. The final conclusion is that LFS can be applied in soil stabilization as efficiently as conventional soil stabilizers.

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1. Introduction

The pressing need for greater sustainability of human activity, in view of the debate over global warming, especially in the final decade of the 20th century, has driven the reuse of suitable industrial by-products with the right qualities. Since the pioneering papers of Motz, Geiseler and Koros [1–3], iron and steelmaking slags have been considered very promising materials in several fields of human activity, and particularly in construction and building. Faced with this situation, the role of the engineer should be to optimize the reuse of these by-products in as many applications as possible in an efficient and appropriate manner [4–10].

Several works on the use of steelmaking slags have been published over the last decade, mainly concerning mortar and concrete (rigid-stiff matrices) [11–29]; in the field of soil stabilization slags and other by-products have been profitably used (compliant-flexible and porous matrices) [30–45].

Ladle furnace basic slag is a by-product of the steelmaking process, generated after the secondary or basic refining of steel. Its main components, in a total amount of approximately 60%, are magnesium and predominantly calcium oxide. The slag contains silicium and aluminium oxides in amounts of about 30%, which act as fluxes to produce the melting of these two refractory oxides. So, the compounds of this LFS (and, in general, of all ferrous slags) are silicates and aluminates of calcium and magnesium. Variations in the proportion of these oxides are determined by the kind of steel heat treatment, the refractory materials of the furnace and any technological advances. Minor components of LFS are calcium fluoride and sulphide, iron, manganese, titanium, and alkaline oxides. The attempt to “almost saturate at high temperature” the

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composition of LFS slag with silicium and aluminium oxides, produces LFS in general with an outstanding content of free-CaO and free-MgO at ambient temperature, accompanying calcium silicates and calcium aluminates. Several works, in the scientific literature, have described the phases present in the LFS [46–49].

The unquestionable similarity between the oxides that are present, even in similar proportions, in both LFS and Portland clinker and the dusty presentation of the LFS at room temperature, with no need for further grinding, mean that its use as a substitute for Portland cement has been proposed. Various alternative uses have been widely reported in the literature [50–55]. In 2009, a study on the weathering of LFS was published by this research group [56]. The study mentioned the expansivity of this material, due to its content of free-CaO and free-MgO, although this aspect was neither described nor analysed in detail.

This study examines the results of accelerated aging of LFS submerged in water at a temperature of 70 °C. The hydration, carbonation and combination of its compounds are related to the volumetric expansivity of the slag and its ability to stabilize the clayey fraction of the soils. The long-term behaviour of LFS [57–59] in terms of its chemical and volumetric changes is studied in this work through a series of standard analytical techniques: X-ray diffraction, thermogravimetric and differential calorimetric analysis, SEM microscopy and EDX analysis. The results and conclusions are described in the following sections of this paper.

1.1. Initial approach

It is a well-known question that the presence of free-CaO and free-MgO in the mass of an engineering material can produce notable, long-term volumetric swelling, due to the volumetric expansion produced by spontaneous hydration of both substances at room temperature, absorbing the necessary water from any source, including water vapour in the atmosphere. Moreover, these calcium and magnesium hydroxides can potentially turn into carbonates, absorbing carbon dioxide from the atmosphere, which eventually causes further volumetric expansion.

When a complex material such as LFS, containing free-CaO and free-MgO and other compounds, is weathered, several complex chemical reactions are likely. These reactions may be modified or changed, if the LFS is mixed with natural mineral-bearing soils and the best results are obtained with clayey soils. The chemical equilibrium of the entire reactions is affected by the presence of all the compounds coming from the LFS and from the soil, and the final result is not always favourable.

The “a priori” determination of the volumetric expansion of a specific kind of slag is not easily feasible. Firstly, the free-CaO and -MgO content of the slag cannot be determined in a satisfactory way; and secondly, the diversity of possible chemical reactions between these oxides and the environmental agents is very high. Concerning the first point, the physico-chemical analyses now available to determine free-CaO and free-MgO content in these sorts of products are notoriously poor.

