Methodology for a Safe and Low-Cost Large-Scale Application for Bauxite Residue in association with Portland Cement in Compositions Applied in Civil Construction

Roberto Cesar de Oliveira Romano [1], Lance Myers[2] and Rafael Giuliano Pileggi[3]
1. Researcher
3. Professor
Polytechnic School of the University of São Paulo, São Paulo, Brazil
2. Research Program Manager
Alcoa of Australia, Australia
Corresponding author: rcorjau@gmail.com

Abstract

Using bauxite residue (BR) in association with Portland cement (PC) presents an opportunity to address challenges facing the aluminium and cement industries: the roadmap of the International Aluminium Institute identifies this application as one of the most impactful uses for BR in large-scale. The route developed in this study, with support from the Alcoa Foundation, focuses on developing a large-scale and low-cost application for the BR without the requirement for additional treatment of the residue, such as energy intensive calcination or additives addition. This study has investigated the properties and compositional variability of BR collected from two different alumina refineries, and the synergistic interactions of the BR with different Portland cements. The chemical reactions and formation of hydrated products were monitored during the development of eco-friendly compositions, with the performance and durability of the components produced being a key output of this study. This methodology has facilitated the production of components at a pilot-scale, without a negative impact on the development of microstructure.The material was easily molded, demonstrated high performance, and was environmentally safe. This paper presents the methodology, and illustrates the overall strategic approach and challenges faced relating to the production of large-scale cement components exposed to environmental conditions.

Keywords: Bauxite residue, Portland cement, Chemical reaction, Rheology, Performance, and methodology of development.

1. Global Bauxite Residue Overview

Over 95% of the alumina produced globally is through the Bayer process. On average, for every ton of alumina produced, approximately 1 to 1.5 tonnes of BR are produced. Annual production of alumina in 2021 was over 138 million tonnes, resulting in the generation of over 180 million tonnes of BR [4]. The BR is deposited and stored in specially engineered facilities commonly called impoundments [1]. These impoundments securely contain the tailings to avoid BR contact with surface or underground water [2,3] and otherwise serve to store BR safely and efficiently.

The aluminium industry is actively investigating options to reduce the quantity of BR produced and the land area required for storage. An important enabler to this is identifying and developing opportunities for value adding uses of BR [5]. Presently, the main applications evaluated for BR include element recovery (heavy metals, rare earth elements, and other critical minerals), synthesis of zeolites, landfill capping, soil amelioration, production of Portland cement clinker, manufacture of building materials, concretes and cementitious components, tiles and bricks, road construction (sub-base and sub-grade), geopolymers, water treatment, production of red ceramics, selective filters for SO_2 or H_2S, and others [3,6–26]. The main challenges relating to BR reuse are high alkalinity and the presence of heavy and alkaline metals. This explains, in part, the reason for why less than 4Mt of BR produced annually is being utilized [17].

The physical properties of BR vary significantly between alumina refineries due to the bauxite mineralogy and processing conditions [27]. For example, the specific surface area (SSA) reported by [28] ranged from 64 - 187 m^2/g, according to the BET method [29], highlighting the difference between BR generated from a Bayer process versus a sintering process. In a separate study, the average SSA of BR was ~ 35 m^2/g for BR generated in the Bayer process, with a range of 15 and 55 m^2/g. Generally BR contains a large proportion of fine particles, varying from 100 nm - 200 μm [5,17,27,28,30], with a d_{90} <75 μm.

Similarly, BR chemical composition potentially changes with time when stockpiled. Typical BR chemical compositions reported in the literature are presented in Table 1, separated by country and the results for Brazil highlighted.

Table 1. Survey of the range of chemical composition of bauxite residue in different countries.

