



The viability of calcined clays and volcanic scoria from western Cameroon as Supplementary Cementitious Material (SCM)

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Abstract

In order to promote the use of calcined clays and volcanic scoria from the western Cameroon as Supplementary Cementitious Material (SCM), the physical, chemical and mechanical properties of fresh and hardened cements were investigated. The cement was formulated by substituting 10, 20, 30, and 40% of clinker by calcined clays from Mayouom (Mkm) and Balengou (MKb), and volcanic scoria from Foubot (PNf). For each of the three raw materials, the loss on ignition is less 1%, the sum $\%SiO_2 + \%Al_2O_3 + \%Fe_2O_3$ is greater than 70%, amorphous phase is present and pozzolanic reactivity with the Chappelle test is greater than 80% of $Ca(OH)_2$ consumed. This makes it possible to classify MKm, MKb and PNf among the pozzolanic materials. The addition of calcined clay to the clinker, result to an increase in the water to cement ratio, unlike the Foubot pozzolan, which does not really affect this ratio. The three raw material act as setting retarders, with PNf having a greater retarding effect than MKm and MKb. The compressive strengths of the cements formulated in this study shows that with 10% clinker substitution, cements of class 42.5 can be obtained, and that from 20% onwards, the cements obtained are of class 32.5. However, an addition of more than 20% PNf in the clinker produces cements with strength less than 30 MPa at 28 days. Calcined clay from Balengou and Mayouom could be used as a viable alternate source of SCM for cement production with better performances compared to volcanic scoria from Foubot.

Keywords Portland cement · Calcined clay · Volcanic scoria · Supplementary Cementitious Material · Western Cameroon

1 Introduction

Portland cements is among the widely used hydraulic binders in concrete. Their use dates back more than 200 years and they are mainly made up of ordinary Portland clinker (OPC), resulting from the calcination at about 1450 °C of a mixture of limestone and clay [1]. For many decades, OPC was the reference hydraulic binder in ancient civilizations, particularly in Egypt and ancient Rome, but also in the rest of Europe and the United States of America [1, 2]. The raw consumption of clinker quickly posed the problem of pollution of the atmosphere because its production is associated with a very high-energy consumption and a high production of greenhouse gases [3–5]. Indeed, producing one ton of clinker implies a consumption of about 3000 kJ/kg and an emission of about 0.866 ton of CO_2 in the atmosphere [3, 6, 7]. Similarly, the use of OPC instead of Roman cement, which was made from limestone and pozzolan heated at low temperatures, led to an increase in the cost of construction

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[3, 8]. In view of these limitations, research work has been undertaken for decades to develop binders that consume the least amount of clinker possible while guaranteeing acceptable mechanical properties. Thus, the common solution used is the substitution of a quantity of OPC by pozzolanic material known as Supplementary Cementitious Materials (SCM) [2–4, 7]. Through this approach, the proportion of clinker in cement has been reduced from nearly 95% in the 1920s to less than 70% in 2018 [9]. This solution has led to a reduction over time in CO₂ emissions per ton of cement produced, from 0.75 t per ton of cement in 1990 to 0.59 t of CO₂ per ton of cement in 2020, representing a reduction of about 21% [4, 10]. Despite this progress, the very high demand for cement, linked to the rapid urbanization of societies, lead to an increase in the global production of CO₂ per year proportionally to the cement production: 2.6Gt CO₂ in 2021 against 2.4 Gt CO₂ in 2019 and 0.9Gt in 1990 corresponding to a cement production of 4.4 Gt, 4.1 Gt and 1.2 Gt respectively [10–12]. The replacement of 45–50% of clinker by a mixture of limestone—calcined kaolinite clay reduced about 30% of CO₂ emission associated to the cement manufacture and not compromise the performance of the resulted cement [13, 14]. These results are leading to more investments in the research and the promotion of SCMs that can be located in various parts of the world. Indeed, SCMs are aluminosilicates materials, which have the capacity to react with lime in OPC during the hydration phase (consumption of portlandite) to form calcium silicates hydrates (C–S–H). They are characterized by their pozzolanic properties i.e. $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \geq 70\%$, presence of amorphous silica and loss on ignition $\text{LOI} \leq 10\%$ [15–17]. SCMs include natural pozzolans (volcanic scoria and volcanic ash) and artificial pozzolan (rice husk ash, calcined clays, fly ash, silica fume) [18–21]. Due to their relatively low costs, volcanic scoria are widely used SCMs in cement production [13, 17]. In the other hand volcanic SCM are not always available. Several studies have shown that volcanic scoria have excellent characteristics for use as SCMs. Other studies have demonstrated the ability of calcined clays and other raw materials to serve as cementitious substitute materials [6, 13, 14, 18, 20, 22–27]. Most cement producers used about 25–35% of volcanic scoria for substitution of clinker in cement manufacture, while the rate of calcined kaolinite clay used for the same function is around 30–45% [13, 14]. However, the effectiveness of SCMs remains a function of their origin (chemical and mineralogical composition of the original magma or source rock) and of the influence of their direct environment on their composition (impurity level in the original material, condition of the volcanic eruption) [2, 8, 28]. That is why pozzolans are continuously studied for their viability in Portland cement manufacturing.

In Cameroon, volcanic scoria is usually used by cement factories as SCM. However, their exploitation is not yet fully

extended to all the deposits in the country. Volcanic scoria deposits are found along the ‘Cameroon’s line’, particularly in the south west region (on the slopes of Mount Cameroon, the Kumba plain, the Tombel plain), in the Littoral region (the slopes of Mount Manengouba with the Djoungou site), in the western region (the Noun plain with the Foubot site), in the Adamawa plateau [18, 29] with an exploitation preference for that of Djoungou. It was very recently in 2018 that the Foubot site was requested for the first fair by a local cement factory with a view to launching its clinker grinding plant located at Nomayos in Yaounde at about 400 km. Because of the increasing demand of SCMs by the cement industry, the search of alternate sources of these Material was found important.

However, this study aims to contribute to promoting the use of calcined clay and volcanic scoria from the western region of Cameroon as SCM in the cement industry by determining their physical, chemical and mechanical properties in the fresh and hardened Portland clinker.

2 Methodology

2.1 Presentation and characterization of raw materials

The calcined clay used in this study was obtained by firing, at 750 °C for 1 h with a temperature rise of 3 °C/min, two raw clays from western region of Cameroon: kaolin from Mayouom and halloysite from Balengou. These different clays were previously characterized by Njoya [30] and Njopwouo [28] respectively. These authors claimed that the Mayouom clay contains approximately 79% kaolinite and Balengou clays contain nearly 70% halloysite. The calcination process was carried out in an electric furnace and after activation, the calcined clay obtained (noted MKm and MKb respectively for Mayouom and Balengou) underwent slow cooling for 24 h before being taken out from the furnace. The artificial pozzolans thus obtained, as well as the volcanic scoria from Foubot (PNf) and the Portland clinker (CL) obtained from a local cement plant, are finely ground using a ball mill and sieved to 63 μm. The powder obtained are used for the formulation of the cements studied in this work, and for the chemical and mineralogical analysis of the raw material. The X-ray Fluorescence (XRF) method was used to determine the chemical characteristics of different raw material while their mineralogy was determined by the X-ray diffractions (XRD) method. The Fourier Transform Infra-Red Spectrometry (FT IR) method was used to determine the main chemical bonds in our different raw material. XRF tests are performed using the ARL 9400 sequential XRF XP spectrometer, while XRD are performed using an Empyrean PANalytical diffractometer (Malvern

Panalytical Ltd, Malvern, UK) with filter Ni, CuK α radiation ($K = 1.540598 \text{ \AA}$) and FT IR are carried out using a Fourier FTS185 Biorad and Vertex 70 Bruker transform spectrometer. The pozzolanic reaction of each of the raw materials is determined using the chapele test, in accordance with standard NF P 18-513. This test consists of reacting 1 g of pozzolan with 2 g of CaO in the presence of 250 ml of water for 16 h at a temperature of 90 °C. The quantity of uncombined lime is then dosed with an HCl solution to deduce the quantity of lime consumed, expressed as mg of Ca(OH) $_2$ consumed per gram of pozzolan or as a percentage of Ca(OH) $_2$ consumed compared to that of a blank solution (without pozzolan) taken as a reference.

