
Physical and Geochemical Characterisation of Pongo Pitti and Bossambo Farm Clays (Littoral Region, Cameroon) for use in Ceramics

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ABSTRACT : *The main objective of this work is to discern the physico-chemical and mechanical behavior of the Pongo Pitti and Bossambo Farm clay formations, located on either side of the Sanaga river in the littoral region of Cameroon. To achieve this, two field campaigns and laboratory works were carried out. Four clay materials were collected and brought back to the laboratory. The laboratory investigations involved physico-mechanical and geochemical analyses, followed by ceramic testing. The materials studied have a clayey texture, with clay percentages ranging from 26.89% to 80.3%, silt from 13.2% to 57.6% and sand from 1.58% to 47.26%. The plasticity index ranges from 11.9% to 24.2%. From a geochemical standpoint, the materials studied show a predominance of silica (49.6% to 63.5%), alumina (20.5% to 27.1%) and iron (2.39% to 8.6%), with the SiO₂/Al₂O₃ ratio varying from 1.96 to 3.1. The Al₂O₃/Fe₂O₃ ratio is 8.4 for Pongo Pitti clays and 2.9 for Bossambo Farm clays. The geochemical weathering indices (ICV, CIA, PIA, CIW, CIW) show a high degree of weathering, with values in excess of 90%. Alkali and alkaline-earth proportions are lower, and the K₂O/Na₂O ratio varies between 8.45 and 14.24, showing an enrichment of potassium in relation to sodium. Lantane is the most abundant rare-earth element (323.84 ppm). The REE study shows a predominance of light REEs over heavy REEs (LREE/HREE~4.51) and a negative Europium anomaly. Infrared spectroscopy showed poor kaolinite crystallinity. Mechanically, the specimens studied, fired at temperatures ranging from 950°C to 1050°C showed good cohesion and metallic soundness. Linear shrinkage was 4.8%. Mass loss increases with temperature. Its value is 12.5% for Pongo Pitti materials and 8.5% for Bossambo Farm materials. Water absorption decreases with temperature and is 20.27% for Pongo Pitti samples and 15.79% for Bossambo Farm samples. Bulk density increases with temperature (2.11 at 950°C to 2.51 at 1050°C). Flexural strength increases with temperature and is 6.66 MPa for materials from Pongo Pitti and 8.89 MPa for those from Bossambo Farm. These materials can be used to make fired bricks and roof tiles, and Pongo Pitti materials can be used to make refractory ceramics.*

KEYWORDS : physical and geochemical characterisation, pongo pitti, bossambo farm clays, ceramics

INTRODUCTION

Used since centuries, clay is one of the most abundant and easy to work with natural resources (Faycal, 2015). Nowadays, more particular attention is paid to these materials due to their use in many scientific and technological fields such as industries, agriculture, engineering and construction, environmental remediation (Murray, 2007; Pialy, 2009; Onana et al., 2019) as well as in the ceramics industry. In Cameroon, several studies have been carried out on the various clay deposits with the aim of valorizing them in the ceramics industry. These include the work of Diko et al.(2011) on Limbé clays, Tassongwa et al.(2017) on Balengou and Lembo clays, Bomeni et al. (2018) on Ngwenfon black clays, Kagonbé et al. (2021) on Sekandé and Gashiga clays, Ndjigui et al. (2021) on Lokoundjé alluvial clays, Fadil-Djenabou et al.(2023) on Kodeck clays, Ngo Mapuna et al. (2023) on Mbalmayo lateritic clays. In the Littoral region, in particular, the abundance of clay materials is unquestionable. Nevertheless, very little work has been carried out on the study of clays and their applications in ceramics. To efficiently and responsibly utilize the clay reserves at Pongo Pitti and Bossambo Farm requires a prior mastery of their various characteristics. Local populations use these materials for artisanal pottery and unfired bricks. These types of pottery and bricks are of poor quality, have a high rainwater absorption rate and short lifetimes on the time scale because their mechanical strengths are lower. The aim of this project is to investigate the physical-mechanical and chemical behavior of the clay formations at Pongo Pitti, near Lac Ossa, and Bossambo Farm, with a view to their use in the ceramics industry. In the Pongo Pitti clay formation, the materials are greyish, obviously with a lot of organic matter, while in the Bossambo Farm clay formation, the materials are yellowish and rich in goethite. The present study has therefore the advantage of contributing to the promotion of local materials in the improvement of ceramic quality.

Geographical and Geological Setting

This study was carried out in two areas of Cameroon's Littoral region. The village of Pongo Pitti, in the rural commune of Dizangué, and Bossambo Farm, in the commune of Mouanko, in the department of Sanaga-Maritime. These villages, located on either side of the Sanaga River, are situated around 20 km west of Edéa, at an average altitude of 8 m above sea level, some 30 km away. Total annual rainfall is around 2,535 mm and the average temperature is 27°C (Ekoa Bessa et al., 2021). The basement is partly metamorphic, composed of biotite, amphibole, grénat and muscovite gneisses and sometimes migmatitic, and a certain quantity of sedimentary rocks, notably ferruginous sandstones and black marls. Soils in the study area are ferrallitic yellow soils, but also hydromorphic (Segalen, 1994).

