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AMAZON KAOLINS AS RAW MATERIALS FOR NEW BLENDS OF LIMESTONE CALCINED CLAY CEMENT

Caulins da Amazônia como matéria-prima para novas misturas de cimento de calcário e argila calcinada

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Abstract

The use of supplementary cementitious materials constitutes one of the main strategies by the global cement industry to limit global warming. In the Amazon, between 1990 and 2018, cements were produced with 14-30% calcined kaolin and 5-10% limestone. Posteriorly, the use of calcined clays and limestone was replaced only by limestone up to 25%. A local solution for reducing costs and improve environmental indicators would be a large-scale use of limestone calcined clay cements (LC^3) with other calcined kaolin/limestone ratios. The objective was to investigate the feasibility of new blends of LC^3 from the ratio of calcined kaolin to limestone below 2 and clinker replacement percentages above 50%. The results point to the possibility of using a greater amount of limestone in LC^3 compositions while incorporating less clinker and calcined kaolin, bringing environmental benefits and reducing production costs. Changes in the Brazilian standards are necessary to include new compositions of LC^3.

Keywords: Amazon kaolins; News blends; LC^3-binders.

RESUMO

O uso de materiais cimentícios suplementares constitui uma das estratégias da indústria global do cimento para limitar o aquecimento global. Na região amazônica, entre 1990 e 2018, produziu-se cimentos com 14-30% de argila calcinada e 5-10% de calcário. Posteriormente, o uso de argilas calcinadas e calcário foi substituído apenas calcário em até 25%. Uma solução regional para reduzir custos e otimizar indicadores ambientais seria o uso de cimentos de argila calcinada e calcário (LC^3) em larga escala, com outras proporções de caulim calcinado/calcário. O presente estudo teve como objetivo investigar a viabilidade de novas composições de LC^3 a partir da razão caulim calcinado/calcário abaixo de 2 e percentuais de substituição de clínquer acima de 50%. Os resultados apontam para a possibilidade de utilizar maior quantidade de calcário nas composições LC^3 incorporando menos clínquer e caulim calcinado, trazendo benefícios ambientais com redução de custos de produção. São necessárias mudanças nas normas brasileiras para incluir novas composições de LC^3.

Palavras-chave: Caulins da Amazônia; Novas blendas; LC^3.

1 INTRODUCTION

The use of supplementary cementitious materials constitutes one of the main strategies by the global cement industry to limit the increase of the global temperature by up to 2ºC (UN ENVIRONMENT *et al.*, 2018). However, this solution comes up against the limited availability of slag and fly ash. In the Amazon, between 1991 and 2018, the only cost-reducing alternative found was the production of composite and pozzolanic cements with 14-30% calcined kaolin and 5-10% limestone. The clays used to produce these cements were secondary kaolins, with percentages above 85% of white-burning kaolinite. There are deposits of flint or semi-flint kaolin, located in the northern Amazon, about 150 to 200 km far from the cement plants. These cements achieved compressive strengths greater than 40 MPa at 7 days and 50-58 MPa at 28 days. In the 2000s, studies carried out at the Federal University of Pará demonstrated that replacing up to 60% of the clinker by mixtures of calcined kaolin/limestone ratio less than 2, preferably 1, with higher limestone content, showed better mechanical properties in both initial and final ages compared to ordinary Portland cement (LIMA, 2004). This performance was attributed to the high quality of the Amazonian kaolin, which allowed the admixture of up to 30% limestone to the composition (LIMA *et al.*, 2005).

Since 2018, limestone calcined clay cements (LC^3) are no longer produced in the Amazon in favor of Portland-limestone cements (PLC) due to the change in the Brazilian standard, which increased the percentage of limestone in CEM II from 10% to 25%, thus becoming more economically attractive. However, this scenario does not meet the Brazilian targets for reducing CO_2 emissions foreseen for the period of 2020-2050 (SNIC, ABCP, 2019). Meeting the CO_2 emission targets associated with low production costs for regions such as the Amazon, with low industrialization and vast territorial extension, will only be possible by using LC^3, with higher percentages of clinker replacement and greater incorporation of limestone. Within this context, the objective of this work was to reproduce the scientific study of the 2000s (LIMA *et al.*, 2005), this time evaluating the technical, economic, and environmental feasibility of new mixtures of calcined flint kaolin cement and limestone.

