

# Valorization of Pozzolans as Partial Additive of Portland Cement: A Case of Pozzolans from the Localities of Foubot, Penja and Tombel (Cameroon)

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## Abstract

The objective of this study is to find alternative materials that can be used as an addition in cement in order to produce ecological and economical cement. Three pozzolans coming from different volcanic regions of Cameroon (Penja, Tombel and Foubot) were sampling. Mechanical compressions on  $40 \times 40 \times 160 \text{ mm}^3$  mortar specimens were made with partial replacements of 2%, 4%, 6% and 8% of the pozzolans in Portland cement and physical analyzes on the mortar powders were carried out. The values of the activity indices of different pozzolans obtained are in the normative range. The compressive strength of mortars decreases at all ages with the proportion of cement substitution. The compressive strength values up to 40 Mpa are obtained for a substitution of 6% for the pozzolans from Penja, Tombel and 8% for the pozzolan from Foubot. Pozzolan from Foubot which contains the highest percentage of  $\text{SiO}_2$  offers a maximum substitution rate and therefore optimally reduces the production costs of Portland cement. Physical tests show that specific surfaces increase with an additions of pozzolans from Tombel and Penja.

## Keywords

Pozzolan, Mortars, Compressive Strength, Tensile Strength

## 1. Introduction

Concrete is a mixture of material made up of aggregates (fine and coarse), water,

cement and additives. Its mechanical performance, fire resistance and competitive cost are properties that make it one of the most widely used building materials in the world [1].

The cement industry is involving in various strategies to limit, mitigate and minimize the production impacts on the ecosystem. In terms of strategy, we can note, among other things, the optimization of production processes, the modernization of cement kilns and the replacement of traditional fossil fuels used for the benefit of renewable energies and industrial waste. The implementation of these solutions, among others, has allowed the cement industry to reduce by 20% of CO<sub>2</sub> emissions per ton of cement for the period 1990-2000 [2].

Another strategy would be to find scientific solutions to limit the CO<sub>2</sub> emissions generated by the clinker manufacturing process. Materials with chemical and mineral compositions comparable to those of clinker seem to occupy a prominent place. They are grouped under the name pozzolanic materials [3] and used as partial substitutes for clinker. They are of natural origin or industrial waste [4]. In the literature, the most commonly used pouzzonlanic products are silico-aluminous or sulpho-calcic fly ash, silica fumes, high-furnace slags, sulfoalumin, metakaolin, sugar cane, etc. [5]. This substitution allows the realization of many cement matrixes and thus diversifies the performance, quality and use of the finished product that is cement. The work done by Gumma *et al.* [6] shows that the use of natural pozzolana as a partial substitution makes it possible to increase by 20% of the compressive strength of the mortar for a substitution of 20% by the weight of cement. Similarly, Mbessa *et al.* [7] show that natural pozzolana powder can effectively substitute up to 20% of cement without reducing the strength class of this cement. Volcanic scoria deposits are abundant in Cameroon. Cameroon has been affected by a gigantictectonic accident linking the Sao Tome and will continue until the Tibesti [8]. This accident is observed by the alignment of forty massifs over a distance of more than 500 km, from the Atlantic Ocean to Lake Chad which is called the "Cameroon Volcanic Line" (CVL). The CVL is a suite of volcanic and sub volcanic devices, that are aligned in the direction North 30° East. 1600 km long, it is dotted with volcanic massifs of the Southwest to Northeast. It comprises Gulf of Guinea islands, mostly volcanic: Bioko Pagalu, Sao Tome, Principe and also some seamounts; the region of West Cameroon, with alternating mountains: Mount Cameroon (Altitude: 4100 m), the Manengouba Mountains (shield volcano of 20 km in diameter, with no known historic activity presents some Strombolian cones Bamboutou, Mbam and Oku and grabens (Kumba, Tombel, Mamfe, Mbos and Ndop) and end the Tikar lowland (Foumban in Banyo) [8].

These materials are in general very little used as an addition for the manufacture of composite Portland cement, the reinforcement of certain unpaved roads or as an aggregate for the formulation of concretes. Volcanic slags or natural pozzolans are fragments of low density vesicular magma and are projected during volcanic explosions [9]. The ability to use these materials in their natural state can be an important economic asset for countries with abundance of those

materials. Many works have investigated and characterized some pozzolans found in Cameroon and their applications in civil engineering [8]-[23].

In 2008 Demirdag *et al.* [13] investigated the control lightweight concrete (CLC) mixtures containing volcanic slag aggregates (VSA) with only normal portland cement (NPC) and finally with fly ash lightweight concrete (FALC) mixture containing 20% of FA as a replacement of the cement by volume.

Their research showed that, masonry units having desired properties can be produced by using fine and coarse VSA lightweight aggregate in the mixture with 10% cement by volume.

In 2009 Kaid *et al.* [14] studied the application of a performance-based approach on the durability of concrete made with an Algerian natural pozzolan. The evaluation of the durability of concrete was based on the comparison of durability indicators with a reference concrete usually found in Algeria. The results of specific indicators for corrosion and acid attacks showed that increasing the pozzolan content led to higher resistance of the concrete. Thus, it is possible to improve the durability of typical concretes currently made in Algeria by using local materials.

