

Physico-Chemical and Mineralogical Characterization of Two Clay Materials of the Far North Region of Cameroon (Makabaye, Maroua)

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Abstract

To contribute to the valorization of local materials, the physico-chemical and mineralogical characterization of two clay materials MJ and MN collected in the Mayo Tsanaga river which crosses the Makabaye district of Maroua (Cameroon) was carried out. For this purpose, various methods of characterization have been used, namely granulometric analysis, Atterberg limits, X-ray fluorescence spectrometry and X-ray diffraction. It is apparent from the granulometry that the clay materials studied titrate 33.77% of clays for MJ against 44.13% for MN. The plasticity indices I_p with values $I_{p_{MJ}} = 19.27\%$ and $I_{p_{MN}} = 23.4\%$ place the materials in the plastic domain and offer them the possibility to being shaped into objects. The chemical composition of the MJ and MN materials reveals that the silicon oxide SiO_2 , the aluminumoxide Al_2O_3 and iron oxide Fe_2O_3 are their main constituents. The X-ray diffraction of the MJ and MN materials shows that they consist mainly of quartz with associated kaolinite, illite, montmorillonite, perialite, dickite, nacrite, amesite, albite, brookite and anorthite. In addition to these, 2/1 minerals such as muscovite, nontronite, glauconite, and phlogopite are also identified in the MJ material. The peaks of sanidine, microcline and gismondine are also found in the MN material. The materials being rich in clay minerals 2/1 can be valorized in the adsorption and the absorption of the oils and greases and in the waterproofing of the grounds. The presence of quartz, kaolinite and illite is undoubtedly favorable for the manufacture of ceramic products in terracotta. These products will be obtained at a relatively lower temperature due to illite, feldspars and iron minerals that provide vitrification during firing by forming eutectics. The aluminosilicate amorphous phases contained in the

studied materials can be exploited to produce geopolymer cements and concretes.

Keywords

Characterization, Physico-Chemical, Mineralogical, Clay Materials, Mayo Tsanaga, Maroua-Cameroon

1. Introduction

Clays are more or less hydrated, aluminosilicates; majority of which belong to the phylitic silico-aluminates group [1]. These materials which dominate the 2- μm fraction of soils are an integral part of our daily lives. This is how they are found from the white layers of the paper on which we write, to the storage of harmful waste that we want to confine through cosmetics, tires, paints and building materials [2]. Their enormous external surface compared to their volume makes them privileged materials for catalysis, the retention of toxic or the supports of composites.

Clay materials exist in almost all regions of Cameroon [3]. In the Far North Region, clay soils are mainly used for the manufacture of different pottery items and building materials such as bricks. These activities, practiced by craftsmen during the dry season, bring them finances to meet their needs.

The efficient and rational use of these materials is most often limited by the low durability and mechanical resistance of their products. This is compounded by the fact that the mineral and chemical compositions of these abundant clay materials are unknown which makes it difficult to improve on the types and yields of the products manufactured from these clays. Without knowledge of chemical and mineralogical composition, it is difficult, for example, to know if a clay is fusible or refractory. The aim of this project therefore was carried out, the mineral and chemical composition of some clays of the Far North Region of Cameroon.

To do this, two representative clay materials MJ and MN, which are superimposed, were sampled in Maroua town in the Far North Region of Cameroon. The chosen zones represent areas of high concentration of activities that employ clay the confection of pottery or construction materials. Chemical and mineral composition as well as granulometric analysis and the Atterberg limits were carried out on these materials. The results of this research will go a long way to contribute to the enrichment of the limited data base on clay materials in Cameroon.

The results of the work will be used to feed a database to support the start-up of industrial projects for local clay materials. The long-term wish is that this experimental and scientific approach, applied to a current raw material, contributes to the valorization of local materials and to sustainable development.

2. Materials and Methods

2.1. Materials

For this work, two representative clay materials MJ and MN were sampled in the Mayo Tsanaga river in Maroua town in the Far North Region of Cameroon. The chosen zone represents area of high concentration of activities that employ clay for the confection of pottery or construction materials. The clay material was located 70 cm deep below the sand layer. Maroua is located on latitude $10^{\circ}34'83''\text{N}$ and on longitude $14^{\circ}17'34''\text{E}$ and is 414 m above sea level. The MJ sample is brownish yellow (Munshell Code 10YR 6/6) while the MN sample is black (Munshell Code N2.5/). One of the major reasons for the choice of these clays is that the reserves are so enormous that they can satisfy an industrial demand.

