Bauxite By-Products as Mineral Admixtures for Portland Cements

Marcio Barata[1], Euler Arruda Junior[2], Caio Melo[3], Marcelo Montini[4] and Raphael Costa[5]
1. Associate Professor
2. Doctoral Student
Universidade Federal do Pará, Belém, Brazil
3. R&D Specialist
4. Senior Chemical Consultant
5. Head of Technology B&A
Hydro, Belém, Brazil
Corresponding author: marciobarata@ufpa.br

Abstract

In emerging countries, Portland cement plays an extremely significant role in the expansion of infrastructure. Global cement production is expected to grow between 12 and 23 % by 2050 compared to its current level, which will produce approximately 11 % to 15 % of global anthropogenic CO_2 emissions, per turn if the way of cement production doesn't change. The use of mineral admixtures as a partial replacement of clinker in Portland cement has been one of the main strategies for reducing CO_2 emissions by global cement industries. However, the availability of blast furnace slag and fly ash is limited compared to the demand for Portland cement. In addition, Brazil is a country of continental dimensions, with great regional differences, where the same mitigation actions will not necessarily be applied in all regions. Nowadays, in regions where slag and fly ash are not available, such as the Amazon, pozzolanic and Portland-composite cements are manufactured with up to 30 % calcined clays or 25 % limestone filler. Another alternative for these regions would be the manufacture of cement with active or inert mineral admixtures from mining by-products. The aluminum production chain, responsible for generating significant amounts of waste, could meet the demand of the local building industry, since some wastes such as the gibbsite-kaolinite waste (GKW) and the bauxite residue (BR) have demonstrated their potential use in previous studies. The incorporation of GKW increased the compressive strength by 44 % in relation to Portland cement. Mortars with 25 % replacement of clinker by BR showed compressive strengths at early ages higher to those obtained with limestone fillers. These results are promising, but require more in-depth studies, especially on durability aspects, dimensional stability, alkali-aggregate reaction and others.

Keywords: CO_2 emissions, Bauxite by-products, Gibbsite-kaolinite waste, Bauxite residue, Mineral admixtures.

1. Introduction

In emerging countries, Portland cement plays a significant role in dwelling construction and infrastructure expansion, where concrete is the most widely used material. The production of concrete is responsible for about 5 to 8% of the world's CO_2 emissions, and cement production is responsible for 95% of this total [1]. In 2016, emerging countries, including China, India, Russia, South Africa, and Brazil, accounted for 81% of the total global cement production, whereas industrialized countries accounted for only 9% [2]. Global cement production is expected to grow between 12 and 23% by 2050 from its current level, which will make cement manufacturing directly responsible for approximately 11 to 15% of global anthropogenic CO_2 emissions [3] if the cement production way doesn't change.

The use of mineral admixtures as a partial replacement of clinker in Portland cement has been one of the main strategies for reducing CO_2 emissions by the global cement industry [4-7]. In

Brazil, the reduction of clinker-cement ratio from the use of mineral admixtures could represented 69% of CO_2 total mitigation emissions in the country's cement sector by 2050 [8]. However, the availability of ground blast furnace slag and fly ash is not enough afford the demand for Portland cement [9].

In addition, Brazil is a country of continental dimensions, with enormous regional differences, in which the same mitigation actions will not be necessarily applied in all Brazilian regions [8]. Currently, in regions where ground blast furnace slag and fly ash are not available, such as the Amazon region, composite and pozzolanic cements are manufactured with up to 25% limestone filler and 30% calcined kaolin, respectively.

Another alternative for the region would be the cement manufacturing with active or inert mineral admixtures from mining by-products. The aluminum production chain produces by-products that can fit this description and can potentially meet the demand of the local building industry.

At HYDRO group, two by-products are generated with great application potential as active and inert mineral admixtures in Portland cements, namely, the gibbsite-kaolinite waste (GKW) and bauxite residue (BR), respectively. The first is generated from the bauxite ore beneficiation process in order to remove kaolinite from gibbsite; the resulting by-product is enriched with kaolinite [10], whose quantities generated are close to 5.4 Mtpy. Bauxite residue (BR) is a by-product of the Bayer process, containing mostly phases from bauxite ore such as hematite, goethite, gibbsite and anatase, in addition to sodalite formed during the process and soluble sodium. Approximately 4.7 Mt of this residue is generated annually. The pozzolanic activity of BR is not satisfactory [11].

