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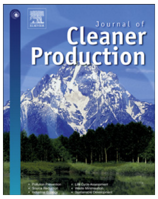

Ladle metallurgy stainless steel slag as a raw material in Ordinary Portland Cement production: a possibility for industrial symbiosis

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ABSTRACT

Ladle metallurgy (LM) slag is generated during the refining process step in stainless steel making. In view of its very fine particle size, due to the transformation of β- to γ-C_2S, and the Cr content, the slag is challenging in terms of handling and disposal and is used in only few applications. The current work explores the utilisation of the LM's fine fraction in Ordinary Portland Cement (OPC) clinker production. Three sets of samples containing LM slag, in 0 wt% (OPC – reference), 6 wt% (OPC6) and 14 wt% (OPC14), were investigated. The sintering temperature was 1450 °C with 40 min soaking time. The clinkers containing LM slag, showed a slight increase in C_3S and a decrease in C_3A and C_4AF. The formation of the C_3S initiated at a lower temperature probably due to the presence of F and C_2S. Longer setting times were found for OPC6 and OPC14. The compressive strength results were found to be comparable at 2 d (22–25 MPa), 7 d (36–38 MPa) and 28 d (44 MPa) of curing, falling into 42.5R CEM I category. The emission of kgCO_2/t of clinker during production, is estimated to decrease at least 12% for OPC14. A processing step for the pre-treatment of the slag is also presented, aiming to reduce the initial Cr content.

1. Introduction

Cement production approaches 3700–4000 Mt/y (U.S. Geology Survey, 2013), corresponding to a substantial CO_2 footprint. Considering the process of cement clinker production, half of the carbon footprint originates from the dissociation of limestone during clinkering, whereas the other half is due to fuel combustion. This accounts for about 8% of global CO_2 emissions according to the latest 2012 report (Olivier et al., 2012). As a consequence, both the industry and academia are exploring strategies to minimise and/or capture CO_2 emissions and a wide portfolio of options appear feasible (Benhelal et al., 2013; Brunke and Blesl, 2014; Gao et al., 2014; Ishak and Hashim, 2014). One of the paths with great potential involves the use of alternative raw materials, preferably Ca-bearing so as to minimise the use of limestone, and the above may become more realistic and sustainable in an industrial symbiosis context (Ammenberg et al., 2014). Examples of industrial symbiosis already exist for decades, the use of ground granulated blast furnace slag and that of fly ash from coal-burning power plants, being two of the most well established. In the paper herein, a new proposal is put forward, aiming to widen the envelope of possibilities.

Stainless steel slags include EAF (Electric Arc Furnace), AOD (Argon Oxygen Decarburization) and LM (Ladle Metallurgy) slags. The last two types of slag are generated during the refining process step in stainless steel making. Stainless steel slag (EAF S – stainless slag) is registered at the European Chemicals Agency (CAS 91722-10-0; Einecs 294-410-9; submission number HQ948325-18) as non-hazardous waste. However, their status in Belgium, Flanders region, is somewhat different. For two specific applications (use in concrete and in asphalt concrete), EAF S slag has the status of raw material instead of waste (Ministrieel besluit, 2012). The quantity of stainless steel produced worldwide in the first half of 2012 accounts to 17.2 Mt (International Stainless Steel Forum). It is estimated that the slag/steel ratio is around 0.33 (t_{slag}/t_{steel}) (Durinck, 2008). Both the AOD and LM generated slags consist of a high content in CaO, SiO_2, MgO but also some Cr_2O_3 and fluorine (F). The crystalline phase composition is mainly C_2S, especially in γ-polymorphic form, with lower levels of merwinite, bredigite, cuspidine and periclase (Kriskova et al., 2012). The major problem with LM slags is the high content in γ-C_2S which is less dense than the other polymorphs of C_2S. This phase causes a

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volume increase of about 12% on cooling, generating a voluminous powder; this phenomenon is known as dusting (Taylor, 1990). An important issue resulting from this transformation is the disposal and downstream utilisation of stainless LM slag.

Both cement and steel industries take action to address their environmental footprint. The former, according to the EU ETS (EU Emissions Trading Scheme), aspire to reduce the overall emissions by at least 20% by 2020 and 50% by 2050, compared to the 1990 levels (European Commission, 2008). With respect to the latter, the amount of steel slag produced in 2010 accounts to approximately 21.8 Mt (The European Slag Association, 2012). From this amount, only 6% was used in cement production, 48% for road construction and the rest was deposited or used for other purposes. The challenge lies in the development of integrated, "zero-waste" flow sheets, which recover both metals and utilise the various residues into building applications.

Considering the above, a push and pull scheme appears possible for the metallurgical and cement industrial sector, where residues from metallurgies could become raw materials for the cement industry. Conceptually, this is an example of industrial symbiosis and has been happening for years, e.g. ground granulated blast furnace slag. The use of other slags however does not appear to be straightforward, as presented below for the case of EAF, AOD and LM slags from stainless steel production.

