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CALCINED CLAY AS CONSTRUCTION MATERIAL: A REVIEW

Murilo Miguel Narciso
Military Engineering Institute

Antônio Carlos Rodrigues Guimarães
Military Engineering Institute

Lisley Madeira Coelho
Military Engineering Institute

Sergio Neves Monteiro
Military Engineering Institute

Abstract: The use of clay to produce stone material by heating at high temperatures dates back to the first people. The calcined clay samples have heating temperatures from 600°C to 1,100°C and good prospects for mechanical strength as aggregates as well as high pozzolanic activity, making them an interesting cementitious product. The use of Artificial Calcined Clay Aggregate (ACCA) is beneficial for being an alternative to crushed stone in remote places where transportation makes any work very expensive, such as the north of Brazil, and for providing a sustainable solution to waste from iron mining, also known as red mud. The correct characterization, using in-depth knowledge of the minerals involved and the physical and chemical characteristics of calcined clay and iron ore, allows us to study the feasibility of applying these compounds in road construction according to pavement mechanics. Calcined clay can be used in different parts of the pavement, and its application as ACCA is discussed here. The literature review gathers studies and research conducted on the correct characterization of calcined clay, and details on the properties achieved during calcination, in addition to presenting a production methodology and its research history.
Keywords: Calcined Clay, Artificial Calcined Clay Aggregate (ACCA), Calcination.

INTRODUCTION

The utilization of clay to produce stone materials by heating to high temperatures dates back to ancient times, as mentioned in Genesis 11:3. Calcined clay aggregates, subjected to heating temperatures between 600°C and 1,100°C, demonstrated in the research of Cabral, for example, compliance with the mechanical properties recommended in the literature. Thus, the use of ACCA is favorable [1].

Currently, two main benefits of using ACCA stand out. In the northern region of Brazil, the civil construction sector faces significant challenges, especially concerning the transport of crushed material, such as coarse aggregates for concrete or paving, including in base layers of road pavements. This situation was explored by Barbosa in the state of Acre [2]. The exploration of clay deposits for the production of aggregates emerges as a viable and economically advantageous alternative, especially in remote areas, where transporting traditional materials is expensive. In this context, technical knowledge about the use of calcined clay becomes of great relevance.

In addition to the previously mentioned benefits in aggregate production, another significant advantage stands out, especially given the increasing incidents involving the failure of tailings dams in Brazil. Between 1996 and 2005, mining generated approximately

2.180 billion tons of waste, of which iron mining stands out as the largest contributor [3]. In this context, the search for sustainable solutions for the reuse or adequate disposal of these wastes becomes crucial.

As for scientific research in the area of calcined aggregates, the Brazilian Army (BA) was a pioneer in the production of artificial calcined clay aggregates in Brazil, with the first studies carried out at the Military Engineering Institute (IME). The use of these materials in pavement construction has become significantly important due to the challenges faced by the Department of Engineering and Construction (DEC) regarding the scarcity of rock deposits in the northern region of the country. Studies such as those carried out by Cabral, which explored an industrial approach to the production of calcined clay aggregate, and Nascimento, which used the aggregate in soil-aggregate and asphalt mixtures, have already demonstrated viable ways of incorporating clay calcined into paving [1,4].

In an analysis of the use of calcined clay combined with limestone to replace clinker, the compound proved favorable and reduced the emission of carbon dioxide into the atmosphere. Some clay minerals stand out for their pozzolanic activity. Studies carried out in the search for minerals with this activity led to the identification of a new group of pozzolanic materials - calcined clay.

Clay is a material widely distributed around the world, cheap, and easily accessible. At the same time, it is a material with great diversity in mineralogical composition, which has led to numerous works dedicated to analyzing the possibility of using clays from specific deposits for the production of Supplementary Cementitious Material (SCM) in the calcination process. [5-10].

Therefore, this study represents an essential review for researchers interested in producing calcined clay, as well as characterizing the thermal activity, physical, chemical, and mineral characteristics, in addition to the pozzolanic activity of the clay to be researched.

CALCINED CLAY AS ARTIFICIAL AGGREGATE

EVOLUTION OF TECHNOLOGY AND BIBLIOGRAPHIC FRAMEWORK

Research on calcined clay is closely linked to research on expanded clay aggregate. Several studies address the topic of expanded clay aggregate in detail, discussing its origin, necessary raw material, obtaining methods and their applications in paving [11-15,1,4].

These discussions derive from pioneering research carried out in Brazil, especially in the Amazon region, coordinated by IPR/ DNER between the end of the 1970s and the beginning of the 1980s [16,17]. This research involved collecting samples of clayey soils in several states in the region, economic studies on the demand for aggregates, making experimental sections, and even implementing a mobile plant to produce expanded clay aggregates.

Countries such as the United States, which had already used expanded clay aggregates since the 1950s, served as a base for the research conducted by DNER in Brazil. An important stage of this study was a technical visit to the United States in 1979, where engineers visited the states of Texas and Louisiana. During these visits, tests were made with aggregates made from clay, mainly expanded clay, in addition to the discovery of a new possibility with what was called "synthetic aggregates".

"Synthetic aggregates", produced by burning clay at lower temperatures than those required for traditional expanded clay, have shown promise for road use [17]. Conclusions drawn from this experience highlighted the stability and economic viability of these aggregates, compared to synthetic expanded clay aggregate. This resulted in the development of a classification system for fired and expanded clay aggregates, adapted to Brazilian environmental conditions, with specific tests to evaluate aggregates and clay. For Brazil, three tests for aggregates were brought and adapted, and the test for evaluating clay is shown below, in Table 1.

