Construction and Building Materials 123 (2016) 404–413

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Effect of high-alumina ladle furnace slag as cement substitution in masonry mortars

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HIGHLIGHTS

- Ladle furnace slag (LFS) is a non-uniform by-product, and can be high-alumina or high-silica slag.
- High-alumina LFS has a better hydraulic reaction in mortars than high-silica LFS.
- Partial substitution of cement by LFS in amounts of 20% by weight has no negative effects.
- LFS-mortar mixes show useful properties for building sector applications.

ARTICLE INFO

Article history:
Received 10 March 2016
Received in revised form 26 May 2016
Accepted 7 July 2016

Keywords:
Ladle furnace slag
Cement additions
Paste
Masonry mortar
Durability

ABSTRACT

Ladle furnace (white or basic) slag is a significant by-product of the steelmaking industry; nowadays the manufacturing process yields two types of basic slag that are either low or high in alumina. The present research focuses mainly on the composition of the high-alumina slag and the reactivity of its compounds such as calcium aluminates, free calcium oxide, and free magnesium oxide, when aged at room temperature and at water steam temperature (accelerated aging). Additionally, a characterization was performed of pastes and masonry mortars that incorporate high alumina ladle furnace slag as a supplementary cementing material in partial substitution of Portland cement in amounts of 10% and 20% by weight. Different properties are studied such as porosity distribution, volumetric stability, mechanical strength and durability, mainly referring to wetting-drying aging cycles. The study concludes that high-alumina ladle furnace slag can induce slight hydraulic reactivity and its partial addition has no negative effect on the fundamental properties of cement masonry mortars.

1. Introduction

Nowadays, Spain produces steel in 19 steelmaking factories, approximately 45% of which are situated in the north of the country, where the authors conducted this research. This industrial sector produces at least eight different types of slags [1], which have been studied by many research groups ever since the pioneering papers of Motz, Geiseler and Koros [2–4], to identify reliable applications for each slag type.

In this scenario, the construction sector has taken action to respond to this challenge and reuse industrial by-products, as recently done in other sustainable approaches [5–10]; thereby exploiting materials, which would otherwise be of no economic value, giving them an environmental friendly value with a functional utility [11–18].

One of the slag types is reducing, basic or white Ladle Furnace Slag (LFS), produced in copious amounts as a by-product of the steelmaking industry in the secondary or basic steel-refining process; this steel-refining process yields basic slag which is either low or high in silica or alumina, depending on the saturation method of melting fluxes. Nowadays, the alumina saturation method is applied in approximately 25% of the steelmaking industry. However, its future is promising, in view of the cheaper and cleaner steel that this novel steel-refining process can produce. The present work is focused mainly on the study of the properties of this alumina-rich slag.

As has been stated in the literature, in general the main components of LFS are magnesium and calcium oxides accompanying silica and aluminum oxides that act as fluxes. Hence, the compounds of LFS are mainly silicates and aluminates of calcium and

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http://dx.doi.org/10.1016/j.conbuildmat.2016.07.014

magnesium, as already described and characterized in the scientific literature [19–28]. Obviously, calcium aluminates are preponderant in the high-alumina slag, while in the high-silica slag calcium silicates are more abundant. Free calcium oxide and free magnesium oxide are also always present in these two types of LFS slags.

This kind of industrial by-product can be used in various construction and civil engineering applications in which a binder is needed, for various reasons. First, due to the similarity between the oxides that are present (also in similar proportions) in both LFS and Portland clinker and the eventual hydraulic properties that they can have. Secondly, the dusty morphology of the LFS in its original state can facilitate its use as a substitute for dusty binders. Over the past decade, it has already reported in the literature initial studies on the use of LFS in cement matrices [1,18,23,24,27,31] followed by studies on soil stabilization for civil works [19,29–31]. In general, the use of LFS basic slag that is high in silica, as a binder or an aggregate or even as raw material of clinker [32], has been relatively successful; on the contrary, LFS high in alumina has only been studied by itself [22,28] until today. The present work presents a pioneering study on its behavior in hydraulic mixes.

For a better comprehension of both LFS types, mainly in terms of hydraulicity, the present research will examine their volume stability [33] and the reactivity of their main components at outdoor temperatures: calcium aluminates, free-CaO and free-MgO. Various analytical techniques are applied to record their chemical and volumetric changes: X-ray diffraction (XRD), thermogravimetric and differential calorimetric scanning analysis (TG-DSC), swelling tests, and SEM (scanning electron microscopy) with EDAX (dispersive energy of X-ray) micro-analysis.

This research also studies cement pastes and masonry mortars containing both white slag types in partial substitution of binder (cement). It focuses on analyzing their performance from two perspectives; firstly, their mechanical strength is tested; secondly, the dimensional stability of mixtures and durability issues are examined by exposure to wetting-drying cycles in the laboratory. It could be used in the preparation of layering mortars (façades), rendering and plastering (partitioning), and bonding (masonry) mortars.

Table 1
Chemical composition and other physical properties.