The aim of this research was to investigate the effect of incorporating GKW and BR as mineral admixtures to Portland clinker. The first as a supplementary cementitious material in pozzolanic cements and the second as a filler, replacing limestone in Portland-composite cements, CP IV and CP II F, according to Brazilian cement standard ABNT NBR 16697. Both are equivalent to CEM IV and CEM II/BL on European cement standard EN197-I, respectively.

2. Experimental

2.1 Raw Materials

There were four raw materials analyzed in the experimental program. The first one was BR from ALUNORTE, generated in Barcarena. The second, the residue from the bauxite washing process in Paragominas (Mineração Paragominas), rich with kaolinite and gibbsite, called here GKW [10]. The others were included in the experimental for comparison purposes. The flint kaolin (FK), extracted from the deposits in the middle Capim River valley in Ipixuna do Pará, is recognized as a high-grade kaolin for the production of high-performance pozzolans [12-13]. And finally, the limestone (LS), as it is the inert mineral admixture used at the production of Portland-composite cement, mining from the Northeast region of Pará, from calciferous occurrences denominated Pirabas Formation.

2.2 Production of Mineral Admixtures

The active mineral admixtures produced in the experimental program were derived from calcination and grinding of kaolins (GKW and FK). The inert mineral admixtures (BR and LS) were only dried and ground. Two and a half kilograms of each kaolin were thermally treated at 800 ºC with a 2-hour plateau. The calcined kaolins were ground for 3 hours in a ball mill using 10 liter porcelain jars with alumina spheres in a 1:9 ratio (ore:spheres). The BR and the limestone were dried in an oven at 105 ºC until reaching the constant mass and ground under the same conditions as the calcined kaolins. Table 1 summarizes the studied mineral admixtures and their respective production processes.

Table 1. Summary of mineral admixtures.

Type of mineral admixture	Production Condition
MK-GKW	calcined GKW 800 ºC, milled 3 hours
MK-FK	calcined FK 800 ºC, milled 3 hours
BR	non-thermally treated BR, dried and milled 3 hours
LS	limestone filler, dried and milled 3 hours

2.3 Methods

The characterization methods were carried out on raw materials, mineral admixtures and Portland cement. The rapid-hardering Portland cement was used, consisting of 92.5% of clinker, 5% of limestone filler and 3.5% of gypsum. The mineralogy was evaluated by X-ray diffractometry (XRD) by the powder method (model *Empyrean*, Panalytical). The chemical characteristics were carried out using energy dispersive X-ray fluorescence spectrometry (Model *700 HS*, Shimadzu). The particles size distribution (PSD) obtained by laser grain size measurements (Model *Mastersizer* 300, Marvern). The specific surface area (SSA) obtained was measured using the BET method (Model *Nova 220*0e, Quantachrome Instruments). The densities were determined according to the requirement of Brazilian standard NBR 16605.

The reactivity of mineral admixtures was evaluated through a test to determine the pozzolanic activity with Portland cement (performance index at 28 days - PI), according to Brazilian standard ABNT NBR 5752. The PI is the ratio between the compressive strength of mineral admixtures mortars, and of control. For metakaolin to meet the reactivity minimum requirement, Brazilian standard NBR 15894 establishes a minimum PI at 7 days of 105%. Compressive strengths of mortars were evaluated for ages 3, 7 and 28 days.

Five mortars were molded, one relative to Portland Cement (control mix) and four with 25% substitutions of the cement by the mineral admixtures described in Table 1. Mortars were molded with binder to sand ratio of 1:3 (in mass) and a water/binder ratio of 0.48. In mortars with mineral admixtures the superplasticizer additive (polycarboxylate ether based) was used so that they exhibited slump flow on the Graff table between 185±2mm. (Table 2). The fine aggregate used was normal Brazilian sand, according to Brazilian standard ABNT NBR 7215.

Table 2. Percentage of superplasticizer in mineral admixture mortars.

Mortar	additive (%)	slump flow (mm)
Control	0,08	185.0
MK-GKW	0,48	182.0
MK-FK	0,40	182.0
BR	0,19	183.5
LS	0,24	184.0

3. Results and Discussions

3.1 Characterization of Raw Materials and Mineral Admixtures

The physical, chemical and mineralogical characteristics of raw materials, mineral admixtures and Portland cement are shown in Table 3 and Figures 1-2. Figures 3-4 show the cumulative PSD of kaolins and their pozzolans, as well as of BR, limestone and Portland cement.