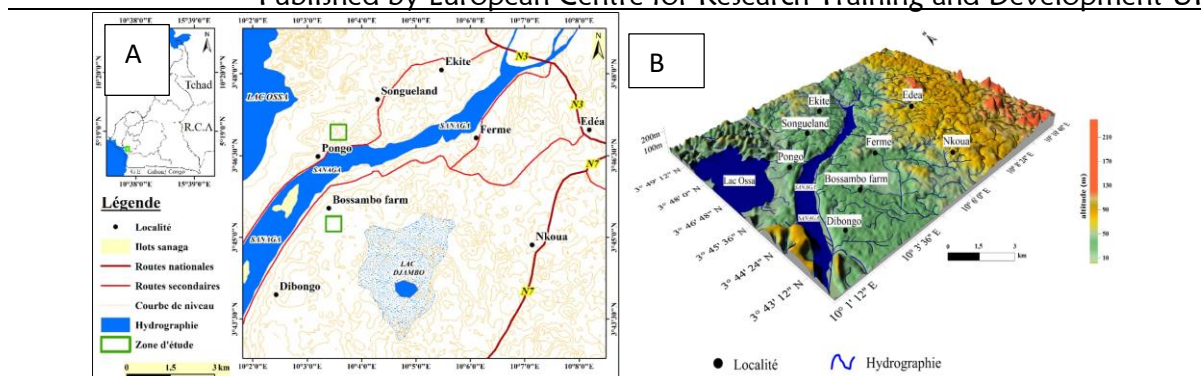


Fig.1. A) Localisation of Pongo Pitti and Bossambo Farm in the Littoral Region, Cameroon.
B) Hydrography and Geomorphology of the Littoral Region.

ANALYSIS TECHNIQUES

Physical-Mechanical Analysis

Physical-mechanical analyses were carried out at the Department of Earth Sciences, University of Yaoundé 1. Colors were determined using the Munsell soil color chart. Particle size analyses were carried out using the Robinson-Koln pipetting method. After drying in the open air for a week, then in an oven for 24 hours, 20 grams of each sample were placed in a beaker, with the addition of 10 ml of bleach to eliminate organic matter and 20 ml of sodium hexametaphosphate to disperse mineral constituents, and put through a rotary shaker for 2 hours. Three elemental fractions were thus determined : clays, silts and sands. Atterberg limits were used to determine the plasticity of the Pongo Pitti and Bossambo clays. The liquidity and plasticity limits were calculated using the Casagrande apparatus according to the method described by Andrade et al. (2011). The plasticity index is the difference between the liquidity limit and the plasticity limit. It is determined by the empirical formula: $IP = LL - LP$.

Chemical Analysis

Infrared spectroscopy (FTIR) and geochemical analyses were carried out as part of the chemical analyses. Infrared spectroscopy was carried out at the University of Yaoundé 1 using a BURKER OPTIK ALPHA spectrometer. Wavelengths ranged from 4000 to 400 cm^{-1} . Geochemical analyses were carried out in South Africa by ALS Laboratory Group. Major elements, expressed as percentage of oxide weight, were determined by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). Trace elements, including REE, expressed in ppm, were determined by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS).

Ceramic Testing

Experimental parallelepiped briquettes (2 cm x 4 cm x 8 cm) were made at the inorganic chemistry laboratory of the University of Yaoundé 1 by adding 12ml of distilled water and using a 10-ton hydraulic press. Two samples were selected (B20 and PP06), one specimen from Pongo Pitti and another from Bossambo Farm. The resulting specimens were air-dried for seven days, then oven-dried at 105°C for 24 h, to avoid sudden drying and cracking during firing. Heat treatment was carried out at two temperature levels: 950°C and 1050°C in a programmable Nabertherm electric furnace (RHF 1500), at temperature increase rates of 5°C per minute.

Linear shrinkage (LS) is calculated by the formula: $LS = [(L_0 - L) / L_0] \times 100$ where L_0 is the length of the briquette before firing and L is its length after firing. The mass loss is the difference between the mass of the briquette before and after firing. After the briquette has been made, the test piece is weighed, giving the mass of the wet briquette. After firing, the test piece is weighed again, and the mass obtained is the mass of the fired briquette. The mass loss PM is calculated using the formula: $ML = [(M_h - M_c) / M_h] \times 100$ where M_h is the mass of the briquette dried at 105°C and M_c is its mass after firing. Bulk density is the ratio between the mass of the specimen and its volume. Volume is calculated by multiplying the dimensions of the briquette: length, width and thickness. $d \text{ (g/cm}^3\text{)} = M/V$, where M is the mass of the briquette at different temperatures and V is its volume ($V = \text{length} \times \text{width} \times \text{thickness}$). The cohesion of the specimens was determined. Cohesion is said to be poor when the specimen crumbles. It is said to be good when the specimen is resistant to crumbling. Sound was determined by tapping the briquette against a metal object. Water absorption was determined in accordance with ASTM C-20-2000. The principle consists in determining the difference in mass of the test specimen before and after immersion in water for 24 hours. Water absorption (WA) is obtained using the formula: $WA = [(W - M_c) / M_c] \times 100$, where W is the mass of the briquette soaked in water for 24 hours. Flexural strength was determined according to the formula: $\sigma_f = 3LP / 2le^2$ where L (mm) is the distance between supports, P is the breaking load, l (mm) is the specimen width and e (mm) is the specimen thickness.

