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

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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 billons 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 ºC 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 picnometry using a Quantachrome MVP 5DC multipicnometer (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 ºC and pressure of 100 mmHg was applied for 24h (Table 2).

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

	Al_2O_3	SiO_2	CaO	Na_2O	K_2O	Fe_2O_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: $SiO_2+Al_2O_3+Fe_2O_3$ >70%, SO_3 <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 (40ºC) 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 ºC due to the acceleration of pozzolanic reaction. This means, that the heat released after only 1 day at 40 ºC is approximately the heat released during 6 days at 20 ºC [9]. As a control sample, silica powder was used with high quartz content, and, therefore, almost totally inert. Eighty grams of homogeneous paste were produced by mixing all the components for 2 min using an overhead laboratory mixer at 1600 rpm. As soon as possible, 15 g of paste were transferred into a glass ampoule, sealed and placed in the calorimeter. The heat flow was recorded during 3 days with the operation temperature kept at 40 ºC.

The mixes were prepared varying the amount of BR from 3.5 to 15 % and gypsum from 0.5 to 3 %. To assure a good pre-homogenization of each blend, the raw materials were put in a zip lock bag and then they were shaken manually for 5 minutes.

The blended cements were mixed with distilled water (water / solid ratio of 0.4) at 1600 rpm for 2 minutes to produce about 80 grams of the paste. The heat flow rate of blended cements was measured using an isothermal calorimeter. The heat flow was recorded during 10 days with the operation temperature kept at 20 ºC.

Based on the instructions of EN-196-1, the produced blended cements were mixed with standard sand and distilled water (water/solid ratio of 0.5) to produce mortar samples [10]. Compressive strength tests were performed with mortars in accordance with EN 196-1. The mortars were demoulded after 24 h and cured in the humidity chamber at room temperature until achieving the desirable hydration time (1, 2, 7, 28 and 90 days). Testing was carried out in triplicate.

4. Results and Discussions

A comparison of cumulative heat release over time for isolated raw materials is shown in Figure 1. While the reactivity of FA increased progressively, BR released heat only at an early age (1 day). Therefore, the BR curve had an opposite behaviour when compared to regular pozzolans since the residue reacted rapidly at the beginning of hydration and acted as inert material at later ages. On the other hand, as it was already expected, the heat release of the quartz sample kept itself practically constant during all the time, evidencing that this raw material did not react with added chemical substances. It is also worth noticing that, between 8 and 9 days of hydration, a small sharp peak appeared in the three curves, which were not interpreted as heat release, but as "unexpected noises" of the equipment. This affirmation might be corroborated after looking at the quartz curve, which also showed a similar peak at the same range, even though it is undoubtedly an inert material.

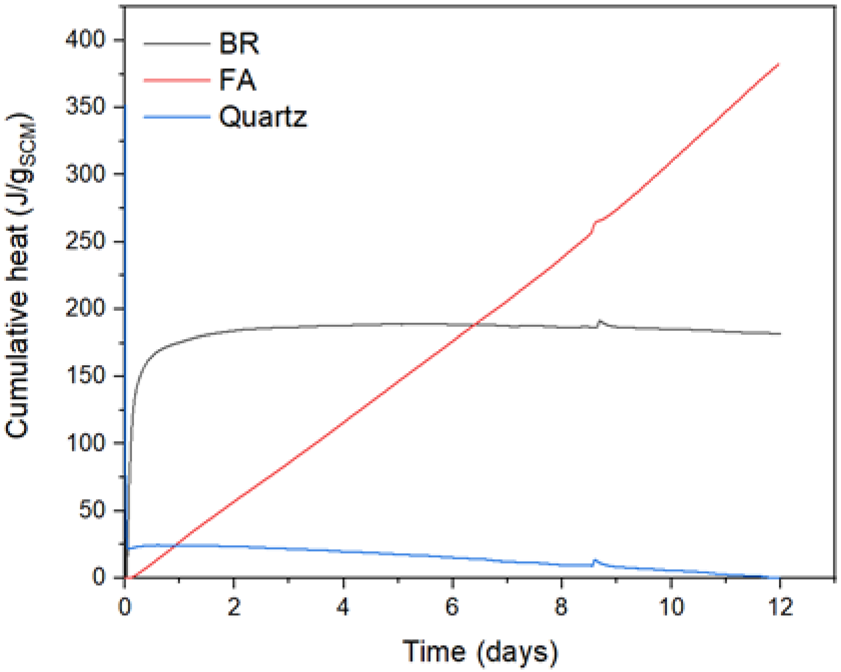

Figure 1. Cumulated heat release of the SCM reaction in the portlandite-SCM model system with added alkalis and sulfates. Obtained by isothermal conduction calorimetry at 40 oC (R3 method). Cumulative heat was normalized per gram of solid (SCM).