Country	**Fe_2O_3**	**Al_2O_3**	**TiO_2**	**SiO_2**	**Na_2O**	**CaO**	**K_2O**	**LOI**	**References**
Australia	24-44	15-40	3-10	9-32	0.4-9	2-4.5	-	-	[22,31]
Brazil	**20-49**	**10-25**	**3-10**	**3-50**	**2-12**	**1-4.8**	**0.1-2**	**9-14**	[18,25,31–34]
China	5-47.5	6.5-26	0.7-7.3	15-25.9	5.2-12.2	2.6-47	0.1-0.77	7-16.3	[35]
Germany	25-35	22-28	8-24	6-16	4-9	0.5-4	-	-	[31]
Greece	41-47	15-26	5.3-5.5	6.8-7.5	~2.9	~10	-	~9.2	[31,36]
Hungary	38-51	14-15	4.5-8	10-13	5-8	>3.5	-	-	[22,31]
India	33-53	14-27	3-23	5-9	4-6	2.7-3.3	-	-	[22,31]
Italy	4-35	10-20	0.5-9	11-37	1.9-7.5	6.5-22	2	7-19	[26,37]
Jamaica	~50	~15	~6.7	1.5-3.4	1-3.2	7	-	-	[22,31]
Japan	39-45	17-20	2.5-4	14-16	7-9	-	-	-	[31]
Russia	~23	~29	~4	~17	~11	~1			[31]
Suriname	24-33	19-24	3.5-12	12-16	8-9	~5			[22,31]
Taiwan	~41	~20	~3	~18	~4				[22]
Turkey	~36	~23	~4	~12	~7	~3	~0.3	~9	[38]
USA	10-60	5-29	3.5-11	4-23	2-8	5-47	-	-	[22,31]
IAI	24-45	10-22	4-20	5-30	2-8	0-14	-	-	[36]
Liu and Wu[2]	6-28	9-17.7	3.2-7.3	8.3-22.7	2.9-4	20-41	0.05-0.4	11.8-17	[28]
Evans	5-60	5-30	0.3-15	3-50	1-10	2-14	-	5-20	[17]

The main mineralogical phases of BR are presented in Table 2. These predominantly consists of oxides and hydroxides of iron, aluminium, silica, calcium and titanium [2,5,39,40].

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[2] Considering both process of bauxite residue generation, Bayer and sintering.

In addition to the main mineralogical phases presented in Table 2, minor/ or trace amounts of vanadium, scandium, gallium, chromium, phosphorous, manganese, copper, cadmium, nickel, uranium, thorium, strontium and barium oxides are typically present.. In general, the oxides contained in bauxite residue constitute approximately 70% w/w crystalline phases and 30% w/w amorphous materials [39].

Bauxite residue contains aluminosilicates in a vitreous phase that can be solubilized in an alkaline solution. Reaction of these materials with Ca^{2+} solubilized from Portland cement can result in the formation of hydrated calcium silicates, aluminates and silicoaluminates. However, this alone does not determine if the BR will behave as a pozzolan in Portland cement manufacture. According to some standards, or using Chapelle's method [41], BR does not exhibit pozzolanic activity.

Table 2. Main minerals found in the bauxite residue worldwide [2,5,39,40].

Oxide	Mineralogy	Chemical formula	Range (%)
Iron	Hematite	α-Fe_2O_3	7 – 29
	Goehtite	α-FeOOH	7 - 25
	Magnetite	Fe_3O_4	5 – 8
Aluminium	Diaspore	α-AlO(OH)	0,5 – 1
	Boehmite	γ-AlO(OH)	1 – 10
	Gibbsite	$Al(OH)_3$	1 – 5
Silicon (amorphous and crystalline)	Quartz	SiO_2	1 – 5
Titanium	Rutile	TiO_2	1 – 6
	Anatase	TiO_2	0,3 – 11
Sodium	Sodalite	$Na_8(AlSiO_4)_6Cl_2(S)$	16 – 24
	Cancrinite	$Na_6[Al_6Si_6O_{24}].2CaCO_3$	0,5 - 50
Calcium	Calcite	$CaCO_3$	1 – 12
Blends	Muscovite	$KAl_2[Si_3AlO_{10}].(OH,F)_2$	1 – 15
	Perovskite	$CaO \cdot TiO_2$	0,5 – 12
	Anorthite	$3CaO.Al_2O_{3}.3Si_2O_2$	2 – 20

The pH of BR, ranges from 9.2 to 12.8 [22]. This alkalinity is due to the presence of alkaline anions, including OH^-, CO_3^{2-} / HCO_3^-, $Al(OH)_4^-$ / $Al(OH)_{3(aq)}$ and $H_2SiO_4^{2-}$ / H_3SiO_4. The alkalinity of the BR is a function of bauxite digestion conditions (ratio between bauxite and caustic soda) and BR tailings management.

The salinity of BR is mostly dictated by the sodium concentration, and can vary from 17-200 mmol/L. This forms the main challenge for utilizing BR in different sectors. Successive washing of BR can result in mass losses, but no change in pH [42]. The authors concluded that solid phase alkalinity within the BR buffered the pH until the point at which the alkaline solids were completely removed.

