POZZOLANIC ACTIVITY OF THERMALLY TREATED BAUXITE RESIDUE IN BLENDS WITH ORDINARY PORTLAND CEMENT

Tobias HERTEL, Silviana ONISEI, Pithchai Pandian SIVAKUMAR, Yiannis PONTIKES

Department of Materials Engineering, KU Leuven, 3001 Heverlee, Belgium

tobias.hertel@kuleuven.be, silviana.onisei@kuleuven.be, pithchaipandian.sivakumar@student.kuleuven.be, yiannis.pontikes@kuleuven.be

Introduction

Bauxite residue (BR), the digestion residue of the alumina production, has found several applications, for instance, in ceramics, metals' recovery or cements.[1-3] Next to the use as part of the raw meal for clinker production or as hydraulic component, the use as pozzolanic material has been studied by several research groups. Ribeiro *et al.*[4] replaced 50 wt% ordinary Portland cement (OPC) by BR in mortars and achieved with these a compressive strength of 12.75 MPa (64% of OPC reference sample). Pera *et al.*[5] prepared mortars with up to 30 wt% replacement of OPC by calcined BR. It was demonstrated that the activated BR shows pozzolanic activity. As an example, 51 MPa were reached for a mix of 70 wt% OPC and 30 wt% BR (calcined at 650°C) after 28d (reference sample 66 MPa). A promising work was patented by Votorantim Cimentos and Companhia Brasileira De Alumínio[6] who modified BR by adding calcia and silica followed by firing, preferably above 1250°C, in order to generate a BR-based reactive pozzolana. Up to 30 wt% of the processed material was used in blends with OPC, with strengths exceeding the required 28 d-strength of 32 MPa (according to Brazilian standards). The contribution of pozzolanas to strength development is due to the formation of additional C-S-H phase, formed by the release of portlandite ($Ca(OH)_2$) from cement hydration and the reaction with reactive silicate species of the pozzolana. Dissolved aluminium species can react additionally with portlandite forming, for instance, calcium aluminate hydrates.[7] BR can contain a minor quantity of total silica content, most often <15 wt%. Most of the crystalline silicates present in BR are found to be not prone to dissolution in the alkaline environment as set by the cement hydration pore solution, which limit the use of BR as a pozzolanic material. Additionally, durability aspects and environmental considerations, such as leaching of heavy metals (*e.g.* Cr, V), are often not covered in the studies of BR-based pozzolanas. In this study, a process is suggested to modify BR in mix with additions of C and SiO_2 at high temperature in order to form on the one hand stable crystalline phases, such as spinels, which become host phases for heavy metals like V and Cr[8], and on the other hand promote the formation of a silica-rich amorphous phase. The resulting material is mixed with OPC and potentially reacts with the cement reaction product portlandite to form C-S-H phase. The modification was carried out based on the findings in a

previous study.[9] The potential pozzolanic activity of the treated material is investigated in comparison with an established pozzolanic material, in this case class C fly ash (FA).

Experimental Methods

The chemical composition of OPC and FA was analysed using XRF. For both, the specific surface area (SSA) was determined according to EN 196-6. BR was dried before its characterisation using XRD and XRF. Based on thermodynamic calculations (with the aim to maximise the amount of formed liquid phase at 1200°C; described more in detail in a previous study[10]), a blend of BR (88.6 wt%), graphite (1.4 wt%) and silica (10 wt%) was mixed before further processing. The sample was heated up at 5°C/min till 1200°C, followed by an isothermal step of 1 h. An alumina crucible was used which was closed with an iron lid containing a gas inlet and outlet in order to maintain an inert atmosphere by flushing N_2 and to release forming gases. After the isothermal step, samples were water-quenched in order to transform the forming melt phase into a vitrified fraction. The obtained precursor was analysed with XRD, EPMA and the SSA was determined according to the Blaine method EN 196-6. Mortar samples (dimensions 4 x 4 x 16 cm^3) were prepared according to EN 196-1 by blending the precursor with OPC, standard sand and water in a water to solid (w/s) ratio of 0.5. Reference mortars of conventional OPC CEM I 52.5 and OPC in mix with FA were prepared to compare the results of the modified BR containing mortars (Table 1). The samples were cured according to EN 196-1.

