Optimizing the Potential of BR Slag in Blended Cement

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Abstract

Bauxite residue (BR) has in principle a great potential to be used in the construction industry considering its large availability. However, BR originating from the Bayer process lacks reactivity, i.e., hydraulic/pozzolanic activity in alkaline conditions, which is required in cementitious applications. Therefore, BR is commonly heat treated through either calcination (<1000 °C), (partial) vitrification (1100 - 1300 °C) or smelting combined with iron extraction (1500 - 1700 °C) to form crystalline or amorphous phases that are soluble at neutral or high pH. Smelting of BR is of much interest as it offers the advantage of combining both metal recovery and valorization of the slag as supplementary cementitious material. However, it has been shown that the purity of the metal and the price of the slag is crucial for the financial feasibility of the process. In this work, the potential of the slag for its use in blended cement was investigated and compared to blast furnace slag (BFS), which is considered a high value supplementary cementitious material. A mix of BR (>80 wt.%), SiO_2, CaO and C was treated in an electric-arc furnace (EAF) at 1550 – 1600 °C to form slag (EAFS) and pig iron. The reactivity of the EAFS was found to be significantly higher than BFS in a simulated cementitious environment. Optimization of the mix design showed that a similar 7 and 28 d strength to 100 % Portland cement (PC) could be obtained using only 55 wt.% PC, 30 wt.% EAF slag and 15 wt.% limestone. The latter shows that EAFS has large potential as supplementary cementitious material and should be considered for further investigation.

Keywords: Bauxite residue, Slag, Glass, Reactivity, Blended cement.

1. Introduction

Supplementary cementitious materials (SCMs) are crucial to reduce the amount of Portland cement (PC) for economic and environmental reasons. These materials are blended with PC and are classified as either pozzolanic (react with $Ca(OH)_2$ and water) or latent hydraulic (reacting with water) for the formation of cementitious hydrates and have the benefit of increasing the late age strength development, durability and reduction in thermal cracking [1]. Blast furnace slag (BFS), fly ashes and limestone are the SCMs that are already widely used [2]. However, due to the climate transition, processes for the production of BFS and fly ash will change and reduce significantly its availability [3]. Surprisingly, this is in contrast with the enormous pressure to decarbonize the cement industry, which actually requires a larger amount of SCMs [3–5]. Bauxite residue (BR) could play a vital role as SCM due to it large locally available volumes. However, currently BR originating from the Bayer process is only used as Fe and Al source in the production of PC (< 5 wt.%) and is not considered as SCM [6]. Major reasons are the alkaline nature, being classified as (hazardous) waste, small particle size, and from a technical point of view its low reactivity (hydraulic/pozzolanic activity), e.g., in a cementitious environment [7].

Bayer already mentioned in his original process patent the potential for iron recovery from bauxite residue [8]. Extraction of iron would require a carbothermic reduction for the production of pig iron (1500 – 1700 °C) or a low temperature reduction for the formation of magnetite through alkali roasting [9] or H_2 reduction [10], which can be later converted to pig iron. It has been shown that direct carbothermic reduction of BR with an electric arc furnace (EAF) is feasible at lab [11] and pilot scale [12]. Because an EAF requires a large amount of energy, the valorization of the extracted slag is crucial to make the process profitable [12]. However, the slag was mainly investigated for Al, Ti or rare earth recovery [11,13,14] and as the slag can be granulated, resulting in an fully amorphous material, it is actually of much interest as cement replacement in concrete and mortars. If a precursor with similar reactivity to BFS could be obtained, the potential is enormous as BFS is considered a high value SCM nowadays with similar price as PC with demand expected to increase in the near future.

This work investigated the treatment of BR in an EAF, with the focus of optimizing the reactivity of the slag phase. The optimal mix of fluxes, reported in Giels et al. [15] for vitrification of BR, was used as it has been shown to result in a reactive amorphous phase. Only partial reduction of Fe was targeted as Fe^{2+} has a positive effect on the depolymerization degree of the glass [16,17], which can increase the reactivity as SCM. This way of thinking deviates from traditional concepts by minimizing the addition of Ca or Mg through substitution with Fe. This can decrease the CO_2 footprint of the process considerably as Ca and Mg are commonly added as carbonates. The reactivity of the EAF slag (EAFS) was afterwards evaluated using the rapid, relevant and reliable (R^3) reactivity test method, which allows to measure the reaction degree of materials in a simulated cementitious environment. Using the data of the R^3 test, the mix design of a blended cement was optimized with respect to compressive and flexural strength. Finally, the reactivity of the EAF slag was compared to BFS and its potential discussed.

2. Methodology

2.1 Characterization and Processing

BR slurry originating from the Tulcea plant was filtrated and the solid BR was dried at 300 °C for 24 h and milled below 500 µm using a rotary disk mill. After drying, the LOI was measured through thermogravimetric analysis (TGA) using a TA SDT Q600 up to 1000 °C with a heating rate of 10°C/min under nitrogen atmosphere. The chemical analysis of the residues was performed using a Bruker S8 Tiger Wavelength Dispersive X-ray fluorescence spectrometer (WDXRF) following a lithium borate and lithium bromide fusion with 10 wt.% BR sample at 1050 °C to form fusion beads.

BR was mixed with CaO and SiO_2 in the weight ratio BR:CaO:SiO_2:C as 100:10:10:3.6 g. The amount of CaO and SiO_2 was based on the work of Giels et al. [15]. Carbon was fluxed under the stoichiometric ratio to keep as much as Fe^{2+} in the slag. Smelting was conducted in a refractory lined 100 kVA DC EAF, within a graphite crucible (Figure 1A). Experiments were triplicated and the material was heated till 1550-1600 °C and the melt was held for 31, 20 and 11 min, respectively. Afterwards, the slag was poured in water as shown in Figure 1B and was dried at 105 ± 5 °C for 24 h. Remaining metallic iron was removed through dry magnetic separation using a Nd magnet. Metallic iron at the bottom of the crucible was solidified in the crucible.

5. References

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