2.2 Formulation and characterization of cements

2.2.1 Formulation of the cements

Four cement formulations were made for each of the three available raw materials. These formulations consisted of a mass substitution of the OPC by 10, 20, 30 and 40% pozzolan and calcined clay powder obtained as described above. A control formulation containing only OPC was also prepared. The homogenization of the mixtures was carried out using a ball mixer for 1 h and the formulations obtained are listed in Table 1. The products formed are isolated from the ambient air in perfectly closed packaging.

2.2.2 Characterization of the formulated cements

2.2.2.1 Determination of water-to-cement (W/C) ratio and setting time The W/C ratio is determined for the calculation of the amount of water required by each of the formulated cements to obtain a paste of normal consistency. It is at this consistency that the optimum values of the physical and mechanical properties of the specimens are achieved (porosity, water absorption, compressive strength, etc.) In this study, the W/C ratio was determined in accordance with the ASTM C187-16 procedure, using the Vicat apparatus [31, 32].

The setting times of the different cements were also determined, after determination of the W/C ratio, by means of the Vicat apparatus and according to the procedure of the ASTM C191-13 standard [32, 33]. This test allows to evaluate the reaction speed of the different raw material with the OPC.

2.2.2.2 Preparation of hardened samples The cement pastes are prepared as in the case of the determination of the W/C ratio with the only difference that the quantity of water is previously known for the mass of cement used. The said paste is immediately introduced into a cylindrical mould of 25 mm diameter and 50 mm length. These moulds are obtained by cutting 50 mm long pieces from a PVC (Polyvinyl Chloride) pipe of 25 mm diameter with a metal saw. The paste is clamped in the moulds by pricking (25 strokes) with a metal rod of 3 mm diameter. The inner walls of the moulds are previously coated with oil to facilitate removal from the mould after drying, and the base is closed with a waterproof plastic. The moulds were filled in two layers in order to reduce any air bubbles and pores, and the surface was smoothed with a ruler after filling. The moulds were then kept at room temperature (23 °C, laboratory temperature) for 24 h, and the hardened samples obtained were immersed until the day of their compression (7, 28 and 56 days).

2.2.2.3 Determination of compressive strength and water absorption rate Before compression with a hydraulic press, the specimens taken out of the water were left in the open air for 4–6 h to have a dry surface. On each day of compressing, three specimens are compressed for each of the formulated cements and the strength retained is the average of the strengths of the three specimens. The Eq. (1) calculates the strength of the specimen:

$$f_{cj}(MPa) = \frac{F(N)}{S(mm^2)} \quad (1)$$

With f_{cj} = compressive strength at j days expressed in MPa, F = compressive breaking strength expressed in Newton (N)

Table 1 Composition of the different cements formulated (2000 g)

Samples codes			Proportion of pozzolans		Proportion of clinker		Quantity of water (g)			
			Mass (g)	%	Mass (g)	%	CL	CMkm	CMkb	CPNf
	CL		0	0	2000	100	468	/	/	/
CMkm1	CMkb1	CPNf1	200	10	1800	90	/	624	632	514
CMkm2	CMkb2	CPNf2	400	20	1600	80	/	730	724	520
CMkm3	CMkb3	CPNf3	600	30	1400	70	/	778	786	524
CMkm4	CMkb4	CPNf4	800	40	1200	60	/	814	806	526

CL, clinker whitout SCM; CMkm, Clinker + Calcined clay from Mayouom; CMkb, Clinker + Calcined clay from Balengou; CPNf, Clinker + Volcanic scoria from Foubot

and S = compressed surface of the specimen expressed in mm^2 .

The measurement of water absorption is carried out in accordance with ASTM C948-81 [32, 34]. In this case, two samples are used per formulation of cement to determine the water absorption rate of the different hardened cements. The samples were first dried in an oven at 105 °C for 24 h, then weighed (md) and immersed again for 24 h. After immersion, their surfaces are dried and the specimens are weighed (mh). The Eq. (2) then gives the water absorption rate:

$$W_A = \frac{mh - md}{md} \times 100 \quad (2)$$

Table 2 Chemical composition of calcined clays and pozzolans used

Oxydes	Samples			
	MKm	Mkb	PNf	CL
SiO ₂	68.68	62.24	47.30	16.719
Al ₂ O ₃	26.05	32.71	14.83	3.229
Fe ₂ O ₃	0.74	3.03	13.09	4.905
MnO	0.01	0.02	/	0.062
MgO	0.22	0.00	6.68	1.121
CaO	0.05	0.06	8.17	68.899
Na ₂ O	0.00	0.00	3.22	0.187
K ₂ O	2.22	0.00	1.12	0.969
TiO ₂	1.02	0.36	2.99	0.251
P ₂ O ₅	0.06	0.04	/	0.46
LOI	/	/	0.84	/
Total	99.05	98.46	98.24	96.802
SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃	95.47	97.98	75.22	/

2.2.2.4 Chemical and mineralogical analyses These tests are carried out on a 56-day old hardened cement powder. In fact, the 56-day old specimens are dried for 48 h in an oven at 75 °C, then crushed using a ball mill and sieved to 63 μm , to obtain the powder subjected to XRD and FT IR test as in the case of the raw material.

3 Results and discussions

3.1 Characteristics of raw materials

Table 2 gives the chemical composition of the material used in this study. It shows that silica (SiO₂ > 60%) and alumina (Al₂O₃ > 26%) are the most abundant major elements in MKm and MKb. The level of Fe₂O₃ (3.03%) in MKb could justify its pink color (10R 8/4), while this oxide is almost zero in MKm with a pale yellow color (2.5Y 8/1.5). In PNf there is a high concentration of SiO₂ (47.30%) CaO (8.17%), MgO (6.68%), Na₂O (3.22%), K₂O (1.12%) and TiO₂ (2.99%) unlike the case of MKm and MKb in which these oxides, leached during the weathering process which gave rise to the Mayouom and Balengou clay, are very weakly represented (% < 1). This testifies to the presence in PNf of primary minerals resulting from the cooling of volcanic debris. For each of the three pozzolans, the loss on ignition is very low (% < 1) and the sum% SiO₂ + % Al₂O₃ + % Fe₂O₃ is greater than 70%. Figures 1, 2 and 3 show the XRD results of the MKm, MKb and PNf samples respectively. There indicates that calcined clay of Mayouom is mainly made up of quartz, illite, anatase and hematite, while that of Balengou is made up of quartz, hematite and microcline. For each of these calcined clays, we observe the absence of

Fig. 1 X-ray diffractogram patterns of calcined clay from Mayouom (MKm)

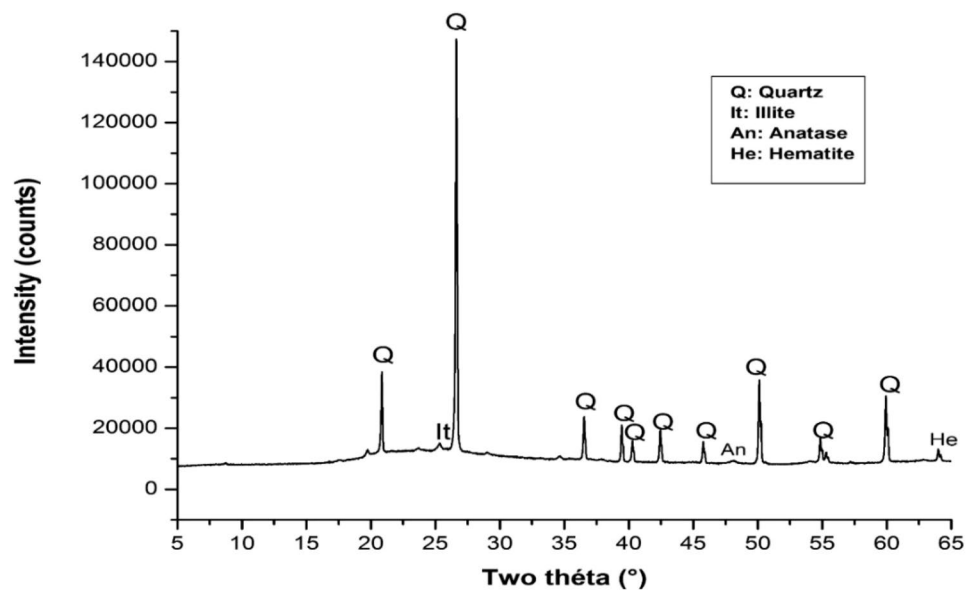


Fig. 2 X-ray diffractogram patterns of calcined clay from Balengou (MKb)

