

## Low-Carbon Cements from Aluminum Chain By-Products

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### Abstract

In emerging countries, Portland cement plays an extremely significant role in the expansion of infrastructure. Global cement production is expected to grow considerably in the next decades, heavily contributing to the global anthropogenic CO<sub>2</sub> emissions, if the way of producing cement will not change. The use of supplementary cementitious materials (SCM) as a partial replacement of clinker in Portland cement is one of the main strategies adopted to reduce CO<sub>2</sub> emissions by global cement industries. However, the availability of conventional SCM like blast furnace slag and fly ash is regional and globally limited compared to the demand for Portland cement. In Brazil, a country of continental dimensions with great regional differences, the same mitigation actions will not necessarily be applied in all regions and 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. An alternative for these regions would be the manufacture of cement with active or inert SCM from mining by-products. Some materials like the gibbsite-kaolinite waste (GKW) and the bauxite residue (BR) have demonstrated their potential use in previous studies. In this experimental investigation, blended cements were produced with clinker replacement levels of 50 % by a combination of metakaolin produced from the calcination of GKW and bauxite residue. The results demonstrated the high mechanical efficiency of these binders compared to ordinary Portland cement. The incorporation of metakaolin provided very high compressive strengths, while the bauxite residue accelerated the clinker hydration and pozzolanic reactions. The combination of the two by-products from the aluminum chain resulted in an increase in both initial and long-term strength, allowing clinker replacements of up to 50 % and reductions of 35 % in greenhouse gas emissions and 50 % in the consumption of non-renewable natural resources (NR<sup>2</sup>). The results are promising and noteworthy with respect to early-age compressive strengths, as they increase construction productivity, but also in minimizing the use of NR<sup>2</sup>. However, more in-depth studies on durability and dimensional stability are essential.

**Keywords:** CO<sub>2</sub> emissions, Aluminum Chain by-products, Gibbsite-kaolinite waste, Bauxite residue, Low-carbon cements.

### 1. Introduction

Due to the accelerated process of urbanization in large cities and their surroundings, especially in emerging countries, there is a growing need for raw materials to meet the demands of the construction industry. In 2020, for example, the global consumption of natural aggregates and cement, fundamental for the construction market, exceeded 48 billion and 4 billion tonnes, respectively [1].

Concrete production is responsible for 5 to 8 % of global anthropogenic CO<sub>2</sub> emissions, with cement being the main contributor, accounting for up to 95 % of the environmental impacts associated with this sector [2]. Global cement production is expected to increase by 12 to 23 % by 2050 compared to its current level, which will make cement production directly responsible for approximately 11 to 15 % of global anthropogenic CO<sub>2</sub> emissions if the method of cement production does not change. Thus, the main challenge is the immediate need to reduce CO<sub>2</sub> emissions related to the production of clinker, the main component of cement, responsible for a large portion of the pollutant gas emissions. In this context, reliance on traditional raw materials also contributes to environmental impacts, highlighting the need to explore more sustainable options.

The use of supplementary cementitious materials (SCM) as a partial replacement of clinker in Portland cement is one of the main strategies adopted by the global cement industry to reduce CO<sub>2</sub> emissions [3]. However, the availability of ground blast furnace slag and fly ash to produce blended cements is not enough to offset the demand for Portland cement [4]. In addition, Brazil is a country of continental dimensions, with enormous regional differences, in which the same mitigation actions will not be necessarily applied everywhere [5].

The development of more sustainable alternatives for cement production must then consider the use of locally and regionally available raw materials. The state of Pará, in Amazon region, is one of the most privileged regions on the planet in terms of mineral resource exploitation. Mining projects in Pará stand out for the quality of their products, the commercial values, and the magnitude of production, also making them responsible for generating significant amounts of waste or by-products. Among the various types of waste from its intense mineral activity, flint kaolin (FK) prevails. FK has excellent technical characteristics, as demonstrated by various studies, indicating its potential application not only in the construction sector but also in the refractory and advanced ceramics industries [6-11]. It is essentially composed of extremely fine kaolinite, has high uniformity, and is easy to handle. All these requirements are excellent to produce a highly reactive pozzolan, called metakaolin, by calcination and grinding of pure kaolinite clays with very few inert minerals.