Method	Title of the test
DNER-ME 222/94	Synthetic clay aggregate – abrasive wear
DNER-ME 223/94	Clays for manufacturing synthetic calcined clay aggregate – quick selection through boiling
DNER-ME 225/94	Synthetic calcined clay aggregate- determination of mass loss after boiling

Table 1 – Tests from the Texas Highway Department and adopted by the DNER [16].

Source: Cabral [17].

Table 1 presents the Texas Highway Department tests adopted by the DNER in 1981. One of the pioneers in the study of calcined clay in Brazil was the Military Engineering Institute (IME),

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which began this research in 1997, registering its first patent in the area.

Table 2 presents a summary of the development of research on calcined clay, from its beginnings in the 90s to final undergraduate projects and some master's theses from the first decade of the 2000s. This analysis covers studies conducted in several institutions, in which the authors made their research data fully available, allowing a significant exchange of experiences on the topic. Table 2 lists the work carried out in this context.

PRODUCTION METHODOLOGY

CABRAL carried out a survey on the production processes of red ceramics in his master's thesis at IME Cabral looking for correlations with calcined clay [1]. This study developed a methodology to guide technicians in selecting materials for road projects, mainly related to production. The methodology was structured in three phases, with suggestions for alternative solutions and a main flowchart for better visualization and understanding of the phases. Figure 1 illustrates the flowchart representing the three phases of the proposed methodology.

The methodology proposed by Cabral is divided into three distinct phases, each addressing specific aspects of the calcined clay aggregate production process [17].

In the first phase, the focus is on the detailed characterization of the raw material, aiming to ensure the final quality of the aggregate. This marks the beginning of a process aimed at achieving optimized industrial production. The second phase focuses on suggesting how to produce the aggregate, highlighting the importance of precise control of the raw material's moisture and firing temperature. Furthermore, the alternative to this step is a conventional pottery unit, which can reduce the initial investment compared to acquiring a prefabricated plant.

Finally, the third phase involves the definition and use of the calcined clay aggregate produced, following current standards and meeting specific engineering demands. This phase includes comparing costs with the use of stone aggregates, in addition to suggesting specification ranges for the raw material and aggregates produced, based on bibliographical and normative references. Table 3 presents the fire loss of the chemical composition and the range of values accepted by this test for the production of ACCA.

Component	Range of Values (%)
Fire loss	0.10 to 27.00
SiO2	15.0 to 77.8
Al2O3	11.9 to 56.0
TiO2	0.01 to 3.5
Fe2O3	0.08 to 9.62
CaO	0.01 to 20.1
MgO	0.10 to 16.3
Na2O	0.01 to 11.8
K2O	0.01 to 16.9

Table 3 – Suggested ranges for the chemical composition of the raw material for ACCA production [1].

Source: Cabral [17].

Clay minerals belonging to the illite, kaolinite, and montmorillonite groups, as well as their combinations, show the best performance in the quality of the calcined clay aggregate.

Concerning the mechanical strength required for the aggregate, Table 4 summarizes some specific tests together with their respective acceptance criteria.

Reference	Place	Type	Title
SOARES et al. (1997)	IME	RI	Technical feasibility study on the use of calcined clay aggregate in the Urucu region (AM)
SOARES et al. (1998)	IME	FP	Technical feasibility of calcined clay aggregate for paving in the Amazon
COSTA et al. (2000)	IME	FP	Calcined clay aggregate from the Amazon: analysis of fatigue and resilience parameters in asphalt mixtures
BATISTA (2004)	IME	MD	Physical and mechanistic characterization of calcined clay aggregates producedwith fine soils from BR-163/PA
CABRAL (2005)	IME	MD	Production methodology and use of calcined clay aggregates for paving
NASCIMENTO (2005)	COPPE	MD	Solutions for paving with calcined clay aggregate in Rio Branco (AC)
SILVA (2006)	IME	MD	Behavior of hot asphalt mixes using calcined clay aggregate
NUNES (2006)	UFC	MD	Mechanical characterization of asphalt mixes produced with synthetic calcinedclay aggregates regarding permanent deformation
SANTOS (2007)	UNB	MD	Study of the behavior of synthetic calcined clay aggregate for use in asphalt coatings in Manaus
CABRAL (2008)	UFAM	MD	Manufacture of concrete with calcined clay aggregate produced with soil from the pottery hub in the Amazon

Table 2 - List of studies carried out on calcined clay aggregate.

RI = Research initiation; FP = Final project; MD = Master's dissertation [17].