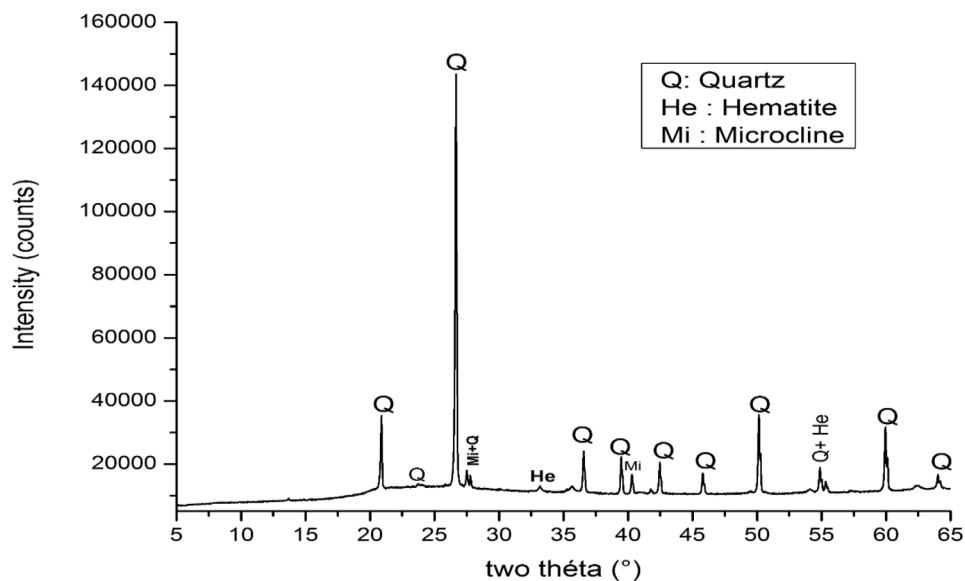
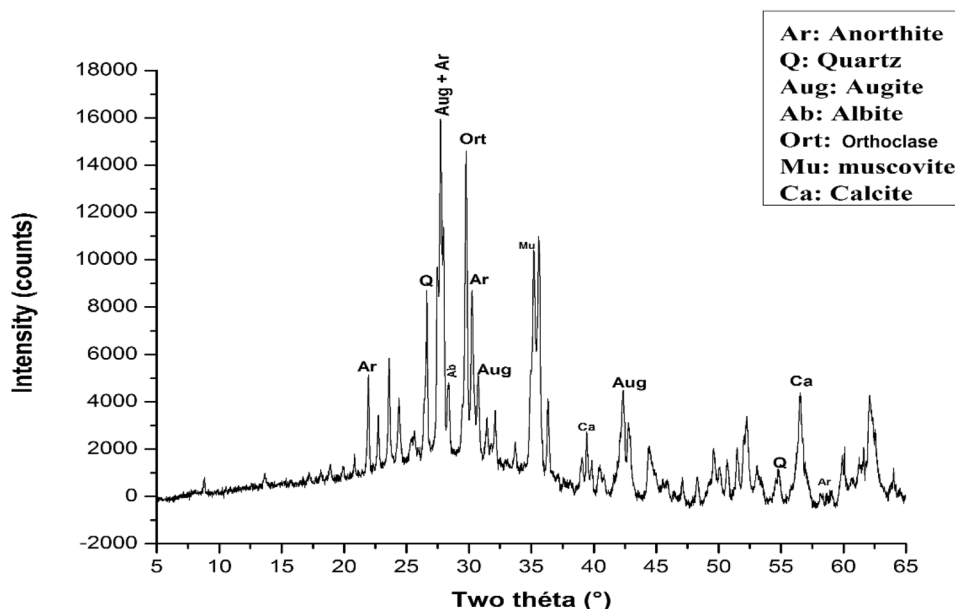


Fig. 3 X-ray diffractogram patterns of volcanic scoria from Foubot (PNf)



kaolinite, the main mineral in Mayouom clay [30] and halloysite, the main mineral in Balengou clay [28]. The absence of kaolinite in MKm can be linked to the calcination which would have transformed it into amorphous metakaolinite, undetectable by XRD analysis [6]. The base of each of the XRD patterns of these two calcined clays shows the presence of a broad hump between 15° and 40° 2θ , peaking at an intensity of about 19,000 counts. This confirms the presence, in these calcined clays, of the amorphous phase that can fix lime during the hydration reactions of cement.

PNf is made up of quartz, anorthite, albite, augite, orthoclase, muscovite and hematite. In addition to these minerals, at the base of the XRD curve of the volcanic scoria, a large hump between 17° and 37° 2θ is observed,

peaking at about 2000 counts. This also indicates the presence of amorphous phase in the volcanic scoria of Foubot.

Figure 4 show the results of FT-IR, which confirm the presence of the amorphous silica represented by the bands 1056 , 796 and 775 cm^{-1} for the case of MKb [35], and the bands 1055 , 798 and 774 cm^{-1} for the case of MKm [37, 38]. This bands indicates the vibrations of asymmetric and symmetrical elongation of the Si–O–Al and Si–O–Si bonds of the amorphous silica. This amorphous phase would be an indicator of the presence in these materials of amorphous metakaolinites and metahalloysites undetectable by XRD analysis. The results above, together with those of the pozzolanic reactivity test presented in Fig. 5, allow MKm, MKb