Two other by-products with great potential for application as active and inert mineral admixtures in Portland cements are the gibbsite-kaolinite waste (GKW) and bauxite residue (BR), respectively. The former is generated in the beneficiation process of bauxite ore to remove kaolinite from gibbsite; the resulting by-product is then enriched with kaolinite [12], with amounts close to 5.4 Mtpa. Bauxite residue (BR) is a by-product of the Bayer process, mainly containing bauxite ore phases such as hematite, goethite, gibbsite, and anatase, as well as sodalite formed during the process and soluble sodium. Approximately 4.7 Mt of this residue are generated annually. The pozzolanic activity of BR is not satisfactory [11].

The mining sector and the aluminum industry have been making many attempts to utilize their by-products instead of simply depositing them, due to the high disposal costs in residue disposal areas or sedimentation ponds.

The aim of this research was to assess the feasibility of producing low-carbon cements (LC<sup>2</sup>) through the combined use of GKW and BR as SCM to partially replace clinker in Portland cement, aiming at meeting engineering goals and simultaneously achieving favorable environmental indicators in terms of reduction of both CO<sub>2</sub> emissions and demand for NR<sup>2</sup>.

## 2. Experimental Program

### 2.1 Raw Materials

Three raw materials were 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 in kaolinite and gibbsite, here referred to as GKW. The third was included in the experiment for comparison purposes, namely the FK. The FK, extracted from deposits in the Capim River valley, Ipixuna do Pará, is recognized as a high-quality kaolin to produce high-performance pozzolans [13-14].

### 2.2 Production of Supplementary Cementitious Material

The active SCM produced in the experimental program were derived from calcination and grinding of kaolins (GKW and FK). The inert SCM (BR) was only dried and ground. Two and a half kilograms of each kaolin were thermally treated at 800 °C for 2 hours. 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 was dried in an oven at 105 °C until reaching constant mass and ground under the same conditions.

### 2.3 Production of Blended Cements

The production of blended cements consisted of mixing Ordinary Portland cement (OPC) with the SCM described in section 2.2. The cementitious mixtures were designed to produce ternary blends, in which fixed amounts of 47 % clinker, 3.0 % gypsum, and 50 % SCM were set, varying the proportions between pozzolans and BR (2:1 and 1:1) and the type of metakaolin, whether originating from the calcination of KF or GKW. Table 1 shows the composition of low-carbon blended cements.

**Table 1. Composition of Low-Carbon Blended Cements.**

Cement	Mass composition (%)				
	Kk	Gp	FK	GKW	BR
OPC	96.5	3.5	-	-	-
LC <sup>2</sup> KF 2	47.0	3.0	33.0	-	17.0
LC <sup>2</sup> KF 1	47.0	3.0	25.0	-	25.0
LC <sup>2</sup> GKW 2	47.0	3.0	-	33.0	17.0
LC <sup>2</sup> GKW 1	47.0	3.0	-	25.0	25.0

Note: Kk: clinker; Gp: gypsum.

### 2.4 Experimental Program

The characterization methods were carried out on raw materials, SCM and binders. 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 particle size distribution (PSD) obtained by laser grain size measurements (Model Mastersizer 300, Malvern). The specific surface areas (SSA) of the cements were determined by two different procedures. The first, by the air permeability method (Blaine Method), according to the prescriptions of ABNT NBR 16372 standard. The second by the BET method (Model Nova 2200e, Quantachrome Instruments). The specific gravity was determined according to the Brazilian standard NBR 16605.