RESULTS AND DISCUSSION

Particle size distribution and atterberg limits.

The clay fraction predominates over the other elemental constituents. Table shows the proportions of different particle size fractions in the materials studied. It can be observed that all granulometric proportions are represented. At Pongo Pitti, the percentage of clays in the materials varies from 50.33% to 80.93%, that of silts from 17.18% to 28.35% and that of sands is not very marked and varies from 1.88% to 21.31%. At Bossambo Farm, the percentage of clays varies from 49.66% to 59.01%, that of silts from 22.94% to 29.43% and that of sands from 11.56% to 27.40%. It can be seen that clays and fine silts account for a large proportion of the materials studied, 98.11% for material PP06, 78.68% for material PP08, 88.44% for material B20 and 72.60% for material B09. Based on the proportions of clays, silts and sands, the Picard (1971) textural diagram was drawn up (Fig. 2). This diagram shows that the materials studied have a clayey texture. Three materials, PP08, B20 and B09, with clay proportions of around 55%, are suitable for use in roof tiles and bricks. The PP06 material, very rich in clay granulometry (over 80%), could be used as a refractory ceramic.

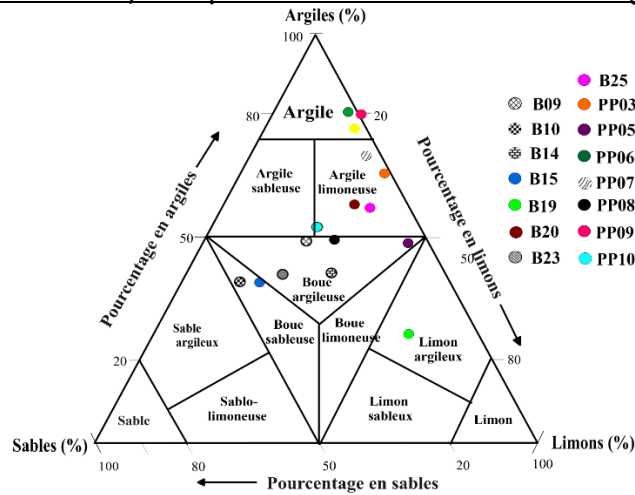


Fig. 2. Textural diagram of Picard (1971)

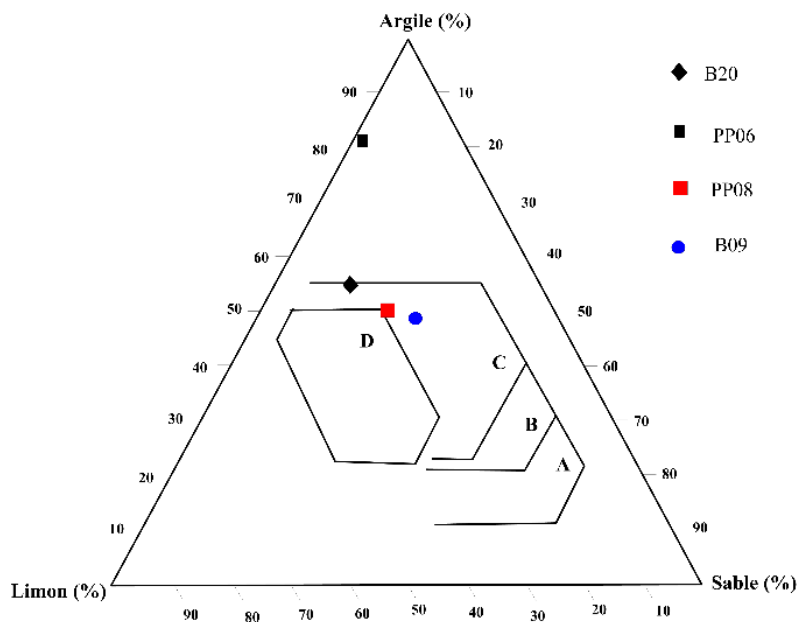


Fig. 3. Diagramm of Winkler (1954)

Atterberg limits

Atterberg limits were used to determine liquidity limits (LL), plasticity limits (LP) and plasticity index (PI). The liquidity limit ranged from 61% to 49.6%, the plasticity limit from 45.5% to 28.9% and the plasticity index from 21.4 to 11.9. The various materials studied, plotted in the Casagrande plasticity diagram (Fig. 4), are in the medium-to-high plasticity domain. The values of the liquidity limits are in correlation with the Particle size distribution. Thus, materials containing a high proportion of clays are those with high liquidity limit values. The plasticity of a material depends on both particle size and mineralogical composition (McNally, 1998). It appears, therefore, that high plasticity index values are related to fine particle sizes. In his work, Abajo (2000) suggested that the plasticity index of clay materials should be greater than 10%. Values below 10% can lead to inappropriate dimensional characteristics and even breakage of manufactured products. The clay materials studied have plasticity indices well above 10% and,

Published by European Centre for Research Training and Development-UK in accordance with the distribution of elementary particles, are suitable for use in the manufacture of fired tiles and bricks. However, specimen PP06 is suitable for use in the refractory ceramics industry.