In 2011 Siddique [15] analysed the comprehensive details of the physical, chemical properties of volcanic ash, and its micro-structure and hydration products. It also covers effect of volcanic ash on consistency, setting times, workability, compressive strength, electrical resistivity of cement paste and mortar.

In 2013 Tchakouté *et al.* [16] characterized two types of volcanic ash (chemical and mineralogical compositions, amorphous phase composition, particle size distribution and specific surface area) and then used as raw materials for the synthesis of geopolymer cements cured at ambient temperature ( $24^{\circ}\text{C} \pm 3^{\circ}\text{C}$ ). The volcanic ash sample with large  $(\text{Al}_2\text{O}_3 + \text{SiO}_2)\%$  wt of amorphous phase, high specific surface area ( $15.7 \text{ m}^2/\text{g}$ ) and synthesized products with  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  molar ratios between 1.04 and 1.31 led to more effective geopolymers: setting time was between 490 and 180 min and 28-day compressive strength between 23 and 50 MPa at ambient curing temperature ( $24^{\circ}\text{C} \pm 3^{\circ}\text{C}$ ).

In 2014 Kemal *et al.* [17] compared the effects of Portland cement replacement on the strength and durability of self-consolidating concretes (SSC). The two replacement materials used are high-volume natural pozzolan (HVNP), a Saudi Arabian aluminum-silica rich basaltic glass and high-volume Class-F fly ash (HVFAF), from Jim Bridger Power Plant, Wyoming, US. The HVNP and HVFAF concrete mixes showed strength and durability results comparable to those of the reference concretes; identifying that both can effectively be used to produce low-cost and environmental friendly SCC.

In 2015 Kilic *et al.* [18] evaluated the suitability of finely ground ( $-20 \mu\text{m}$ ) and/or heated (at  $1000^{\circ}\text{C}$ ) volcanic pumice powder to be used as a supplementary cementitious material. The results from their study showed that the heat treatment significantly affected the pozzolanic activity of VP, and use of heated-ground pumice as a supplementary cementitious material increased the strength of mortar

up to 7% in 90 days as well as 7- and, 28-day strengths.

In 2016 Djobo *et al.* [19] evaluated the mechanical properties and durability of volcanic ash based geopolymer mortars synthesized at 27°C and 80°C. Their results showed that the pore structure and permeability are the key factors affecting the durability of volcanic ash based geopolymer mortars.

In 2017 Zhang *et al.* [20] manufactured the fired hollow clay bricks (FHCBs) by firing a type of highly expansive soils, the black cotton soil (BCS), and natural volcanic ashes (VA), which were both collected from Kenya. This research provides a strategy in making use of vast resources BCS in Kenya obtained from municipal constructions.

In 2017 Djobo *et al.* [21] investigated the role of chemical composition and mineral contents of volcanic ash on their reactivity during geopolymerization reaction and, consequently, mechanical properties.

Their works showed that there are still many works such as durability tests (carbonation, freeze-thaw, resistance, etc.), life cycle analysis, etc. that need to be done in order to satisfy both suitability and sustainability criteria for a large-scale or industrial application.

In 2018 Kupwade-Patil *et al.* [22] studied the effect on Embodied Energy (EE) of concrete when Ordinary Portland Cement (OPC) is partially substituted with natural Pozzolanic Volcanic Ash (VA) at the material and the building scale. The work aims to demonstrate potential improvements to the EE of buildings by comparing the EE of the cement mix with VA replacement to that of baseline case of traditional concrete. The demonstrated reduction in EE values were calculated when natural supplementary cementitious materials (SCM) such as volcanic ash are used as a partial replacement to OPC, and it can be adapted to design and build energy-efficient systems tailored for structural and non-structural applications.

Recently in 2018 Lemougna *et al.* [23] summarized the main interesting research outcomes on volcanic ashes in the fields of cements and concretes, geopolymers, ceramics, low grade refractory materials, lunar soil stimulants and adsorbents. Factors affecting their suitability for specific applications are screened and possible areas of interest for future research suggested.

However few of them have made a comparative study between the pozzolans of the different regions of Cameroon is done, in order to choose the best pozzolanas additive for producing economical and ecological cement. The objective of this work is to assess the pozzolanic response of volcanic ash from the volcanic areas of Penja, Tombel and Foubot and then compare their contribution in the development of composite cements while contributing to reduce pollution due to cement production.

## 2. Materials and Experimental Methods

### 2.1. Materials

#### 2.1.1. Clinker and Gypsum

Clinker and gypsum used in this paper are coming from DANGOTE Cameroon

cement Factory in accordance with the standard ASTM C150-07 [24].

### 2.1.2. Natural Pouzzolona

The different pozzolans are from volcanic eruptions and they have black color. They are coming from the localities of Foubot (Fpo), Penja (Pjpo) and Tombel (Tpo) all respectively located in the West regions (Mount Mbapit), the Littoral (Mount Koupé), and the Southwest (Mount Cameroon). **Figure 1** shows the pozzolan sampling map.

The different pozzolans were firstly characterized in order to determine their chemical composition and physical properties. The different samples were obtained by a quartering and grinding process in a ball mill for a grinding time of 4 hours followed by a particle size analysis using a 45 microns sieve.

### 2.1.3. Cement

The cement used for this study is ordinary Portland cement type 42.5 R of the company Dangoté Cameroon in accordance with the standard ASTM C150-07 [24]. It consists only of clinker (95%) and gypsum (5%).