Four ternary blended cements were produced with 50 % clinker replacement and compared with ordinary Portland cement with respect to the compressive strength. Regarding the environmental indicator, CO<sub>2</sub> emissions and consumption of non-renewable natural resources (NR<sup>2</sup>) were also evaluated, as well as the compressive strength for each of these index ratios, reported here as yield of the binder. CO<sub>2</sub> emissions were calculated for a BAT Scenario (Best Available Technology) in Brazil, using 6-stage preheater and precalciner kilns, in addition to vertical roller mills. In determining the NR<sup>2</sup>, only the raw material necessary for the manufacture of all cements (OPC and LC<sup>2</sup>) were considered. The wastes used in the production of SCM (GKW and BR), as well as fuels and energy were not included in the NR<sup>2</sup> inventory. The environmental indicators were obtained from environmental inventory of local industries' data base.

The compressive strengths of the cements were determined according to the ABNT NBR 7215 standard. The evaluation was carried out on mortar specimens made acc.to Brazilian standard with cement and sand in a 1:3 mass ratio and a water-to-cement ratio of 0.48 for ages of 1, 3, 7, and 28 days. To provide similar plasticity, due to the higher fineness of the blended cements, polycarboxylate superplasticizer admixtures were used in the blended cement mortars at dosages of 0.2 % by mass of cement, while in the reference mortar (with OPC), only 0.08 % was used. Twelve cylindrical specimens of 50 × 100 mm were molded for each type of cement, three for each age (1, 3, 7 and 28 days).

The specimens were air-cured for the first twenty-four hours and then kept under moist curing until the specific testing date. The exception was for the 1-day test specimens, which were tested only under air curing. The molding of the mortars was acc. ABNT NBR 5752 standard, specifying procedures for mixing, molding, curing and testing of strength.

### 3. Results and Discussions

#### 3.1 Characterization of Raw Materials and SCMs

The physical and chemical characteristics of the raw materials and SCM shown in Table 2 are discussed together with the mineralogy (Figures 1 and 2), to address their advantages and challenges as alternative resources to produce low-carbon cements.

**Table 2. Chemical and physical characteristics of raw materials and SCM.**

Oxides (wt.%)	BR	GKW	FK	M-GKW	M-FK
SiO <sub>2</sub>	13.43	24.30	43.55	-	-
Al <sub>2</sub> O <sub>3</sub>	16.28	37.68	38.75	-	-
Fe <sub>2</sub> O <sub>3</sub>	46.74	16.87	1.57	-	-
TiO <sub>2</sub>	4.82	2.26	2.09	-	-
Na <sub>2</sub> O	8.32	0.00	0.00	-	-
CaO	1.12	0.00	0.00	-	-
L.O.I.	7.78	18.52	13.70	0.30	0.50
Physical Parameters					
Specific gravity (kg/dm <sup>3</sup> )	3.07	2.72	2.53	2.83	2.63
SSA <sub>BET</sub> (m <sup>2</sup> /g)	15.76	19.92	24.64	25.00	42.66
D <sub>10</sub> % (µm)	1.70	3.05	4.60	1.81	3.95
D <sub>50</sub> % (µm)	8.07	6.74	9.87	4.73	21.30
D <sub>90</sub> % (µm)	63.10	18.70	27.10	18.20	75.20

BR is composed of hematite, goethite, gibbsite, anatase and sodalite. Fe is present in the form of hematite (Fe<sub>2</sub>O<sub>3</sub>) and goethite (FeOOH), and it is responsible for the intense red color of BR. Al<sub>2</sub>O<sub>3</sub> present in the BR is in the form of aluminum hydroxide of the gibbsite type (Al(OH)<sub>3</sub>) as

well as in the crystalline structure of sodalite ( $\text{Na}_{7,6}(\text{Al}_6\text{Si}_6\text{O}_{24})\cdot(\text{CO}_3)_{0,93}\cdot(\text{H}_2\text{O})_{2,93}$ ), a mineral formed during the bauxite digestion process.  $\text{SiO}_2$  and  $\text{Na}_2\text{O}$  present in BR are also part of the structure of sodalite.  $\text{TiO}_2$  is in the form of anatase and  $\text{CaO}$  is part of the structure of calcite (not detected by XRD). The high content of Fe explains the high density of  $3.07 \text{ kg/dm}^3$  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 GWK, 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 GWK (high-grade kaolin) [15]. The LOI of 18 %, very high for kaolin, is due to the presence of gibbsite and goethite (Figure 1). Regarding FK, it is extremely pure kaolin, consisting essentially of kaolinite, in addition to anatase and goethite as trace minerals (Figure 1).

