Use of Bauxite Residue Slurry as Single Activator in a Hybrid Binder System

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Abstract



The use of bauxite residue (BR) slurry as an activator in a hybrid system is explored in this paper. The strong alkaline nature of the slurry, which is considered as a major barrier for most valorization routes, is beneficial in this approach, where it is used as single source of water and alkalis to activate a hybrid cementitious precursor blend. Moreover, the fineness of the solid fraction of the slurry is expected to improve the particle packing, enabling reduction of the water content and thus of the final system porosity. Experimentally, ≥ 33 wt% of BR slurry, was homogenized and subsequently mixed with either non-ferrous metallurgy slag or ground granulated blast furnace slag (GGBFS), ≤ 10 wt% of ordinary Portland cement (OPC) and minor additives. The raw materials were mixed and the resulting pastes were cured at ambient conditions. Satisfactory mechanical properties were reached, exceeding 35 MPa already after 3 d of curing at room temperature. The results are promising, also considering that the slag mix can be potentially replaced by a thermally processed BR, thus leading to a maximization of total BR content in the newly formed binder.

Keywords: Alkali/OPC activation, bauxite residue, red mud, non-ferrous metallurgy slag, GGBFS, mortar, mix design.

1. Introduction

Bauxite residue (BR) is the alkaline residue which is generated in a high volume, exceeding 150 Mt/year worldwide, during the Bayer process for the production of alumina [1]. Negative public perception, costs and scarcity of disposal areas, are some of the main drivers for research on the reuse of BR as a resource for novel materials. Next to the recovery of base metals and rare earth elements from BR [2], the production of construction materials seems to be a reasonable way to incorporate large volumes of BR [3]. Various literature is published on using BR in geopolymers or inorganic polymer, a binder which is generally formed by the alkali activation of an aluminosilicate precursor [4]. Most studies dealing with the use of BR in geopolymers, suggest a combination of BR with other reactive raw materials, such as fly ash [5] or metakaolin [6]. In most of these cases dried BR was used which mainly acted as a fine filler material merely contributing physically to the strength and microstructure. A significant decrease in these properties is reported when large volumes of BR are used. In order to activate BR so that it participates in the reactions for the inorganic polymers, different treatments, such as a chemical and thermal transformation [7] have proven to be a suitable alternative. Another approach was pursued by Krivenko et al [8] who prepared various alkaline cements including high fractions of BR with ground granulated blast furnace slag (GGBFS) and cement in combination with Na₂CO₃, sodium silicate or Na₂O·SiO₂·5H₂O as alkaline components. Promising compressive strengths of 60 MPa were reached for mortar samples incorporating 60 wt% BR, 30 wt% GGBFS, 10 wt% OPC, activated using sodium silicate solution according to a liquid to solid ratio of 0.4. Several pressed concrete samples were prepared and up to 90 wt% of BR was incorporated in a mix with 9.2 wt% of GGBFS, 1.2 wt% of alkaline reagents with an addition of 16 wt% of water over the total mix. A compressive strength of 4 MPa was achieved after 28 days, while higher GGBFS contents lead to higher strengths. In another approach, spent Bayer liquor (= after precipitation of gibbsite) consisting mainly of NaOH and dissolved Na-aluminates is used as alkaline activator of fly ash [9]. Satisfying compressive strength of about 42 MPa was reached after 28 days. The liquid fraction of BR slurry (as it leaves the Bayer process), which still consists of a considerable amount of alkaline liquid, is believed to act as an activator for the precursor materials.

In this paper a novel hybrid binder system is studied incorporating waste streams from different industries in a synergistic way. A bauxite residue slurry in an "as-produced" state from the Bayer process is used as an alkaline activator for a GGBFS or a non-ferrous metallurgical slag (NFMS),. NaOH additions and their influence on the total alkalinity and reactivity of the systems are investigated. OPC was added to accelerate the hydration by a rapid formation of hydration products in an alkaline environment. These hydration products potentially act as nucleation sites for the reaction products formed with the dissolved slag species and thus cause a faster strength development [8]. Basanite also proved to be beneficial for the strength development [10] whereas the workability was improved by adding superplasticizer.

2. Material and Methods

2.1. Raw Materials

A synthetic iron-silicate slag (NFMS) was produced by melting iron ore, quartz sand, limestone and chamotte at a temperature of 1300 °C followed by water quenching in order to obtain a glass with a chemistry comparable to non-ferrous metallurgical slags, such as copper, lead, zinc and ferro-nickel slag [11-13]. A commercial ground granulated blast furnace slag (GGBFS) from Orcem and a CEM-I 52.5N cement from Vicat were used in this study as additions. Bauxite residue (BR) slurry was supplied from RUSAL Aughinish (Ireland). The solid content of the slurry was 59 wt%.