Compounds	CEM I 52.5 R	CEM II/A-M 42.5 R	LFS1	LFS2
SiO_2 (%)	18.56	20.83	3.77	22.94
Al_2O_3 (%)	5.05	6.40	28.82	4.42
Fe_2O_3 (total) (%)	3.29	3.51	3.82	1.01
MnO (%)	–	–	0.29	0.22
MgO (%)	1.49	1.62	6.36	5.99
CaO (%)	63.40	58.29	53.96	61.64
Na_2O (%)	0.21	0.20	–	–
K_2O (%)	0.71	0.90	–	–
TiO_2 (%)	–	–	0.14	0.34
P_2O_5 (%)	–	–	0.04	0.01
SO_3 (%)	1.8	1.2	2.80	3.43
Loss on ignition (%)	2.72 (C+ CO_2 + H_2O)	4.53 (C + CO_2 + H_2O)	26.2	3% gain
Blaine fineness (cm^2/g)	4975	4060	2820 (after crushing)	1650
Specific gravity (Mg/m^3)	3.13	3.05	2.75	3.03

2. Materials

2.1. Water, cement, and natural aggregates

Clean water from the urban mains supply of the city of Bilbao was used that contained no elements that might negatively affect the quality of the hydraulic mixes.

Two Portland cement types were used in present research. Cement type I (CEM I 52.5 R) consisting of 90% Portland clinker, 5% calcium carbonate powder fines, and 5% gypsum, with a unimodal particle-size distribution of around 20 μm (checked by a LS 13320 laser diffractometer). Cement type II (CEM II/A-M (V-L) 42.5 R) consisted of 80% Portland clinker, 15% high-silica fly ash, 2% calcium carbonate, and 3% gypsum, with a bimodal particle-size distribution of around 19 μm and, more frequently, 34 μm. Their chemical composition and other physical properties of both cement types, analyzed by X-ray fluorescence (XRF), are shown in Table 1.

A commercial crushed natural limestone aggregate sized between 0 and 4 mm, with a fine fraction (<0.063 μm) of 20%, was also used. Its main mineral compound was calcite (95%), with a specific gravity of 2.68 Mg/m^3 and a fineness modulus of 2.4 units. Fig. 1 includes the fine limestone sand morphology, supplied by Morteros Bikain Company.

2.2. Slags

High-alumina and high-silica ladle furnace slags, by-products from two different steelmaking industries, were labeled LFS1 and LFS2, respectively. LFS1 is a high-alumina slag weathered on factory grounds over several weeks; its aging level was 'a priori' uncertain at the moment of its reception, but its morphology was no longer dusty (original situation), but agglomerated in particles of some centimeters in size (see Fig. 1). LFS2 was a dusty high silica slag taken from the factory immediately after cooling, with no aging at all. Fig. 1 shows the morphology of both LFS types: LFS1 presented an irregular-shaped material, with powder and pieces of low cohesion formed of small aggregated particles, while LFS2 presented a powdery-dusty appearance with disaggregated particles. Their chemical composition obtained by X-ray fluorescence analysis, on slags in their "as-received" state, is shown in Table 1, in which the "loss of ignition" gives an approximate idea of the degree of aging of each slag type. Additionally, Table 2 details their mineralogical analysis by XRD, which indicates the presence-absence of hydration-carbonation

Table 2
XRD analysis of Ladle Furnace Slags.

Mineral constituents	LFS1	LFS2
Tricalcium aluminate ($Ca_3Al_2O_6$)	•••	
Calcium-olivine (Ca_2SiO_4)	••	•••••
Brucite ($Mg(OH)_2$)	•	
Calcite ($CaCO_3$)	••••	
Hydrotalcite (Mg_6 Al_2 $(CO_3)(OH)_{16}$·$4H_2O$)	•••	
Mayenite ($Ca_{12}Al1_4O_{33}$)	••	••
Katoite ($Ca_3Al_2(OH)_{12}$)	•••	
Sjögrenite (Mg_6 Fe_2 $(CO_3)(OH)_{16}$·$4H_2O$)	••	
Periclase (MgO)	••	••
Jasmundite (Ca_{22} $(SiO_4)_8O_4S_2$)	•↓	•
Fluorite (CaF)		••
Oldhamite (CaS)		•

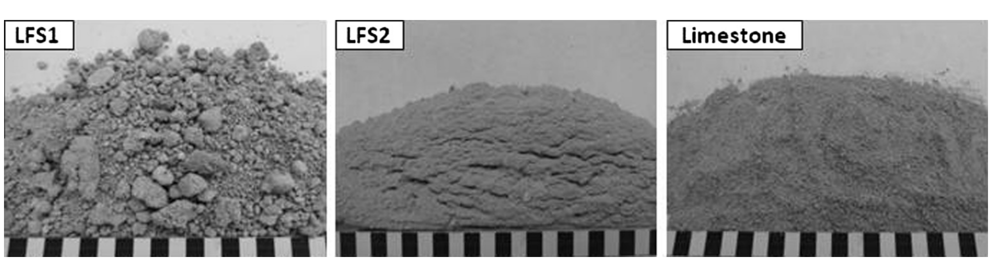

Fig. 1. Morphology of limestone and LFS1/LFS2 slag. Black and white stripes are centimeters.