In an overview with respect to the utilisation of EAF and AOD slags from the stainless steel industry (Huaiwei and Xin, 2011) claim that these slags can be very stable on a long term after a stabilisation/solidification process, being further suitable for utilisation in cement production, road construction, civil engineering work. Moosberg-bustnes (2004) has investigated the properties of AOD slag as a filler in concrete. The results revealed a clear potential, provided some of the negative aspects such as activation (effect on cement hydration) and durability can be overcome. Manso et al. (2006) and Pellegrino et al. (2013), find EAF slag suitable as aggregate in concrete production with better or comparable mechanical properties when compared to a reference sample, if the substitution of the aggregate is lower than 50 wt%. Kriskova et al. (2012) have shown that the hydraulic properties of AOD and LM slag can be enhanced through mechanical activation. More work in this area has in fact demonstrated that both mechanical and alkali activation of LM slag appears to be a promising path for delivering an alternative binder (Kriskova et al., 2014; Muhammad et al., 2014). Maslehuddin et al. (2011) have used EAF dust as replacer of 2 wt% OPC in blended cements, indicating improved mechanical properties and durability in their studies. Xuefeng and Yuhong (1998) and Hilton (1998) have also used stabilized EAF dust as raw material in clinker cement production. To the best of our knowledge, there is no work available regarding the utilisation of LM slag as raw feed material in clinker production.

The envisaged work therefore explores an alternative path which seeks to overcome some of the existing issues of the stainless steel and cement industry. The production of OPC cement clinker with addition of 6 wt% and 14 wt% of the fine fraction of LM slag is investigated. A benchmark sample was also produced for comparison. The central aim was to understand the influence of LM slag in the clinkering process, on the microstructure of clinker, on the mechanical and physical properties of the final cement mortars as well as on the environmental performance of these new cements.

2. Materials and methods

2.1. Characterisation of raw materials

The raw materials used in this study were LM slag fraction below 160 µm (called also "the fine fraction"), limestone, flysch and bauxite residue (red mud). The fine fraction of LM slag amounts to about 73 wt%, and it has been used as received. This was determined by sieving approximately 50 kg of a representative batch of LM slag. To investigate the variation of slag chemistry for different particle sizes, the LM slag was sieved at different fractions and characterised. The chemical analysis (Tables 1 and 2) was performed by X-ray fluorescence (Philips PW 2400), whereas only for fluoride (F) in the case of slag, ion chromatography (ICS-2000 Ion Chromatography System, Dionex) was used. Cr_2O_3 was analysed with inductively coupled plasma optical emission spectrometry (ICP-OES, Varian 720-ES) after selective (≥160 µm, 160 µm–125 µm, 125 µm–80 µm and ≤80 µm) sieving. The lithium metaborate ($LiBO_2$) method was used for sample preparation. For X-ray diffraction analysis (Siemens D500 SC40), the parameters used were 2θ range of 10°–70°, CuKα radiation under 40 kV and 40 mA, 0.02° step size and 4 s step time. The crystalline phases were identified by using Highscore X'pert® software based on the Powder Diffraction files from the International Centre for Diffraction Data (ICDD). Quantitative X-ray diffraction analysis (QXRD) was performed using TOPAS® Academic software (Bruker-AXS) based on normalized Rietveld method (Table 3).

Table 1
Chemical composition of raw materials (in wt%).

Raw materials	LM slag (fine fraction)	Limestone	Flysch	Bauxite residue
CaO	56.4	54.5	5.6	14.6
SiO_2	32.5	0.9	58.3	7.8
MgO	7.5	0.6	2.9	0.2
MnO	0.4	n.d.	n.d.	n.d.
Al_2O_3	1.3	0.4	13.8	20.4
Fe_2O_3	0.4	0.1	5.9	35.4
Na_2O	n.d.	n.d.	1.1	2.0
K_2O	n.d.	0.1	2.5	0.1
SO_3	0.2	0.1	0.1	0.4
Cr_2O_3	0.5	n.d.	n.d.	0.2
TiO_2	0.4	n.d.	n.d.	4.6
F	2.9	n.d.	n.d.	n.d.
LOI	0.0	43.3	9.8	13.0
Total	102.4	99.8	99.8	98.7

LOI: loss on ignition, n.d.: not determined.

2.2. Design and methodology for the synthesis of clinkers

For clinker production all raw materials were individually milled in a centrifugal mill (Retsch ZM100) at a particle size <80 µm. The LM slag was used as it came out of sieving (<160 µm) and there was no need for milling as the d_{50} was below 50 µm. Particle size distribution of LM slag was analysed by laser diffraction (MasterSizer Micro Plus, Malvern). The synthesis of the raw meals was calculated by means of a Microsoft Excel© worksheet based on cement quality indexes. Three types of clinker were prepared, one as a reference (OPC), and two more

Table 2
The chemical composition of different particle sizes of LM slag; main oxides, Cr and F.

Analysis	Fractions	≥160 µm	160–125 µm	125–80 µm	≤80 µm
XRF	CaO	56.5	56.3	56.9	57.7
	SiO_2	29.8	32.4	32.3	31.2
	Al_2O_3	1.6	1.2	1.2	1.3
	Fe_2O_3	1.2	0.4	0.3	0.3
	MgO	9.0	7.4	7.3	7.4
ICP-MS	Cr_2O_3	0.70	0.46	0.44	0.41
Ion chromatography	F	n.d.	2.95	3.22	3.17

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