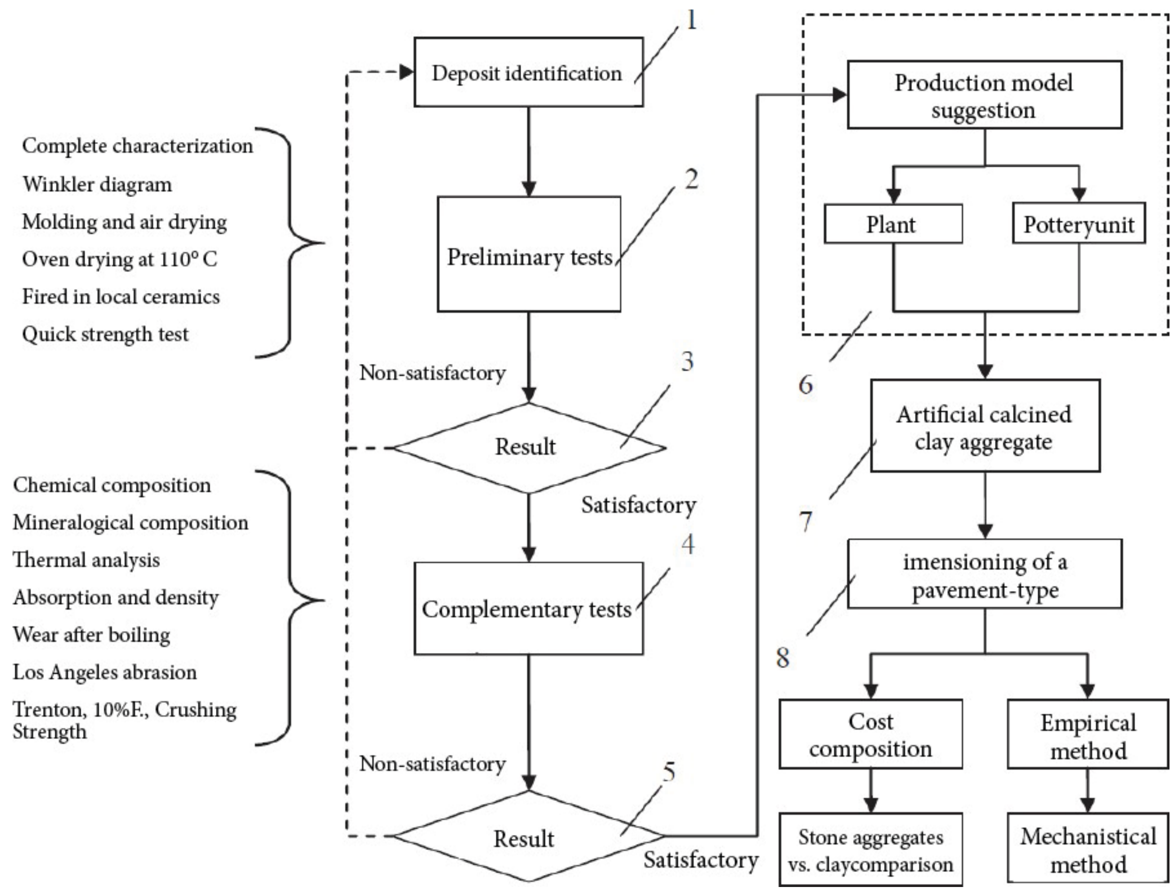


Figure 1: Flowchart representing the methodology(CABRAL, 2005).

Method	Title of the test	Limits of Results
DNER-ME 222/94	Synthetic clay aggregate - abrasive wear	Less than 50%
DNER-ME 225/94	Synthetic calcined clay aggregate - determination of mass loss after boiling	Less than 6%
DNER-ME 197/97	Aggregates - determination of crushing strength of coarse aggregates	Less than 40%
DNER-ME 081/98	Aggregates - determination of absorption and density of coarse aggregates	Absorption less than 18%
DNER-ME 096/98	Coarse aggregate - assessment of mechanical strength using the 10% fines method	Greater than60 kN
DNER-ME 399/99	Aggregates - determination of shock loss in the Trenton device	Less than 60%

Table 4 – Suggested limits for some ACCA mechanical strength parameters [1].

Source: Cabral [17].

CHARACTERIZATION TESTS OF THE CLAY TO BE CALCINED:

Recently, a series of studies aimed at characterizing raw materials in the ceramic industry have benefited from the following tests, which can be applied to characterize calcined clay aggregate.

Mineralogical Analysis by X-ray Diffraction (XRD):

XRD is an essential technique for the microstructural analysis of crystalline materials. When a beam of X-rays is incident on a crystal, diffraction occurs, allowing the identification of the phases present. Bragg's Law is fundamental in this context, relating the wavelength of X-rays to interplanar distances. Computational tools help interpret the spectra, identifying the phases accurately [18]. Figure 2 shows an example of X-ray diffraction of clay with kaolinite and other samples.

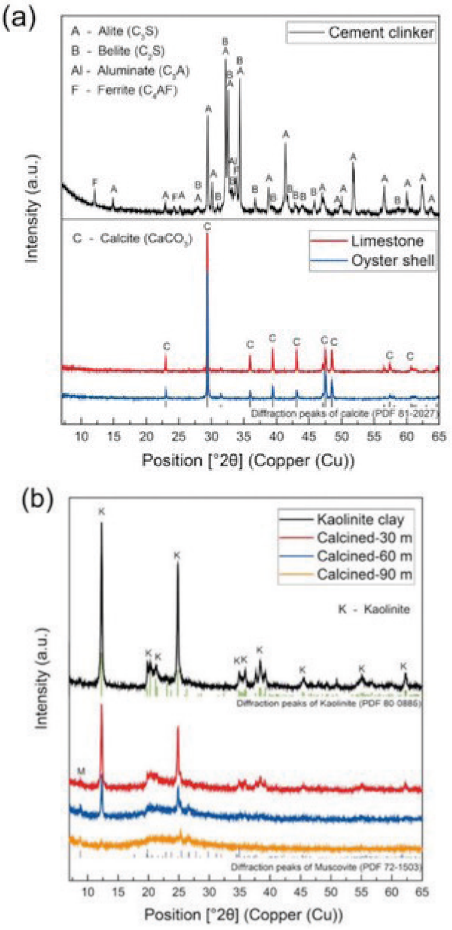


Figure 2: Example of XRD patterns of raw materials: (a) cement clinker, limestone, and oyster shell; (b) raw clay and calcined clays [19].