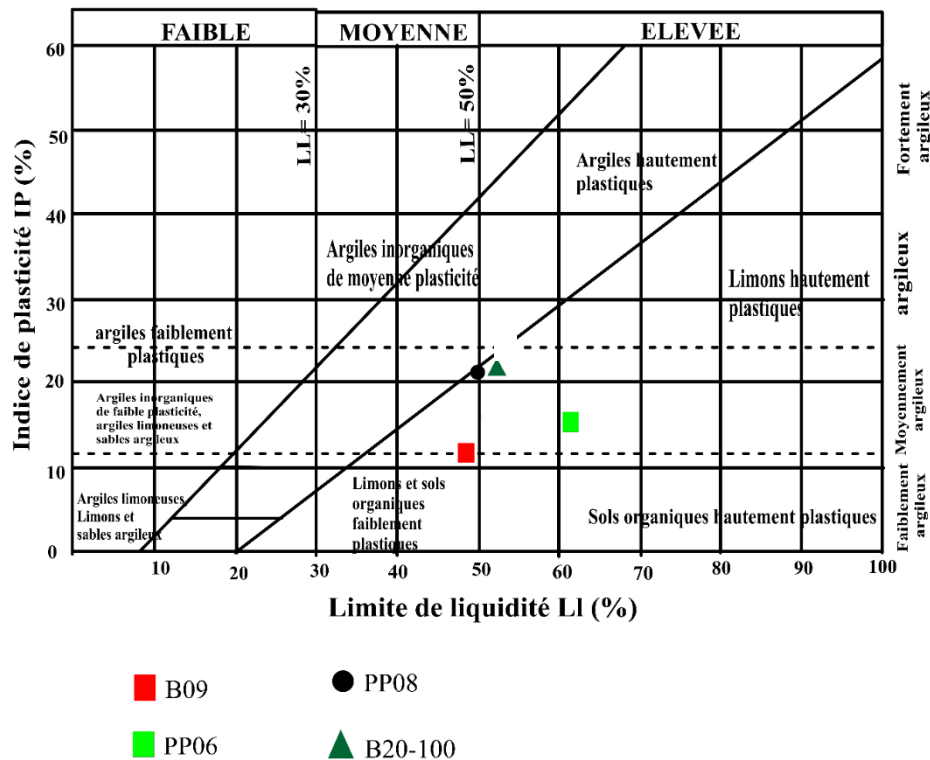


Fig. 4. Plasticity diagram of Casagrande

Chemical Characterization

Infrared spectroscopy

The spectra of the materials studied are spread out between wavelengths of 3800 cm^{-1} and 3300 cm^{-1} , as well as between 1300 cm^{-1} and 400 cm^{-1} . The kaolinite elemental lattice contains four hydroxyls, resulting in the presence of four absorption bands centered on frequencies 3655 , 3670 , 3695 cm^{-1} for external OH and 3620 cm^{-1} for internal OH (Ledoux and White, 1996). The spectroscopic analyses illustrated in figure 5 show that the Pongo Pitti and Bossambo Farm materials exhibit the bands around 3694 and 3621 cm^{-1} , those around 3655 cm^{-1} being weakly materialized and those around 3670 cm^{-1} being non-existent. The weak development of internal OH vibration bands at 3650 cm^{-1} and the non-existence of bands around 3670 cm^{-1} are evidence of the low crystallinity of the materials studied. The deformation vibrations of the Al-O bond are localized around 910 cm^{-1} and those of Si-O around 1018 cm^{-1} .