Fig. 4 FT IR patterns of samples MKm, MKb and PNf

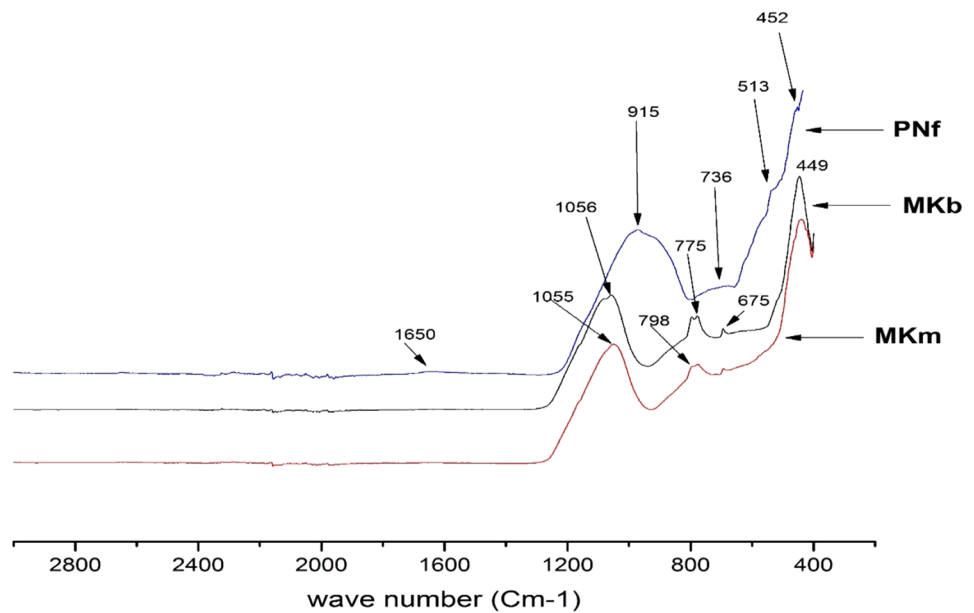
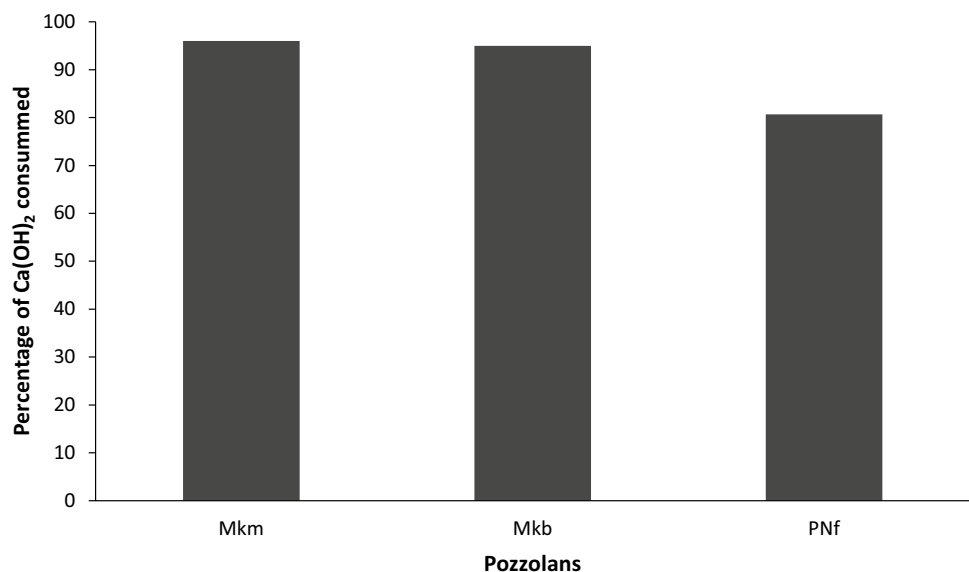


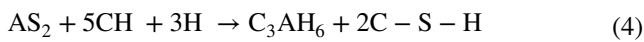
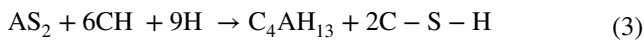
Fig. 5 Reactivity of Mkm, Mkb and PNf with $\text{Ca}(\text{OH})_2$ in the presence of water



and PNf to be classified among the pozzolanic material that can be used in concrete [15, 16, 35]

The study of the pozzolanic activity of the raw material in solution gave the result shown in Fig. 5. This result shows that the calcined clays of Mayouom (MKm) and Balengou (MKb) are more reactive than the volcanic scoria of Foubot (PNf): $\text{Ca}(\text{OH})_2$ consumption rate being 96%, 95% and 80% respectively for Mkm, MKb and PNf. This high reactivity of MKm and MKb can be explained by their great fineness. Indeed, according to [18], when the samples came into contact with the CH solution, their acidic and amphoteric compounds reacted through an acid–base reaction. In the case of volcanic scoria, [18] report the mechanism that was proposed by R. Dron, using

orthoclase (KAlSi_3O_8) which is a feldspar whose structure consists of three SiO_2 tetrahedral units and one AlO_2^- unit. He believes that in solution, the O^{2-} ions externs to the SiO_2 units are confronted with the presence of water molecules, leading to the formation of OH^- ions. The negative charges produced in this reaction can find compensation outside the surface and inside the tetrahedron. As a result, the tetrahedral units can become less and less bound, move from their initial positions and enter solution as H_3SiO_4^- ions. It is these latter ions that react with Ca^{2+} ions to form calcium silicates hydrates (C–S–H). In the case of calcined clays, it is the metakaolin (AS_2) that reacts with CH to form C–S–H and aluminosilicates as indicated by the theoretical Eqs. (3)–(5).

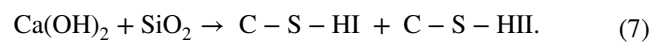
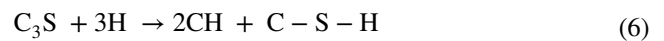


where C, CaO; S, SiO₂; A, Al₂O₃; H, H₂O.

3.2 Characteristics of formulated cements

Figures 6, 7 and 8 show the results of XRD analysis of each formulation group obtained, as indicated in Table 1. The presence of cement minerals such as portlandite, belite, alite and tetracalcium aluminate hydrated is observed. The presence of quartz in CMkm and CMkb cements is mainly due to the addition of calcined clay MKm and MKb. CPNf cements, in addition to the minerals mentioned above, include wollastonite, anorthite and hematite. The hydration of alite (C₃S) lead to the production of portlandite (CH) and calcium silicates hydrates (C–S–H) according to Eq. (7) shown below [20, 21]. The portlandite thus produced leads to the formation of additional calcium silicates hydrates (C–S–HI and C–S–HII) and of gehlenite (C₂ASH₈) after consumption of the amorphous silica and the aluminosilicates of calcined clay, according to Eqs. (5) and (7) [6]. Indeed, according to [39], metakaolins, cause the consumption of portlandite produced by cement during the hydration

process. This reaction is not very extensive in CPNf because the pozzolanic reactivity of PNf are very low compared to that of MKm and MKb, which are higher. This explain why, in the XRD curves of CMkm and CMkb cements, the intensity of the peaks of certain cement minerals (portlandite, alite) decreases with an increase in the level of calcined clay, unlike the case of CPNf cements in which the addition of pozzolan does not have enough impact on the peak intensities of these minerals. This observation is also made on the FT-IR curves of Figs. 9, 10, and 11 where, the peak of the 3640 cm⁻¹ band which represents the vibration of the OH bond of portlandite [40], almost constant in CPNf tends to disappear with an increase in the level of calcined clay.



where CSHI, CaO_{0.8-1.5} SiO₂ (H₂O)_{1.0-2.5}; CSHII, CaO_{1.5-2.0} SiO₂ 2(H₂O).

The C–S–H thus formed are generally in amorphous form [41] and are mainly responsible for the strength of cements. On the FT-IR results curves of the cements obtained (Figs. 9, 10 and 11), the 1640 cm⁻¹ band (observed on CMkm and CMkb) and the 1650 cm⁻¹ band (observed on CPNf) correspond to the vibration of the OH bond of C–S–H [40] and the bands 950 and 667 cm⁻¹ correspond to the vibrations of asymmetric elongation of the Si–O bond of the C–S–H [40].