### 2.1.4. Sand

The sand used is standardized sand. It complies with ASTM C-128 [25].

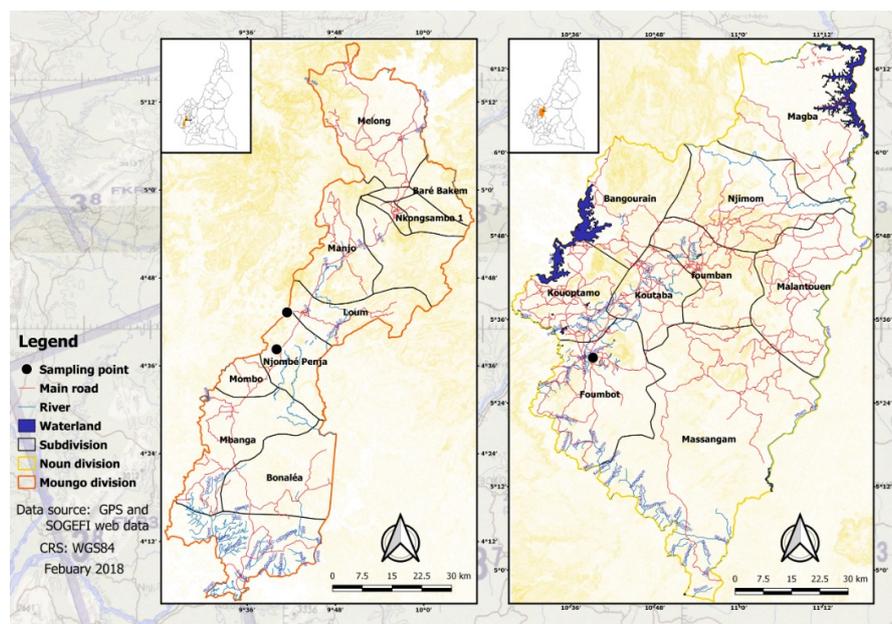
### 2.1.5. Water

The water used comes from the analysis laboratory. It is generally used for making concrete.

## 2.2. Methods

### 2.2.1 Preparation of Samples

Volcanic ash from Foubot, Tombel and Penja was used as a partial substitute



**Figure 1.** Sampling map of different pozzolans.

for 2%, 4%, 6%, and 8% of clinker by the weight of cement. The cement-sand ratio (C/S) has been kept constant at 1/3 and the water-cement ratio (W/C) at 0.5. In order to determine the compressive and flexural strengths, different mortars were made in accordance with ASTM C618 [26] and stored in a water bath at room temperature of  $20^{\circ}\text{C} \pm 1^{\circ}\text{C}$ . The flexural and compressive strength tests were carried out at 7, 14 and 28 days, according to the EN 196-1 standard [27] for compression testing procedures on cement mortars.

### 2.2.2. Consistency Tests

The consistency test is carried out with the Vicat machine. The test is carried out in an air conditioned room maintained at  $20^{\circ}\text{C} \pm 2^{\circ}\text{C}$  and at a relative humidity of at least 65%. This test was carried out on cement paste according to the European standard EN 196-3 [28].

### 2.2.3. Setting Time Test

The sampling tests are done using the Vicat needle which gives two practical references: the initial setting and final setting time. This test was carried out on cement paste according to the European standard EN 196-3 [28].

### 2.2.4. Mortars

These mortars are made up according to EN 196-1 [27]. Mortar is the mixture of sand and cement composed in a proportion of 1:3 with a W/C ratio = 0.5.

Mortar specimens of  $40 \times 40 \times 160 \text{ mm}^3$  were manufactured and formulated with partial replacements of 2%, 4%, 6% and 8% of pozzolans in portland cement.

### 2.2.5. Mechanics Strengths

The mechanical compression tests were carried out on  $40 \times 40 \times 160 \text{ mm}^3$  mortar specimens. Compressive strength of the cube was measured by compression testing machine (Perrier) having a capacity of 6000 kN at the age of 7, 14 and 28 days. For each mixture three specimens were tested and tests were carried out according to the relevant IS standards.

## 3. Results and Discussions

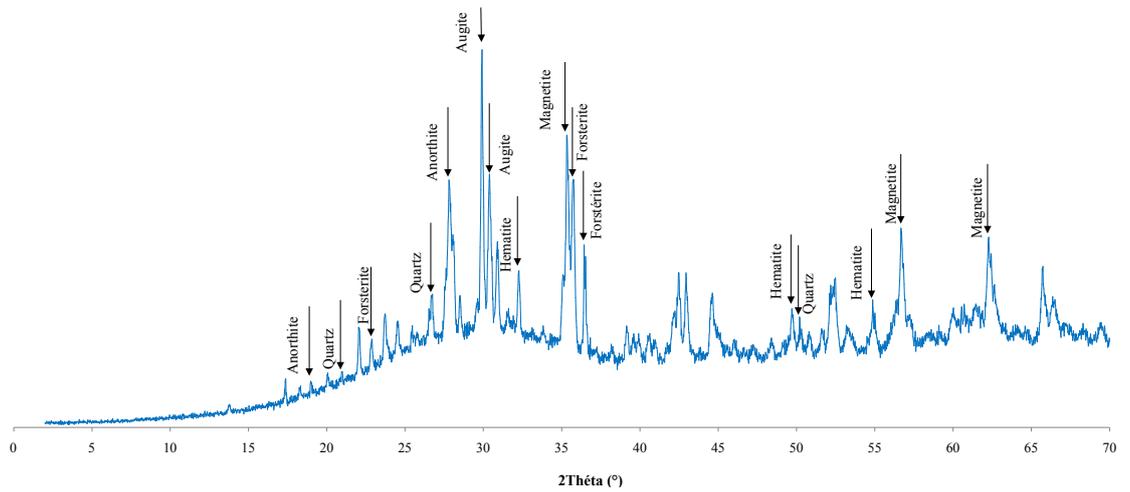
### 3.1. Physical, Chemical and Mineralogical Properties of Materials