2.2. Methods

2.2.1. Granulometric Analysis

It reflects the determination of the weight proportions of particles contained in the clay materials according to their sizes. Wet sieving of samples and the sedimentation of the fraction less than $100\ \mu\text{m}$ were carried out according to French standards NF P18-560 [4].

2.2.2. Determination of the Atterberg Constant

Atterberg constant was determined by passing the clay material through a $400\ \mu\text{m}$ aperture using the mechanical Casagrande apparatus according to the French standard NF P94-057 [5].

This constant determines the water content W which characterizes the following change:

Solid \rightarrow Plastic: W_p

Plastic \rightarrow Liquid: W_l

The plasticity index I_p of the material was then determined from the Equation (1):

$$I_p = W_l - W_p \quad (1)$$

2.2.3. X-Ray Fluorescence Spectrometry

The chemical composition of the clay materials was determined by X-ray fluorescence spectrometry using the Panalytical AXIOS PW4400 spectrometer. The molten pearl method was used. The beads were obtained from the dissolution of the materials in lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) and homogenized at 1150°C .

2.2.4. X-Ray Diffraction

X-ray diffraction was obtained using a diffractometer suitable for the characterization of polycrystalline plane samples, the X'PER PRO MDP diffractometer from Panalytical. The scanned angular range is between 5 and 70° in 2θ (angle of incidence). The copper $\text{K}\alpha_1$ radiation (wavelength = $1.540598\ \text{\AA}$) used was produced at a voltage of $40\ \text{kV}$ and an intensity of $40\ \text{mA}$.

The diffractograms are plotted with the Panalytical X'PERT Highscore plus 3.0 software. Their stripping was done using the P.D.F. (Powder Diffraction File) of Materials Data Inc's MDI JADE 6.5 software that maps inter-reticular distances d to recorded 2θ angles and mineralogical phases contained in material samples.

3. Results and Discussion

3.1. Particle Size Fractions

Figure 1 gives the variation of cumulative size with diameter of MJ and MN clay materials. By projection on the various axes, these curves show that the MJ material consists of approximately 47.76% sand ($2 \text{ mm} > \varnothing > 0.006 \text{ mm}$), 16.20% silt ($0.006 > \varnothing > 0.002 \text{ mm}$) and 33.77% clay ($\varnothing < 0.002 \text{ mm}$) while MN consists of 37.76% sand, 16.20% silt and 44.13% clay [6]. \varnothing is the diameter of each size fraction.

The MN material is therefore richer in clay minerals than the MJ material, even though they have the same amounts of silt. Generally, the more a material is rich in fine fraction, the more it requires water to pass from a solid paste to a plastic paste and from it to a liquid paste [7]. In other words, the material will tend to retain more water between its particles, which will cause a relatively long drying time. As a result, it will take more energy to dry products made from MN material [8].

3.2. Atterberg Limits

Table 1 presents the results of the Atterberg limits of the samples.

These results show that the MJ material is less plastic than the MN material. The MJ and MN materials can resist flow under its own proper weight up to moisture contents of 35.8% and 46.6% respectively. However, the plastic deformation, corresponding to its normal consistency (between 15% and 40%), requires less than 16.53% water for MJ and 23.2% water for MN. These results (plasticity index 19.27% and 21.5%) show that these materials are plastics [9]. This explains why the quantity of water they retain without becoming fluid is high. These results are in agreement with the results of the granulometric tests presented in Section 3.1.

3.3. Chemical Analysis

The results of the chemical analysis expressed as mass percentages of the oxides of MJ and MN materials are presented in **Table 2**.