The surface charge of BR is predominantly negative in alkaline pH, with an isoelectric point of ~pH 6. This is an important parameter, as the dispersion/coagulation forces, ionic charge, redox reactions, rheological properties and other factors can affect the BR processing and making it difficult to use in some applications [5].

Typical BR conditions, as described above, show significant variability in physicochemical, mineralogical, and surface properties of bauxite residue, including high alkalinity and salinity, all of which can directly impact on the viability of utilizing BR.

This paper presents a path to developing a large-scale and low-cost application for BR without the requirement for additional treatments, such as energy-intensive calcination, or additives addition.

2. Development of Large-Scale Applications for the use of BR in Cement Materials

2.1 Evaluating the Raw Material Properties

Development of cementitious compositions requires the comprehensive characterization of the raw materials. Particle size distribution (PSD) and morphology, specific surface area (SSA), density, mineralogy, chemical composition, surface charge, solubility, and leaching, are just some of the key physical parameters. These parameters determine the rheological behavior of concretes, impacting on the yield stress, viscosity, and thixotropy [43,44]. Mineralogy, solubility and chemical composition all contribute to the chemical reactions of the cement, which is ultimately governed by a balance between dissolution and precipitation [45].

The particle size distribution, volumetric surface area and solids content [46,47] assist with predicting the input material properties, which is an important consideration in the production of concretes. Some researchers consider BR unsuitable for use in cement formulations, citing that the BR is responsible for low performance in the hardened state, in part due to the additional water required to achieve the desired rheological properties. BR tested in this study (Alcoa – Poços de Caldas, Minas Gerais State, and Alumar – São Luis, Maranhão State) presented a considerable range in particle size (from 0.1 to 70 μm, with d_{50} around 20 μm, depended on the treatment) and particle morphology/surface roughness (from 10 to 22 m^2/g). Based on these physical properties, the samples would likely require additional water to achieve similar workability when compared to reference compostions. The focus of this research was to develop formulations that produce concretes that are easy to cast, ecofriendly, and demonstrate similar performance to reference compositions, without increasing the amount of water required. [44,46,48,49].

BR tested in this study contained high alkalinity (pH 11.5 - 13.0), low concentrations of Ca, intermediate concentrations of Ti, and high concentrations of Al, Si, Fe and Na. High concentrations of Al, Si, Fe will not negatively impact association with the cement provided they have adequate solubility to contribute with the chemical reaction of the clinker phases. The presence of up to 12% sodium will limit the quantity of BR that could potentially be used in the compositions, unless the BR and cement is combined with other reactive powders, such as pozzolans and slags [34,50,51]. Decreasing the moisture content of the BR using pressure filtration, or equivalent, will positively impact the Na content due to increased removal of water-soluble Na.

2.2 Understanding Material Characteristics and their Impacts on Chemical Reactions

It is essential to understand the chemical reaction mechanisms that occur when the binder contacts water when working with Portland cement. The hydrated clinker products will always remain the same, but the kinetics of reaction will vary as a function of the cement type, presence of supplementary materials and admixtures, water content, temperature, and other variables [52–54]. Using BR further increases the complexity of the system [23,34].

The physicochemical and mineralogical properties BR impart different effects on the kinetics of the hydration reaction. It dilutes the clinker phases and impacts nucleation processes, which in turn affects the chemical reaction of the clinker silicate phases. The formation of ettringite (Aft) and conversion to monosulfoaluminate (Afm) is affected by the precipitation of calcium silicate hydrate (C-S-H) and calcium hydroxide (CH) and aluminate phases. Sodium silicoaluminate and calcium silicoaluminate phases are also formed [34].

Figure 1 illustrates the heat flow released during the reaction of four different Portland cements with 10% w/w BR from Minas Gerais state[3]. Also included is a chart illustrating the chemical reaction of compositions containing cement with 65% w/w of slag and different proportions of BR from Maranhão[4] state (labelled as BR2 to differentiate).