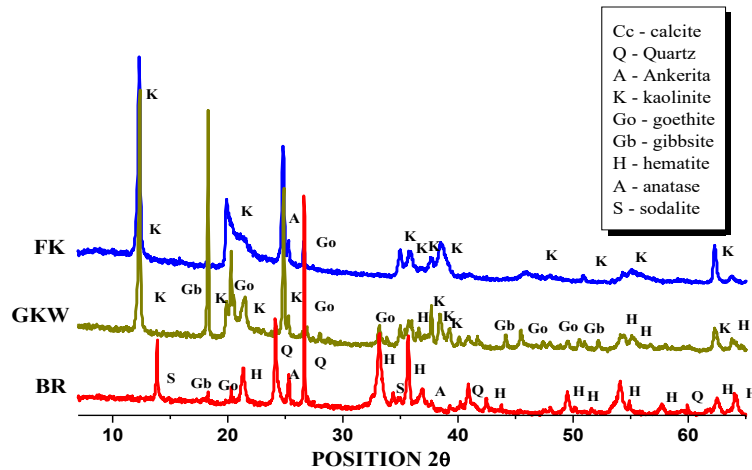


Figure 1. XRD patterns for BR, GWK and FK.

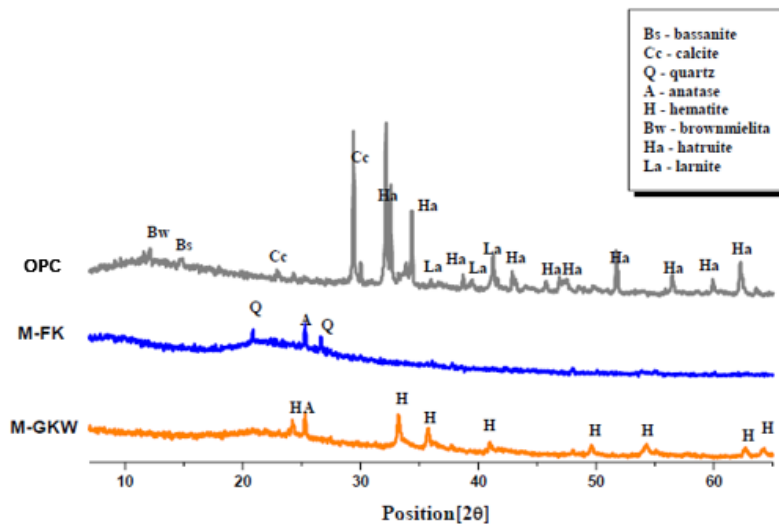


Figure 2. XRD patterns for M-GKW, M-FK and OPC.

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 [13].

In the X-ray diffractogram of the GWK (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 GWK is a kaolinite with a high degree of defects due to the first triplet, located between 19.9° and 23.8° (2θ), where a unique peak was found, and the other two triplets were located between 35° and 40° (2θ), where only two bad-defined reflections were found. Regarding 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 (GWK and FK), complete dehydrolysis occurred from the thermal treatment, reflected in low values of LOI (Table 2). In the X-ray diffractogram of M-GWK, only the amorphous halo related to metakaolinite, the hematite and anatase were identified. Calcination at 800 °C converted goethite into hematite and the gibbsite disappeared. However, no peaks were identified in XRD referring to boehmite or γ-alumina, which are minerals formed from the dehydration of gibbsite at temperatures above 300 °C (Figure 2).