From a qualitative point of view, the materials have the same kinds of oxides quantitatively, apart from silicon oxide; the difference in the percentage composition of the oxides in the two materials is relatively small or non-existent in some cases (SO_3 and P_2O_5). SiO_2 , Al_2O_3 and Fe_2O_3 are the major oxides in these materials. The oxide SiO_2 is of a preponderant proportion in several studied

Cameroonian clay materials [10] [11] [12] [13]. The MJ and MN clays have less SiO_2 , almost the same amount of Al_2O_3 , and more Fe_2O_3 than the vertisolic materials of the Logone Valley (69.5% SiO_2 , 11.5% Al_2O_3 , 4.35% Fe_2O_3 on average) [14]. The relatively high potassium oxide content relative to other alkali metal oxides is a favorable factor for illitization and a decrease in the maturation temperature of ceramics that could be elaborated from these materials [15]. These ceramics will naturally be colored red because of the presence of iron between 800°C and 1100°C [16].

3.4. X-Ray Diffraction of MJ and MN Samples

Table 3 illustrates the analysis of X spectra using PDF files while Figure 2 and Figure 3 respectively show the diffractograms of MJ and MN materials.

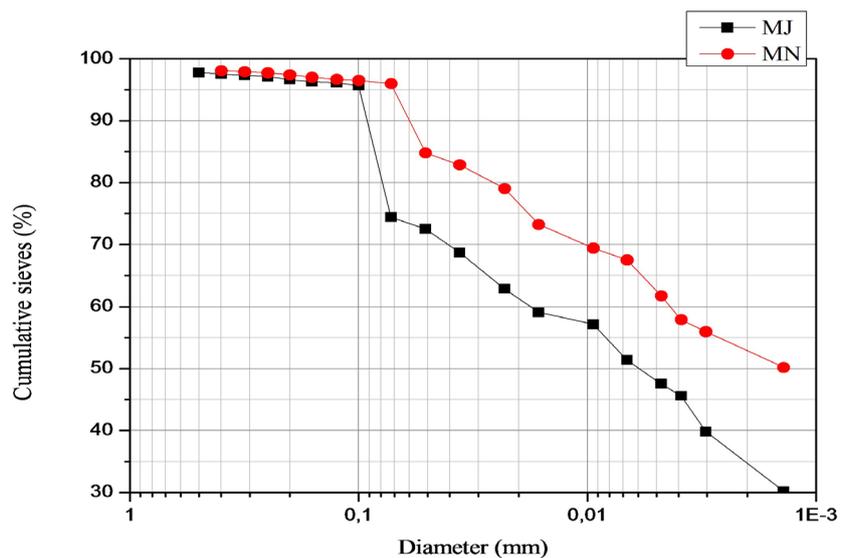


Figure 1. Granulometric curves of materials MJ and MN.

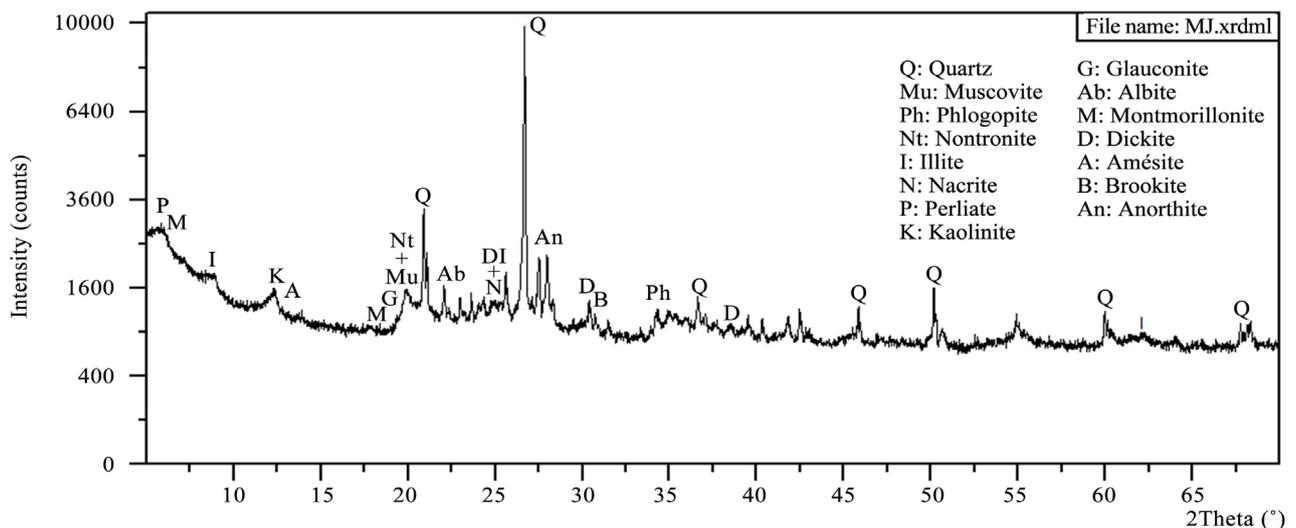


Figure 2. X-ray diffractogram of MJ material.

