

Characterization of Low-CO₂ Ferrite-Belite Cements Incorporating High Volumes of Bauxite Residue as a Raw Material

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Abstract

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Bauxite residue (BR) is the main waste of the alumina sector. It is produced at rates of 170 million tons per year, out of which only 4 million tonnes are used in other industrial processes. Currently, less than 3 % is used as a raw material in Portland cement production, mostly due to limitations imposed by the clinker chemistry itself. Hence, research is being carried out to develop Fe-rich cements, and by doing so, incorporate higher levels of BR. In the work herein, a low-CO₂ ferrite-belite cement clinker was developed by incorporating more than 35 wt% BR as a raw material. Two sets of clinker mixtures were designed using thermodynamic modelling, and limestone, kaolin, and BR as raw materials. A low-BR clinker (38 wt% BR) and a high-BR clinker (50 wt% BR) were synthesized at 1250-1260°C, followed by rapid cooling. The results obtained from quantitative X-ray diffraction and electron probe microanalysis indicated that the low-BR content clinker had more Ca₂(Al_xFe_{1-x})₂O₅ and C₂S (reactive phases) with some minor gehlenite, whereas a higher BR content increased the content of gehlenite and perovskite. Apart from the particular phase assemblage and the amount of each phase formed, the amount of BR in the clinker's raw meal also affects the particular solid solutions formed. This is due to the variability in the Al/Fe ratio in the Ca₂(Al_xFe_{1-x})₂O₅ phase influencing the reactivity, but also due to the presence of Na⁺, transition metals such as Fe³⁺ and Ti²⁺ in the Ca₂(Al_xFe_{1-x})₂O₅ as well as C₂S reactive phases, being able to stabilize the reactive polymorphic phases. In addition, an interstitial face such as reactive mayenite is formed at lower temperatures due to rapid cooling. Moreover, it is also expected that the solidification path will play a role, and that higher cooling rates will most likely lead to enhanced overall hydraulic activity.

Keywords: Bauxite residue, Clinker, Ferrite-belite cement, Rapid cooling, Reactivity, Stabilize

1. Introduction

The utilization of BR is roughly about 10 % in China and 2-3% globally [1]. The use of bauxite residue in the manufacturing of construction materials is a path of considerable interest for the alumina producer since it may absorb vast amounts of waste and provide a new revenue stream. Few alumina refineries in the world such as Hindalco in India, Mykolaiv in Ukraine and Mytilineos in Greece are supplying unmodified-BR as a raw material to the cement plant for Portland cement production (OPC). Hindalco achieved an 100% utilization of bauxite residue from three of its refineries by sending it to more than 40 cement plants in India, achieving a sale of 2 million tonnes of its BR production [2]. It is estimated that a total of 3 million tonnes of BR are used in the production of clinker worldwide. However, the use of BR as a raw material component in the OPC production varied between 0.8-3.5 wt.% [3]. Low-valorization values of BR has encouraged various organizations such as the International Alumina Institute to reach the strategic target goal of 20% valorization of BR by 2025.

Currently in the laboratory scale, more than 20% of BR has been successfully valorized in the production of cements. In one of the research works, the amount of BR that has been valorized

accounted up to 23 wt.% in the raw meal production of OPC [4]. In this work, dealkalinized BR obtained from the sintering process was used instead of the Bayer process. The dealkalinized BR accounted for higher content of CaO and SiO₂, thus making it suitable for large quantities allocated in the raw meal of OPC. BR has also found its ways as a raw material in the production of inorganic polymers. In the recent works of Giels et al. [5], a compressive strength of 131MPa was achieved in 28 days by incorporating 81 wt% of BR. The BR was thermally modified at 1200–1300 °C with minor additions of C, CaO and SiO₂ to develop a reactive precursor. Thus, opening the possibility of upscaling the work. In the production of calcium sulfo-ferroaluminate cements (CSA-F), the maximum amount of BR valorized in the clinker production was 65 wt.% [6], nevertheless the highest 2 days compressive strength achieved was 28.5 MPa which is comparatively lower than the market produced standard CSA cements but still better than OPC 52.5N. In the works of Hertel et al. [7], a 35.5 wt% BR as a raw meal component of CSA cement achieved a 2d compressive strength of 43MPa almost similar to the market produced CSA cements. In the production of ferrite-belite cements, incorporation high volumes of BR > 30 wt % to achieve a considerable compressive strength is still in progress. Currently, Montoya et al. [8] only achieved a compressive strength of 10 MPa after 28 days. Hence to understand the poor compressive strength results, it is important to characterize the clinker phase composition in depth.