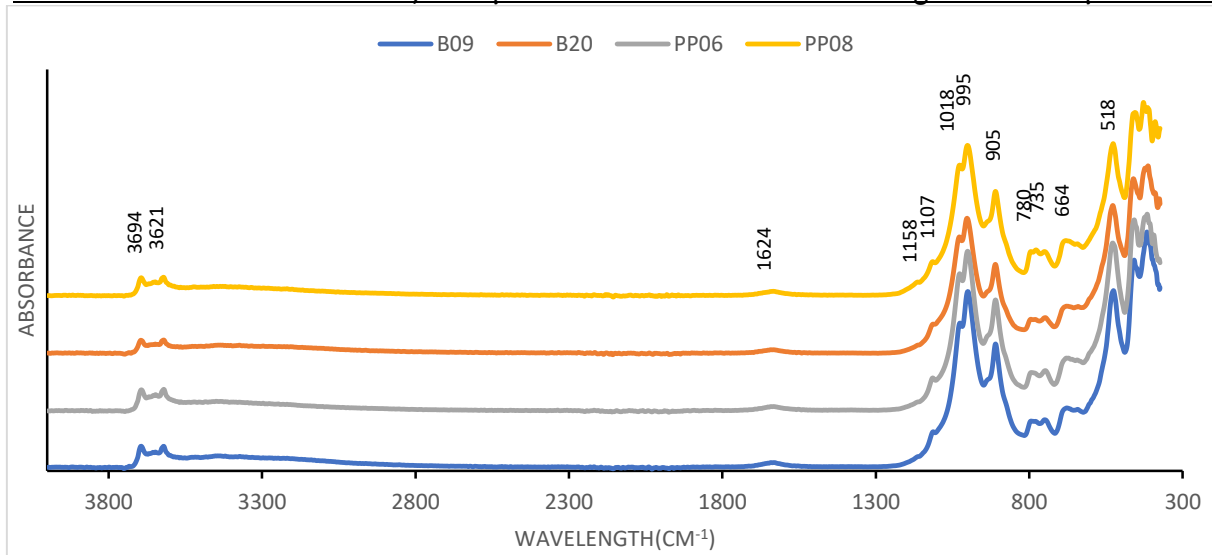


Fig. 5. IR spectra of materials from Pongo Pitti and Bossambo Farm

Broad, low-intensity absorption bands are also observed around 1641 cm^{-1} in all four materials analyzed. These bands are attributed to water molecules or other radicals making up amorphous aluminosilicates. At low frequencies, the wavelengths observed around 905 cm^{-1} , 995 cm^{-1} and 1018 cm^{-1} are those specific to quartz and kaolinite. The bands observed at 780 cm^{-1} , 735 cm^{-1} in the clay materials analyzed are typical of Al-O vibrations in aluminosilicates. According to the spectra studied, the main minerals present in materials are kaolinite, illite and quartz (Caillère et al., 1982). Superimposing the infrared spectra of all four materials shows good agreement between different peaks. This similarity of infrared spectra reflects the almost homogeneous crystallinity of kaolinites and other minerals in the materials analyzed.

Geochemics

Major elements

The results of Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) analysis of four samples of clay materials from Pongo Pitti and Bossambo Farm are shown in table..... The most abundant oxides in the samples analyzed are SiO_2 , Al_2O_3 and Fe_2O_3 . Silica content ranged from 49.6% to 63.5%, alumina from 20.50% to 27.10% and iron from 2.29% to 8.60%. The highest silica content was observed at Pongo Pitti (63.5% for sample PP08).

Table 1. geochemical composition of Pongo Pitti and Bossambo Farm clays

Analysed elements	Ld	Pongo Pitti		Bossambo Farm	
		PP08	PP06	B09	B20
SiO ₂	0,01	63,50	53,00	55,50	49,60
Al ₂ O ₃	0,01	20,50	27,10	20,60	24,20
Fe ₂ O ₃	0,01	2,39	3,29	7,03	8,60
CaO	0,01	0,03	0,04	0,16	0,12
MgO	0,01	0,20	0,25	0,59	0,59
Na ₂ O	0,01	0,05	0,07	0,22	0,11
K ₂ O	0,01	0,61	0,73	1,86	1,57
TiO ₂	0,01	1,91	1,88	1,56	1,76
MnO	0,01	0,06	0,03	0,04	0,07
P ₂ O ₅	0,01	0,09	0,16	0,20	0,32
LOI	0,01	11,75	14,85	11,00	13,50
Total	-	101,09	101,40	98,76	100,44
SiO ₂ /Al ₂ O ₃	-	3,10	1,96	2,69	2,05
K ₂ O/Na ₂ O	-	12,20	10,43	8,45	14,27
K ₂ O+Na ₂ O	-	0,66	0,80	2,08	1,68
Al ₂ O ₃ /Fe ₂ O ₃	-	8,58	8,24	2,93	2,81
K ₂ O+Na ₂ O+MnO+P ₂ O ₅	-	1,04	1,28	3,07	2,78
TiO ₂ +Fe ₂ O ₃	-	4,30	5,17	8,59	10,36
CIA	-	96,74	96,99	90,19	93,08
PIA	-	99,60	99,58	98,01	98,99
CIW	-	99,61	99,60	98,19	99,06
ICV	-	0,26	0,23	0,56	0,53

ICV = (Fe₂O₃ + K₂O + Na₂O + MgO + CaO + TiO₂)/Al₂O₃, Cox and al.(1995) ;

CIA(%) = [Al₂O₃/(Al₂O₃ + K₂O + Na₂O + CaO) x100], Nesbitt and Young (1984) ;

PIA(%) = [(Al₂O₃ - K₂O)/(Al₂O₃ - K₂O + Na₂O + CaO)x100], Fedo and al. (1995)

CIW(%) = [(Al₂O₃/(Al₂O₃ + Na₂O + CaO) x100], Harnois (1988)

The high SiO₂ content in sample PP08 is due to the high sand content observed during the grain size distribution. Similarly, the highest alumina content is obtained in the same locality (27.1% for PP06). An abundance of iron is more marked at Bossambo Farm (average 7.8%) than at Pongo Pitti (average 2.8%), which leads, after firing, to the red coloration of specimens from these materials, certainly due to the transformation of goethite into hematite. This coloration is more pronounced with higher TiO₂ contents. For illustration, the Bossambo Farm materials, for which the sum of TiO₂ + Fe₂O₃ is much higher than that obtained on the Pongo Pitti materials, show briquettes with a red coloration. Concentrations of alkalis, alkaline earths, MnO and P₂O₅ are low, averaging 0.19% and 0.49% respectively for Pongo Pitti and Bossambo Farm clay materials, except for K₂O, which varies from 0.61% to 1.86%. Loss on ignition (LOI) values ranged from 11% to 14.85%. The highest value for sample PP06 is due to the presence of clay minerals and a high level of organic matter. The ICV (Index of Compositional Variability) is used to determine sediment maturity (Cox et al., 1995). In materials from Pongo Pitti and Bossambo Farm, it ranges from 0.26 to 0.56. At Pongo, its values are the lowest, with an average