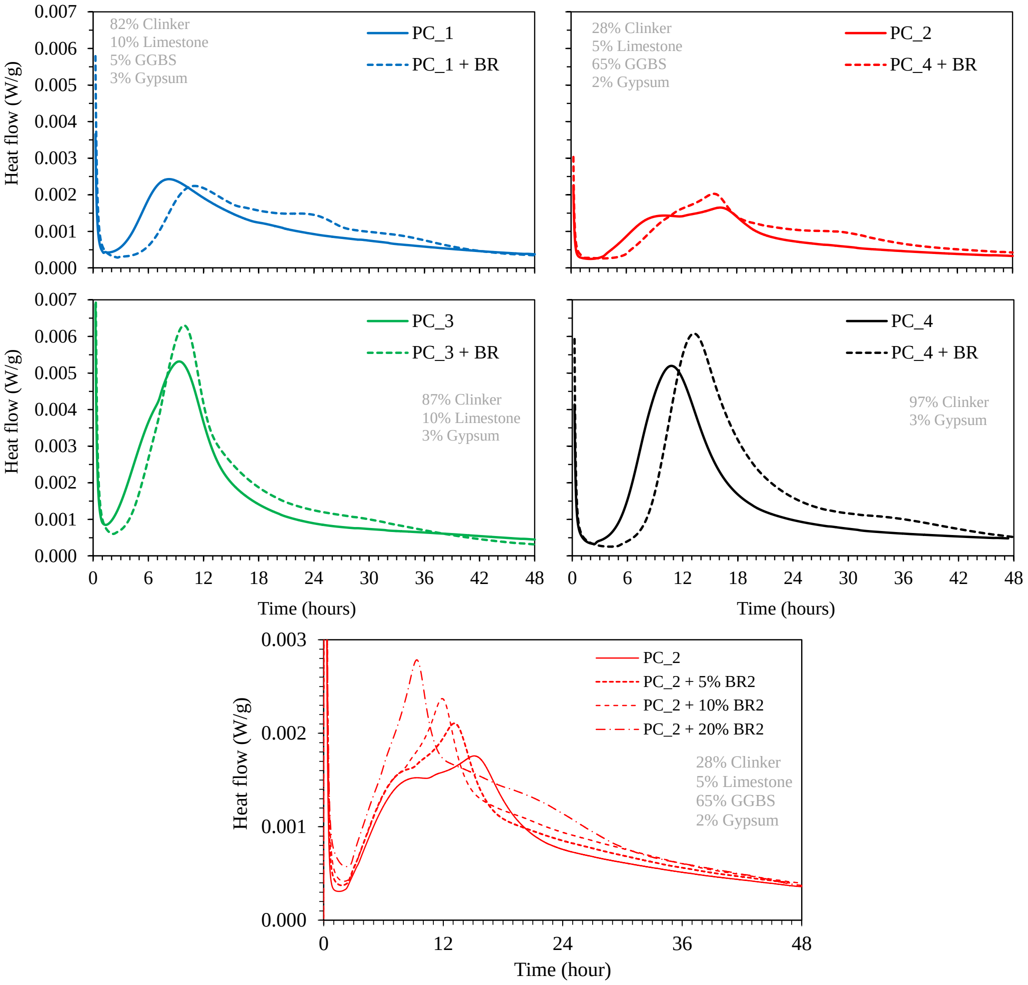

Figure 1. Monitoring the heat flow of compositions with the same BR (from the Minas Gerais state) and different Portland cements (above), or with the same Portland cement (PC_2) and different contents of BR2 (below) from Maranhão state (see that the y-axis scale for this graph is different of the others).

Use of Minas Gerais BR caused a delay in the chemical reaction for all cements, mainly due to the impact of aluminates and alkalis, and the presence of flocculant. The Al-ion may be incorporated into the C–S–H layer, alternatively the presence of Al-ions may poison the C-S-H crystal formation. [55] due to the aluminate ions strongly inhibiting dissolution due to the precipitation of aluminosilicate at the surface of the alite (C_3S). Despite that, these Si–O–Al bonds are preferentially formed in low alkaline conditions and stabilized at higher pH by calcium ions in the coordination sphere of aluminium ions [56,57].

Interestingly, using a high quantity of slag [34], with the same cement and Maranhão BR accentuated the chemical reaction, due to the lower quantity of free ions (in this case, the BR was

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[3] The BR was received was ~ 50% w/w solids, with high concentrations of aluminates, alkalis, and soluble salts.
[4] BR was provided as filter cake from a pressure filter.

obtained from a press filter). Increasing BR content elevated the suspension alkalinity and the rate of the slag dissolution. This intensified the formation of ettringite and the released heat (peak overlaps with C–S–H). After ~30 hours, once any sulfate was consumed by ettringite formation, the excess aluminate then reacted with this hydrate to form calcium monosulfoaluminate, again slightly increasing the released heat. Importantly, this BR sample had a much finer particle size distribution, thereby increasing the available nucleation points [58].