Table 1: Investigated mortar samples

Sample	OPC (wt%)	FA (wt%)	BRCS10 (wt%)	w/s
Reference OPC	100	-	-	0.5
FA	60	40	-	0.5
BRCS10	60	-	40	0.5

Uni-axial compressive strength (load cell 250 kN; crosshead speed 2 mm/min) of the prepared mortars (3 specimens for each mortar) was tested in order to evaluate the contribution of the modified precursor mortar to the strength development.

Results and Discussion

The dried BR in this study is iron-rich (Fe_2O_3: 47 wt%), still containing a substantial amount of alumina (23 wt%) as well as calcia (9 wt%) and silica (9 wt%), among other components such as TiO_2 and Na_2O. Hematite, diaspore, katoite and cancrinite are the main mineral phases found. Minor components comprise gibbsite, goethite, calcite, boehmite and rutile. A detailed quantification is listed elsewhere.[10] The modified BR contains 50 wt% amorphous fraction besides Fe-rich spinel solid solutions and a minor fraction of metallic Fe. Results of EPMA analysis verified that minor heavy metal components such as Cr and V are encapsulated in spinels, which can be interpreted as

promising with respect to leaching. The SSA was 6100 ± 300 cm^2/g. The OPC is a CEM I (SSA: 5400 ± 270 cm^2/g) and the FA (SSA: 6000 ± 300 cm^2/g) is class C and thus expected to show pozzolanic activity[11] (Table 2).

Table 2: Normalised XRF data of OPC and FA

Component in wt%	CaO	SiO_2	Al_2O_3	SO_3	Fe_2O_3	MgO	Other
OPC	63	21	5	4	4	2	<3
FA	17	40	18	6	12	3	<4

The compressive strength of the OPC mortar exceeded the characteristic 28d minimum strength of 52.5 MPa[7], while the FA mortar is characterised by a decrease in strength (Figure 1). Nevertheless, 78% of the strength with respect to the reference sample was reached, which proves the pozzolanic activity of the used FA. Concerning the BRCS10 sample a loss of 45% in strength was noted after 28d of hydration, which suggests that the modified precursor only acts as an inert filler material and does not contribute to any additional strength development.

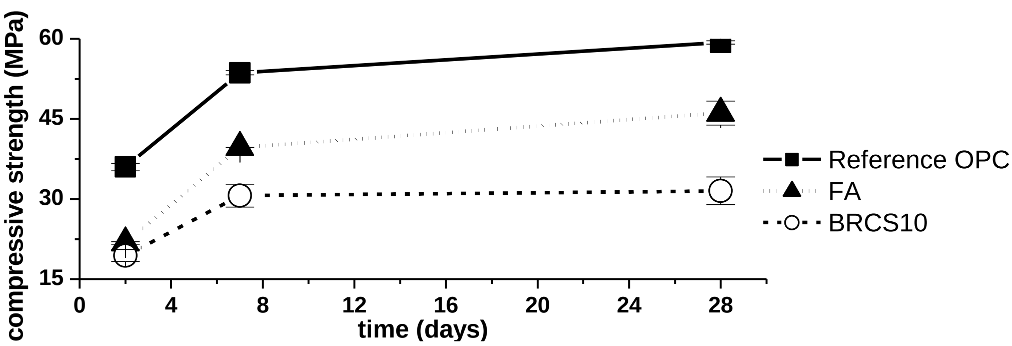

Figure 1: Compressive strength of tested mortar samples, w/s 0.5

A possible explanation for the results, is that the amount of amorphous phase is, compared to FA, either too low or its chemical composition is not suitable to promote pozzolanic reactions with the formed portlandite. A combination of both factors is also conceivable.

Conclusions

The use of other than OPC hydraulic or pozzolanic materials is a possible way to save energy and reduce the CO_2 emissions in the cement industry. In this regard, BR is a potential candidate and its large-scale use can contribute to a decrease of the global inventory. An attempt was carried out herein to transform BR in such a pozzolanic material. Based on the obtained results, it was shown that the synthesised material was not suitable as a pozzolanic material for OPC. Further investigations are needed with respect to alternative modifications and firing conditions (potentially the use of suitable fluxes) to obtain more reactive amorphous fraction. An optimisation of the mortar formulation is also planned to investigate its influence on the strength development. Moreover, a critical evaluation of such a chemical and thermal

modification of BR has to be carried out in order to assess the environmental impact as well as the economic feasibility.

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http://www.etn.redmud.org.

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