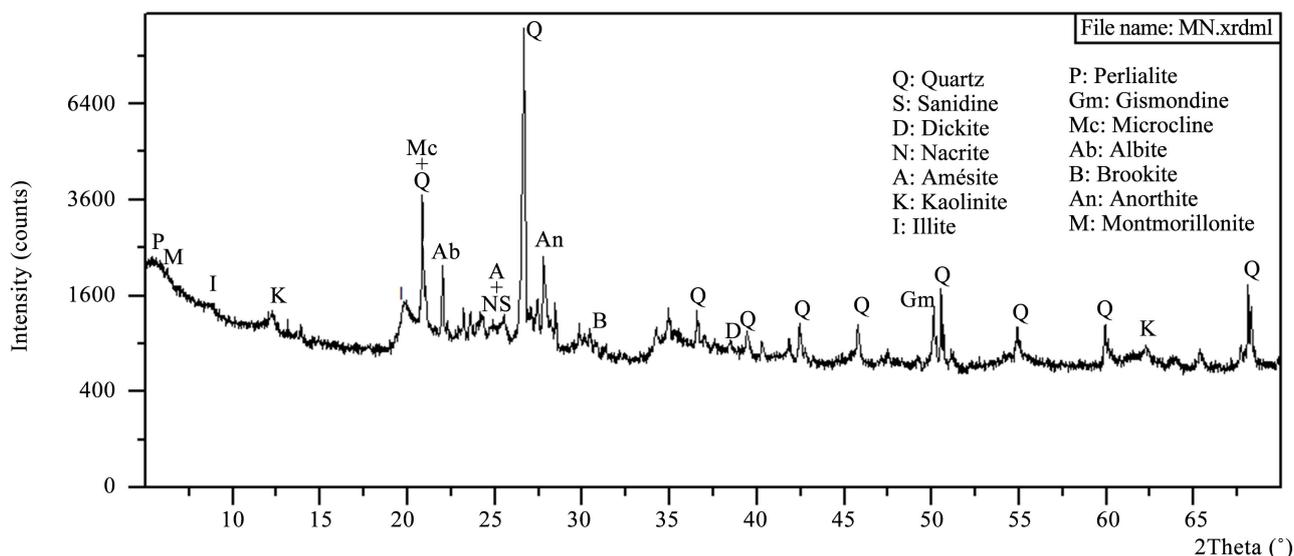


Figure 3. X-ray diffractogram of MN material.

Table 1. Atterberg limits of MJ and MN materials.

	Liquid limit W_L (%)	Plastic limit of W_p (%)	Plasticity index I_p (%)
MJ	35.8	16.53	19.27
MN	46.6	23.2	23.4

Table 2. Chemical composition of MJ and MN materials (Percentage by mass relative to the material dried in air, L.O.I. = Loss on Ignition).

Oxides	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	Mn ₂ O ₃	L.O.I.	Total
MJ	51.43	15.34	11.02	3.60	1.48	0.66	2.38	4.26	1.92	0.08	0.20	7.62	99.99
MN	41.89	14.64	17.47	2.92	1.75	0.66	2.15	4.88	2.26	0.08	0.26	11.04	100

Table 3. X spectrum analysis of MJ and MN materials.