Table 3. Chemical and physical characteristics of raw materials, mineral admixtures and the Portland cement.

Oxides (wt%)	**BR**	**GKW**	**FK**	**LS**	**PC**	**M-GKW**	**M-FK**
SiO_2	13.43	24.30	43.55	5.95	21.00	-	-
Al_2O_3	16.28	37.68	38.75	1.80	3.56	-	-
Fe_2O_3	46.74	16.87	1.57	0.22	2.56	-	-
TiO_2	4.82	2.26	2.09	0.91	0.19	-	-
Na_2O	8.32	0.00	0.00	0.04	0.85	-	-
CaO	1.12	0.00	0.00	48.24	63.45	-	-
MgO	0.53	0.00	0.00	2.34	1.47	-	-
MnO	0.02	0.00	0.00	0.00	0,00	-	-
K_2O	0.24	0.00	0.00	0.20	0.45	-	-
SO_3	0.00	0.00	0.00	1.66	2.98	-	-
SrO	0.00	0.00	0.00	0.00	0.00	-	-
ZrO_3	0.80	0.13	0.20	0.00	0.00	-	-
P_2O_5	0.03	0.00	0.00	0.10	0.00	-	-
Others	0.02	0.00	0.00	0.00	0.10	-	-
LOI	7.78	18.52	13.70	38.45	4.62	0.30	0.50
Physical Parameters							
Density (kg/dm^3)	3.07	2.72	2.53	2.73	3.17	2.83	2.63
SSA_{BET} (m^2/g)	15.76	19.92	24.64	11.90	4.10	25.00	42.66
d_{10} (μm)	1.70	3.05	4.60	2.18	1.70	1.81	3.95
d_{50} (μm)	8.07	6.74	9.87	7.01	8.06	4.73	21.30
d_{90} (μm)	63.10	18.70	27.10	33.40	28.90	18.20	75.20

BR is composed of hematite, goethite, gibbsite, anatase and sodalite. Fe is present in the form of hematite (Fe_2O_3) and goethite (FeOOH), and it is responsible for the intense red color of BR. Al_2O_3 present in the BR is in the form of aluminum hydroxide of the gibbsite type ($Al(OH)_3$) as well as in the crystalline structure of sodalite ($(Na_{7,6}(Al_6Si_6O_{24}).(CO_3)_{0,93}.(H_2O)_{2,93})$), a mineral formed during the bauxite digestion process. SiO_2 and Na_2O present in BR are also part of the structure of sodalite. TiO_2 is in the form of anatase and CaO is part of the structure of calcite (not detected on XRD). The high content of Fe explains the high density of 3.07 kg / dm^3 of BR. Another relevant aspect is the high concentration of sodium, either free or weakly bound to the sodalite structure, which can cause problems related to surface efflorescence.

In GKW, in addition to kaolinite, other minerals such as goethite, gibbsite, hematite, anatase and quartz were observed in the X-ray diffractogram (Figure 1). The kaolinite concentration was estimated at 61% through semi-quantitative analysis by XRD (Rietveld method). This kaolinite concentration is satisfactory to provide adequate pozzolanic activity to GKW (high-grade kaolin) [14]. The LOI of 18%, very high for kaolins, is due to the presence of gibbsite and goethite (Table 3). Regarding FK, it is extremely pure kaolin, consisting essentially of kaolinite, in addition to anatase and goethite as trace minerals (Figure 1).

Another relevant point about the reactivity of metakaolin produced from thermally treated kaolin is the number of defects in the kaolinite crystal structure. Kaolinites with higher quantity of defects are the most appropriate for metakaolin production because they provide higher dehydroxylation rates and, consequently, greater reactivity [12-13].

