The efficiency of quartz addition on electric arc furnace (EAF) carbon steel slag stability

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HIGHLIGHTS

- A method to stabilize EAF slag was implemented in an actual steel plant.
- The stabilization treatment lead to the formation of slag with gehlenite matrix.
- The stabilization process efficacy was confirmed by several leaching tests.
- Gehlenite inhibits heavy metals leaching.

ARTICLE INFO

ABSTRACT

Electric arc furnace slag (EAF) has the potential to be re-utilized as an alternative to stone material, however, only if it remains chemically stable on contact with water. The presence of hydraulic phases such as larnite ($2CaO\ SiO_2$) could cause dangerous elements to be released into the environment, i.e. Ba, V, Cr. Chemical treatment appears to be the only way to guarantee a completely stable structure, especially for long-term applications. This study presents the efficiency of silica addition during the deslagging period. Microstructural characterization of modified slag was performed by SEM and XRD analysis. Elution tests were performed according to the EN 12457-2 standard, with the addition of silica and without, and the obtained results were compared. These results demonstrate the efficiency of the inertization process: the added silica induces the formation of gehlenite, which, even in caustic environments, does not exhibit hydraulic behaviour.

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1. Introduction

Today steel slag is considered effectively equivalent to the common stone material employed in civil engineering applications. Its physical and mechanical properties are often higher than those of traditional raw materials [1–6] and, in recent decades, its use has increased exponentially [7]. In particular, electric arc furnace slag (EAF) offers several advantages when compared to other aggregates: it lacks clay and organic ingredients in its composition, has a rough and porous surface and provides good adhesion and good abrasion resistance.

Road construction [6,8–12] and concrete/clinker production [13–16] are common applications in which EAF slag could be mixed with or completely replace traditional raw materials. EAF slag could

be used as an aggregate in Hot Mix Asphalt (HMA) pavements, as an aggregate in concrete pavements, as a base or sub-base material, as an embankment material and as a railway ballast [17]. Slag aggregates are not directly exposed to the environment when mixed with other substances, i.e. bituminous binders or cement. For such applications, the standards do not generally require elution tests because the slag does not come in contact with water. On the contrary, leaching behavior characterization is mandatory for slag use in unbound applications, i.e. unpaved roads, armourstone or gabions. In such conditions, slag are subject to continuous cycle of wetting and drying. Several studies [4,10,18–20] have investigated the leaching behavior of slag aggregates and highlight that such aggregates could potentially release dangerous chemical elements (especially Ba, V and Cr), as well as unbound slag, when coming into contact with water.

Other investigations of the leaching behavior of EAF slag [21–25] have tried to identify the major mineralogical phases responsible for the dangerous species release. Electric arc furnace slag has a chemical composition close to that of the cement clinker, mainly

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constituted by calcium-silicates and calcium-ferrites, which makes steel slag potentially usable as a cementitious material [26]. Experimental tests have identified calcium silicates, especially larnite[1], hartrurite and bredigite, as the principal phases reacting with water and thus responsible for the releasing of elements, i.e. barium [22,23]. Other phases might also contribute to an increase in the amount of elements in the eluate: brownmillerite, calcium aluminate and non-stoichiometric spinels could be associated with Cr release. Barium oxide is a substitutional chemical compound of CaO in calcium silicates whereas chromium (in both trivalent or hexavalent form) could replace iron and aluminum oxide in a brownmillerite-type phase [27] and in calcium aluminates [28]. The hydration process facilitates the migration of species such as Ca, Mg or Ba into water. In a basic environment, chromium oxide could be easily dissolved into a hexavalent form, which is the most reactive and dangerous (it is classified as carcinogenic by the World Health Organization).