2 METHODOLOGY

Six ternary cements were produced, divided into two groups with different percentages of clinker replacement. Group I, with 45% replacement, was compared with Portland-limestone cement (CEM A/L 42.5), aimed at the industrial segment, which comprises 30% of the Brazilian market. Group II, with 60%, was compared with Portland-limestone cement (CEM B/L 32.5) intended for self-construction (bagged cement segment), which represents 70% of the Brazilian market. In addition to Portland-limestone cements, ordinary Portland cements (CEM I 32.5 and 42.5) were also used as a reference. The property evaluated was the compressive strength.

Regarding the environmental indicator, CO_2 emissions, electrical intensities and consumption of non-renewable natural resources (NR^2) were also evaluated, as well as the compressive strength for each of these index ratios, reported here as yield of the binder. CO_2 emissions and electrical intensities (EI) were calculated for a BAT Scenario (Best Technology Available) in Brazil, using 6-stage preheaters and precalciners, in addition to vertical roller mills. In determining the NR^2, all the raw material necessary for the manufacture of clinker, pozzolana and limestone were considered, i.e., blistering, humidity and loss of crystallization water. The environmental indicators were obtained from environmental inventory with local industries data base.

The standardized mortars were molded in a 1:3 ratio (binder: IPT sand) by weight, with a water/binder ratio of 0.50 (by weight), the binders being fully mixed before making the mortars. Superplasticizer (PCE) was used to maintain the same consistencies at flow table for all mortars (230±5mm). The Specific Surface Area was measured using the Blaine´s air permeability method (SSA_{Blaine}). Compressive strengths at 1, 3, 7, 28 and 91 days were determined according to ABNT NBR 7215. Table 1 shows the six different binder compositions, the SSA_{Blaine}, the dosage of superplasticizer used ((w/w of the total mass of cement) and the environmental indicators for each of the evaluated binders. The global assessment of the production cost considered the costs of materials (raw materials, fuel), energy, operation and maintenance, and equipment depreciation.

3 RESULTS AND DISCUSSIONS

Table 1 shows compositions and environmental indicators of the binders. The LC^3 binders required more than double the superplasticizer than the reference cements due to the higher SSA_{Blaine}. All LC^3-binders showed lower compressive strengths at early ages (1-3 days) than the reference cements, regardless of the type of segment or group (industrial or self-construction) (Figure 1). This is a disadvantage of LC^3, mainly in the industrialized construction segment, which requires high resistance in the early ages. From the 7th day onwards, LC^3 overcame the OPC and PLC strengths. It is worth mentioning the performance of LC^3 50 1, with a higher amount of limestone in the composition (22.5%) and a lower percentage of calcined kaolin, which also presented higher compressive strengths than the reference cements at 7 days of age (Figure 1a). The high concentration of kaolinite in flint kaolin provided the calcined clay with high reactivity, allowing the incorporation of limestone above the ideal stoichiometric calculation without impairing the initial and final strengths of these cementitious compositions, which were 38 MPa at 7 days and 49 MPa at 28 days, quite high and appropriate for the industrialized construction segment.

Table 1. Compositions and environment indicators of binders.

	CEM I 32.5/42.5	CEM II A/L 42.5	CEM II B/L 32.5	LC^{3}50 2	LC^{3}50 1.5	LC^{3}50 1	LC^{3}35 2	LC^{3}35 1.5	LC^3 35 1
Clinker (%)	95	82	74	50	50	50	35	35	35
Calcined clay (%)				30	27	22.5	40	36	30
Limestone (%)		13	21	15	18	22.5	20	24	30
Gypsum (%)	5	5	5	5	5	5	5	5	5
SSA_{Blaine} ($cm^2.g^{-1}$)	4200	4950	4780	6210	5850	5670	7370	6910	6410
PCE (%)	0,4	0,9	0,9	1,6	1,7	1,9	2,4	2,5	2,6
CO_2 emissions (kg/tbinder)	810	727	663	530	525	515	430	422	411
EI (kwh/tbinder)	110	83	78	65	65	64	58	57	57
NR^2 (ton NR^2/tbinder)	1.93	1.76	1.70	1.58	1.58	1.57	1.50	1.49	1.48