of 0.24, in contrast to those at Bossambo, which are high, with an average of 0.54. These low values, below 1, prove that these materials are mature. The CIA (Chemical Index of Alteration) is used, firstly, to understand and measure the intensity of chemical alteration of source rocks and, secondly, to discriminate the depositional environment of sediments (Nesbitt and Young, 1984). In the materials studied, the CIA value varies in percentage from 90 to 97. This suggests intense alteration of the source rock. The PIA (Plagioclase Index of Alteration) is also used to assess the intensity of alteration (Fedo et al., 1995). The PIA value varies in percentage terms between 98.01 and 99.60. These data suggest intense alteration of plagioclase in the source rock. This intense alteration is also confirmed by CIW values, which range in percentage from 98.19 to 99.11. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio ranges from 1.96 to 3.10. This may indicate to the presence of 1/1 and 2/1 clay minerals (Deramne, 2021). CIW, PIA, CIA, ICV values and the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio suggest intense alteration of the source rock, but also the maturity of the materials studied. The sum of weak alkalis ($\text{Na}_2\text{O} + \text{K}_2\text{O}$) ranges from 0.66 to 2.08, with lower values at Pongo Pitti and below 1. The $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratio ranges from 8.45 to 14.27, showing an enrichment of K_2O over Na_2O . The sum of alkalis and alkaline earths is low (0.99 on average for material from Pongo Pitti and 2.61 on average for samples collected at Bossambo Farm), coupled with a high silica content, this may induce insufficient sintering during the briquette firing process (Onana et al., 2019). Alumina content can be used to determine the refractoriness of clays. Depending on the alumina content, two classes can be identified: (i) the first with alumina contents below 25%. These are PP08, B09 and B20. These materials are used in the manufacture of earthenware and pottery and (ii) the second with alumina contents above 25%. This is PP06. These are low-fusibility materials. This alumina content will also lead to an improvement in the physical-mechanical characteristics of fired briquettes during the sintering phase, as Al_2O_3 will contribute to the formation of mullite (Ukwatta and Mohajerani, 2017). The $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ mass ratio can be used, in industrial valorization, to define the use of clays in ceramic paste formulation. Two classes can be distinguished: (i) Pongo Pitti materials have an $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ ratio greater than 5.5. These clays are said to be alumina-rich, with colors tending towards white. They can therefore be used to manufacture refractory ceramics. (ii) Bossambo Farm materials have an $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ ratio of less than 5.5. These clays are rich in iron and are predisposed for the manufacture of building materials (Garcia-Valles et al., 2020).

Trace elements

The various trace elements measured by ICP-MS are shown in table The lithophilic elements with large ionic radius (LILE) have very varied concentrations in the materials studied. The most abundant is barium, with concentrations ranging from 324 to 842 ppm. This element is much more enriched in Bossambo Farm clays (average 777 ppm) than in Pongo Pitti clays (average 393 ppm). Strontium is the second most abundant LILE element in the materials studied, varying in ppm between 59.2 and 135.5, again with a high concentration in the Bossambo Farm clay materials (average 123.25 ppm).

Table 2. Trace element concentrations in the materials studied

	PP08	PP06	B09	B20
Ba	324	462	842	712
Cr	123	149	131	157
Cs	3,69	4,39	3,87	4,77
Ga	29,4	38,9	29,8	34,8
Hf	23,4	12,7	17,1	14,05
Nb	46,7	44,4	35,9	41,1
Rb	33,5	42,8	79,2	83,7
Sn	4,9	5,5	3,7	4,3
Sr	59,2	75,1	135,5	111
Ta	2,7	2,9	1,9	7,9
Th	21,6	24,4	22,1	24,7
U	6,33	5,35	4,71	5,47
V	116	150	144	170
W	2,9	2,7	2,1	2,5
Y	47,1	23,1	41	28,8
Zr	971	522	707	543
U/Th	0,29	0,22	0,21	0,22
Rb/Sr	0,57	0,57	0,58	0,75

Then there's rubidium, with concentrations ranging from 33.5 to 83.7 ppm. Caesium concentrations are very low, averaging 4.18 ppm. Elements with a small ionic radius and a large charge, the HFSE (uranium, thorium, zirconium, Hf, Ta, Nb...) have highly variable concentrations. In this category of chemical elements, Zr is the most abundant, with ppm concentrations ranging from 522 to 971. The others are less abundant: U has an average concentration of 5.47 ppm, while Th is more abundant than uranium, with an average concentration of 23.2 ppm. Sn, Ta and Hf have average concentrations of 4.6, 3.85 and 16.81 ppm respectively. Trace elements with an affinity for iron, such as vanadium, gallium and chromium, vary widely in concentration. Vanadium and chromium are the most represented elements, with average concentrations of 145 ppm and 140 ppm respectively. The U/Th ratio varies around 0.20, reflecting the abundance of thorium relative to uranium. The Rb/Sr ratio values in the materials studied from Pongo Pitti and Bossambo Farm range from 0.57 to 0.75.