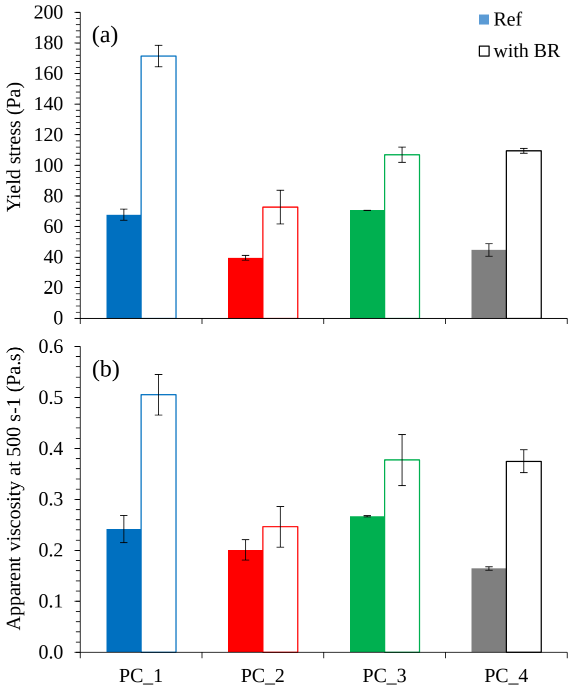
2.3 Evaluating the Fresh State Properties of Pastes Containing Bauxite Residue

Evaluation of the fresh state properties of cement compositions is necessary during the development of eco-efficient formulations. Reducing the quantity of cement content by using supplementary cementitious materials increases the complexity of the system. This complexity is further increased when incorporating BR, due to the significantly different physicochemical properties relative to Portland cement.

Both BR PSD and SSA can impact on the fresh state properties of pastes. As discussed previously, BR contains a considerable quantity of fine material, with a d_{90} ranging from 100nm - 200 μm. SSA can also vary considerably, with a survey of Brazilian BRs reporting a range of 15 - 55 m^2/g. This is a factor of ~10 - 37 times higher than Portland cements, even with similar density. The PSD, SSA and real density all affect the mobility of particles during the flow or start of flow, governing the viscosity and yield stress respectively [47]. While the PSD affects the packing of particles, the SSA dictates how much liquid will be required to separate them.

The flow of suspensions using BR is presented in Figure 2, with the same compositions used as those presented in Figure 1. Chart (a) illustrates the comparison for the yield stress, and Chart (b) illustrates the comparison for apparent viscosity. The difference in the physical parameters of the particles is presented in the table on the right of the charts.

The data clearly indicates that the high SSA and fine PSD of the BR increases both the viscosity and yield stress of the paste. A similar trend was also reported in [32,59,60]. These rheological assessments are important as they are used to match flowability with the possible applications for the paste. Increasing water content can maintain the consistency of products and overcome the impact that BR has on the rheological properties, however this can also decrease the strength and the durability of the final product due to an increase in porosity and permeability after hardening [61–64]. This can also facilitate the leaching of soluble ions.



Physical property	PC_1	PC_2	PC_3	PC_4	BR
Density (g/cm^3)	3.01	2.95	2.99	2.94	2.87
SSA (m^2/g)	1.97	2.10	1.20	1.25	22.6
d_{10} (μm)	3.10	2.70	3.60	4.90	0.60
d_{50} (μm)	19.3	17.5	20.5	24.0	5.00
d_{90} (μm)	54.0	49.0	55.0	60.0	35.6

Figure 2. Yield stress (a) and apparent viscosity (b) of suspensions with and without bauxite residue. The physical parameters of the particles are presented to the right.

The quantity of water required may be reduced by using a superplasticizer, or applying a treatment to the BR. The use of i) superplasticizers, ii) BR calcination, and iii) BR alkalinity to promote alkaline activation of slag was investigated.

The use of superplasticizers based on melamine sulfonates or polycarboxylate molecules successfully produced flowable suspensions with low quantities of water, but this significantly delayed the chemical reaction [18,65]. The slowing of the chemical reaction is undesirable as it can affect strength development and production rate.