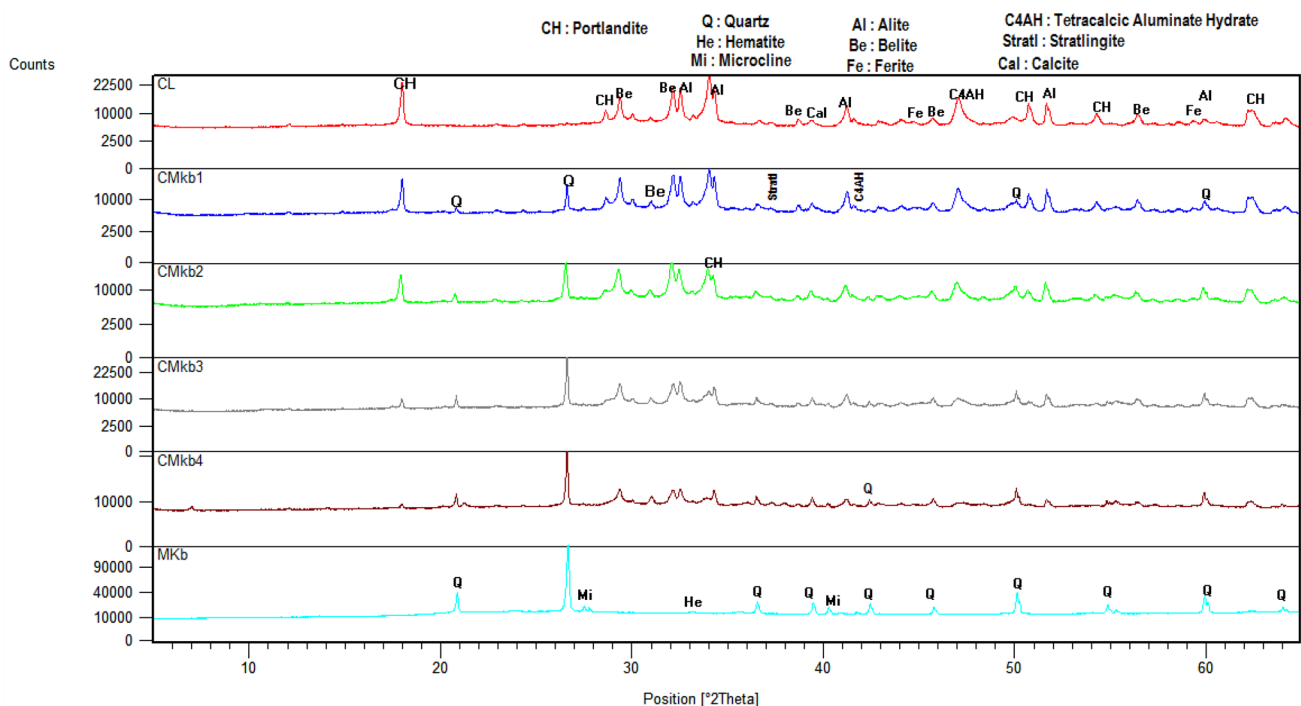


Fig. 6 X-ray diffractogram patterns of clinker and CMkb cements

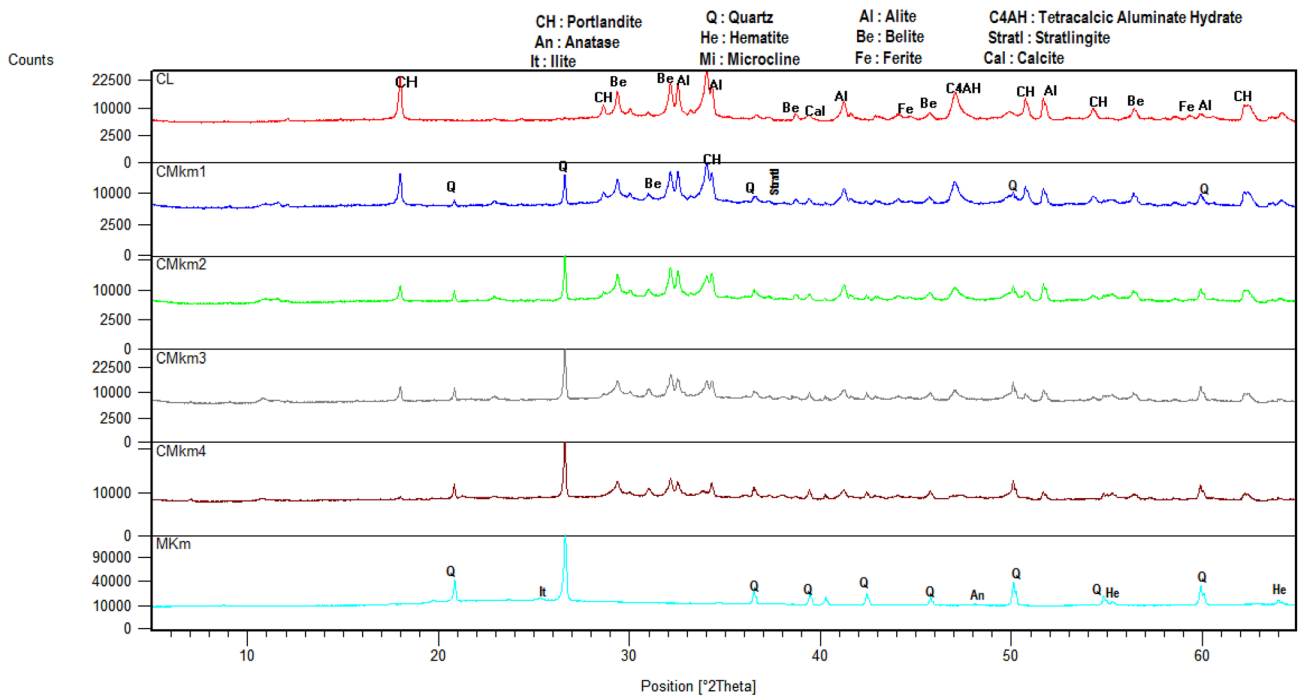


Fig. 7 X-ray diffractogram patterns clinker and of CMkm cements

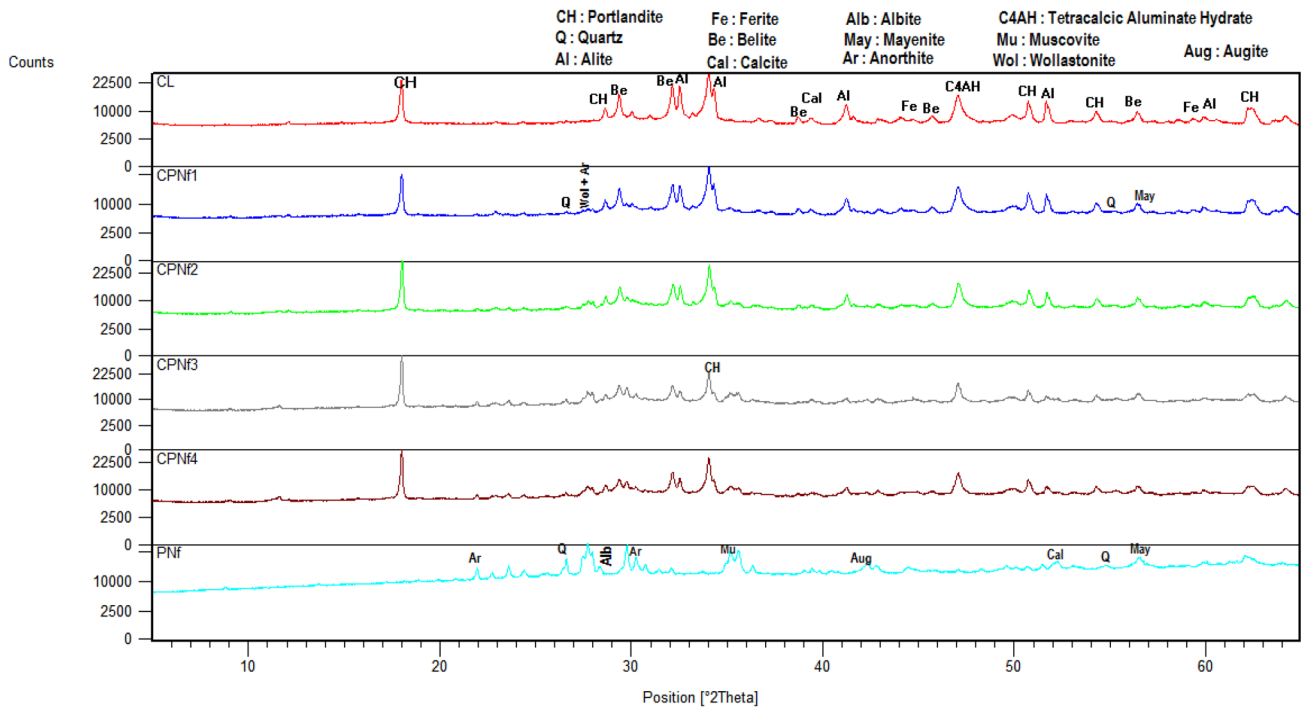
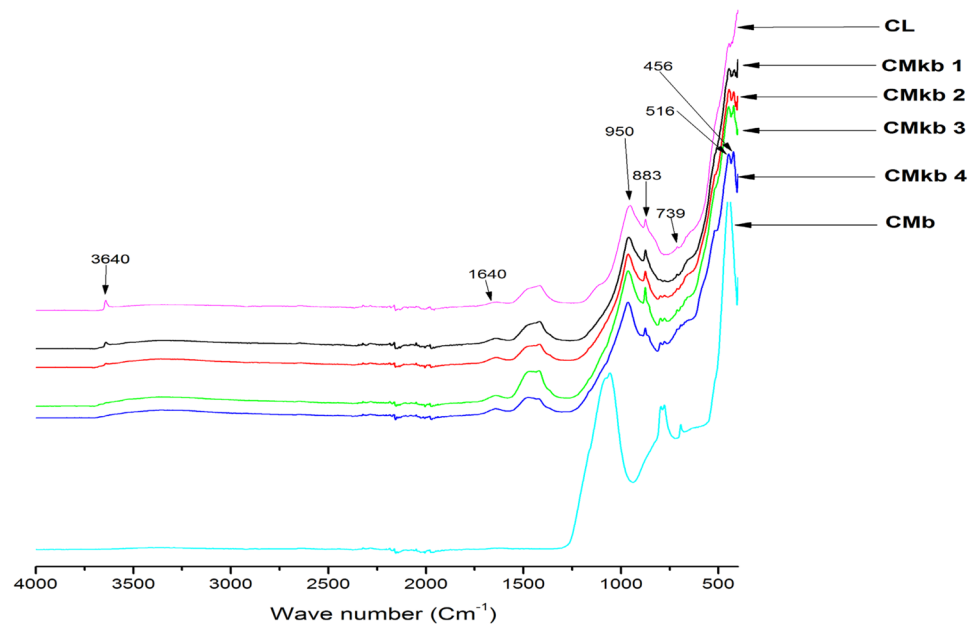
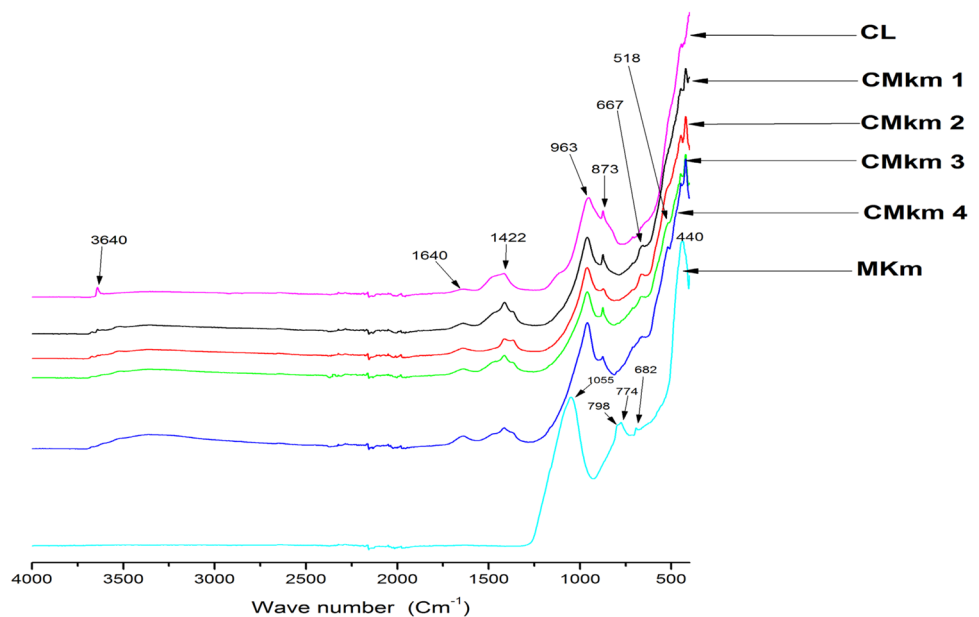


Fig. 8 X-ray diffractogram patterns of clinker and CPNf cements

The effect of calcined clay and volcanic scoria of western region of Cameroon as SCMs can also be seen on the physical and mechanical properties of the products obtained.

Figure 12 shows that the CMkm and CMkb cements have a W/C ratio, which increases as a function of the level of calcined clay while this ratio seems stable for the CPNf.

Fig. 9 FT IR patterns of clinker and CMkb cements**Fig. 10** FT IR patterns of clinker and CMkm cements

This is due to the presence in calcined clay, of very fine clay minerals (illite and hematite), which have a high absorbance due to their sheet structure.

