

Cementitious Activity Evaluation of Bauxite Residue and Fly ash combination on Portland Blended Cement

Marcelo Montini¹, Xuerun Li², José A. Rodrigues³, Rafael G. Pileggi⁴
and Karen Scrivener²

1. Chemical Consultant, Technology Area, Hydro, Belém, Brazil

2. Swiss Federal Institute of Technology of Lausanne (EPFL)

3. Federal University of São Carlos (UFSCar)

4. São Paulo University (USP)

Corresponding author: marcelo.montini@hydro.com

Abstract



The aluminum industry is responsible for the management of a massive volume of bauxite residue (BR) on a global scale (120 million tons of generation and 3 billion tons of inventory). However, less than 4 % of BR has been applied industrially since its high alkalinity is harmful to several applications. The most promising way of employing the BR is to utilize it as supplementary cementitious material (SCM) in cement. The objective of the present study is to investigate the chemical activation of fly ash (FA) by bauxite residue, aiming to maximizing the incorporation of BR to SCM. Isothermal conduction calorimetry and compressive strength were carried out to investigate the six Portland blended cements containing different ratio of BR/FA mixture (%w / w): 0/30, 3/27, 7/23, 15/15, 23/7 and 30/0. The results showed that BR may be incorporated in the maximum limit of 7% in the blended cement. At this BR dosage, the early strength of the blended cement was enhanced and the long term strength did not decrease considerably. The reaction of fly ash was significantly promoted when BR was added. On the other hand, high BR addition showed a higher compressive strength at 1 day, but suffered from a considerable reduction on long-term properties.

Keywords: Bauxite Residue, Supplementary Cementitious Materials, Portland Cement.

1. Introduction

The aluminum industry is responsible for the management of a massive volume of bauxite residue on a global scale (120 million tons of generation and 3 billions tons of inventory) [1]. However, less than 4 % of BR has been reused industrially as its high alkalinity is harmful for many applications. The most potential way of using the BR is to use it as supplementary cementitious materials in cement [2].

The reuse of bauxite residue as partial substitute of Portland blended cement in mortar and concrete formulations has been studied by the Laboratory of Microstructure and Eco-Efficiency in São Paulo University. The researchers have proven that it is technically feasible to replace up to 20% of cement by bauxite residue, resulting in porosity reduction, increase of compressive strength and decrease of air permeability [3] [4]. However, the lack of evidence concerning the behaviour of alkalis (mainly sodium) from bauxite residue in the hardened state did not allow the authors to predict whether long term deterioration and leaching could happen or not.

One hypothesis to decrease the soluble sodium from the bauxite residue is to combine this residue with regular supplementary cementitious materials (e.g. fly ash, blast furnace slag) in order to react its alkalis with silicon and aluminum phases of SCM [5]. This mechanism is not very well understood, and it is called “alkaline activation”. As an additional advantage, the bauxite residue could contribute with the formation of hydrated products and improve the packing of cementitious system [3] [4].

Therefore, the objective of the present study is to investigate the activation of fly ash (FA) by bauxite residue.

2. Materials

Portland cement (OPC), bauxite residue (BR), fly ash (FA), quartz powder (Qz) and gypsum (> 98% of purity) were used in this study. The chemical and mineralogical composition of raw materials were analyzed by XRF (Table 1). BR is from an alumina refinery located in the northeast of Brazil. BR was initially collected from the last thickener and then had its solid content increased from 40 to 70 % by using a filter press. In the sample preparation step, BR and fly ash were dried at 100 °C for 24h and sequentially were ground in a ball mill for 15 min, which was adjusted to operate as close as possible to industrial cement grinding (rotational speed: 41 rpm; specific charge: 37 %; sample/ball (wt.% / wt.%): 10) [6]. Finally, the physical characterizations of raw materials were carried out by the following procedures: particle size distributions by laser diffraction using Malvern MasterSizer S; real density by helium pycnometry using a Quantachrome MVP 5DC multipycnometer (Table 2); and specific surface area (SSA) according to BET method (Braunauer, Emmet and Teller) using a Gemini 2375 micromeritics machine, where samples were pre-treated at 60 °C and pressure of 100 mmHg was applied for 24h (Table 2).

Table 1. XRF-analysis [wt.%]. *loss on ignition.

	Al ₂ O ₃	SiO ₂	CaO	Na ₂ O	K ₂ O	Fe ₂ O ₃	SO ₃	TiO ₂	LOI*	Total
OPC	3.7	16	65.4	0.2	1.1	3	3.8	0.2	4	98.6
BR	19.2	15	1.03	10	0.02	38.6	0.2	4.8	10	98.9
FA	27.1	61	2.5	0.3	2.2	2.8	0.3	1.3	1.5	99.6

*loss on ignition

Table 2. Physical characterization of BR and fly ashes.