Mineralogical analysis using scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS):

Mineralogical analysis by scanning electron microscopy in conjunction with energy-dispersive X-ray spectroscopy (EDS) is a widely used technique to examine the composition and structure of materials at a microscopic level. The SEM generates high-resolution images of the material's surface, allowing the visualization of detailed characteristics, while the EDS identifies the elements present in the sample through the analysis of the energy of the emitted X-rays. This combination provides qualitative information about the chemical composition and distribution of elements in the sample. Figure 3 shows examples of SEM images of calcined clay samples, and Figure 4 illustrates examples of EDS of the same samples:

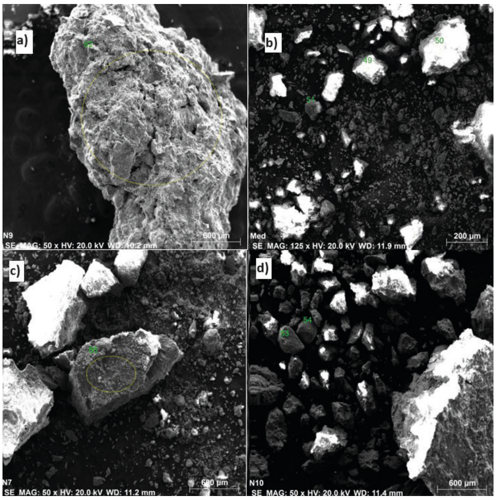
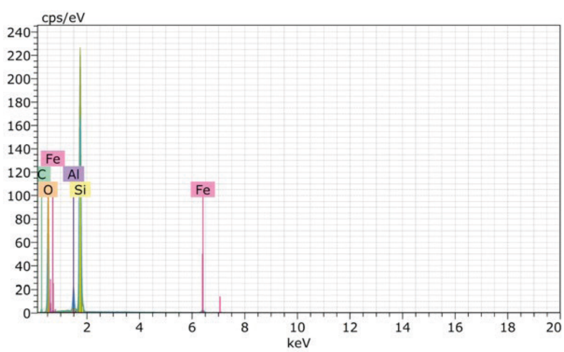


Figure 3: Exampled of SEM images of calcined clay mixtures: a) Clay calcined at 1,100 °C with 34% waste; b) Mixture of clay dried in the open air and in an oven; c) Clay calcined at 1,100 °C without mixing time of clayey soil with fine sandy soil; d) Clay calcined at 1,100 °C with 30-min mixing time of clayey soil with fine sandy soil.



Norm. mass percent (%)

Spectrum	C	O	Al	Si	Fe
53	6.45	38.70	5.87	45.59	3.40
54	5.28	47.42	0.73	45.74	0.83
Mean value:	5.86	43.06	3.30	45.67	2.11
Sigma:	0.83	6.17	3.63	0.11	1.81
Sigma mean:	0.58	4.36	2.57	0.07	1.28

Figure 4: Example of EDS of clay mixtures calcined at 1,100 °C with a 30-min mixing time of clayey soil with fine sandy soil.

Chemical Analysis by X-ray Fluorescence (XRF):

XRF is a multi-element technique that determines the chemical composition of samples based on the detection of X-rays emitted by the constituent elements. The main oxides are analyzed, with a precision that varies according to the element and concentration. At the same time, the fire loss test complements the chemical analysis, allowing the determinationof water, carbonate, and organic matter [18].

Differential (DTA) and Thermogravimetric (TGA) Thermal Analysis:

These techniques characterize the thermal properties of materials, such as mass variations and melting temperatures. DTA records temperature differences between the sample and an inert substance, while TGA monitors the variation in mass as a function of temperature. They are crucial to understanding the firing processes in ceramic masses [20-21]. Figure 5 shows the results of the DTA and TGA on limestone, oyster shells, and clay samples.

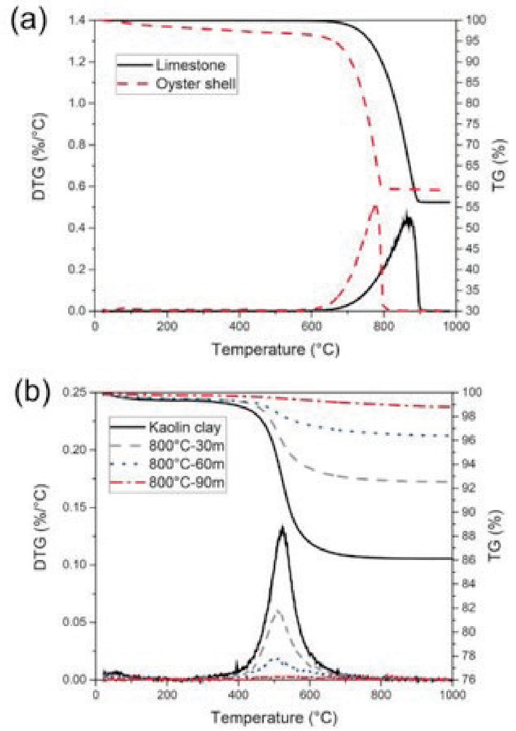


Figure 5: Example of a DTA-TGA result of raw materials: (a) limestone and oyster shells; (b) kaolinite clay and calcined clay after heating [19].

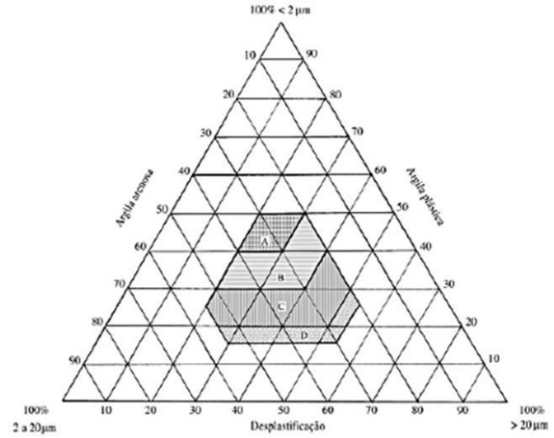


Figure 6: Winkler Triangle Diagram (PRACIDELLI and MELCHIADES, 1997)

Regions	particle size composition		
Types of products	2	2 a 20	20
Quality material	40 a 50	20 a 40	20 a 30
tiles, covers	30 a 40	20 a 50	20 a 40
holey bricks	20 a 30	20 a 55	20 a 50
solid bricks	15 a 20	20 a 55	20 a 55

Figure 7: Particle size composition of red ceramic products, according to the Winkler Diagram [22].