A similar behavior was observed for LC^3 35 compositions, with calcined kaolin/limestone ratio lower than the stoichiometric ideal (1.5:1 and 1:1). Despite the low clinker to cement ratio, these compositions showed similar strengths to OPC and PLC cements at 7 days, surpassing them after the 28th day (Figure 1b). Strength gains were more expressive for long-term ages, reaching between 39 and 42 MPa at 28 days and 43 and 49 MPa at 91 days. These LC^3 35 could be used in the segment of bagged cement, self-construction or informal construction, which represents about 70–75% of the national market and intended for the production of low-compressive strength concretes, mortars prepared on site and based-cement products (pavers, blocks and roof tiles), where there are no trained personnel or rational dosage.

In this paper, binders were compared not only considering mechanical properties, but also from the perspective of yield of the binder, indicators that associate how much CO_2 is emitted, or how much electrical intensity or NR2 is consumed to achieve the same level of strength, as shown in Figures 2-4. Regarding CO_2 emissions, LC^3-binders showed lower yields at early ages compared to OPC and PLC. However, at 28 days, due to the higher strength development from the 7th day in relation to the reference cements, the performance of LC^3-binders surpassed the OPC binders and PLC, all of which with yields of around 100MPa/ton CO_2, while OPC only achieved 45-53MPa/ton CO_2 and PLC, 56-61MPa/ton CO_2 (Figure 2).

The behaviors of electrical intensity and NR^2 consumption exhibited order of magnitude similar to that of CO_2 emissions, with LC^3-binders exhibiting lower yields at early ages and higher in the long term. At 28 days, LC^3-binders presented yields greater than 690 MPa/Mwh whereas the OPC and PLC below 535 MPa/Mwh (Figura 3). Regarding the consumption of NR2, LC^3-binders reached yields greater than 26 MPa/tonNR2 whereas the OPC and PLC below 25 MPa/ tonNR2 (Figure 4).

Fig. 1. Compressive strength of cements at 1, 3, 7, 28 and 91 days. a) Industrial segment; b) Self construction segment.

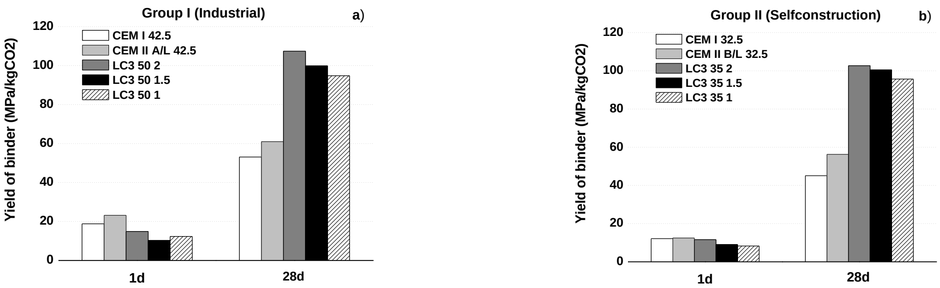

Fig. 2. Yield of binder (CO_2 footprint) at 1 and 28. a) Industrial segment; b) Self construction segment.

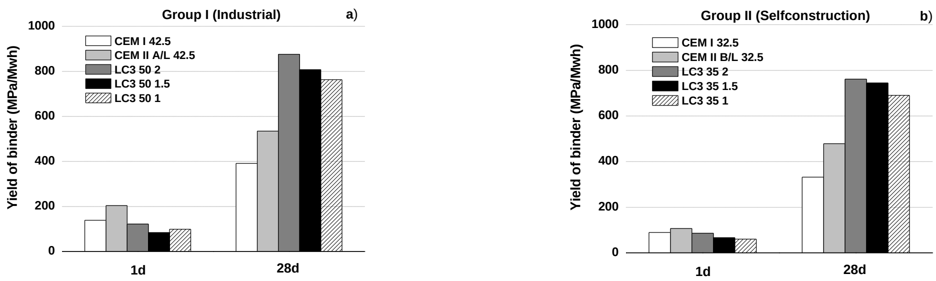

Fig. 3. Yield of binder (E.I.) at 1 and 28. a) Industrial segment; b) Self construction segment.