The chemical compositions of pozzolans are shown in **Table 1**.

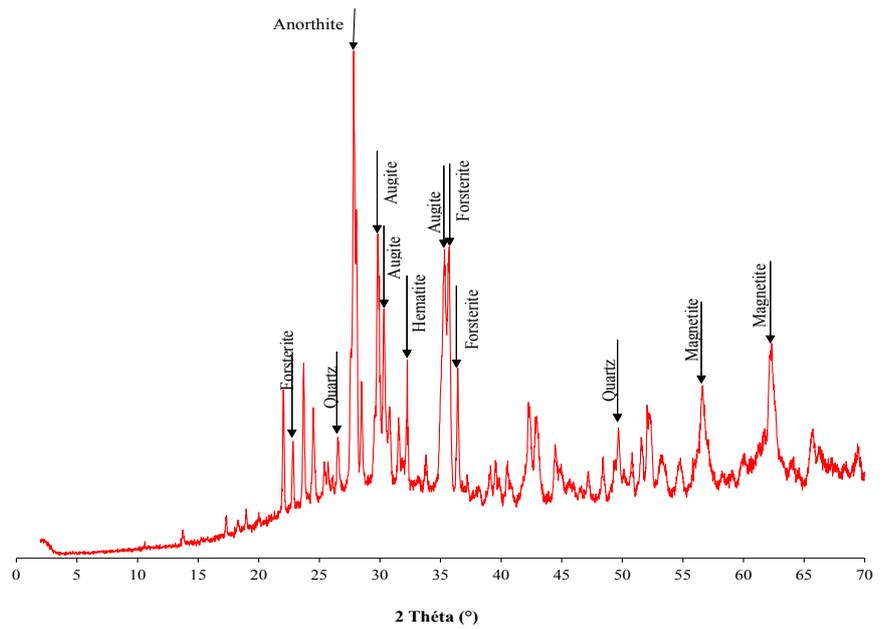
The mineralogical analysis of these different pozzolans shows that pozzolan from Foubot (FPo) have the highest percentage of  $\text{SiO}_2$  followed by pozzolan from Penja and pozzolan from Tombel. It can be noted that for pozzolans from Foubot and Penja,  $\% (\text{Al}_2\text{O}_3 + \text{SiO}_2 + \text{Fe}_2\text{O}_3) > 70\%$  then, these volcanic ashes can be used as pozzolanic materials. All these materials have semicrystalline phases and amorphous phases.

**Figures 2-4** show XRD of different pozzolans.

The XRD analysis of the pozzolans (see **Figure 1** and **Figure 2**) shows that other than the amorphous phase, the crystalline phases presented in the pozzolans



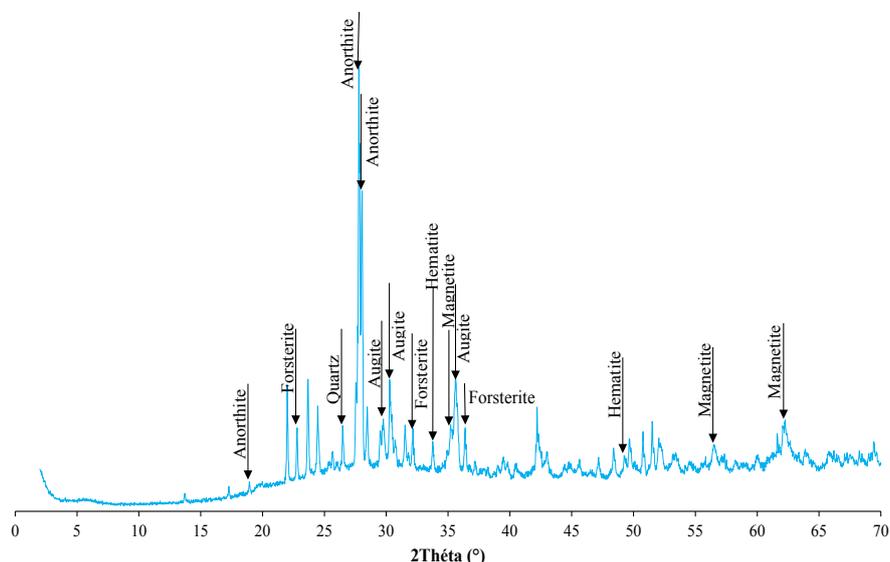
**Figure 2.** XRD of pozzolans from Foubot.