	OPC	BR	FA
Density (g/cm ³)	3.3	2.9	2.2
SSA (m ² /g)	1.3	15	1.2
D ₁₀ (µm)	-	0.7	3
D ₅₀ (µm)	-	3	27
D ₉₀ (µm)	-	45	137

Portland cement can be classified as high alkali cement once its sodium equivalent content is 0.96 % (Table 1). The main chemical elements of BR are Fe, Al, Si and high sodium equivalent content (10%). From the chemical point of view, the fly ash might be classified as class F, low calcium, as this material meets the requirements of standard specified by ASTM C618, such as: SiO₂+Al₂O₃+Fe₂O₃ >70%, SO₃ <5 % and LOI <6 % [7].

Comparing the physical characteristics of BR to the other raw materials, it can be observed that: the specific surface area of BR is almost 14 times higher than that of OPC and FA; the D50 of FA is 9 times smaller than that of BR (Table 2).

3. Methods

The investigation of reactivity of BR and fly ashes as supplementary cementitious materials was carried out by short-term calorimetry experiments according to the rapid, relevant and reliable (R3) method [8]. The R3 test differs completely from the traditional calorimetry experiment, since in the former, rather than combining the SCM with cement powder, the pozzolan is mixed with specific chemical reagents (calcium hydroxide, calcium sulphate and alkalis) at a higher temperature (40°C) in order to minimally reproduce the chemical reaction of hydration of blended cements. According to the developers of R3 methodology, it was chosen to work at 40 °C due to the acceleration of pozzolanic reaction. This means, that the heat released after only 1 day at 40 °C is approximately the heat released during 6 days at 20 °C [9]. As a control sample, silica powder

5. Conclusions

The R3 calorimetric test showed that, even though, the BR does not behave like a typical pozzolan (slow and later reaction), its chemical influence on phase formation cannot be neglected, once its cumulative heat is peaked at the beginning of reaction (1 day). After 1 day of hydration, BR does not release heat anymore, and, acts, thus, like an inert material.

We could use maximum 7 % of BR in the blended cement with fly ash. At this BR dosage, the early strength of the blended cement was enhanced, and the long-term strength did not decrease substantially. On the other hand, high BR addition also showed a higher compressive strength at 1 day but suffered from a considerable reduction on their long-term properties.

Finally, from the business point of view for cement and aluminium sector, this study is highly relevant as it may reduce the cost and land footprint for residue storage as well as to decrease the carbon and non-renewable raw material footprint at cement plant.

6. Acknowledgements

Marcelo Montini and Prof. Rafael G. Pileggi acknowledge the financial support given by Alcoa Foundation.

7. References

1. Instituto Internacional do Alumínio (IAI). Bauxite Residue Management: Best Practice. 2015. p. 31.
2. Evans, K (2015). Success and challenges in the management and use of bauxite residue. Leuven. *Bauxite residue valorisation and best practices conference*.
3. Romano, R. C.O. et al (2013). Evaluation of transition from fluid to elastic solid of cementitious pastes with bauxite residue using oscillation rheometry and isothermal calorimetry, *Appl.Rheol* 23, 23830.
4. Romano, R. C.O. et al (2016). Acompanhamento da hidratação de cimento Portland simples com resíduo de bauxita, *Cerâmica* 62, 215-223.
5. Hairi, S.N.M, et al (2015). Synthesis and properties of inorganic polymers (geopolymers) derived from Bayer process residue (red mud) and bauxite. *Journal of Materials Science*, Vol. 50, pp. 7713-7724.
6. Ene G (2007). The Grinding Charge of Rotary Mills, *the Annals of Dunarea de Jos of University of Galati*.
7. ASTM. Standard specification for coal fly ash and raw or calcined natural pozzolan for use in concrete. 2001, Vol. 04.
8. Snellings, R; Scrivener K.L (2016). Rapid screening tests for supplementary cementitious materials: past and future, *Materials and Structures* 49, 3265-3279.
9. Avet, F; Snellings, R; Diaz, A.A; Haha, M.B; Scrivener, K (2016). Development of a new rapid, relevant and reliable (R3) test method to evaluate the pozzolanic reactivity of calcined kaolinitic clays, *Cement and Concrete Research* 85, 1-11.
10. British Standard (BS) – BS EN 196 1:1 (1995). Methods of testing cement – Part 1: Determination of Strength.