MJ Material			
Mineral	Formula	Inter-reticular distance d in angström	PDF file number
Quartz	SiO ₂	4.24 Å, 3.33 Å, 2.45 Å, 1.98 Å, 1.81 Å, 1.54 Å and 1.38 Å	PDF 46-1045
Muscovite	KAl ₂ Si ₃ AlO ₁₀ (OH) ₂	10.05 Å, 4.46 Å, 3.34 Å and 2.56 Å	PDF 07-0025
Phlogopite	KMg ₃ (Si ₃ Al)O ₁₀ (OH) ₂	10.05 Å, 3.35 Å and 2.61 Å	PDF 10-0493
Nontronite	Na _{0.3} FeSi ₄ O ₁₀ (OH) ₂ 4H ₂ O	15.04 Å and 4.46 Å	PDF 29-1497
Illite	(K,H ₃ O)Al ₂ Si ₃ AlO ₁₀ (OH) ₂	9.98 Å, 5.01 Å, 4.48 Å, 3.72 Å, 3.45 Å, 3.33 Å, 3.19 Å, 2.98 Å, 2.56 Å and 1.50 Å	PDF 26-0911
Nacrite	Al ₂ Si ₂ O ₅ (OH) ₄	7.19 Å, 3.60 Å and 1.48 Å	PDF 07-0350
Perliolite	K _{2.02} Al ₂ Si _{4.76} O _{13.53}	15.75 Å, 4.57 Å, 3.47 Å, 3.17 Å and 2.90 Å	PDF 39-0294
Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	7.23 Å and 1.49 Å	PDF 14-0164
Glauconite	K(Fe, Al) ₂ (SiAl) ₄ O ₁₀ (OH) ₂	10.13 Å, 4.54 Å and 2.58 Å	PDF 09-0439
Albite	Na(AlSi ₃ O ₈)	4.04 Å	PDF 99-0001

Continued

Montmorillonite	$\text{Ca}_{0.2}(\text{Al}, \text{Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$	15.21 Å, 5.01 Å, 4.51 Å and 1.49 Å	PDF 13-00135
Dickite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	7.23 Å, 3.60 Å and 2.33 Å	PDF 10-0446
Amesite	$(\text{Mg}, \text{Fe}, \text{Al})_{3-x}[\text{SiAlO}_5](\text{OH})_{4-2x}$	7.15 Å and 3.54 Å	PDF 37-0429
Brookite	TiO_2	3.51 Å and 2.90 Å	PDF 29-1360
Anorthite	$\text{CaAl}_2\text{Si}_2\text{O}_8$	3.22 Å, 3.21 Å and 3.19 Å	PDF 41-1486
Material MN			
Quartz	SiO_2	4.25 Å, 3.34 Å, 2.45 Å, 2.28 Å, 2.23 Å, 2.12 Å, 1.98 Å, 1.81 Å, 1.80 Å, 1.67 Å, 1.54 Å, 1.45 Å, 1.38 Å and 1.37 Å	PDF 46-1045
Sanidine	$\text{K}(\text{Si}_3\text{Al})\text{O}_8$	4.27 Å, 3.81 Å, 3.47 Å, 3.34 Å, 3.29 Å, 3.27 Å, 3.24 Å, 3.01 Å, 2.92 Å, 2.77 Å, 2.61 Å, 2.59 Å, 2.39 Å, 2.18 Å, 2.02 Å, 1.93 Å and 1.79 Å	PDF 25-0618
Dickite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	7.23 Å, 3.60 Å and 2.33 Å	PDF 10-0446
Nacrite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	7.23 Å, 3.60 Å and 1.48 Å	PDF 07-0350
Amesite	$(\text{Mg}, \text{Fe}, \text{Al})_{3-x}[\text{SiAlO}_5](\text{OH})_{4-2x}$	7.15 Å and 3.54 Å	PDF 37-0429
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	7.23 Å, 3.59 Å and 1.49 Å	PDF 14-0164
Illite	$(\text{K}, \text{H}_3\text{O})\text{Al}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2$	10.05 Å, 5.03 Å, 4.48 Å, 3.72 Å, 3.46 Å, 3.34 Å, 3.20 Å, 2.99 Å, 2.56 Å and 1.50 Å	PDF 26-0911
Perillite	$\text{K}_6\text{Na}_3\text{Al}_9\text{Si}_{27}\text{O}_{72} \cdot 21\text{H}_2\text{O}$	15.94 Å	PDF 39-0224
Gismondine	$\text{CaAl}_2(\text{Si}_2\text{O}_6)_4 \cdot 4(\text{H}_2\text{O})$	7.31 Å, 4.92 Å, 4.27 Å, 3.34 Å, 3.19 Å, 3.13 Å and 1.82 Å	PDF 20-0452
Microcline	KAlSi_3O_8	4.24 Å and 3.26 Å	PDF 99-0067
Albite	$\text{NaAlSi}_3\text{O}_8$	4.04 Å, 3.66 Å and 3.22 Å	PDF 19-1184
Brookite	TiO_2	3.51 Å and 2.90 Å	PDF 29-1360
Anorthite	$\text{CaAl}_2\text{Si}_2\text{O}_8$	3.22 Å, 3.21 Å and 3.19 Å	PDF 41-1486
Montmorillonite	$\text{Ca}_{0.2}(\text{Al}, \text{Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$	15.21 Å, 5.01 Å, 4.51 Å and 1.49 Å	PDF 13-00135