**Figure 3.** XRD of pouzzolans from Penja.

**Table 1.** Chemical composition of pozzolans from Tombel, Foubot and Penja.

Oxyde (%)	TPo	FPo	PjPo
SiO <sub>2</sub>	32.61	55	43
TiO <sub>2</sub>	5.78	1.8	3.3
Al <sub>2</sub> O <sub>3</sub>	12.48	15	15
Fe <sub>2</sub> O <sub>3</sub>	22.65	8.5	14
MgO	6.58	2.9	5.8
CaO	13.58	6.1	11
K <sub>2</sub> O	1.01	3.1	1.7
Na <sub>2</sub> O	1.16	5.3	4.1
SO <sub>3</sub>	0.18	0.9	0.8



**Figure 4.** XRD of pozzolans from Tombel.

were calcite, gypsum, anhydrite, quartz, tridymite, magnetite, hematite, rutile, muscovite, and some evidence of portlandite.

The XRD of pozzolans presents high quantity of amorphous phase (**Figures 2-4**). This is probably due to the nature of such materials that result from rapid cooling of volcanic lavas [9]. The peak identification shows common minerals for all pozzolans as diopside, enstatite, anorthite, albite and quartz.

### 1) Specific Surface

The specific surfaces of pozzolans from Foubot, Penja and Tombel are designated as SSF, SSP, SST, respectively was determined in accordance with ASTM C 618 [12].

The various results obtained are summarized in **Table 2**.

The highest specific surface at 6% to 8% of addition is obtained with pozzolan from Foubot followed by Pozzolan from Penja.

### 2) Activity Index

**Figure 5** shows the evolution of the activity index (Id) obtained at 28 days as a function of the degree of substitution in weight of cement by different pozzolans.

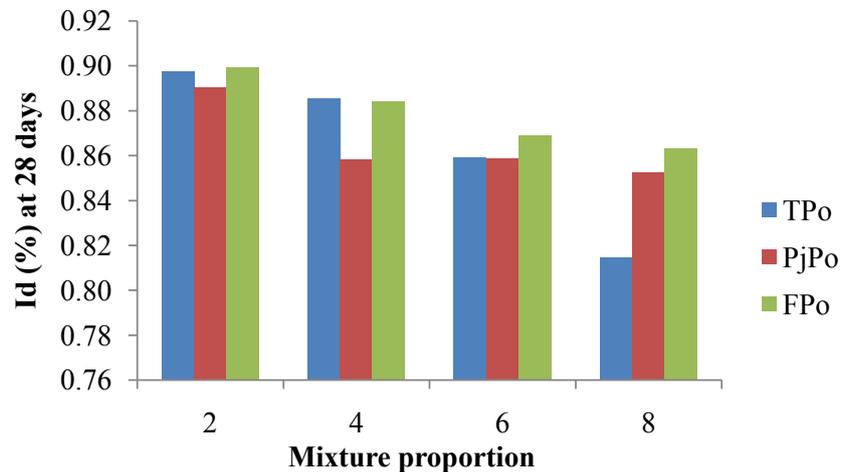
In **Figure 5**, it is noted that at 28 days of age, from 0% to 8% of addition, activity indices of all pozzolan are above 80%. All these values are above the normative limit (67%), we can conclude that all these pozzolans have pozzolanic material. We also observe a decreasing of the activity index when the percentage of addition increases. It goes from 90% for 2% of addition for pozzolans from Foubot and Tombel to 86% for 8% of addition and 81% for 8% of addition of pozzolan from Tombel. Then we can conclude that, the black pozzolan from Foubot could presents better mechanical results, followed by pozzolan from Penja and finally pozzolan from Tombel

## 3.2. Mechanical Results

### 1) Case of Pozzolan from Foubot

**Table 2.** specific surface.

Mixture proportion of pozzolana	0%	2%	4%	6%	8%
SSF (g/cm <sup>2</sup> )	2986	3210	3420	3567	3650
SST (g/cm <sup>2</sup> )	2986	3212	3345	3461	3502
SSP (g/cm <sup>2</sup> )	2986	3230	3335	3542	3632

**Figure 5.** Activity index as function of the percentage of addition.

The consistency tests were carried out on cement pastes formulated from cements manufactured by adding black pozzolan from Foubot according to European and Cameroonian standards. The results of the consistency and setting tests are recorded in **Table 3**.

In **Table 3**, it can be seen that the initial setting time decreases with the percentage of addition of the pozzolan.

The rate of hydration for the initial setting time is fast. However, the final setting time curve increases with the percentage of pozzolan addition. This can be explained by the fact that the rate of hydration decreases the reaction time of pozzolan, which has a long-term effect.

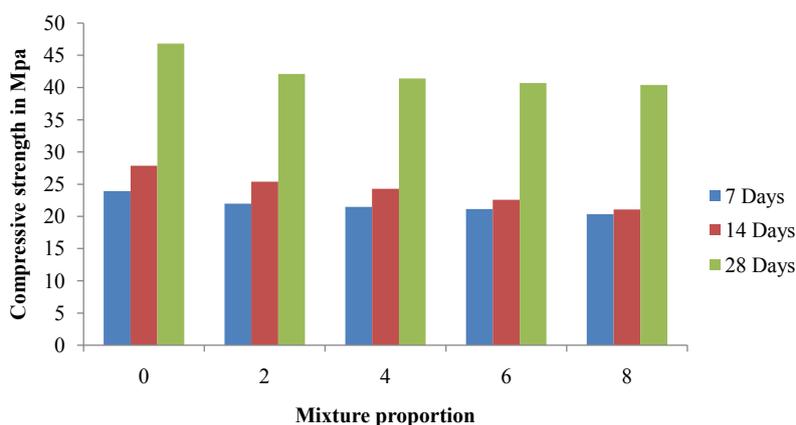
**Figure 6** and **Figure 7** show the evolution of the compressive strength and tensile strength of mortars containing a variable rate of additions of natural pozzolana (2%, 4%, 6% and 8%) at different ages: 7, 14 and 28 days.