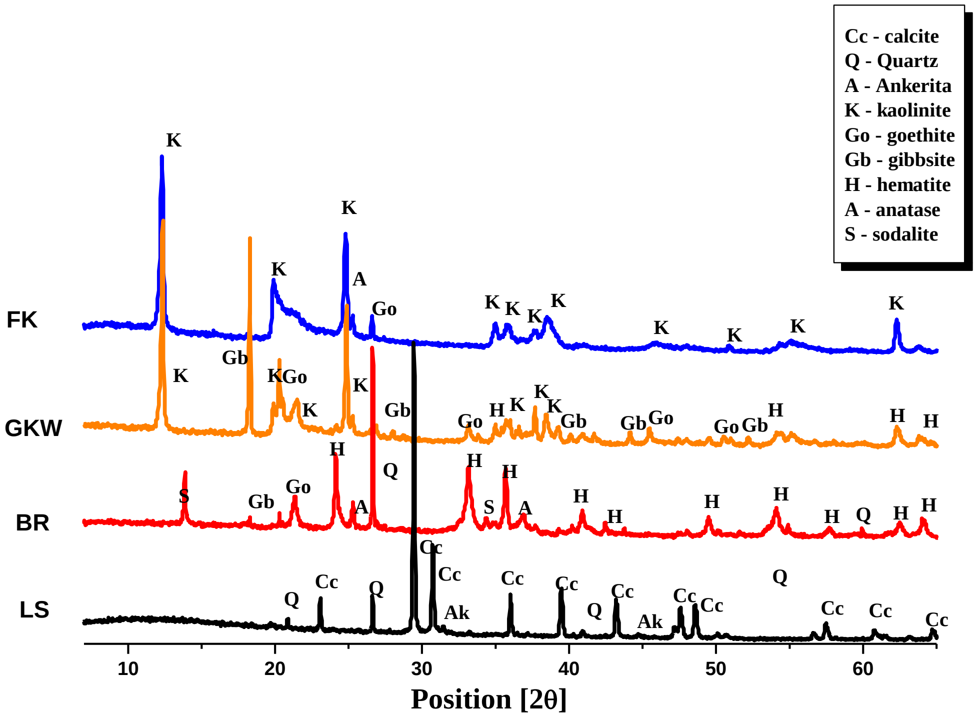

Figure 1. XRD patters for LS, BR, GKW and FK.

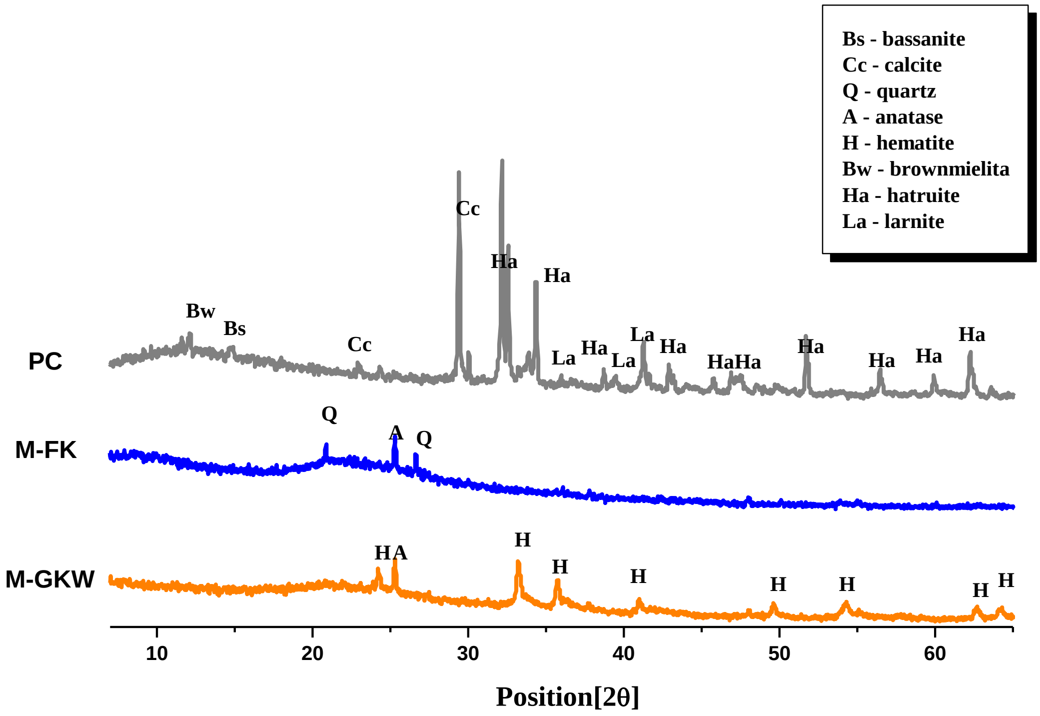

Figure 2. XRD patters for M-GKW, M-FK and PC.