The MJ and MN materials consist mainly of quartz with associated kaolinite, illite, montmorillonite, perillite, dickite, nacrite, amesite, albite, brookite and anorthite. In addition to these, 2/1 clay minerals such as muscovite, nontronite, glauconite, and phlogopite are identified in the MJ material. These minerals are present in the vertisols found in the North [17] and Far-North of Cameroon [18]. The peaks of sanidine, microcline and gismondine appear also in the MN material. The minerals are diversified and varied in both samples. The sand layer, entrained by water, which covers the MJ and MN materials along the river bed may have an impact on their chemistry and mineralogy. Montmorillonite and kaolinite are also present in Logone materials while other minerals are not listed.

The kaolinite peak at 7.2 Å on the MJ diffractogram was resolved indicating the presence of a crystallized kaolinite.

A similar peak in the material MN is represented by a dome, characteristic of a mineral with a lower degree of crystallinity: such a peak denotes the presence of a poorly crystallized or amorphous kaolinite which does not have a microstructural organization [19]. Montmorillonite and illite also present domes at 14

and 10 Å, which are indicative of poor crystallinity.

The 2/1 clay minerals have been used in the adsorption and absorption of oils and greases and also in the waterproofing of soils [20]. Quartz, kaolinite and illite are favorable for the manufacture of terracotta ceramic products. These products are obtained at a relatively lower temperature because of the presence of illite, feldspars (albite and anorthite) and iron minerals which provide vitrification by the formation of eutectics [21]. Amorphous minerals, especially aluminosilicates, are potential materials to produce cements and geopolymer concretes [22].

4. Conclusions

This work characterized two samples of clay material obtained from the Tsanaga River of the Far North Region of Cameroon. Granulometric analysis showed that the clay contents of samples MJ and MN were 33.77% and 44.13% respectively. The materials are essentially plastics in nature which make them amenable for the fabrication of different articles as suggested by their plasticity values, 19.27% and 23.4% for MJ and MN. Major oxides present in the two samples are SiO₂, Al₂O₃ and Fe₂O₃. The presence of quartz, kaolinite and illite is undoubtedly favorable for the manufacture of ceramic and assimilated products.

From a perspective of sustainable local development, this study is part of the contribution to the promotion of local materials. It is therefore an important scientific contribution in the knowledge and characterization of industrial mineral resources of Cameroon.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

- [1] Velde, B. (1992) Introduction to Clay Minerals: Chemistry, Origins, Uses and Environmental Significance. Chapman and Hall Ltd., London.
<https://doi.org/10.1007/978-94-011-2368-6>
- [2] Meunier, A. (2003) Argiles. Contemporary Publishing International-GB Science.
- [3] Sieffermann, G. (1959) Premières déterminations des minéraux argileux des sols du Cameroun. *Conférence Interafricaine des Sols*, Dalaba, 2-11 November 1959, 139-150.
- [4] AFNOR (1990) Granulats-Analyse granulométrique par tamisage. NF P18-560.
- [5] AFNOR/SOLS (1993) Sols: Reconnaissance et essais—Détermination des limites d'Atterberg—Limite de liquidité à la coupelle—Limite de plasticité au rouleau. NF P 94-051.
- [6] Anger, R., Fontaine, L., Houben, H., Doat, P., Van Damme, H., Olagnon, C. and Jorand, Y. (2011) La terre, un béton comme les autres? Quelques mécanismes de stabilisation du matériau terre. In: Rainer, L., *et al.*, Eds., *Terra 2008: The 10th International Conference on the Study and Conservation of Earthen Architectural Heritage*, Getty Publications, Bamako, 222.