Table 3 gives the initial and final setting time of the various cements formulated. Generally, it shows that the variation of this parameter with the increase of the pozzolan content in the cement is negligible (a few minutes). However, it would be interesting to note that the cements containing calcined clay have a shorter setting time (on average 95 min for the initial setting time and 145 min for the final setting time) than that of cements containing volcanic scoria from Foubot (on average 110 min for the initial setting time

and 180 min for the final of setting time). With regards to the setting time of the control mixture, the calcined clay and volcanic scoria from western Cameroon act as setting retarders, with PNF having a greater retarding effect than MKm and MKb.

Figure 13 shows that calcined clays and volcanic scoria from western Cameroon induce a decrease in the compressive strength of ordinary Portland clinker. Also, it shows that for all formulations tested, the compressive strength decreases as the SCM content increases. The control mixture (OPC + 0% SCM) has the following compressive strengths 45.16 MPa at 7 days, 54.12 MPa at 28 days and 60.04 MPa

Fig. 11 FT-IR patterns of clinker and CPNf cements

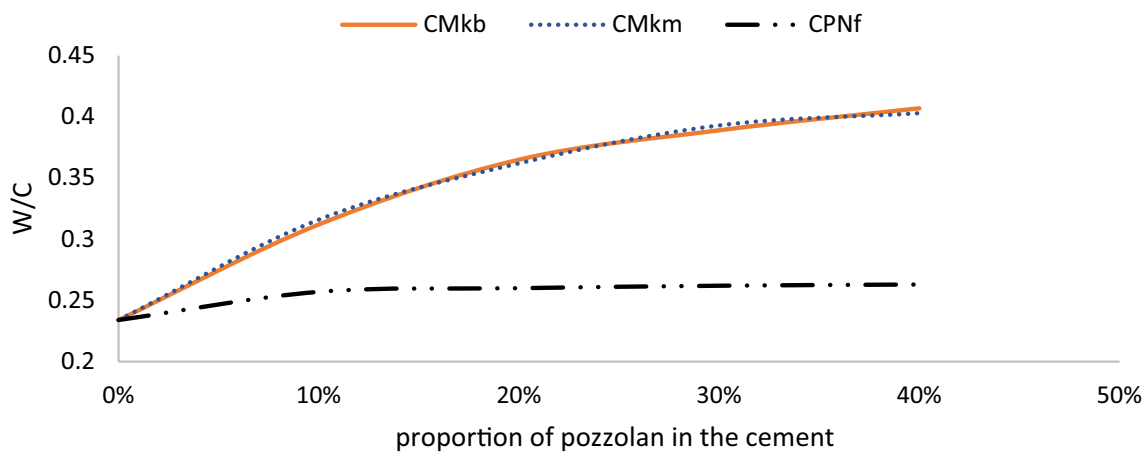
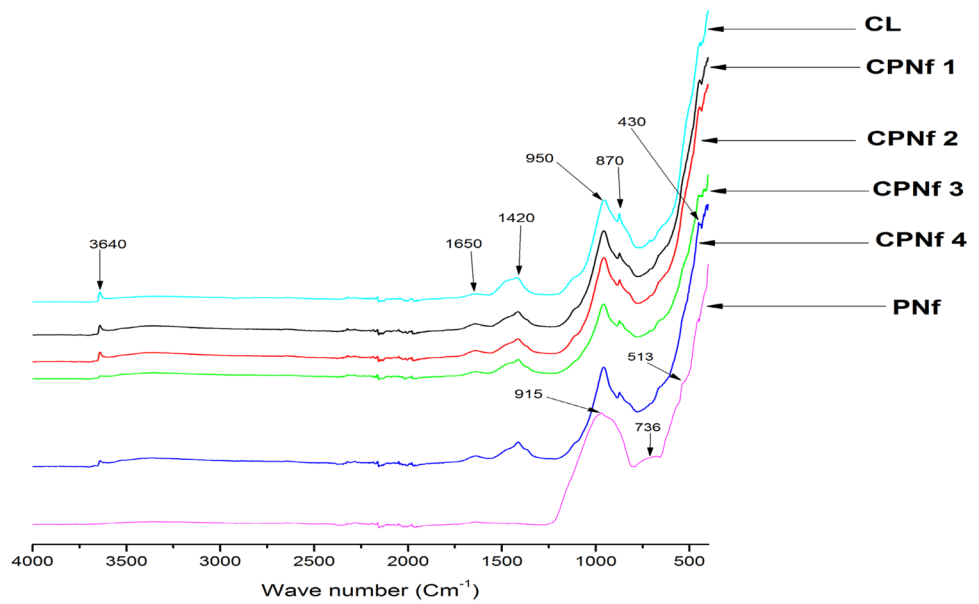