The particle size distributions of untreated kaolins showed that both are extremely fine and have similar SSA<sub>BET</sub> (Table 2). However, when thermally treated and milled, M-GWK presented fineness and SSA<sub>BET</sub> superior to M-KF. The SSA<sub>BET</sub> of the M-GWK was extremely high, around 40 m<sup>2</sup>.g<sup>-1</sup>, aspect that may cause severe problems of shrinkage and creep in cementitious products.

The particle size distribution of BR is compatible with those of Portland cement. However, the SSA<sub>BET</sub> of 15 m<sup>2</sup>/g of BR was three times higher in relation to Portland cement (Table 3). The incorporation of BR in cement, at levels above 25 % may increase the fineness excessively and result in problems associated with the dimensional stability of mortars and concretes. However, further research is needed to assess this issue.

### 3.2 Characterization of Low-Carbon Blended Cements

The physical characteristics of the produced cements are presented in Table 3. The specific gravity, regardless of the type of metakaolin used with the incorporation of BR, were below 3.00 kg/m<sup>3</sup> due to the lower specific gravity of these SCM compared to OPC. However, among the blended cements, those with higher incorporation of BR had the highest specific gravity values, preferable in construction due to the lower dispersion of particulate material, as well as for the ease of bagging. The specific gravity of the cement increases with the higher specific gravity of those residues (GWK and BR) and the cements produced from the combination of metakaolin derived from the calcination of GWK with BR showed the highest specific gravities, with values close to 3.00 kg/m<sup>3</sup>.

**Table 3. Physical characteristics of Low-Carbon Blended Cement.**

Parameters	OPC	LC <sup>2</sup> KF 2	LC <sup>2</sup> KF 1	LC <sup>2</sup> GWK 2	LC <sup>2</sup> GWK 1
Specific gravity (kg/dm <sup>3</sup> )	3.17	2.86	2.86	2.97	2.99
SSA <sub>BLAINE</sub> (cm <sup>2</sup> /g)	3 980	6 580	6 460	8 080	7 340
SSA <sub>BET</sub> (m <sup>2</sup> /g)	4.1	12.3	10.9	18.5	16.1
Particle Size Distribution					
D <sub>10</sub> % (µm)	1.70	2.87	3.98	3.87	1.87

D <sub>50</sub> % (µm)	8.06	12.74	9.46	7.00	7.51
D <sub>90</sub> % (µm)	28.90	35.97	38.87	30.78	33.57

The cements with M-GKW (LC<sup>2</sup> GKW) exhibited extremely high BET specific surface areas (SSA), between 16 and 18 m<sup>2</sup>/g, while the binders with calcined KF had SSA values between 10 and 12 m<sup>2</sup>/g. Both are very high and significantly superior to the SSA<sub>BET</sub> of OPC, 4.15 m<sup>2</sup>/g. In terms of SSA<sub>Blaine</sub>, the values for binders with M-GKW ranged between 7 340 and 8 000 cm<sup>2</sup>/g, while those with calcined KF ranged between 6 460 and 6 580 cm<sup>2</sup>/g. The SSA<sub>Blaine</sub> of OPC was 3 980 cm<sup>2</sup>/g. Further investigations into the calcination process would be necessary to cause more significant particle agglomerations to reduce the SSA.

The increase in SSA of about 2 to 4.5 times compared to the OPC by the BET method and 1.5 to 2 times by the Blaine method prompts that these cements are much more susceptible to issues related to dimensional stability than the reference cement.

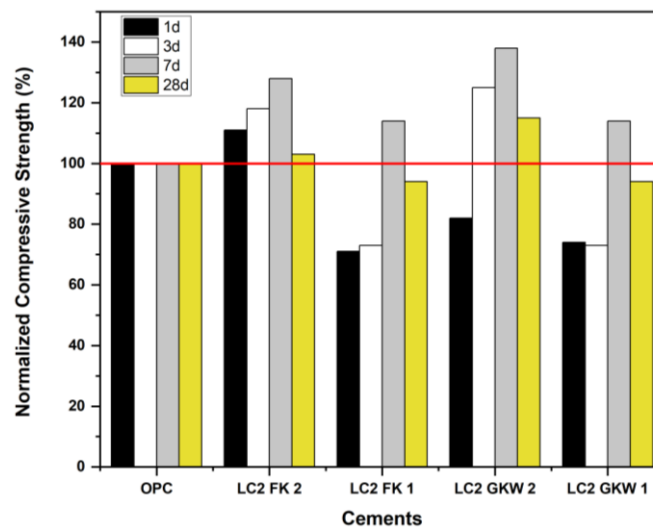
### 3.3 Compressive Strength and Environmental Indicators