Moreover, the calorimetry curves of blended cements evidenced a positive effect of BR on the cumulative heat at early ages but an undesirable impact at later ages (Figure 2). The higher the BR incorporation, the lower the release of heat after 4 days. Consequently, only the mixes with 3.5 and 7 % of BR showed heat release higher than the mix with 30 % FA within 8 days of hydration.

Usually there is a strong relationship between kinetic behaviour and mechanical strength of materials. Because of that, as it was already expected, the compressive strength results matched the same tendency of calorimetry outcomes at early ages. The results may be summarized in the following manner (Figure 3):

- The first day: the higher the amount of BR, the higher the compressive strength. The mixes with 15 % and 30 % of BR showed a compressive strength 20 and 10 % higher than the 30 % FA mix, respectively;
- Later ages (> 2 days): the higher the amount of BR, the lower the compressive strength. Therefore, the mixtures with 3.5 of BR had better performance since its compressive strength was only 15 % and 7 % lower than the 30 % FA mix at 28 and 90 days of curing, respectively.

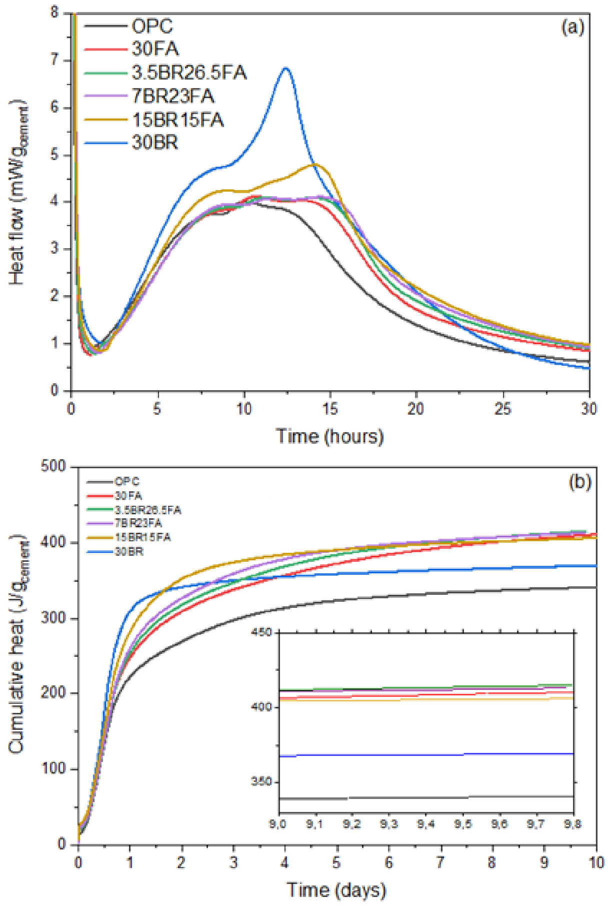

Figure 2. The heat flow (a) and cumulative released heat (b) for four blended cements with up to 30 % of BR and two references (OPC and 30FA). Heat flow and cumulative heat were normalized per gram of blended cement.

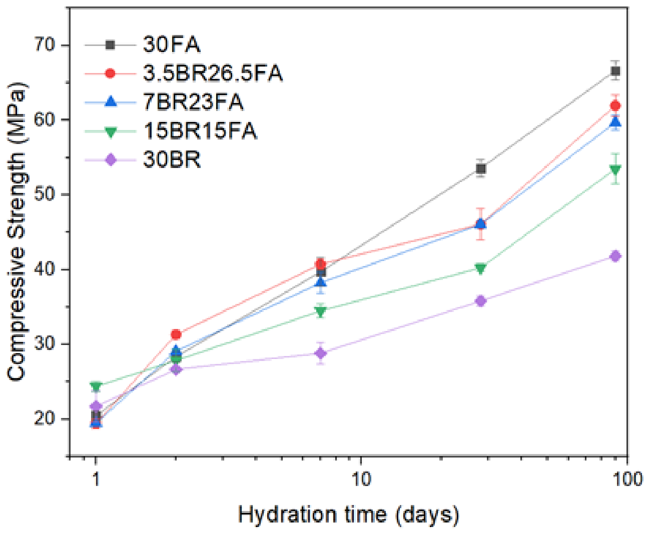

Figure 3. Compressive strength development of mortars produced from BR/FA blended cements with up to 15 % of BR and two references (30FA and 30BR).

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

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