The chemical composition of all raw materials was analyzed using X-ray fluorescence and X-ray diffraction using the Rietveld method for the quantification of the data. Physical properties, such as specific surface area, particle size distribution and density were determined using a Blaine apparatus, a laser diffraction particle size analyzer and a helium pycnometer. The pH and the chemical composition of the liquid fraction of BR, obtained after filtering using 0.45 μ m filter paper, was determined using a pH meter and an ICP-OES, respectively.

2.2 **Preparation of Pastes and Mortars**

Pastes of different compositions were prepared per 500 g in a 3 L Hobart mixer, first mixed for 1 minute at speed 1 and then 4 minutes at speed 2. 1000 kg/m³ of homogenized BR slurry is used as a base material and mixed with 1400 kg/m³ of GGBFS or 2000 kg/m³ of NFMS in order to obtain a similar rheological behavior of the different mixtures. More NFMS had to be added due to the higher density and broader particle size distribution compared to the GGBFS. Considering the liquid fraction of the BR slurry, a liquid to slag ratio of 0.205 for the NFMS samples and 0.293 for the GGBFS samples was used. When cement is added, 200 kg/m³ of the slag is replaced by CEM-I 52.5N. In case of extra alkali activation, 20 kg/m³ of NaOH pellets (> 99 % purity, Sigma Aldrich) were added to the powder mix. 20 to 48 kg/m³ of non-commercial superplasticizer was used to keep the rheological properties of the slurries constant. The amount of superplasticizer was adapted for each mix to obtain a comparable workability. 12 kg/m³ of bassanite (CaSO₄ · 0.5 H₂O) from Knauf was added in all mixes, as this has proven to be beneficial for the strength development in NaOH/OPC activated slags [10]. The compositions in kg/m³ of the eight mixes prepared in this study are given in Table 1.

Mechanical strengths, of the pastes, are obtained from the acoustic reflection described by Lootens [14]. Initial setting and final setting times, respectively, are the moments when the strengths are 0.1 MPa and 1 MPa. Semi adiabatic calorimetry is used to obtain the heat evolution during the hardening phase of 400 g of paste. Mortars were prepared by mixing 1 kg of paste with 1 kg of masonry quartz sand with a maximum grain size of 1 mm for 4 minutes in a Hobart mixer and casted in 4 x 4 x 16 cm³ mortar prisms. The compressive strength at 28 days was measured using an Instron 5985 applying a crosshead speed of 2 mm/min.



Figure 6. Early age adiabatic calorimetry results of samples with NFMS in mW per gram of paste. The cumulative heat release after 72 h in J per gram paste (H 72) is given in between brackets.

The calorimetry data of NFMS-OPC-Na revealed the OPC hydration and slag reaction peaks after 5 and 21 h, respectively. Most of the strength is gained during the slag reaction peak as shown in Figure 3. Due the higher reactivity of GGBFS, the OPC and slag reaction peak in GGBFS-OPC-Na are nearly merged into one peak appearing after 5 h. Although the intensity of the peak (9 mW/g) is much higher than the NFMS-OPC-Na peaks (4 and 2 mW/g) the strength of both samples is similar. This is due to the fact that the NFMS-OPC-Na peaks are much broader, and thus show a longer but slower reaction than the GGBFS-OPC-Na peak resulting in a comparable cumulative heat release after 72 h of respectively 200 and 260 J/g of paste.

4. Conclusion

When combining NaOH activation with OPC, mortars from slags can be made with 500 kg/m³ of fresh BR slurry. Mortars with GGBFS deliver the highest strength at 28 days, but also with synthetic non-ferrous metallurgical slag a strength of 67 MPa was achieved with a self levelling mortar. NFMS slag can easily be replaced by thermally processed BR as proposed by Hertel et al. [7]. In this approach, mortars can be made with 500 kg/m³ of BR slurry combined with 1000 kg/m³ of ground granulated BR. When also the fine aggregates would be replaced by treated but unmilled BR, more than 1250 kg/m³ additional BR can be incorporated. The best mortars in this study were activated with 100 kg/m³ OPC and 10 kg/m³ of NaOH, which is a low-cost and environmentally friendly way to valorize BR and non-ferrous metallurgical slags. Further research is focused on optimizing the activation, incorporating higher volumes of fresh slurry and evaluating the durability of such mortars.

5. References

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