- [7] Mathieu, C. and Lozet, J. (2011) Dictionnaire encyclopédique de science du sol: Avec index anglais-français. Lavoisier, Paris.
- [8] Brosnan, D.A. and Robinson, G.C. (2003) An Introduction to Drying of Ceramics: with Laboratory Exercises. The American Ceramic Society.
- [9] Vulliet, L., Laloui, L. and Zhao, J. (2016) Mécanique des sols et des roches (TGC volume 18): Avec écoulements souterrains et transferts de chaleur. PPUR Presses polytechniques et universitaires romandes, Lausanne.
- [10] Elimbi, A., Founyapte, S. and Njopwouo, D. (2004) Effets de la température de cuisson sur la composition minéralogique et les propriétés physiques et mécaniques de deux matériaux du gisement argileux de Bakong (Cameroun). In: *Annales de chimie*, Vol. 29, Lavoisier, Paris, 67-77. <https://doi.org/10.3166/acsm.29.2.67-77>
- [11] Njoya, D., Elimbi, A., Nkoumbou, C., Njoya, A., Njopwouo, D., Lecomte, G. and Yvon, J. (2007) Contribution à l'étude physico—Chimique et minéralogique des argiles de Mayouom (Cameroun) In: *Annales de Chimie*, Vol. 32, Lavoisier, Paris, 55-68. <https://doi.org/10.3166/acsm.32.55-68>
- [12] Pialy, P. (2009) Etude de quelques matériaux argileux du site de Lembo (Cameroun): Minéralogie, comportement au frittage et analyse des propriétés d'élasticité. Doctoral Dissertation, University of Limoges, Limoges.
- [13] Mache, J.R. (2013) Minéralogie et propriétés physico-chimiques des smectites de Bana et Sabga (Cameroun) Utilisation dans la décoloration d'une huile végétale alimentaire. Doctoral Dissertation, Université de Liège, Liège.
- [14] Balo Madi, A., Nguetnkam, J.P., Bitom, D.L. and Basga, S.D. (2017) Caractérisation géo-mécanique et classification des matériaux vertisoliques de la vallée du Logone au Cameroun. *Proceedings of the 19th International Conference on Soil Mechanics and Geotechnical Engineering, Seoul*, Seoul, 17-21 September 2017, 397-401.
- [15] Meunier, A. and Velde, B.D. (2013) Illite: Origins, Evolution and Metamorphism. Springer Science & Business Media, Berlin.
- [16] Sigg, J. (1991) Les produits de terre cuite: Matières premières, fabrication, caractéristiques, applications: Faïences et grès. Ed. Septima.
- [17] Djoufac Woumfo, E., Elimbi, A., Panczer, G., Nyada Nyada, R. and Njopwouo, D. (2006) Caractérisations physico-chimiques et minéralogiques des vertisols de Garoua (Nord Cameroun). *Annales de Chimie*, **31**, 75-90. <https://doi.org/10.3166/acsm.31.75-90>
- [18] Ekodeck, G.E. (1976) Nature et comportement géochimique des formations superficielles gonflantes du Nord-Cameroun. Th. 3^e cycle, Université de Grenoble, 182 p.
- [19] Hinckley, D.N. (1962) Variability in "Crystallinity" Values among the Kaolin Deposits of the Coastal Plain of Georgia and South Carolina. *Clays and Clay Minerals*, **11**, 229-235. <https://doi.org/10.1346/CCMN.1962.0110122>
- [20] Bergaya, F., Theng, B.K.G. and Lagaly, G. (2006) Developments in Clay Science 1. Handbook of Clay Science, Chapter 10, Elsevier, New York.
- [21] Haussonne, J.M. (2005) Céramiques et verres: Principes et techniques d'élaboration (Vol. 16) PPUR presses polytechniques.
- [22] Elimbi, A., Tchakoute, H.K. and Njopwouo, D. (2011) Effects of Calcination Temperature of Kaolinite Clays on the Properties of Geopolymer Cements. *Construction and Building Materials*, **25**, 2805-2812. <https://doi.org/10.1016/j.conbuildmat.2010.12.055>.