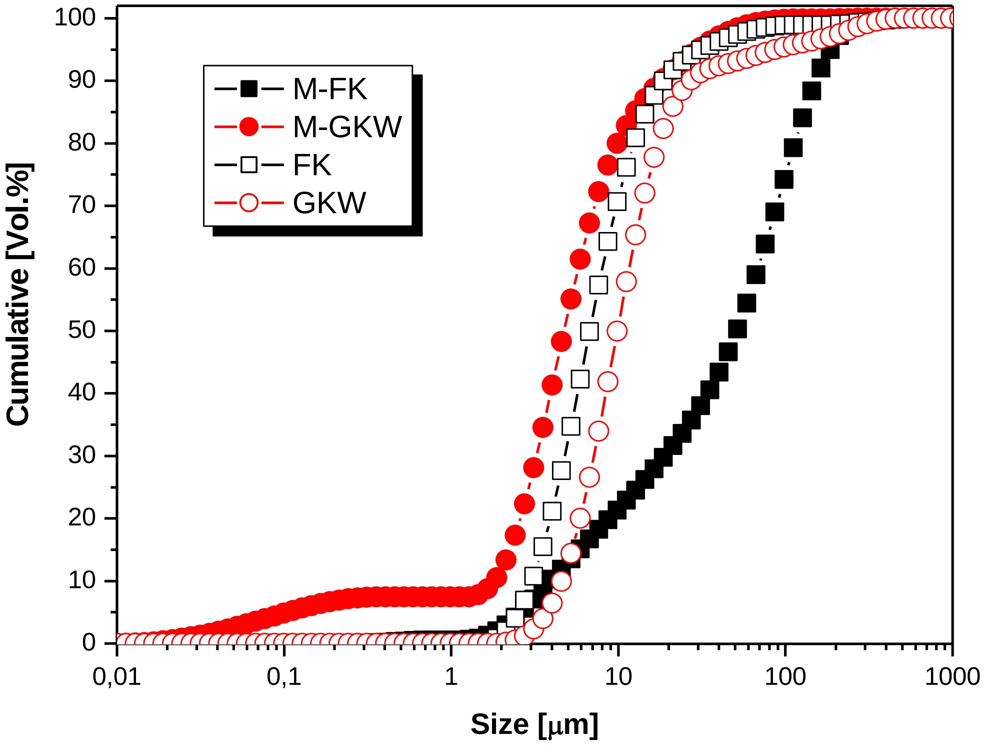

Figure 3. Cumulative particle size distributions curves of the untreated and thermally treated kaolins.

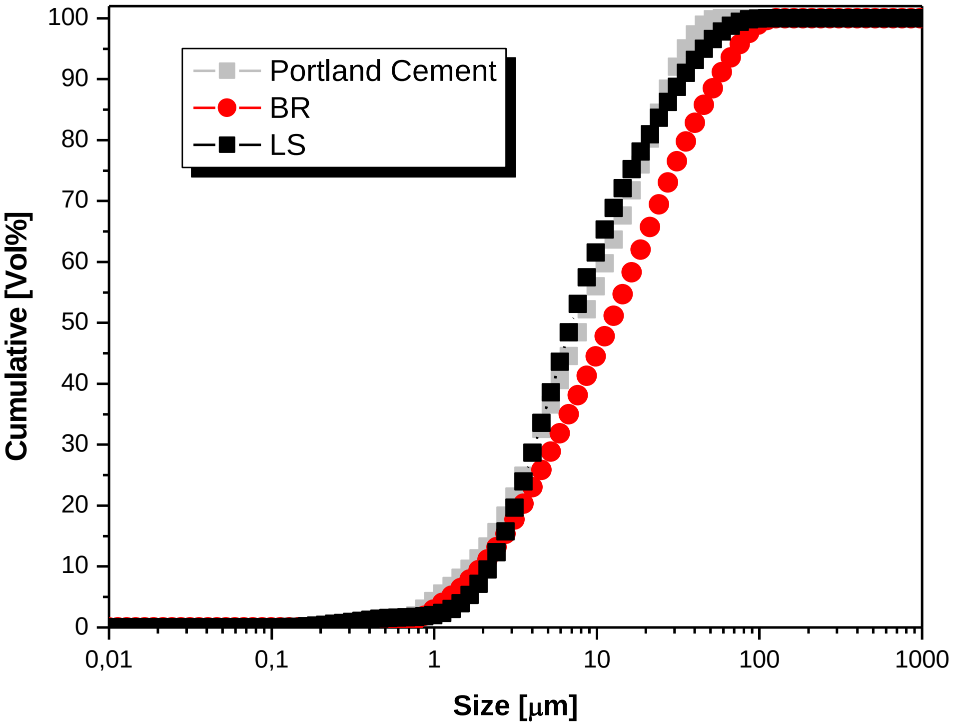

Figure 4. Cumulative particle size distributions curves of the Portland cement, limestone and bauxite residue.