**Figure 6** and **Figure 7** show that the compressive strengths and tensile strength decrease with the addition rate of 2%, 4%, 6% and 8% at 7, 14 and 28 days respectively. At 28 days, we see that all mortars formulated with the addition of Foubot black pozzolan have resistances that remain within the standard range of 40 MPa. Therefore the addition to 8% of this pozzolan in the manufacturing of cement can be recommended.

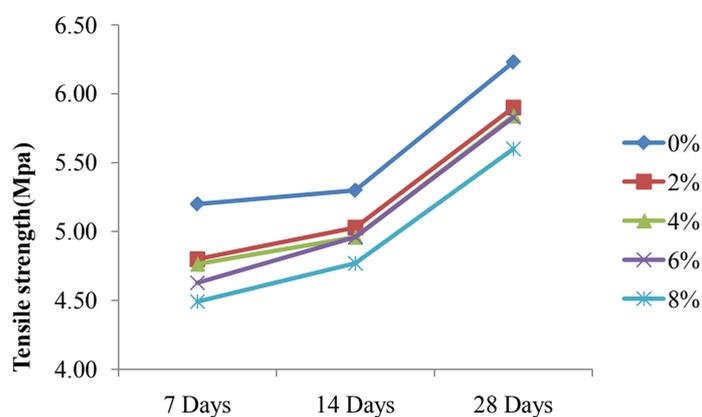
## 2) Case of Black Pozzolan from Penja

The results of the consistency and setting tests are shown in **Table 4**.

In **Table 4**, we observe a decreasing of the setting start time with the rate of addition. This is due to a rapid rate of hydration of the cement paste. We also



**Figure 6.** Compressive strength of mortars as function of percentage of addition: case of Foubot pozolans.



**Figure 7.** Tensile strength of mortars as function of percentage of addition: case of Foubot pozolans.

**Table 3.** Consistency and setting time of black pozzolan from Foubot.

Désignation	% mixture proportion	Consistency (%)	Initial setting time (minutes)	Final setting time (minutes)
CEM II B	0	28	146	349
FPo	2	28	140	352
FPo	4	28	133	394
FPo	6	28	125	388
FPo	8	28	123	386

**Table 4.** Consistency and setting time of black pozzolan from Penja.

Désignation	% mixture percentage	Consistency (%)	Initial setting time	Final setting time
CEM II B	0	28	148	349
PjPo	2	28	142	352
PjPo	4	28	137	394
PjPo	6	28	136	388
PjPo	8	28	129	386

notice an increase of the final setting time for an addition of 0% to 4% of addition, which shows that the rate of hydration is slow for this interval of addition of the black pozzolan from Penja. From 4% to 8% of pozzolan addition, we notice a clear decrease of final setting time, which causes a decrease in the speed of hydration. For the low values of adding black pozzolan from Penja, we observe that it has a delaying effect.

**Figure 8** and **Figure 9** show the compressive and tensile strength of mortars as function of percentage of addition: case of pozzolan from Penja

In **Figure 8** and **Figure 9**, it is noted that the compressive strengths decrease with the addition rate of 2%, 4%, 6% and 8% compared to the control mortar at 7, 14 and 28 days in succession.

At 28 days, we note that the resistance of the mortars with an addition of 8% pozzolan is less than 40 MPa at 28 days. For the additions of 2%, 4% and 6% the resistances obtained are greater than 40 MPa. Therefore an addition from 2% to 6% of this pozzolan in the manufacturing of cement can be recommended.

### 3) Case of Pozzolan from Tombel

The results of the consistency and setting tests are shown in **Table 5** and **Figure 13**.

In **Table 5**, we observe an increasing of the initial setting time with the pozzolan addition rate. This is due to a slow rate of hydration of the cement paste. Moreover, the final setting time decreases with the addition rate of pozzolan, which can be attribute to the low speed of hydration of the cement paste is slow.

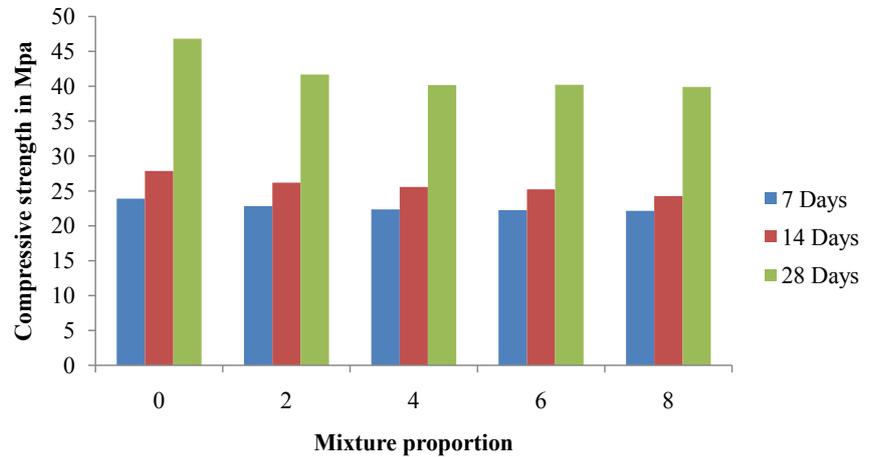
**Figure 10** and **Figure 11** present compressive strength and tensile strength as function of percentage of addition in the case of Tombel pouzzolan.