Fig. 12 Variation of the W/C ratio depending on the amount of calcined clay and volcanic scoria

Table 3 Initial and final setting time of the different formulated cement

Pozzolan content in cements (%)	Initial setting time (minutes)				Final setting time (minutes)			
	CL	CMkb	CMkm	CPNf	CL	CMkb	CMkm	CPNf
0	62	/	/	/	108	/	/	/
10	/	81	89	94	/	133	138	152
20	/	96	97	110	/	146	141	182
30	/	104	98	105	/	150	146	180
40	/	100	99	125	/	152	144	188

at 56 days. At 7 and 28 days of curing, CPNf cements have very low strength compared to CMkb, CMkm and control mixture cements. Their strength vary around 41–43 MPa for CPNf1, 28–33 MPa for CPNf2, 22–26 MPa for CPNf3 and 20–25 MPa for CPNf4. This corresponds respectively to a reduction in the 28-day compressive strength of the control

mixture of 20, 36, 50 and 53%. At 56 days, these cements have compressive strengths approximately equal to those of CMkb and CMkm cements, i.e. 43, 42, 38 and 36 MPa respectively for CPNf1, CPNf2, CPNf3 and CPNf4. These values correspond to the reduction in compressive strength of the control mixture at this age of 26, 28, 35 and 39%

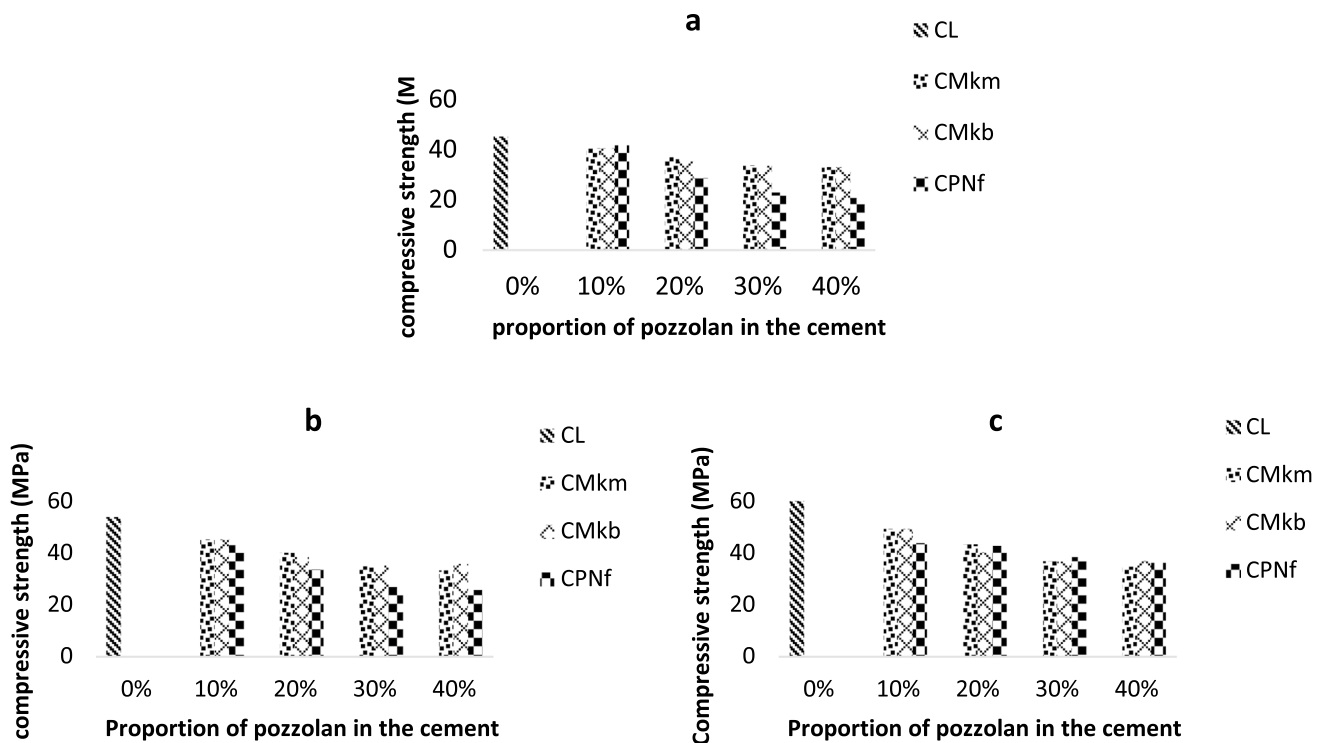


Fig. 13 Compressive strength of formulated cements **a** after 7 days; **b** after 28 days, and **c** after 56 days

respectively. The calcined clays of Mayouom and Balengou seem to have similar effects in reaction with OPC. The average 7-day compressive strengths of CMkm and CMkb are 40.45, 36.05, 33.55 and 32.90 MPa respectively for 10, 20, 30 and 40% substitution. They correspond to a reduction of 10–27% of the compressive strength of the control mixture at the same age. At 28 days, these strengths are of the order of 45.4 MPa for CMkm1 and CMkb1, 35.1 MPa for CMkm3 and CMkb3, 38.5 MPa for CMkb2, 40.2 MPa for CMkm2, 33 MPa for CMkm4 and 35.9 MPa for CMkb4. They correspond to a reduction of 15 to 38% in the compressive strength of the control mixture at 28 days. At 56 days, the compressive strength obtained are 49.6 MPa for CMkm1 and CMkb1, 36.9 MPa for CMkm3 and CMkb3, 43.5 and 40 MPa respectively for CMkm2 and CMkb2, 34.8 and 37 MPa respectively for CMkm4 and CMkb4. These correspond to a reduction of 17–42% in the compressive strength of the control mixture at 56 days. This evolution of the compressive strengths confirms the observations of [16] and [25]. According to these authors, this decrease in compressive strength would be related to the slow hydration process between pozzolan and cement, as well as to the fineness of the particles. [25] show that the substitution of 20% of white Portland cement by metakaolin induces a reduction in compressive strength of about 17% at 28 days. However, the presence of and important crystalline mineral phase in

the Mkm, Mkb and Pnf, can also contribute to the reduction of the compressive strengths, since the latter, inert during the hydration process, leads to an increase in the pore space of the material at the young age. These pores will be subsequently reduced by the production of additional C–S–H in the long term with an increase in the compressive strength. The difference in compressive strength observed between cements containing calcined clays and those containing volcanic scoria may also be related to their pozzolanic reactivity but also to the fineness of the particles of the pozzolans added. At young age, the calcined clays react more quickly with CH and the C–S–H produced, in combination with the clay particles (very fine, $\leq 2 \mu\text{m}$) reduce the voids of the material, with the effect of limiting the reduction in compressive strength compared to that of the control specimens. Unlike volcanic scoria, which has a slow pozzolanic reaction (see Figs. 5 and 8 above) with the absence of very fine particles that can contribute to the reduction of the pore space in the material.