In the X-ray diffractogram of the GKW (Figure 1), the superposition of gibbsite and kaolinite peaks impaired the identification and the shape of the peaks. Even so, it was possible to conclude that the GKW is a kaolinite with a high degree of defects due to the first triplet, located between 19.9 º and 23.8 º2θ, where a unique peak was found, and the other two triplets were located between 35 º and 40 º2θ, where only two bad-defined reflections were found. Regarding to FK, XRD reveals a high degree of defects of kaolinite, which explains the higher reactivity of metakaolin produced from this kaolin over those with low degree of defects in the crystal structure [13].

Due to a high degree of defects in the crystal structure of these kaolinites (GKW and FK), complete dehydrolysis occurred from the thermal treated of the kaolins, reflected in low values of LOI (Table 3). In X-ray diffractogram of M-GKW, only the amorphous halo related to metakaolinite, the hematite and anatase were identified. Calcination at 800 ºC converted goethite into hematite and the gibbsite disappeared. However, no peaks referring to boehmite or γ-alumina were identified in XRD, which are minerals formed from the dehydration of gibbsite at temperatures above 300 ºC (Figure 2).

The particle size distributions of untreated kaolins showed that both are extremely fine (Figure 3), in addition to having similar SSA_{BET} (Table 4). However, when thermal treated and milled, M-GKW presented fineness and SSA_{BET} superior to M-KF. The SSA_{BET} of the M-GKW was extremely high, around 40 $m^2.g^{-1}$, aspect that may cause excessive problems of shrinkage and creep in cementitious products.

The particle size distribution of BR is similar to that LS, both with particle sizes compatible with those of Portland cement (Figure 4). However, the SSA_{BET} of 15 $m^2.g^{-1}$ of BR was three times higher in relation to Portland cement (Table 3) and 35% superior to LS. The incorporation of BR in cement, in levels above 25% may increase the fineness of Portland cement excessively and result in problems associated with the dimensional stability in mortars and concretes. However, further research is needed to assess this issue.

3.2 Performance Index

The compressive strength values of the mortars are shown in Table 4; Figure 5 shows the Performance Index (PI) of thermally treated kaolins, BR and LS. No differences were observed in the reactivity of the metakaolins produced from GKW and FK, the latter being recognized as high-grade kaolin for production of high-reativity metakaolin. The calcined kaolins reached PI at 7 days of 152-153 % and at 28 days between 144 and 148 % (Table 4). In both cases, PI values were higher than the minimum stipulated in Brazilian standard NBR 15894.

Other important aspects to highlight are the early on higher compressive strength values of M-GKW mortar in comparison to those of the control mix. These are extremely important aspects for the cement industry, considering the typical low strengths in the early ages (3 to 7 days) of pozzolanic cements.

At 28 days, the PI of BR mortar was slightly superior in comparison to that obtained by LS mortar, 78.3% versus 76.9% (Table 4). The compressive strengths of BR mortar were higher than those of limestone at all ages evaluated. However, these differences were greater at 3 and 7 days, being reduced at 28 days (Figure 5).

These results were extremely promising, considering the increase of compressive strength at early ages provided by both M-GKW and BR. Low-initial compressive strength has always been the major problem for Portland-composite cements (CEM II / BL) and pozzolanic cements (CEM IV) due to the large incorporations of limestone (≤25%) and pozzolans (≤45%). The use of both BR and GKW may be an alternative for the supply of mineral additives in the Eastern Amazon, either inert or active, as long as the issue of fineness is minimized. Complementary studies on efflorescence, alkali-aggregate reaction, shrinkage and creep are needed to assess the feasibility of incorporating these by-products of the aluminum chain in civil construction.

Table 4. Performance index with Portland cement at 28 days.