Rare earth elements

The sum of REEs ranges from 266.24 to 402.06 ppm (Table ...). The materials studied contain more light rare earths (La, Ce, Pr, Nd, Sm and Eu) than heavy rare earths (Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), with the LREE/HREE ratio oscillating between 10.72 and 13.27.

Table 3. REE concentrations in the materials studied

	PP08	PP06	B09	B20
La	85,8	71,3	79,4	70,5
Ce	172,5	111,5	156,5	119
Pr	19,8	12,8	16,85	12,9
Nd	73	42,9	58,5	43,2
Sm	13,9	7,47	10,2	6,91
Eu	2,75	1,58	2,17	1,58
Gd	10,65	6,01	8,5	6,41
Tb	1,63	0,85	1,32	0,97
Dy	8,92	4,74	7,19	5,27
Ho	1,83	0,94	1,47	1,08
Er	5,08	2,6	4,01	3,29
Tm	0,75	0,44	0,59	0,44
Yb	4,74	2,69	3,57	2,66
Lu	0,71	0,39	0,61	0,44
REE	402,06	266,21	350,88	274,65
LREE	367,75	247,55	323,62	254,09
HREE	34,31	18,66	27,26	20,56
LREE/HREE	10,72	13,27	11,87	12,36
Ce/Ce*	1,01	0,89	1,04	0,95
Eu/Eu*	0,69	0,72	0,71	0,72
(La/Yb)_N	12,30	18,01	15,11	18,00

$$(Ce/Ce^*) = (Ce_{sample}/Ce_{chondrite}) / (La_{sample}/La_{chondrite})^{0.5} \times (Pr_{sample}/Pr_{chondrite})^{0.5} \text{ (Taylor and McLennan, 1985)}$$

$$(Eu/Eu^*) = (Eu_{sample}/Eu_{chondrite}) / (Sm_{sample}/Sm_{chondrite})^{0.5} \times (Gd_{sample}/Gd_{chondrite})^{0.5} \text{ (Taylor and McLennan, 1985)}$$

$$(La/Yb)_N = (La_{sample}/La_{chondrite}) / (Yb_{sample}/Yb_{chondrite}) \text{ (McDonough and Sun, 1995)}$$

This LREE enrichment is also confirmed by the (La/Yb)_N ratio, which varies between 12.30 and 18.01. Normalized to chondrite (Taylor and McLennan, 1985) (Figure), the samples studied show LREE enrichment, with an average LREE/HREE ratio equal to 4.5.

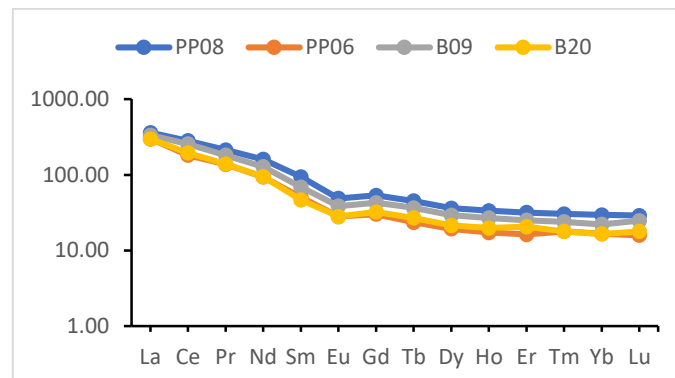


Fig. 6. REE spectra normalized to chondrite (Taylor and McLennan, 1985)

The materials are characterized by a negative Eu anomaly, with an average of 0.71, and a lack of Ce anomaly, with an average of 0.97.

Mechanical Tests

Mechanical tests were carried out on PP06 and B20 materials.

Briquette color

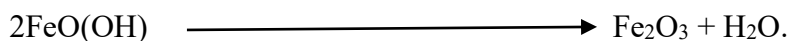
Table 4 shows the coloring of specimens at different temperatures.

At 105°C, specimens of material PP06 have a light gray coloration (2.5YR7/1) and those of material B20 have a light yellow-brown coloration (2.5YR6/4).

Table 4. coloration of Pongo Pitti and Bossambo Farm clays at differents temperatures

Entités	Ech	950°C		1050°C	
		color	code	color	code
Pongo Pitti	PP06	Pink	7,5YR8/6	Pink	7,5YR8/4
Bossambo Farm	B20-100	Red	2,5YR6/8	Red	2,5YR5/8
	B20-90	Red	2,5YR6/8	Red	2,5YR4/8
	B20-80	Red	2,5yYR5/8	Red	2,5YR5/8

The yellow color of the samples before firing is due to the presence of goethite. At 950°C, briquettes from sample PP06 are pink (7.5YR 8/6), those from B20-100 are red. At 1050°C, briquettes from sample PP06 are pink (7.5YR8/4). Those from B20 are red (2.5YR5/8). The red coloration of Bossambo Farm briquettes is due to the transition from goethite to hematite, with loss of the water molecule, by the reaction :



However, Fe₂O₃ is not the only oxide involved in briquette coloring. CaO, TiO₂, MgO, MnO give specific colorations to ceramic products (Kreimeyer, 1987). A small amount of iron oxide in the PP06 sample resulted in colors similar to white (pink) and is suitable for the manufacture of vitreous materials, porcelain, sanitary ware and tableware (Reeves et al., 2006).