To achieve a clinker replacement factor of 30 wt% and a strength activity index above 75%, the EU-funded project - ReActiv (Industrial Residue Activation for Sustainable Cement Production) was implemented to achieve this milestone. In this study, two types of clinkers were produced from limestone (LS), kaolin (K) and bauxite residue (BR), with clinker replacement of 38 wt% and 50 wt% with BR at a chosen clinkering temperature range between 1250-1260°C followed by rapid cooling respectively [9]. The first step of evaluating these clinkers was to characterize them. The mineralogy of the produced clinkers was obtained by X-ray diffraction (XRD). In addition, the X-ray fluorescence (XRF), scanning electron microscope (SEM-EDX) and electron probe micro-analysis (EPMA) was used for characterization. The physical characterization of the clinker was accomplished by measuring the density, blaine fineness and the particle size distribution.

2. Materials and Methods

2.1 Production of Clinker

The raw materials for the ferrite-belite (FB) clinker were limestone (Carmeuse), bauxite residue (Mytilineos) and Kaolin (Imerys). Two mixtures of the FB cements were chosen: (1) LS57BR38CL5 where, 57 wt% of LS was mixed with 38 wt% BR and 5 wt% K and (2) LS45BR50CL5 where, 45 wt% of LS was mixed with 50 wt% BR and 5 wt% K.

Figure 1 represents the schematic representation of the process flow for the preparation of the selected mixtures, based on the modification of the work of Montoya et al. [8]. The weighed raw materials were mixed with ethanol and (a) zirconia grinding elements for 12 hr in an overhead shaker (Turbula WAB T2F) to obtain a homogeneous blend. (b) The mixtures were dried using rotovap (Heidolph 4010) to remove the ethanol. (c) The dried mixture for each selected composition mixed with 15% deionized water in a Hobart mixer to form ~ 2cm spherical pellets by hand. To remove the excess water content, the pellets were dried at 110°± 5 °C for 24h using a drying oven (Binder ED 260).

Figure 2 represents the schematic representation of the process flow for clinker production of the selected mixture. The pellets were placed in an (a) alumina crucible and (b) introduced in a bottom-loading furnace (AGNI ELT 160-02) to reach the target temperature of 1260°C at a rate

4. Conclusion

Based on the characterization of the FB cement clinker, the gehlenite content increases with higher BR content in raw meal of FB clinkers. Moreover, high gehlenite content also diminishes the mayenite that formed at low temperatures (at temperatures < 1300°C). Hence in the high-BR clinker, the mayenite formation was suppressed due to increased gehlenite content in comparison to low-BR clinker. Furthermore, the content of belite in FB-clinkers were higher than the OPC and this is due to the absence of melt formation when sintering at lower temperatures. The chemical composition of the clinker phases revealed that most of the reactive phases such as belite and ferrites were stabilized by metal ions due to rapid cooling of the clinkers. Moreover, the BR content in the raw meal influenced the A/F ratio in the ferrite phase i.e., higher the BR content, lower the A/F ratio and thus reduced reactivity of the ferrite phase. This change in the A/F stoichiometry and the stabilization of the phases can improve the reaction kinetics during hydration of the cement. However, new strategies need to be devised in order to control the content of gehlenite in these clinkers, which are unreactive and do not contribute to the strength of the cement. Thus, raw materials that contain very high alumina and minor amounts of silica can be used with BR to formulate such clinkers.

5. References

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