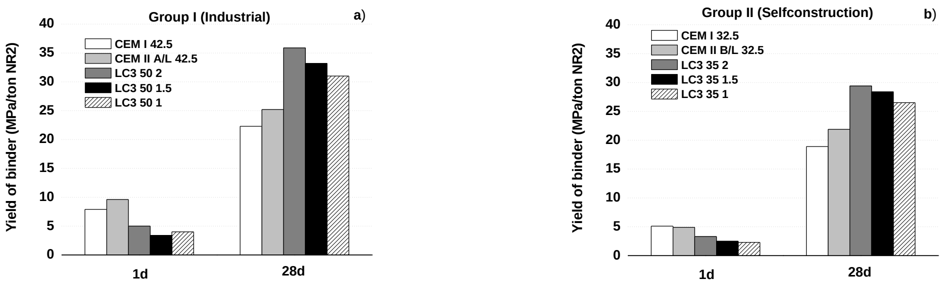

Fig. 4. Yield of binder NR^2 at 1 and 28. a) Industrial segment; b) Self construction segment.

In general, among LC³ compositions, those with the best yields were the ones with the calcined kaolin/limestone ratio equal to 2. The results demonstrate the importance of the binder mechanical efficiency to obtain a good environmental performance. However, the compositions with the highest amount of limestone also showed excellent yields, evidencing the importance of the kaolinite content in the calcined clay pozzolan.

Figure 5 shows the results of the economic analysis, taking into account different transport distances from clays to cement plants. For both segments of the local cement industry, LC³ only becomes viable for binders with a higher limestone content, those with a calcined kaolin/limestone ratio of 1, regardless of the percentage of 45 or 60%, for transport distances of up to 150km from the clay deposits to the cement plant. Despite the excellent results obtained in terms of mechanical properties and environmental indicators, LC³ compositions have economic restrictions due to clay transporting logistics, in addition to the costs associated to calcination. In the Amazon, the scarcity of supplementary cementitious materials, the great distances and the precarious infrastructure are limitations for the implementation of low-carbon cements in the region.

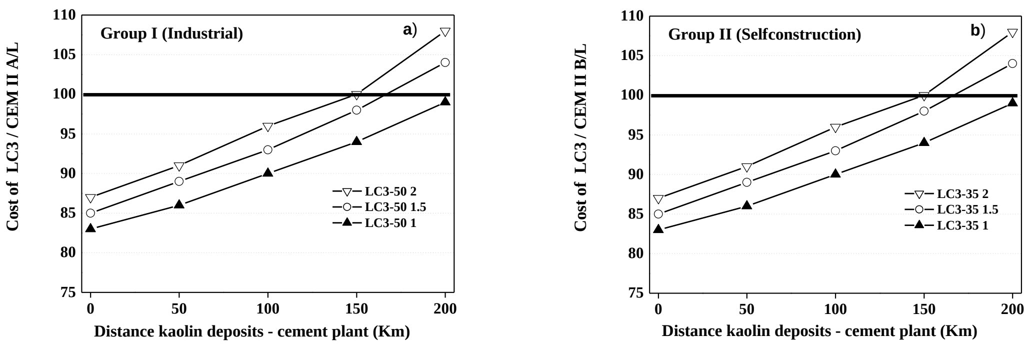

Fig. 5. Economic analysis of production of limestone calcined kaolin cement from Amazon region. a) Industrial segment; b) Self construction segment.

4 CONCLUSION

The results obtained in this paper, in terms of mechanical, environmental and economic aspects, point to the possibility of using a greater amount of limestone in LC³ compositions while incorporating less clinker and calcined kaolin, bringing benefits related not only to environmental issues, but also to investments in equipment, logistics, reducing the amount of fuel and calcined clay and, finally, reducing production costs. This is attributed to the high concentration of kaolinite from the Amazon. Changes in the Brazilian standards are necessary to include these new compositions of LC³.

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