Source: Pracidelli and Melchiades [22] , Motta et al. [23].

Winkler Classification

Furthermore, the Winkler diagram is used to classify the quality of the soil intended for calcination and production of ceramic material. The diagram is used in particle size studies for ceramics, defining the most suitable particle size zones for red ceramic products. The method uses the results of particle size analysis by sieving and sedimentation to determine the proportion of soil that falls into three distinct categories: particles with a diameter of less than 2 micrometers (clay fraction), between 2 and 20 micrometers (silty fraction), and greater than 20 micrometers (sandy fraction). Classification is done using the triangle in Figure 6 and the Table in Figure 7.

These tests provide valuable data for firing planning and quality control in the ceramic industry, contributing to the identification of minerals present in samples. References such as Grim and Souza Santos offer a solid basis for comparing and analyzing results [20,25].

IN-DEPTH ANALYSIS OF THE CHARACTERISTICS OF CLAY MINERALS AND THEIR CALCINATION

There is no uniform definition of the term "clay". However, from a geological point of view, clays are generally unconsolidated sedimentary rocks or in a consolidated form referred to as clay stones, predominantly composed of very fine silicate minerals. According to EN ISO 14688-1, clay is defined by grain size <2 μm. In terms of quantity, clay minerals make up the largest proportion. However, the term "clay" is used here for all sediments containing clay minerals, regardless of total content. Depending on the particle size distribution, some of the "lower grade clays" would be better suited to be classified as "silt". Clay minerals have a lamellar structure with particle sizes mostly smaller than 2 μm and are categorized as phyllosilicates. Their wide availability is because they arise mainly from the weathering of silicate rocks [26-27].

The clay minerals included in this review can be grouped into two main categories, often referred to in the literature as 1:1 and 2:1 minerals. These terms derive from the structure of these minerals, which consists of repeated tetrahedral (T) and octahedral (O) sheets. In the tetrahedral sheet, Si4+, Al3+, and Fe3+ cations are in contact at the corners, while in the octahedral sheet, Al3+, Fe3+, Mg2+, and Fe2+ cations are in contact at the edges, alternating between cis and trans configurations, as shown in Figures 8 and 9.

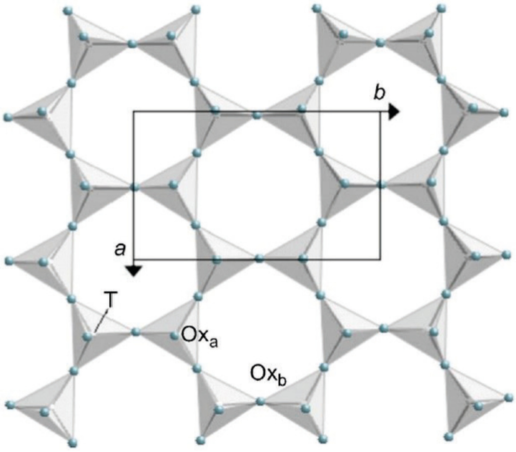


Figure 8: Tetrahedral sheet. T, tetrahedral cations; Oxa, apical oxygen atoms; Oxb, basal oxygen atoms. a and b refer to the unit cell parameters [28-29].

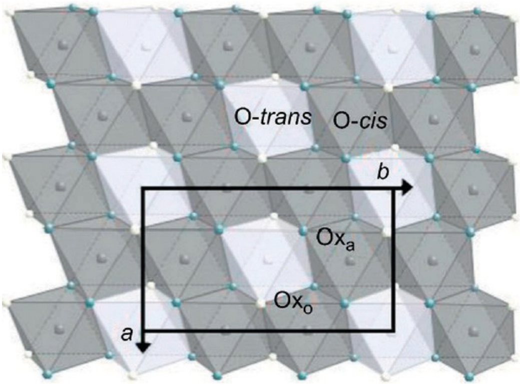


Figure 9: Octahedral sheet. O-trans, trans-oriented octahedra; O-cis, cis-oriented octahedra; Oxa, apical oxygen atoms; Oxo, OH, F, Cl octahedral anion. a and b refer to the unit cell parameters [28-29].

Kaolinite and the product of its calcination, i.e. metakaolinite, are the most widely tested clay minerals that form part of clays subjected to calcination for use as SCM due to their pozzolanic activity.

The effectiveness of the thermal activation process, and consequently the pozzolanic activity of the material obtained, depends on many factors. These include calcination temperature, particle size and shape, time, and others. The greatest attention is paid to the analysis of the influence of temperature. Table 5 presents a summary of research carried out on pozzolanic activity as well as the methods used and the main results:

CONCLUSIONS

In recent decades, studies on the use of artificial calcined clay aggregates have gained prominence in the Brazilian and global academic scene, resulting in an international bibliographic synthesis of this technology. The methodology proposed by Cabral remains relevant and useful for professionals interested in this field, despite the challenges faced due to the need to adapt existing technical standards [13].