The compressive strength of cement obtained in this study, especially at 28 days, are low compared to those of CEM II/A-P 42.5R cements used in Cameroon and studied by [32]. These cements studied by [32] contain 80–94% clinker, 6–20% volcanic scoria and 0–5% secondary components. Furthermore, according to the recommendations of EN 196-1 reported by [32], only CMkm1, CMkb1 and

CPNf1 conform to Portland cement CEM II/A-P 42.5R on the basis of their strength which are between 42.5 and 62.5 MPa. The other formulations, with the exception of CPNf3 and CPNf4, are all CEM II/A-P 32.5R because their 28-day compressive strength are between 32.5 and 52.5 MPa.

The study of the f_{c28}/f_{c56} ratio (f_{cj} = compressive strength at j days of cure) (Table 4) shows that at 28 days, CMkm and CMkb cements (from 10 to 40% of calcined clay), achieve compressive strength greater than 91,5% of those obtained at 56 days as recommended by the [42], unlike CPNf dosed between 20 and 40%, the strengths of which at 28 days are less than 80% of those obtained at 56 days. Indeed, according to [42], Eq. (8) give the compressive strength of concrete between 28 and 60 days.

Table 4 Values of the ratio between the compressive strength at 28 and 56 days (f_{c28}/f_{c56})

Pozzolan content in cements	CL	CMkm	CMkb	CPNf
0%	90	/	/	/
10%	/	92	96	98
20%	/	92	95	79
30%	/	95	95	70
40%	/	96	95	71

$$f_{cj} = \frac{j \cdot f_{c28}}{4.76 + 0.83j} \tag{8}$$

where j is age of concrete (number of day). So, if $j=56$ days, Eq. (8) give $f_{c28}/f_{c56} = 91.5\%$.

This shows that calcined clay allow the maximum compressive strength of cements to be reached more quickly, even with more than 20% substitution, unlike Foubot's volcanic scoria, whose the presence in cements leads to slow growth in compressive strength. This difference can be attributed as the direct consequence of the low chemical reactivity between Foubot's volcanic scoria and OPC, unlike calcined clay from Mayouom and Balengou, which in the clinker, causes the production of additional C–S–H responsible for strength. All of the above places the calcined clay from Mayouom and Balengou as better SCM than the Foubot's volcanic scoria, especially with more than 10% substitution.

Figure 14 shows results of water absorption. The results increases with an increase in the level of pozzolan in the cement, and decreases, for each prototype, with time. At 56 days, water absorption decreases ($WA \leq 8\%$) by more than half compared to that obtained between 7 and 28 days ($10\% \leq WA \leq 20\%$) for each prototype. The difference in water absorption observed between the CPNf samples and the CMkb and CMkm samples at early age may be related to the grainy texture of the volcanic scoria powder, which leads to a high porosity of the CPNf samples compared to the CMkb and CMkm samples, whose metakaolin included,

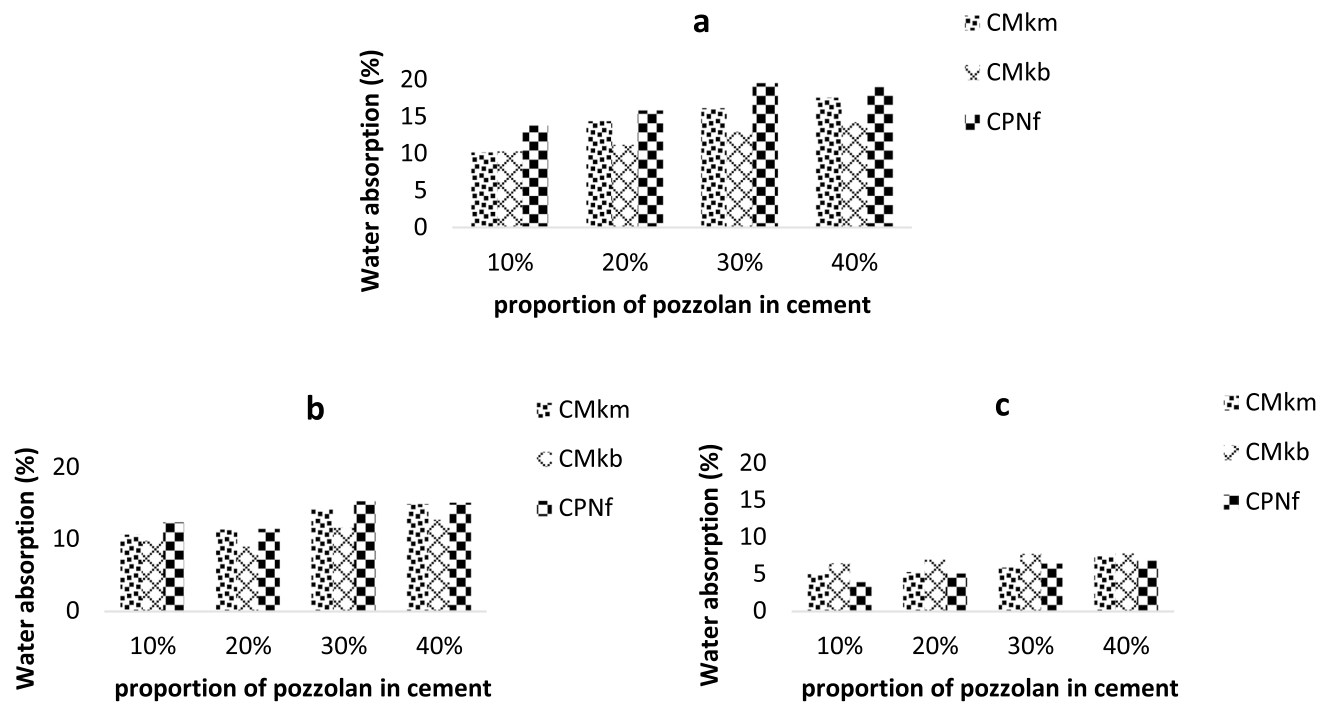


Fig. 14 Water absorption of formulated cements **a** after 7 days; **b** after 28 days, and **c** after 56 days

have a clayey texture. At this age, porosity seems to be the determining factor for water absorption as the reaction between pozzolan and OPC, which give rise to amorphous compounds (C–S–H) that reduce pores and increase strength, are still ongoing. However, at 56 days, after the reactions between the pozzolan powder and the OPC are substantially complete, the development and curing of the C-S-Hs reduces the pore space considerably. This can lead to the fact that water absorption becomes more related to the presence or absence of highly absorbent minerals such as clay minerals in the specimens. Thus, it can be observed that CMkb specimens have a higher percentage of water absorption compared to CPNf.

4 Conclusion

In this study, the purpose was to investigate on physical, chemical and mechanical properties of calcined clays and volcanic scoria from western region of Cameroon as SCM. At the end, following conclusions were made:

- The presence of calcined clay leads to the consumption of portlandite produced by hydration of the cements formed. This leads to the formation of additional C–S–H, unlike the case of cement containing Foubot's volcanic scoria, which visibly react less with portlandite.
- The increase in the level of calcined clay in the Portland clinker leads to an increase in its water-to-cement ratio, while this value is almost invariable with the increase in the level of Foubot's volcanic scoria
- The cements containing 20 to 40% of calcined clay have a shorter setting time than that of cements containing 20 to 40% of Foubot's volcanic scoria. This volcanic scoria and calcined clays from western Cameroon act as setting retarders
- volcanic scoria and calcined clays from western Cameroon shows a decrease in the compressive strength of ordinary Portland clinker.
- CMkm1, CMkb1 and CPNf1 conform to Portland cement CEM II/A-P 42.5R on the basis of their strength which are between 42.5 and 62.5 MPa. The other formulations, with the exception of CPNf3 and CPNf4, are all CEM II/A-P 32.5R because their 28-day compressive strengths are between 32.5 and 52.5 MPa.
- Calcined clay of Mayouom and Balengou allow the maximum compressive strengths of cements to be reached more quickly, even with more than 20% substitution, unlike Foubot's volcanic scoria, whose presence in cements leads to slow growth in compressive strength
- Calcined clays are more viable as SCM in the western region of Cameroon than the volcanic scoria.

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Declarations

Conflict of interests The authors have no relevant financial or non-financial interests to disclose.

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