The compressive strength values of the mortars for the ages of 1, 3, 7, 28, and 91 days and the environmental indicators are presented in Table 4. The normalized strengths relative to the reference mortar values for all evaluated ages are shown in Figure 3.

**Table 4. Compressive Strength and Environmental indicators of Low-Carbon Cements.**

Cement	Incorporation of raw FK or GKW (%) <sup>(1)</sup>	Incorporation BR (%)	Compressive Strength (MPa)					CO <sub>2</sub> emissions (kg CO <sub>2</sub> /t cement)	NR <sup>2</sup> (t NR <sup>2</sup> /t cement)
			1d	3d	7d	28d	91d		
OPC	-	-	19.4	33.9	34.5	45.0	53.1	810	1.93
LC <sup>2</sup> FK 2	38,0	17	21.5	39.9	44.3	46.5	52.8	534	1.40
LC <sup>2</sup> FK 1	28,8	25	13.8	29.0	39.4	45.3	50.2	520	1.30
LC <sup>2</sup> GKW 2	40,2	17	15.9	42.4	47.5	52.0	58.4	534	0.99
LC <sup>2</sup> GKW 1	30,5	25	14.4	24.7	39.4	42.1	51.4	520	0.99

Note: <sup>(1)</sup>Quantities of raw GKW and FK required to produce metakaolin (pozzolan), considering LOI of 18 % and 13.3 %, respectively.



**Figure 3. Compressive strength of mortars normalized to the strength of OPC.**

Blended cements showed a high strength development rate in the first ages, between 1 and 7 days, and more accentuated for 3 and 7 days. These binders, with significant incorporations of SCM (50 %), are comparable to high early strength cement, despite the reduced clinker content, with compressive strengths at 1 day above 14 MPa (ranging between 13.8 and 21.5 MPa), the minimum limit established by ABNT NBR 16679 for rapid-hardening cement. After 7 days the blended cements showed compressive strengths above 39 MPa, and after 28 days between 42 and 52 MPa, which, according to the requirements of Portland cement standard ABNT NBR 16697, would classify them as pozzolanic cement, CP IV, class 40. The blended cements with higher metakaolin content (LC<sup>2</sup> 2), regardless of the type of kaolin used, showed higher mechanical efficiency.

From the seventh day on, there was a slowdown in the strength development of blended cements. However, the soluble sodium released by the sodalite present in the BR did not impair the cement hydration to the point of showing decreases in mechanical properties or interruption of the cement hydration or pozzolanic reactions. In Table 4, both at 28 and 91 days, the blended cements present increases in compressive strength. The blended cements develop strengths at 91 days of 50–58 MPa, quite high and mostly higher than 53 MPa of OPC.

The normalized strength in relation to the reference cement (Figure 3) showed an initial acceleration of strength up to the seventh day and a stabilization from the 28<sup>th</sup> day of age on, demonstrating equivalent long-term strength developments between blended and the reference cements. Strength increments for the most advanced ages (28 and 91 days) indicate that the pozzolanic reactions of calcined clay are still evolving.

The blended cements with higher metakaolin content (LC<sup>2</sup> 2), regardless of the type of kaolin used, showed higher mechanical efficiency. Additionally, the use of metakaolin produced from GWK provided mechanical performance similar or even superior to that of the pozzolan produced from FK, which is recognized as a high-quality material.