Research	Method	Main results
01	RMN, heating up to 1,100 °C	Pozzolanic activity both in the raw state and after heating at any temperature up to 1,100 °C; above 800 °C, there was a decrease in activity.
02	Heating at various temperatures (500 to 950 °C)	The results are ambiguous: while some studies indicate low effectiveness of heat treatment, others show an increase in the heat of hydration of cement; the pozzolanic activity of muscovite calcined at 800 °C was demonstrated, although it was relatively low compared to calcined illite and kaolinite.
03	Different calcination methods (specific temperature)	Mixed-layer minerals, such as illite/smectite and mica/smectite, showed pozzolanic activity after heat treatment; the optimum calcination temperature and the presence of NH4+ ions influenced the pozzolanic activity. The transition of feldspar from a crystalline form to an amorphous form also increased pozzolanic activity in some cases.
04	Calcination at specific temperatures	The kaolinite dehydroxylation process is crucial for its pozzolanic activity; the kaolinite structure affects the dehydroxylation temperature, which varies from 350 °C to 900 °C; prior grinding may be necessary to increase the effectiveness of the calcination process.
05	Calcination at 830 °C	Sepiolite is not active as pozzolan in its raw state, but after calcination at 830 °C, it exhibits distinct, although relatively low, pozzolanic activity and significantly reduced water demand. The low activity can be attributed to the low Al content in sepiolite.
06	Heating to high temperatures (930–950 °C)	Moderate pozzolanic activity after heat treatment at high temperatures; the dehydroxylation process does not lead to the activation of illite, but the destruction of its structure and partial recrystallization results in moderate pozzolanic activity.
07	Calcination at a specific temperature	The results are ambiguous: while some studies indicate low effectiveness of heat treatment, others show an increase in the heat of hydration of cement; the pozzolanic activity of muscovite calcined at 800 °C was demonstrated, although it was relatively low compared to calcined illite and kaolinite.
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13	Heating to high temperatures (930–950 °C)	Apresenta atividade pozolânica moderada após tratamento térmico em altas temperaturas; o processo de desidroxilação não leva à ativação da illita, mas a destruição de sua estrutura e recristalização parcial resulta em atividade pozolânica moderada.
14	Calcination at a specific temperature	The results are ambiguous: while some studies indicate low effectiveness of heat treatment, others show an increase in the heat of hydration of cement; the pozzolanic activity of muscovite calcined at 800 °C was demonstrated, although it was relatively low compared to calcined illite and kaolinite.

15	Different calcination methods (specific temperature)	Mixed-layer minerals, such as illite/smectite and mica/smectite, demonstrated pozzolanic activity after heat treatment; the optimum calcination temperature and the presence of NH4+ ions influenced the pozzolanic activity. The transition of feldspar from a crystalline form to an amorphous form also increased pozzolanic activity in some cases.
16	Calcination at specific temperatures	The kaolinite dehydroxylation process is crucial for its pozzolanic activity; the kaolinite structure affects the dehydroxylation temperature, which varies from 350 °C to 900 °C; prior grinding may be necessary to increase the effectiveness of the calcination process.
17	Thermogravimetric Analysis, Calorimetry, Mechanical Strength and X-ray Diffraction	An increase in compressive strength was detected by the strength activity index test; the X-ray diffraction (XRD) characterization indicated a higher cement replacement factor and a slow pozzolanic reaction; progress of the pozzolanic reaction was observed by thermal analysis.
18	Mechanical Strength	Progression of compressive strength at all ages evidenced by the strength activity index test.
19	Chapelle, Thermogravimetric Analysis, X-ray Diffraction and X-ray Fluorescence	Using compressive strength, the materials, compared to clay, show different performances; TGA indicated that all portlandite was consumed, representing a good pozzolanic reaction of the calcined clay.
20	Mechanical Strength and X-ray Diffraction	XRD was used to characterize the clay to form metakaolin and mechanical strength to measure the progress of the geopolymer's compressive strength.
21	Mechanical Strength	Increase or similarity in the mechanical strength of concrete with calcined clay.
22	Mechanical Strength	Satisfactory behavior of metakaolin with steel fibers and increased compressive strength, especially at advanced ages.
23	Chapelle, Mechanical Strength and X-ray Diffraction	XRD was used to characterize the clays, observing the complete dehydroxylation of kaolinite after calcination at 750 ºC, pointing to pozzolanic reactivity through the chaplet method, confirmed by thermal analysis, and the compressive strengths of the mortars were equal to or higher than the reference.
24	Frattini, Mechanical Strength, X-ray Diffraction and X-ray Fluorescence	Mechanochemical activation enhanced the pozzolanic activity of natural clays, the strength activity index and the Frattini test confirmed the increase in pozzolanic reactivity; XRD tests pointed out the ability of clays to act as pozzolans.
25	Mechanical Strength and X-ray Diffraction	XDR pointed out the dehydroxylation of kaolinite at 600 ºC and the strength activity index showed greater compressive strengths at advanced ages.
26	Calorimetry and X-ray Diffraction	XRD was used for characterization and assessed the presence of kaolinite in the clays, isothermal calorimetry was used to quickly probe the reactivity of kaolinite clays, and thermal analysis quantified the kaolinite showing a strict directly proportional link between the kaolinite content of the raw clay and reactivity of the calcined clay.
27	R3, X-ray Diffraction and X-ray Fluorescence	Calcined clays were characterized by XRD and XFR, pointing out the potential of the material and the R3 pozzolanic test showed that the clays are significantly more reactive than fly ash and comparable to slag and silica fume.
28	Frattini, Luxàn, X-ray Diffraction, X-ray Fluorescence, Thermogravimetric Analysis and Mechanical Strength	XRD indicated the potential of the material in its characterization, electrical conductivity confirmed that natural pozzolans can be classified as having low reactivity, and the Frattini test and thermogravimetric analysis confirmed the pozzolanic behavior of natural pozzolans. These results were confirmed by mechanical tests with a strength gain of around 13 to 15% at advanced ages.
29	R3, X-ray Diffraction and X-ray Fluorescence	XRD allowed the mineralogical characterization of 13 different clayey raw materials, pointing to a previous pozzolanic reactivity confirmed by the R3 calorimetric test where kaolinite influences the heat of hydration.
30	Chapelle, R3, X-ray Diffraction and Mechanical Strength	XRD was a primary analysis to explain the difference in behavior between materials; there was an increase in the strength of mortars with calcined clay measured by compressive strength, and the R3 test also showed the pozzolanic reactivity of the clays.
31	Chapelle and X-ray Diffraction	XRF characterized and identified the pozzolanic activity of the material; XRD revealed that the presence of the material in the system increases the presence of CSH. The Chapelle test confirmed that the increase in compressive strength was due to the pozzolanic reaction of the material.