The free-CaO content is composed of calcium oxides and hydroxides and, in theory, semi-quantitative estimation by X-ray diffraction using suitable reflection power factors as well as other analytical techniques detailed in several technical standards may be used to estimate it. However, neither method is reliable; in fact, the results obtained after the chemical analysis detailed in the relevant standards may introduce significant errors and cannot be relied upon. X-ray diffraction shows low peaks for calcium oxide and a notorious presence is needed to arrive at a rough estimation of the oxide content; the calcium hydroxide content, Portlandite, is determined with more precision by this technique.

As various authors [13,60] have previously noted, two different CaO-oxide morphologies may be distinguished in almost all the iron and steelmaking slags: a “primary” and a “secondary” free-CaO. The “primary” free-CaO comes from undissolved lime added to the flux-slag of the furnace at the start of heating process and was not combined in silicate or aluminate form in the liquid slag at 1640 °C throughout the steel refining process; this CaO is in fact a solid phase in suspension in the liquid slag, the particles, of between 4 and 20 µm in size, appear in SEM and EDAX analyses on the unhydrated slag at ambient temperature. During the cooling of LFS, the allotropic change of dicalcium silicate [61] is expansive and destroys the initial rigid matrix of the slag, leaving a sort of primary CaO exposed to environmental attack.

The “secondary” CaO comes from the decomposition of the high temperature tricalcium silicate into dicalcium silicate during the cooling process, and it remains mainly confined to or embedded in the solid particles of dicalcium silicate, inaccessible to the external environment, its size being less than one micron. This CaO was not detected by any of the above-mentioned methods of analysis; its interaction with the environment, based on diffusion, is very slow; and the amount of this kind of CaO is, in general, less than the amount of primary CaO.

The free-MgO contained in the LFS at room temperature has a very similar origin to that described for the “primary” free-CaO, undissolved particles of burnt periclase in the liquid slag. The presence of these solid particles of lime and periclase in the liquid slag is necessary to protect the refractory wall of the furnace from the chemical attack of the slag.

The content of free-MgO, periclase and brucite (magnesium hydroxide), cannot be evaluated in a reliable way by chemical analysis and, as in the earlier case, only X-ray diffraction gave a semi-quantitative estimation of its presence, using appropriate reflection powers in the calculations after the diffractograms. In general, the particles of periclase in the slag at room temperature are embedded in other abundant components such as, for example, dicalcium silicates.

Chemical interaction between the “primary” free-CaO and the moisture of the environment is fairly fast and amounts of calcium hydroxide (portlandite) coming from the hydration of the “primary” CaO can appear in the LFS within a few hours. Later on, after several weeks, this hydroxide can slowly be converted into calcium carbonate, and other compounds, such as calcium–magnesium carbonate can even appear. Interaction between the “secondary” free CaO and the environment is similar to that mentioned for the primary free CaO, but it is very slow due to the confinement or enclosure of its particles. In fact, observations of the behaviour of other kinds of slags (EAF slag or LD slag) indicate a delay of several years.

The chemical interaction between the free-MgO and the environment is slower than it is between the primary free-CaO and the environment, and periods of several years have sometimes been observed. Additionally, in most cases, the periclase is also embedded in other LFS particles and its enclosure inside arrays that are not hydratable, such as calcium olivine, means that the access of moisture to the periclase is even slower. Magnesium hydroxide or brucite is the simplest of these compounds that are formed, although a wide variety of products can appear and brucite is not always present in the aged LFS.

As stated earlier, the diversity of possible chemical reactions between these calcium and magnesium oxides and the environmental substances is very high. The following schematization shows some of the chemical reactions and compounds obtained from the aging of the LFS. An exhaustive list would occupy too much space as there are multiple possibilities for the resultant compounds.

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