Hydration process by a dissolution precipitation requires ample time to be completed: for example, pure larnite reaches 50% of the hydrated ratio in 100 days [29]. Therefore, larnite hydration and dissolution is very difficult to be noted in EAF slag during the 24 h of a standard leaching test (EN 12457-2 standard) because only a small amount of the slag, less than 1%, reacts with water. However, this amount is enough to solubilize a quantity of Ba, Cr and V that exceeds the limits imposed by environmental regulations. Since the polluting elements are generally bound to the silicates, reducing their amount or reducing their solubility are two ways to overcome the problem. This could be achieved by promoting the transformation of the phases in which the aluminum is in the tetra-coordinated form and increasing the polymerization degree of the structure, namely increasing the number of SiO_4 tetrahedra. Specifically, the resistance of a silicate to hydration and the hydrolysis processes increases with the degree of oxygen sharing between SiO_4 polyhedra of the mineral structure [30]. These microstructural transformations should lead to the formation of more stable phases featured by high degree of condensation of structural tetrahedra, i.e. anorthite or gehlenite. Breaking the bonds is difficult due to an insufficient ion force of the mixing medium. In this case, the aluminum atoms are situated in tetrahedral coordination and behaves like silicon atoms [31]. Thus, a thermochemical inertization process was developed to transform EAF slag into an absolutely safe by-product useful for both aggregates and unbound applications. The treatment consists in the addition of pure quartz into the fluid slag during the deslagging operation, allows producing a continuous flow of treated slag having specific chemical composition and properties. The dosing device consists in a sand storage container equipped with automatic vibrating delivery table and with a chute positioned downstream the delivery device, to continuously carry the sand in the mixing zone. The admixed slag is collected in a slag-pot, which helps to keep it stirred, thus homogenizing the microstructure. This process is based on the same principle adopted by Drissen et al. [32] to stabilize Basic Oxygen Furnace (BOF) slag. Being the slag treatment only possible at the liquid state, the novelty of the proposed technique is to chemically modify the slag, exploiting its residual heat without external heating source or remelting operations. In this way, no modification inside the furnace are provided, avoiding to compromise the steel quality, and no additional investment's costs are need to successfully treat the slag.

The quartz addition should have a two-fold effect: it reacts with calcium aluminates to form gehlenite, inhibiting the formation of larnite, and simultaneously prevents its disintegration, thus

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Table 1
XRF chemical composition (weight %) and samples identification.

Sample ID	SiO_2	Al_2O_3	CaO	MgO	FeO	Cr_2O_3	V_2O_5	Ba	Λ
S1	12.36	8.96	26.10	3.21	37.53	2.46	0.08	0.06	0.800
S2	10.36	7.26	28.67	3.98	39.69	1.96	0.10	0.08	0.820
MS1	18.34	9.25	23.26	2.85	35.93	2.25	0.09	0.11	0.759
MS2	22.39	8.20	19.18	2.24	37.29	2.01	0.09	0.07	0.739

avoiding the "dusting effect" [33]. Larnite undergoes several phase transformations [34], the most important of which is the inversion from β-Ca_2SiO_4 (monoclinic) to γ-Ca_2SiO_4 (orthorhombic). This transformation is accompanied by a volume increase of around 12% [35]. β to γ transformation causes disintegration of the slag, the so called "dusting effect," making slag handling and storage problematic and the achievement of economic value for the slag virtually impossible. Formation of only 4 wt.% of γ-Ca_2SiO_4 is enough to cause slag disintegration. A relatively small amount of SiO_2 is enough to form a large amount of gehlenite [36]. Gehlenite, together with akermanite, is the main crystalline phase in ground granulated blast furnace slag, which is known to have very low hydraulic activity and a low environmental impact [37–39].

This work presents the benefits of silica treatment on slag release behavior. The efficiency of adding silica was experimentally demonstrated by XRD, SEM and leaching test analyses, with regards to liquid-on-solid ratio effects.

2. Experimental procedure

Two batches of carbon steel slag (S1 and S2) were investigated and modified (MS1 and MS2) by the above mentioned inertization process. The added quartz has an average particle size between 1 and 5 mm, with the 90% included in the 1–2 mm range. This size assures the sand to completely melt and dissolve itself in the slag flow. The quartz amount is comprised between 5% and 15% by weight of the slag, with optimal values approximately between 8 and 12 wt.%, depending on the initial chemical composition of the slag to be treated.

Slag chemical compositions were measured by XRF and checked by SEM-EDS and are reported in Table 1 together with the sample identification and optical basicity (Λ) (a basicity index formulated by Duffy and Ingram using spectrographic information coupled with the electronegativity data defined by Pauling [40]).

The analyzed slag are located on the phase ternary diagram shown in Fig. 1.

The comparison between as-received (S1 and S2) and modified slag (MS1 and MS2) was performed from a morphological and microstructural point of view with XRD and SEM analyses.

X-ray diffraction (XRD) data was collected using a Bruker D8 Advance diffractometer in a θ–θ configuration and employing Cu Kα radiation (λ = 1.54 Å) with a fixed divergence slit size 0.5° and a rotating sample stage. The samples of powder were obtained by ring mill grinding (average diameter 15 μm) and were scanned between 10° and 80° with the Vantec detector. The qualitative analysis was performed with EVA software.

Morphological and microstructural characterization was performed by Zeiss EVO50 Scanning Electron Microscopy (SEM) equipped with an Oxford Inca EDS probe. The slag was moulded in an araldite-based resin, grinded and polished. SEM analyses were carried out in backscattered electrons mode (BSE) in order to identify and check the different phases pointed out by XRD. General and local chemical compositions were measured using an EDS probe.

The slag leaching behaviour was investigated by performing the standard leaching test according to EN 12457-2 (24 h in 10 l/kg