32	Unusual Comparative Analysis, X-ray Diffraction and X-ray Fluorescence	XRF and XRD characterized the material, indicating pozzolanic potential. Pozzolanic reactivity was measured by unconventional tests.
33	Chapelle, Thermogravimetric Analysis, X-ray Diffraction and X-ray Fluorescence	XRF and XRD characterized the material, pointing to pozzolanic potential. The combination of XRD with thermogravimetric (TG) techniques evidenced the difference between calcination and grinding. The Chapelle test showed a better pozzolanic reactivity of the material compared to the commercial one.
34	Mechanical Strength	Mechanical strength was adopted to evaluate the pozzolanic development of the material in the cement matrix.
35	Mechanical Strength, Calorimetry and X-ray Fluorescence	XRD was used to measure the crystalline phases. Calorimetry showed the formation of hydrates, pointing to a pozzolanic reaction with the formation of CSH. The compressive strength of cementitious matrices showed a decrease when percentages greater than 30% were replaced, as well as showing the development of pozzolanic reactivity of the material.
36	Mechanical Strength, Luxàn and X-ray Fluorescence	XRF was used to characterize the materials. The Lùxan test indicated a medium pozzolanicity of the material that induces filling behavior in the cement matrix. The incorporation of the waste increased the mechanical strength.
37	Thermogravimetric Analysis, Calorimetry and X-ray Diffraction	The calorimetry, XRD and TG results revealed the pozzolanic reaction of the calcined clay, and due to the pozzolanic reaction, there was a greater production of CSH increasing the mechanical strength.
38	Mechanical Strength, Unusual Comparative Analysis, X-ray Diffraction and Calorimetry	XRD and DTA/TG studies confirmed declines in portlandite content and CSH formation. Using less usual standardized tests, the cements were considered pozzolanic. Mechanical performance analysis reinforced the pozzolanic potential of the material.
39	Mechanical Strength, Unusual Comparative Analysis and Thermogravimetric Analysis	Red clay has a higher potential than the others.
40	Mechanical Strength	The pozzolanic potential of the materials was tested by the mechanical behavior of mortars, showing a positive effect on the properties. Pozzolanic materials can improve the environmental resistance of mortar.
41	Frattini, Chapelle, Mechanical Strength, Thermogravimetric Analysis, Calorimetry, X-ray Diffraction and X-ray Fluorescence	The pozzolanic activity of the clays was evaluated by fixing calcium hydroxide (Chapelle), Frattini test, and compressive strength, indicating that when calcined at 650 ºC, they showed pozzolanic activity and a percentage increase in compressive strength.
42	Chapelle, Mechanical Strength	The evaluation of pozzolanic activity using the Chapelle method showed that this material has the potential to be used as a pozzolan. In the mechanical strength analysis, ternary mixtures with the material and limestone resulted in greater compressive strength.
43	Mechanical Strength, Thermogravimetric Analysis, X-ray Diffraction and X-ray Fluorescence	The thermal transformation of the materials was studied by TG-DTA and XRD, pointing out the transformation temperatures of each phase. Pozzolanicity was measured in 7 days and the strength activity index through mechanical strength had a significant increase. The material, when calcined, appears as a reactive pozzolan, but with subsequent reactions.
44	Chapelle and Mechanical Strength	The Chapelle test and the strength activity index were used to evaluate the pozzolanic activity of the material after heat treatment, indicating higher pozzolanic activity when calcined.
45	Luxán	The assessment of pozzolanicity was necessary to understand how the material behaves in the reactive process with the cement used in the matrix and showed good pozzolanic reactivity according to the Lùxan method, allowing improvements in technological properties such as mechanical strength.
46	Frattini, Mechanical Strength, X-ray Diffraction and X-ray Fluorescence	With characterization tests, such as XRD, mechanical strength analysis, and pozzolanicity tests, it was possible to determine that clays can replace cement in mortars. The incorporation of the material increased the density of the mortar; however, its mechanical strength decreased.
47	Mechanical Strength, Unusual Comparative Analysis, X-ray Diffraction and X-ray Fluorescence	The partial replacement of cement in mortars with clays resulted in a considerable improvement in compressive strength at 28 days. The pozzolanic reactivity of clays A and B is explained by characterizing structural changes after calcination with XRD, thermal, and unconventional analysis.