CO<sub>2</sub> emissions from the evaluated blended cements were between 34 and 36 % lower than those from OPC. Binders with higher metakaolin content (LC<sup>2</sup> 2) showed slightly higher CO<sub>2</sub> emissions compared to binders with lower metakaolin content (LC<sup>2</sup> 1) due to the increased energy required for the calcination of clays (GWK or FK).

The NR<sup>2</sup> consumptions of the blended cements are shown in Table 4, with values between 27 and 49 % lower than those of the OPC. Unlike what was observed in compressive strength and CO<sub>2</sub> emissions, there were significant differences between the use of metakaolin produced from GWK and FK. The NR<sup>2</sup> demand of pozzolanic cements with M-GWK was substantially lower than that of the binder with M-FK, due to the former being composed of 55 to 57 % waste materials.

The synergy between the high reactivity of metakaolin from GWK and the acceleration of hydration and pozzolanic reactions by the soluble sodium from BR provided extremely satisfactory results in terms of both initial and final strengths, as well as in the reduction of CO<sub>2</sub> emissions and NR<sup>2</sup> demand due to the significant utilization of both waste materials. It is noteworthy that LC<sup>2</sup> GWK cements, with 50 % waste from the aluminum production chain, still achieved results superior to those obtained with the OPC and LC<sup>2</sup> FK.

The levels of strength achieved by these cements, regardless of the type of metakaolin (KF or GWK) or the proportion (2:1 or 1:1), qualify them for the industrial segment, which includes the construction and engineering industries, prefabricated elements, as well as art, infrastructure, and industrial works, representing about 30 % of the Portland cement market in Brazil. However, there are no regulatory restrictions preventing this group of cements from also being applicable

in the self-construction segment, despite their high strengths, which could be a very positive aspect and an important differentiator for a new product in the market.



Figure 4. Colors of pastes with low carbon and reference cements.

The high initial strengths, even with proportions of up to 25 % BR, a very significant number, impart a characteristic to pozzolanic Portland cements of high strength at early ages, overcoming a barrier to their widespread use in the building construction market.

A disadvantage is the reddish colour that the cementitious materials acquire. This aspect must be strongly considered in strategic planning for a potential commercial application. Figure 4 shows the colours of some tablets made with these cements. This aspect requires an adequate marketing campaign highlighting the economic and environmental advantages of these cements, with technological properties superior to those of commercial grey cements, which offer chromatic neutrality to the built environment.

### 3.4 Yield of Binder

Binders were compared not only from the point of view of mechanical properties, but also from the yield of the binder, indicators that associate how much CO<sub>2</sub> is emitted, or how much NR<sup>2</sup> is consumed, to achieve the same level of strength (Figure 5).

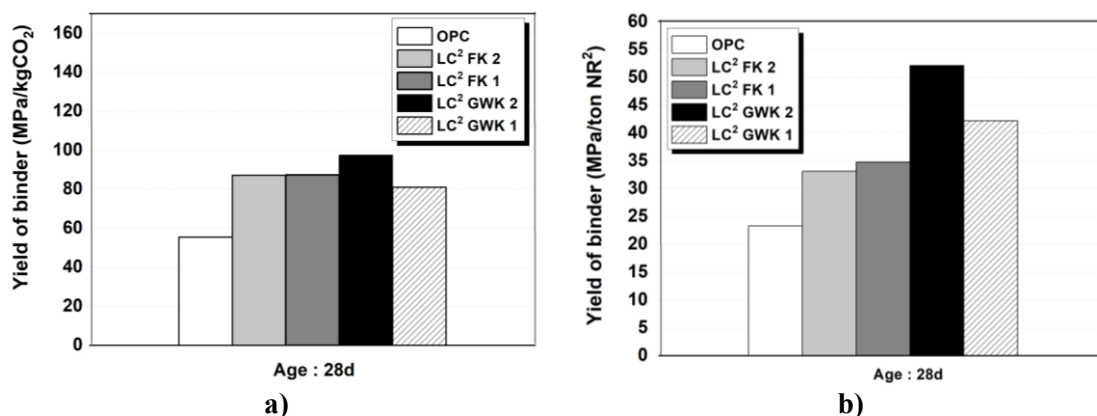


Figure 5. Yield of binder. Left: a) CO<sub>2</sub> footprint, Right: b) NR<sup>2</sup>