For all ages of 7, 14 and 28 days, the compressive strength and tensile strength decrease with the rate of addition of pozzolan. At 28 days, it is noted that the resistance of the mortars with addition of 8% pozzolan is lower than the norm which stipulates that the acceptable limit is 40 MPa (compressive strength) at 28 days for a cement to be validated. While additions of 2%, 4% and 6% additions are still in the cement class since their strengths are greater than 40 MPa. According to these results, we can propose an addition of the range of 0 to 6% of the black pozzolan from Tombel for the manufacturing of cement in order to reduce the cost of cement.

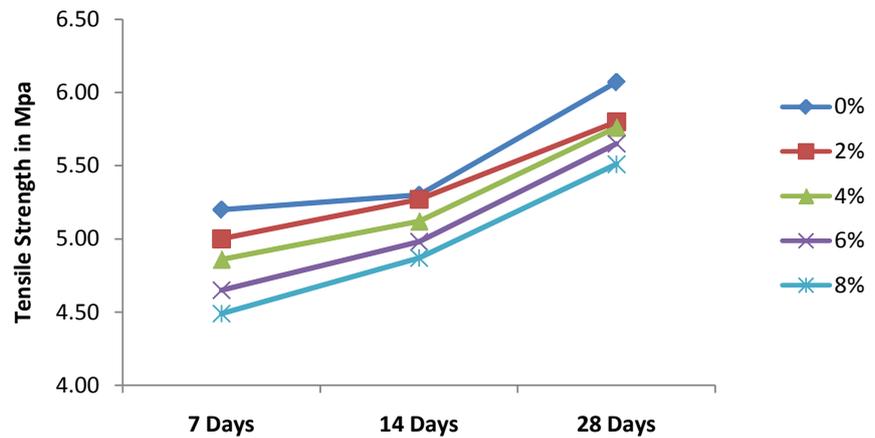
### 4) Comparative Study of Compressive and Tensile Strengths at 28 Days of Age for Different Pozzolans

**Table 5.** Consistency and setting time of black pozzolan from Tombel.

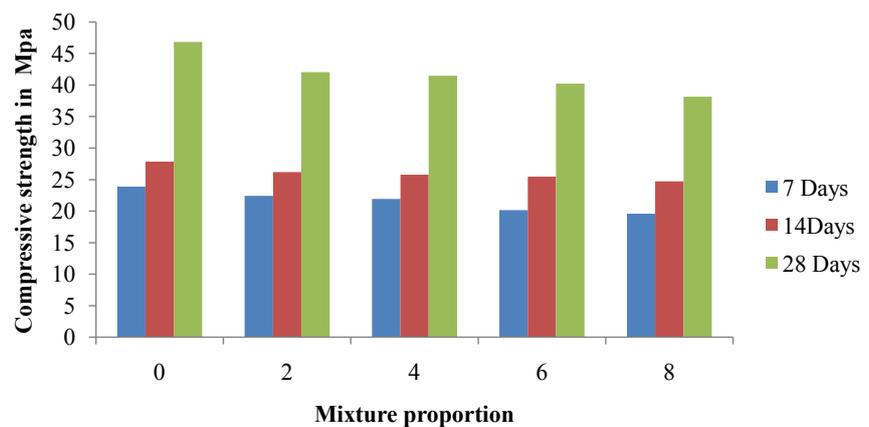
Designation	Mixture proportion	Consistency (%)	Initial setting time	Final setting time
CEM II B	0	28	153	445
TPo	2	28	168	445
TPo	4	28	168	446
TPo	6	28	171	441
TPo	8	28	180	432