Using BR calcined at 800ºC in association with Portland cement did not impact the chemical reaction compared to reference compositions, but the rheological properties were similar to using untreated BR in association with Portland cement, where increasing the quantity of BR increases the yield stress and viscosity [32]. Although the SSA decreased significantly, the surface charge of BR also changed, becoming more negative at the pH of the cement suspension, negatively impacting the flow.

The third alternative, mixing BR with ground blast furnace slag, resulted in a product with good properties, no impact on the chemical reaction, and low impact on the rheological properties. A matrix of different slags and BR/slag ratios were investigated to optimize the composition performance and minimize leaching [5,25].

In summary, using BR in Portland cement can have a significant impact on the fresh state, but there are ways to produce components with good flowability, without the need for increasing the water demand.

2.4 Evaluating the Hardened State Properties Compared to Traditional SCMs

All inputs into the fresh state development will impact on the cement consistency [60], development of mechanical properties [63], and the performance of components during service. live [66].

The objective of this study was to identify large-scale BR applications in the development of eco-efficient compositions that use low quantities of Portland cement. This also positively impacts CO_2 emissions due to the decreased requirement for clinker per ton of cement produced [67]. It is common practice to use supplementary cementitious materials (SCMs) [52], such as the commonly used pozzolans, granulated ground blast furnace slag (GGBS) and limestone.

However, the availability of these products is finite, necessitating the need for alternative sustainable materials. BR has the potential for use as an SCM, but it is not yet commonly used in association with Portland cement. According to Figure 3, BR provides a different Ca:Al:Si ratio when compared with traditional SCMs [34]. The impact of BR on the hardened state properties of concrete compositions also needs to be compared to traditional SCMs.

Concretes were produced maintaining a constant cement content (260 kg/m³) while changing the quantity of SCM (5% and 10%-vol as a function of cement content). The aggregates and the water content were the same for all compositions. The use of BR did not deteriorate the hardened properties of micro-concretes [34], with the micro-concrete product demonstrating similar performance compared to concrete made using traditional SCMs.

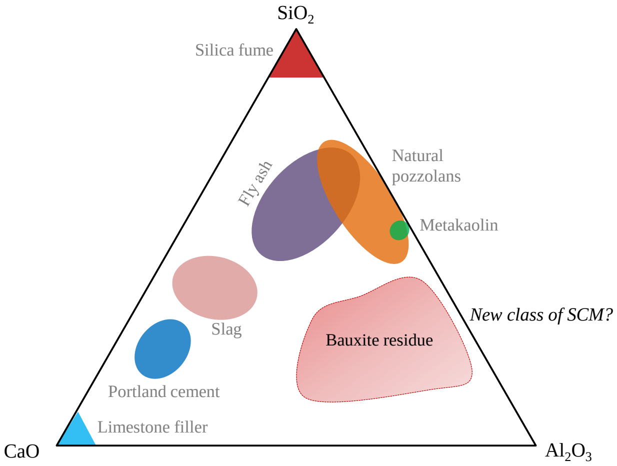


Figure 3. $CaO-Al_2O_3-SiO_2$ ternary diagram of cementitious materials, including BR.

The monitoring of carbonation of these concretes, up to a year, demonstrated similar carbonation to compositions produced with silica fume. The results therefore indicate that BR could be used to produce concretes at up to 10%-vol, however, the evaluation of leaching, shrinkage and alkali-silica reaction was still required.

2.5 Evaluation of Leaching, Shrinkage, and Alkali-Silica Reaction

Almost all research related to concrete durability has focused on the leaching, efflorescence, shrinkage, alkali-silica reaction and steel-bar corrosion [14,24,68–70]. This project focused on the first four parameters.

Untreated BR, calcined BR, and BR combined with slag to promote alkaline activation were all used to assess the impact on fixing soluble ions. All were mixed with Portland cements (the purest commercially available in Brazil and containing the highest content of blast furnace slag, Figure 1) and cured for 28 days before evaluating leaching. Results indicated that pure Portland cement combined with untreated BR produced the worst leaching outcome. The calcination of BR helped to slightly reduce leachability, but the association of BR and slag, before addition to the cement, produced the best outcome. The optimal ratio of BR and GGBS needs to be determined [25,71]. The efflorescence results followed a similar trend [71]. Although Portland cement with slag decreased free ions in all compositions, it is important to note that the content of sodium (and aluminates) leached in each composition were considerably higher than in the reference compositions, with a direct correlation with the BR content. This would limit the quantity of BR that can be used.