Mortars	**Compressive Strength (MPa)**			**Performance Index with PC at 28 days (%)**
	3 days	**7 days**	**28 days**	
Control	30.94	33.73	42.10	100
M-GKW	33.33	51.20	60.96	144.80
M-FK	36.49	51.48	62.42	148.30
BR	27.97	30.23	32.97	78.30
LS	21.85	25.37	32.39	76.93

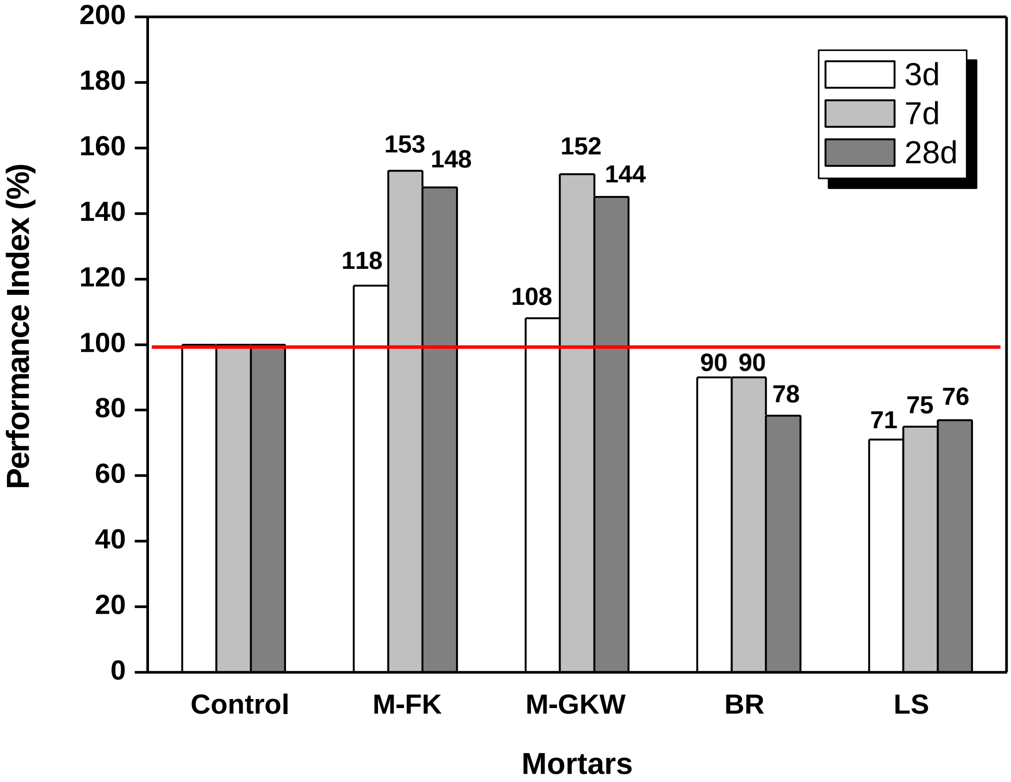

Figure 5. Compressive strength of mortars normalized to the strength of control mix.

4. Conclusions

BR is constituted by a complex assemblage of minerals, highlighting the presence of iron oxides and hydroxides, gibbsite and sodalite, a mineral formed in the bauxite ore digestion process, which has sodium weakly bound to its structure. Particle sizes are in the same order of magnitude as LS and Portland cement. However, BR SSA_{BET} is superior, which can cause problems of dimensional stability when incorporated in large amounts into cement.

In terms of mechanical properties, the replacement of LS by BR increased the compressive strength of the mortar at all ages. However, the difference was more expressive at 3 and 7 days than at 28 days. The results are promising, but they should be viewed with caution, as there are other aspects that must be taken into account when using BR in Portland cement, such as alkali-aggregate reactivity, the appearance of efflorescence, shrinkage and color.

GKW consists mostly (60%) of a kaolinite with a high degree of defects and extremely fine. The SSA_{BET} of untreated and thermally treated GKW were 19 and 42 $m^2.g^{-1}$, respectively. These characteristics, whereas providing high reactivity, can also cause problems associated with dimensional stability such as excessive shrinkage and creep.

Metakaolin derived from GKW obtained a PI at 28 days of 144 %, similar to that calcined FK which is considered one of the most reactive mineral admixtures. In addition, M-GKW also showed a high-value of PI for the early ages, mainly at 7 days. This is an extremely important aspect for the cement industry, considering that the major problem of pozzolanic cements, with large incorporation of mineral admixtures, is the low compressive strength at early ages. The use of GKW may eliminate this problem as long as the issue of fineness is controlled.

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