In terms of CO<sub>2</sub> emissions, pozzolanic cements, regardless of the type of metakaolin (GKW or FK) and the incorporated content (25 and 33 %), exhibited much higher yields of binder compared to the reference cement and were similar to each other. There were no significant differences

between binders with SMC, indicating that the higher mechanical efficiency of cements with higher metakaolin content (LC<sup>2</sup> 2) was offset by the lower CO<sub>2</sub> emissions of binders with lower metakaolin content (LC<sup>2</sup> 1), with all showing yields of binder between 81 and 97 MPa/t CO<sub>2</sub>. Despite the absolute environmental indicators in Table 4, there is no difference in using cements with higher or lower metakaolin content or produced from GKW or FK in terms of CO<sub>2</sub> emissions to achieve the same level of strength.

Regarding NR<sup>2</sup> consumption, pozzolanic cements with M-GKW yielded between 42 and 52 MPa/t NR<sup>2</sup> at 28 days, while those with M-FK and OPC provided 34 and 23 MPa/t NR<sup>2</sup>, respectively. For cements with M-GKW, higher mechanical efficiency associated with large-scale use of industrial waste translated into better environmental indicators in terms of NR<sup>2</sup> demand.

#### 4. Conclusions

Cements with incorporations of 25 to 33 % of MK and 17 to 25 % of BR provided strengths both at early ages and at final ages that far exceeded the requirements for Portland cement, achieving results at 28 days equal to or greater than 42 MPa.

The synergy between BR and metakaolin, regardless of the type of kaolinite used (GKW or FK), showed very attractive preliminary compressive strength results in terms of utilization in the Construction Industry. With reduced proportions of calcined material, they achieved high early-age strengths, an aspect that has always been unfavorable and a barrier to the widespread use of cements with SCM in the construction market. The incorporation of BR provided a *sui generis* characteristic to pozzolanic Portland cements: high early-age strength.

The mechanical performance of cements with calcined GKW in conjunction with BR was very satisfactory, both at early and final ages. This is due to the fact that the residue is a high-grade kaolin, with high concentrations of kaolinite, between 50–60 %. However, this high reactivity is partly due to the extremely high specific surface area, which in turn, when incorporated into the cements, resulted in excessively high SSA<sub>BET</sub> and SSA<sub>BLAINE</sub>, far above the recommended levels for dimensional stability.

CO<sub>2</sub> emissions from the evaluated blended cements were between 34 and 36 % lower than those from OPC. Binders with higher metakaolin content showed slightly higher CO<sub>2</sub> emissions compared to binders with lower metakaolin content due to the increased energy required for the calcination of clays. In terms of yield of binder related to CO<sub>2</sub> footprint, there is no difference in using cements with higher or lower metakaolin content or produced from GKW or FK to achieve the same level of strength.

Regarding NR<sup>2</sup> consumptions, the blended cements showed values between 27 and 49 % lower than those of the OPC, with differences in the use of metakaolin produced from GKW. This aspect affected the yield of binder associated with NR<sup>2</sup>, with pozzolanic cements containing M-GKW showing results 100 % higher than those obtained with OPC at 28 days. The higher mechanical efficiency, resulting from the synergy between BR and GKW, and the fact that they are composed of 55–57 % waste led to significantly lower NR<sup>2</sup> demand.

In summary, the combined evaluation of CO<sub>2</sub> emissions, NR<sup>2</sup> demand, and mechanical efficiency identifies ternary cements made from calcined GKW and BR as promising low-carbon binders. However, the results obtained so far, are preliminary in nature, making it essential to conduct in-depth investigations into the physical requirements of these cements, as well as the mechanical behaviour at more advanced ages (> 180 days) and aspects related to durability and color are also of extreme importance for validating the use of these cements in the Construction Industry.

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