**Figure 8.** Compressive strength of mortars as function of percentage of addition: case of pozolans from Penja.

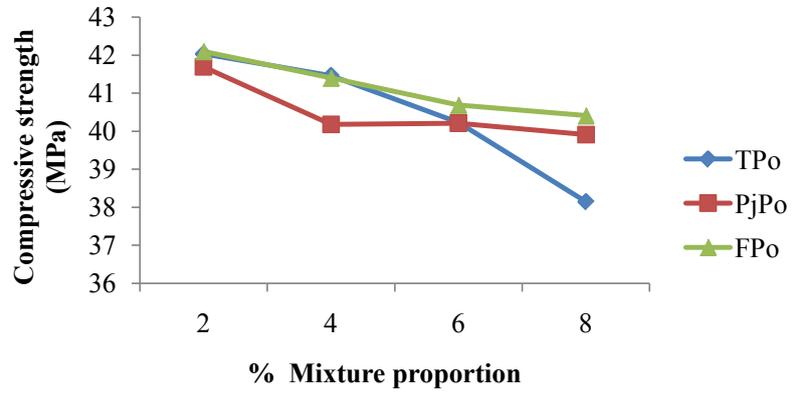


**Figure 9.** Tensile strength of mortars as function of percentage of addition: case of pozolans from Penja.

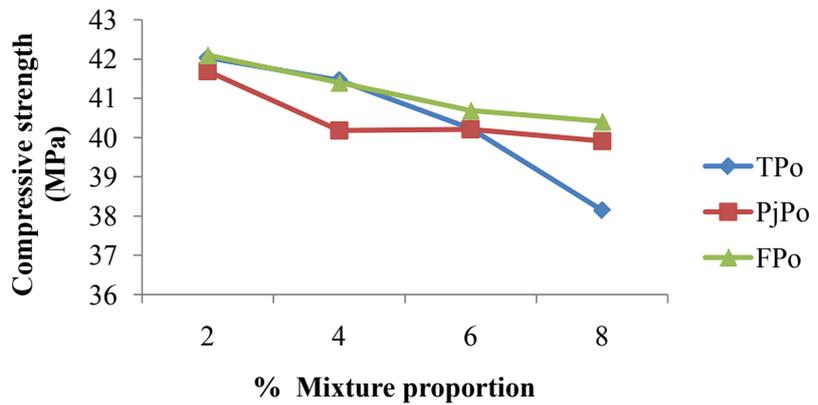


**Figure 10.** Compressive strength of mortars as function of percentage of addition: case of pozolans from Tombel.

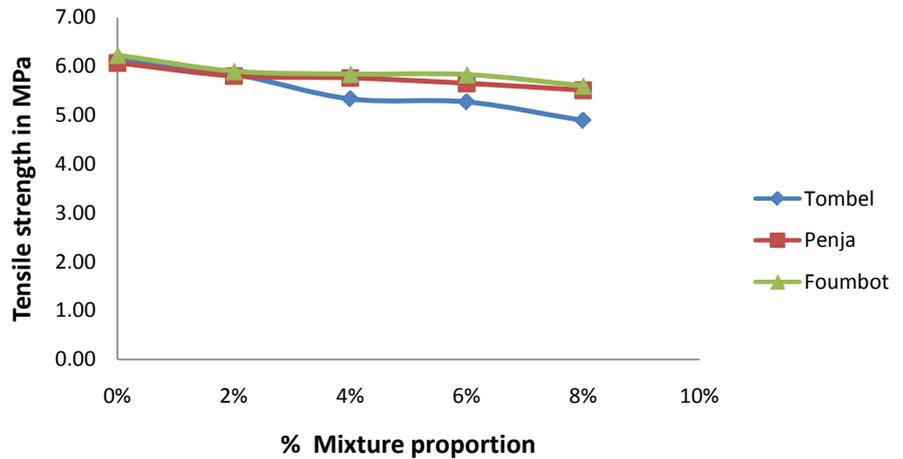
**Figure 12** and **Figure 13** show the results of compressive and tensile strength obtained at 28 days for different pozzolans studied.



**Figure 11.** Tensile strength of mortars as function of percentage of addition: case of pozzolans from Tombel.



**Figure 12.** Compressive strength obtained at 28 days for different pozzolans studied.



**Figure 13.** Tensile strength obtained at 28 days for different pozzolans studied.

For all pozzolans studied the compressive and tensile strength decrease with the rate of addition of the pozzolan. For an addition of 2% to 6% of pozzolans, the compressive strengths of the mortars are greater than 40 MPa. Beyond 6% of addition it is noted that only the resistance of the mortars made from Foubot black pozzolana remains higher than 40 MPa. The black pozzolane from Penja is

slightly lower than 40 MPa and the strength of black pozzolan from Tombel remains below 40 MPa. Then, it is noted that Foubot black pozzolan has better results of mechanical strength. This is due to the fact that it contains a highest percentage of SiO<sub>2</sub> (55%) followed by the Penjapozzolan (44%). In addition, it is noted that the highest specific surface and the highest activity index is obtained with an addition of black pozzolan from Foubot, followed by black pozzolan from Penja and black pozzolan from Tombel.

#### 4. Conclusions

- The activity index shows that all the pozzolans studied present pozzolanic properties and can therefore be used as an addition in the manufacturing of cement.
- The highest specific surface and the highest activity index are obtained with an addition of black pozzolan from Foubot, followed by black pozzolan from Penja and black pozzolan from Tombel.
- Foubot black pozzolan has better results of mechanical strength. This is due to the fact that it contains a highest percentage of SiO<sub>2</sub> (55%) followed by the Penjapozzolan (44%).
- The mechanical strengths of cements decrease with the percentage of pozzolans addition.
- Cement made up with an addition of 2% to 6% of black pozzolan from Penja has strengths greater than 40 MPa at 28 days.
- Cement made up with an addition of 2% to 4% black pozzolan from Tombel has strengths greater than 40 MPa at 28 days.
- The cement manufactured with an addition of 2% to 8% of black pozzolan from Foubot has resistances greater than 40 MPa at 28 days.

#### Confirm

The authors also confirm that in this paper:

- Acknowledgements is not applicable.
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The data used to support the findings of this study are available from the corresponding author upon request.

#### Conflicts of Interest

The authors certify that there's no financial/personal interest or belief that could affect their objectivity and there is no conflict of interest.

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