Linear shrinkage

Linear shrinkage was measured on PP06, B20 materials. For materials from Pongo Pitti, PP06, linear shrinkage values are 4.31% and 4.81% respectively for temperatures of 950°C and 1050°C. For materials from Bossambo Farm, B20, the linear shrinkage values are 1.78% and 4.87%. It can be seen from these results that linear shrinkage values are higher in Pongo Pitti materials than Bossambo Farm at 950°C. This behavior is thought to be due to the large amount of mineralogical clays and organic matter in these materials (Tardy,1993). Linear shrinkage increases with temperature. Indeed, when materials are subjected to heat treatment, dehydration and dehydroxylation reactions take place, generally accompanied by particle packing, which increases linear shrinkage. The higher the linear shrinkage, the more compact and dense the briquette obtained (Ndzana, 2019). Linear shrinkage for Pongo Pitti materials is less than 5% and is less than 2% for Bossambo Farm materials at 950°C. Referring to the work of Adrade et al. (2011), the low values of linear shrinkage would be due to the dominant presence of kaolinite

compared to other minerals. Indeed, as a clay mineral, kaolinite contains less constituent water. But these low values could also be due to the high alkali content ($K_2O+Na_2O\sim 1.68$) in Bossambo Farm materials.

Mass loss

Mass loss is a measure of the amount of material likely to decompose or volatilize during cooking. The mass losses for PP06 are 12.1% and 12.56% respectively for temperatures of 950°C and 1050°C; for B20, the mass loss values are 8.38% and 8.50% respectively. A mass decrease is observed as the temperature increases. This is due to the volatilization of organic matter and the loss of water molecules (existing as hydroxyls) from hydrated minerals. The loss of mass is also greater in Pongo Pitti materials than in Bossambo Farm materials. This loss of mass would be due to a sufficiently high proportion of mineralogical clays and organic matter.

Water absorption

Water absorption is 27.57% and 20.27% for Pongo Pitti materials at 950°C and 1050°C respectively. For Bossambo Farm materials, water absorption is 20.87% and 15.79%. Water absorption decreases with increasing temperature. Water absorption in the Pongo Pitti material, PP06, is higher than that of materials harvested at Bossambo Farm. In fact, B20 records the lowest water absorption value. This lower value means that the material contains a large quantity of clay minerals which, during their transformation into mullite, inhibit the evolution of water absorption and thus porosity (Onana et al., 2019). In the materials studied, water absorption at 1050°C is generally below 20%. These values below 20%, especially for those from Bossambo farm, indicate that these clays can be used in the ceramic industry, especially in the manufacture of fired tiles and bricks in accordance with the Brazilian classification (Souza et al., 2002; Ngun et al., 2011). Water absorption is a key factor affecting the durability of ceramic products, in this case manufactured briquettes. Low water absorption values imply high durability and resistance in a natural environment (Fadil-Djenabou et al., 2023).

Bulk density

For materials from Pongo Pitti, the density is 2.11 and 2.23 for temperatures of 950°C and 1050°C respectively. For those from Bossambo Farm, the density is 2.12 and 2.51. Apparent density increases with the evolution of sintering temperature for the different materials studied (Ndjigui et al., 2016).

Cohesion and sonority

At 950°C and 1050°C, the materials studied do not crumble, so cohesion is good. The sound of the samples studied is metallic.

Flexural strength

Flexural strength is 4.96 MPa and 6.66 MPa in the material harvested at Pongo Pitti, at 950°C and 1050°C respectively. In samples harvested at Bossambo Farm, it is 4.38 MPa and 8.89 MPa for temperatures of 950°C and 1050°C. At 950°C, flexural strength is higher in the Pongo Pitti material. At 1050°C, Bossambo Farm material is stronger than Pongo Pitti material. According to the Brazilian standard (Souza et al., 2002), Pongo Pitti and Bossambo Farm materials are suitable for the manufacture of building bricks, ceramic blocks and roof tiles (flexural strength is greater than 6.5 MPa).

CONCLUSION

The main aim of the present study was to characterize the physico-mechanical and geochemical properties of Pongo Pitti and Bossambo Farm clays, as well as their use in the ceramics industry. Chemical analysis revealed that the clay materials studied are rich in SiO₂, Al₂O₃ and Fe₂O₃, and much less rich in alkalis (Na₂O and K₂O) and alkaline earths (MgO and CaO). The Al₂O₃/Fe₂O₃ ratio showed the presence of aluminous clays at Pongo Pitti, suitable for use in the refractory ceramics industry, and the presence of iron-rich clays suitable for the manufacture of building bricks and roof tiles. Linear shrinkage, mass loss, bulk density and flexural strength increased with rising temperature, while water absorption and porosity decreased with increasing temperature. The results of the post-firing mechanical tests demonstrated that the materials studied can be used in the manufacture of bricks and roof tiles, but that Pongo Pitti's materials can also be used in refractory ceramics.

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