48	Mechanical Strength, Thermogravimetric Analysis and Calorimetry	The strength activity indices meet the requirements for a pozzolanic material. The compressive strength results indicated that the optimum strength to replace Portland cement by up to 30% was viable for the use of brick waste.
49	Frattini	Using the Frattini method, it was possible to evaluate that the material in question presented greater pozzolanic activity than non-activated mixed cement samples, although it was considered non-pozzolanic.
50	Unusual Comparative Analysis and X-ray Diffraction	During the work, material characterization was carried out by XRD and unconventional methods to evaluate the development of pozzolanic reactivity. Calcium adsorption by kaolinite increased with increasing initial hydrated lime concentration, causing a delay in the long-term pozzolanic reaction.
51	Mechanical Strength and X-ray Diffraction	XRD was used for material characterization and mechanical resynthesis to evaluate pozzolanic development. The results showed a drop in the physical properties of the material, as well as in mechanical strength when using larger material.
52	Chapelle, Thermogravimetric Analysis and X-ray Diffraction	Pozzolanic potentials were investigated using a new method involving TGA/DTG and XRD techniques in addition to the Chapelle method. The results provided insights for the development of restoration mortars.
53	Thermogravimetric Analysis and X-ray Diffraction	Mineralogical changes were monitored using X-ray diffraction (XRD) and thermogravimetric analysis. Different lime contents in the treated samples were used to evaluate the development of pozzolanic reactions. The clays exhibited low reactivity, resulting in a delay in the precipitation of new hydrated phases.
54	Frattini, Mechanical Strength and Luxàn	The materials, 3 clays, were selected and characterized. After calcination at 700 ºC and grinding, pozzolanic activity was determined using the electrical conductivity test, Frattini test and compressive strength index. The results show that all calcined clays are classified as highly reactive pozzolans.
55	Mechanical Strength, Thermogravimetric Analysis, Calorimetry, X-ray Diffraction and X-ray Fluorescence	Preliminary analyses such as XRD showed a difference in their metakaolinite content. Isothermal calorimetry and compressive strength tests were carried out, complementing the analysis of the development of pozzolanic reactivity in the matrix, with the hydration reaction being monitored using thermogravimetric analysis (TGA). As a main result, the reactivity of the materials is different.
56	Frattini, Mechanical Strength, Calorimetry, X-ray Diffraction and X-ray Fluorescence	Clay can be calcined to form a technically viable supplementary cementitious material since the compressive strength of concrete showed similar results to other materials already in use. XRD characterization showed a reduction in crystallinity and an increase in amorphous phases in samples calcined at 600 ºC confirmed by thermal analysis. The Frattini test indicates a continuous pozzolanic reaction with curing time.
57	Mechanical Strength	The incorporation and additions to the cement made it possible to obtain mortars with physical-mechanical properties and durability superior to the reference mortar. However, mixtures containing glass dust and/or metakaolin showed greater strength than those containing brick waste.
58	Chapelle and X-ray Diffraction	XRD was performed to characterize and quantify the amount of silica in the material. The modified Chapelle test determined that the greatest amounts of fixed lime were found at 700 and 800 ºC, that is, the greatest pozzolanic reactivity at these temperatures.
59	Frattini and X-ray Fluorescence	XRF and the Frattini method in conjunction indicated that at higher temperatures there was a decrease in reactivity. Clay reactivity increases directly proportional to the calcination temperature, with the limit at a temperature of 900 ºC.
60	Chapelle, Mechanical Strength, R3 and Calorimetry	Very good correlations were detected between the compressive strength of the mortar and both chemical reactivity measurements, presenting a new and fast method indicated especially for calcined clays. Firstly, obtained by measuring the heat release during the reaction using isothermal calorimetry and secondly by determining the bound water.
61	Unusual Comparative Analysis and X-ray Diffraction	XRD showed that the samples have good pozzolanic reactivity, indicating that the reactivity of each clay is different.
62	Mechanical Strength and X-ray Diffraction	The material was characterized by XRD and its pozzolanic behavior was tested by measuring compressive strength. The results showed that the material can be considered as a possible partial replacement for cement in concrete.

63	Frattini, Mechanical Strength and X-ray Diffraction	The pozzolanicity of the samples was evaluated using the Frattini method and by determining the compressive strength. The results showed that the pozzolanic reactivity of the samples complies with the requirements of the Brazilian standard.
64	Unusual Comparative Analysis, X-ray Diffraction and Calorimetry	The mineralogy study was carried out using XRD and XRF, where it was possible to evaluate the influence of montmorillonite. Pozzolanic reactivity was measured by isothermal calorimetry, indicating that the formation of CSH is greater for samples containing montmorillonite.
65	Mechanical Strength, X-ray Diffraction and Calorimetry	The development of pozzolanic reactivity was evaluated based on the compressive strength of the cementitious composites, and it was possible to observe that the sample showed pozzolanic behavior.
66	Chapelle, Mechanical Strength, Thermogravimetric Analysis, X-ray Diffraction and X-ray Fluorescence	The clay samples showed pozzolanic behavior, leading to an improvement in the mechanical properties of cement mortars. Pozzolanic reactivity was confirmed by compressive strength tests and thermogravimetric methods, indicating an increase in the amount of calcium hydroxide fixed by the pozzolanic material.

Table 5: Updated table of reviews of research and testing used to evaluate the pozzolanic activity of clays by Jaskulski et al. and Pinheiro et al. [27-28].

Source: Jaskulski et al. and Pinheiro et al. [27-28].

The practical application of these aggregates offers relevant perspectives for research. The demand for innovations in this sector is evidenced by the search for patents and the interest in improving existing technologies.

The results of large-scale experiments, such as the application of aggregates on highways, demonstrate the viability and benefits of these materials. Despite the technical and regulatory challenges faced, the positive contributions to pavement durability and strength indicate significant potential for the construction industry.

Detailed analysis of production processes, including the selection of raw materials and heat treatment methods, reveals the importance of efficient technological control to guarantee the quality of the aggregates. Collaboration between academia and industry is essential to overcome obstacles and promote advances in this field.

Despite the challenges and uncertainties, studies indicate that calcined clay aggregates have the potential to become a viable and economically attractive alternative to natural aggregates, contributing to the sustainability and efficiency of the Brazilian construction industry.

Numerous studies have indicated that heat treatment is essential to activate clay minerals or enhance their pozzolanic activity. Factors such as time, temperature, and particle size play crucial roles in determining the success of the calcination process. Major advances are expected in the production of LC3 (Limestone Calcined Clay Cement), which requires great knowledge of the characteristics of calcined clay as well as mastery of characterization tests. Therefore, this review is of great value to researchers who seek to work with calcined clay, especially those who focus on calcined clay aggregate.

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