

Low-Carbon Footprint Cements Incorporating High Volumes of Bauxite Residue

David Ariño-Montoya¹, Marios Katsiotis², Giannis Giannakopoulos³,
Remus Ion Iacobescu⁴ and Yiannis Pontikes⁵

2. Group Research & Innovation Manager

3. Head of Quality Support

TITAN Cement Company S.A., Group Research, Development & Quality, Elefsina, Greece

1. PhD student

4. Senior Researcher

5. Professor

KU Leuven, Department of Materials Engineering, Leuven, Belgium

Corresponding author: david.arinomontoya@kuleuven.be

Abstract



The use of large quantities of bauxite residue (BR) to produce two types of low-carbon cement (ferrobelitic and aluminoferrite) was studied in this project. These types of cement are of great interest for the industry because of the lower energy demand and CO₂ footprint as well as the higher possible incorporation of by-products, compared to ordinary Portland cement (OPC). To produce the clinkers, BR was combined with limestone, clays and reagent chemicals in order to achieve a suitable raw meal chemistry. The goal was to keep BR addition constant at 50 wt% in all mixtures. The mineralogical phase formation at different burning temperatures was estimated by means of thermodynamic calculations. Clinkers were produced at different temperatures, 1200, 1250 and 1300 °C, followed by rapid cooling by air. The obtained clinkers were mineralogically quantified by the Rietveld method using X-Ray diffraction analysis. Additionally, microstructural characterisation was performed using SEM-EDS. Hydration kinetics were also studied by isothermal calorimetry. The results show that BR quantities as high as 50 wt% can be used to produce reactive, and environmental friendly cement clinkers.

Keywords: Bauxite residue, red mud, cement clinkers, mineralogy, bauxite residue valorisation.

1. Introduction

Bauxite residue is the by-product obtained after alumina extraction in the Bayer process. It is known that for each tonne of alumina, between 0.4 and 2 tonnes of BR are generated [1]. Most BR is not used in any industrial process and it is subsequently stored. It has been estimated that more than 3 thousand million tonnes of BR are currently stockpiled [2]. This potential source of raw materials could be an opportunity for the fabrication of construction materials. Different approaches have been attempted in order to achieve this goal. Typically, the materials that are produced are ceramics [3], cements [4] and more recently, inorganic polymers [5].

From the candidate materials that could incorporate BR, cement stands out in view of the massive volumes produced. In 2016, the worldwide production was estimated to be over 4 thousand million tonnes [6]. This is associated with a substantial CO₂ burden, which fuels research into new and alternative types of cements. This research activity is needed and thus supported by the European Union (EU) green-house gas reduction policies. These collective efforts aspire to lead to a reduction of CO₂ emissions by 20% by 2020 and 80% by 2050. The use of BR in the production of low-carbon cements can contribute to the realisation of such goals.

With regards to BR, its use in ordinary Portland cement (OPC) production is already happening industrially in selected plants worldwide; in this case, BR is used as an alternative source of Fe_2O_3 and, depending on the origin, Al_2O_3 [7,8]. Going beyond OPC, research effort has been already put in the development of iron-rich cements with BR [9,10]. For example, Singh et al. produced aluminoferrite, ferrobelite and ye'elimite-ferrite clinker [11,12]. In their work, they focused on clinker composition and firing regime, finding that the resulting mechanical properties depended greatly on the raw meal originally used. In another work, Kavas et al. [13] worked for the production of ferrobeltic clinker with activated belite. In order to achieve this, a combination of BR and boron wastes was used. The use of boron stabilizes belite (Ca_2SiO_4) in the α' polymorph, which has higher reactivity with water, and as a result improves the early mechanical properties.

In the work herein, the aim was to utilize high amounts of BR (50 wt%) in clinker cement production. Focus is placed on the interplay of iron with the other elements in the clinker, having as an ultimate goal to develop high-iron containing clinkers with satisfactory performance and low carbon footprint. The increased presence of iron is expected to result in the formation of increased brownmillerite content, which to the best of our knowledge, hydrates poorly compared to the main constituents of conventional clinker, namely alite (Ca_3SiO_5) and belite. This reactivity will be enhanced by additives in a follow-up work.

2. Experimental Methods

2.1. Raw Material Characterisation

For the synthesis of the clinkers, the following materials were used: filter-pressed BR cake provided by Aluminium of Greece (AoG); limestone (cLS) and clay (Cl) provided by TITAN Cement Company S.A.; reagent grade alumina (Al_2O_3 – 99.99% purity) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ – 99.0% purity) were acquired by Sigma-Aldrich. The materials were dried for 48 hours at 105 ± 5 °C and ground in a ball mill to particle size below 250 μm . The chemical composition of the raw materials was determined by quantitative X-ray fluorescence (XRF), using a Bruker S8 Tiger on fused beads.

2.2. Thermodynamic Calculations

Thermodynamic calculations were performed by FactSage 7.0 [14] with the databases FactPS (FACT pure substances database), FToxid (oxide database for slags, glasses, ceramics, refractories and FSstel (steel database)). The objective of the thermodynamic calculations was to estimate the amount of phases formed at different clinkering temperatures following cooling down. To determine the formation of phases upon solidification, the Scheil-Gulliver model was used.

2.3. Clinker Production

According to the thermodynamic calculations, two promising clinkers were selected. The first one, aluminoferritic favouring the synthesis of $\text{Ca}_2\text{Al}_x\text{Fe}_{2-x}\text{O}_5$ and another one ferrobeltic, targeting the formation of $\text{Ca}_2\text{Al}_x\text{Fe}_{2-x}\text{O}_5 - \text{Ca}_2\text{SiO}_4$. The selected materials were mixed together for 30 min in a Turbula mixer T2C (WAB). Following this, the dry materials were mixed with approximately 10 wt% deionized water to form ~ 2 cm spheres; prior to clinkerization, the spheres were dried for 24 h at 105 ± 5 °C. For clinker production, the spheres were placed in platinum crucibles and introduced in a preheated furnace for 30 min at 800 °C; following, the target temperature (1200, 1250 and 1300 °C) was reached by heating at 10 °C/min and held for 30 min. The resulting clinker was then removed from the furnace and was immediately cooled

optimisation tools will be employed, aiming to deliver high performance BR-rich cements for certain applications.

5. Acknowledgements

The research leading to these results has received funding from the European Community's Horizon 2020 Programme ([H2020/2014-2019]) under Grant Agreement no. 636876 (MSCA-ETN REDMUD). This publication reflects only the authors' view, exempting the Community from any liability. Project website: <http://www.etn.redmud.org>. The authors wish to thank Professor Margarita Beazi-Katsioti from NTUA for support with the preparation of clinker specimens.

6. References

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