The alkali-silica reaction (ASR) was monitored according to the Brazilian standard accelerated method (NBR 15577-5), with the results indicating that the expansion obtained for the reference composition after 28 days was similar to that for the compositions formulated with up to 20% of BR. This indicates that at 20% BR content the ASR expansion has not been inhibited, and it is likely that this is a consequence of the high soluble alkali content triggering a more aggressive attack on the aggregate. However, 30% BR reduced the expansion rate of mortars, possibly by causing clinker dilution driving a lower proportion of hydrated products, including calcium hydroxide. These hydrated products are necessary for the formation of expansive products in the ASR reactions. An alternative hypothesis is the availability of soluble aluminate ions in the BR may have a mitigating effect on the ASR.

Finally, the shrinkage in ordinary concretes compared with other common supplementary cementitious materials demonstrated that using BR (both untreated and calcined) produced only minor expansion at rates of up to 10% replacement [5,25,71].

2.6 Development of Products and their Exposure to the Environment

After understanding the physicochemical interactions between BR and different Portland cements, some components commonly used in urban infrastructure and furniture were developed. This included hydraulic tiles, rendering mortars, ordinary concretes, benches, table and chairs and other products. Figure 4 illustrates some of the products produced to assess performance while exposed to the environment.

Compositions were preferentially formulated using Portland cement with slag and replacement of up to 10% of BR. This formulation was selected as it was considered the best combination of raw materials considering the fresh and hardened state properties and leaching aspects. Certain components were produced with calcined BR, and some benches with and without steel-bar. Importantly, the BR content can be increased above 10% if mechanisms for chemical stabilization of alkalis are used e.g., using additional pozzolans, or a product of slag activation produced by the residue.

Mortars with BR presented better adhesion than the reference, even with 10% less cement. The fresh state properties were also improved, expanding the applicability of the formulation. Some efflorescence was observed in hydraulic tiles and the bench, which correlated with the composition of BR and association with cement, as presented previously. Finally, after exposure for three years, a resistance to fungi growth in the hydraulic tiles was observed.

Figure 4. Components developed for monitoring after exposure to environmental conditions.

3. Conclusions

The physicochemical parameters of BR and the other raw materials used in paste compositions define the optimal ratio that can be used in cement and concrete. In this study, the association of BR and slag (from the composition of Portland cement or in its pure form) seemed to be the best practice to produce stable compositions.

The use of untreated BR impacted on the fresh state properties, with increasing BR content proportionally increasing the yield stress and viscosity. This may be overcome by to increasing the quantity of water to obtain an adequate consistency for application, but this will deteriorate the hardened state properties.

Superplasticizers were used to produce compositions with suitable fresh state properties, while BR calcination and combination of BR with a slag for alkali activation were assessed to alter the physicochemical, mineralogical, and surface properties of the BR. The use of superplasticizer improved the flowability with lower water requirements but caused a considerable delay in the chemical reaction. It is important to remark that this does not mean that these compositions cannot be used. It depends on the type of application you intend to do. Calcination of BR (or using the product of alkaline activation of BR) did not interfere in the chemical reaction, but in both cases, changes in rheological properties were observed, increasing yield stress and viscosity with the increase in BR content.

In the hardened state, the performance of microconcretes prepared with BR (untreated and calcined) were statistically similar compared to other traditional supplementary cementitious materials.

Leaching of sodium and aluminates, and consequent efflorescence, was higher with increasing BR additions, but it was possible to fix a considerable proportion of these soluble ions by associating the BR with slag and selecting the most suitable Portland cement.

The monitoring of alkali-silica reaction by the Brazilian standard accelerated method, indicates that at up to 20% of BR addition the trend is similar to that observed by the reference material. However, using a larger amount of BR replacement resulted in a lower reaction compared to the reference, possibly caused by clinker dilution or by the higher availability of soluble aluminate ions that may impart a mitigating effect.

Finally, we produced some cementitious components using the best conditions evaluated for the fresh and hardened state properties, chemical reaction, and leaching. The components were evaluated and exposed to the environment. The results indicated that it is possible to produce safe, large-scale applications for BR by using appropriate criteria for particle properties, choice of raw materials, and the development of compositions with correct proportioning to guarantee the performance in the fresh and hardened state, with good durability and environmental performance with respect to leaching.

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