

Pozzolanic Activity of Old Volcanic Tuffs of Mako Area (Senegal-Oriental, West African Craton): An Economic and Environmental Interest

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How to cite this paper: Ndiaye, M., Diène, M., Diop, M.B. and Ngom, P.M. (2019) Pozzolanic Activity of Old Volcanic Tuffs of Mako Area (Senegal-Oriental, West African Craton): An Economic and Environmental Interest. *International Journal of Geosciences*, 10, 225-237.

<https://doi.org/10.4236/ijg.2019.103014>

Received: January 30, 2019

Accepted: March 12, 2019

Published: March 15, 2019

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Abstract

The volcanic tuffs of Senegal-Oriental in Mako area are produced during a calc-alkaline volcanism which occurs in this region and which is dated from about 2.3 - 1.95 Ga. Despite their altered appearance, the X-Ray diffractions show mineral paragenesis: Quartz-Kaolinite-Illite and an important amorphous phase. On the Ternary Keil-Rankin diagram for the CaO-SiO₂-Al₂O₃, the volcanic tuffs of Mako area are situated between pozzolan and the fly ash. The difference between silica and lime is greater than 34% in these volcanic tuffs. In this study, they have been mixed with Portland cement to obtain pozzolanic cements respectively with 20%, 30%, 35% and 40% of addition of volcanic tuffs. The pozzolanic reactivity is highlighted by the compressive strength increase until 90 days of conservation in water. It supposes that the vitreous phase of the volcanic tuffs reacts with the free CaO (CaOf) of Portland cement to produce new hydrated minerals. This study has a positive economic and environmental impact. Because the time of grinding of pozzolanic cements is reduced. Also, the addition of volcanic tuffs reduces the production of clinker, then the CO₂ emission.

Keywords

Old, Volcanic, Tuffs, Calc-Alkaline, X-Ray Diffractions, Amorphous, Pozzolanic, Cements, Compressive Strength, Economic, Environmental

1. Introduction

Portland cement is the most common type of cement used in construction applications, but it is an expensive binder due to the high cost of production asso-

ciated with the high energy requirements of the manufacturing process itself [1]. Raw materials such as limestone and clay are grinded and heated in a kiln at 1400°C - 1450°C to form predominantly clinker, which is then finely ground together with additives such as gypsum to obtain Portland cement [11] [32] [41]. Also, the heating of the raw material produces important CO₂ emission in the atmosphere. Therefore, to reduce the CO₂ emission and the cost of binder, other cheap inorganic materials with cementitious properties such as natural pozzolans, waste products from industrial plants and silica fume can be used as a partial replacement for Portland cement [2] [11] [12] [13] [14] [20] [22] [23] [24] [26] [37] [39] [41] [44] [45].

The volcanic tuffs of Mako are produced during volcanic eruption dated from about 2.3 - 1.95 Ga [3] [4] [5] [6] [7] [35]. In this paper, the potential use of these volcanic tuffs as a natural raw material in the production of pozzolanic cement is investigated. In Senegal the production of Portland cement is very expensive associated with the important CO₂ emission. To provide all people to access to the cement it is very important to test new raw material. In this study, the physical, chemical and mineralogical characteristics of the volcanic tuffs are first examined, and then the compressive strength of Portland cement is compared with pozzolanic cement to determine the pozzolanic activity of these volcanic tuffs.

2. Geological Context

The volcanic tuffs of Senegal-Oriental in Mako area dating from Birimian (about 2.3 - 1.95 Ga) [3]-[8] [10] [15] [16] [19] [21] [33] [36]. They are described as pyroclastic rocks which are produced during a submarine explosive volcano (**Figure 1**).

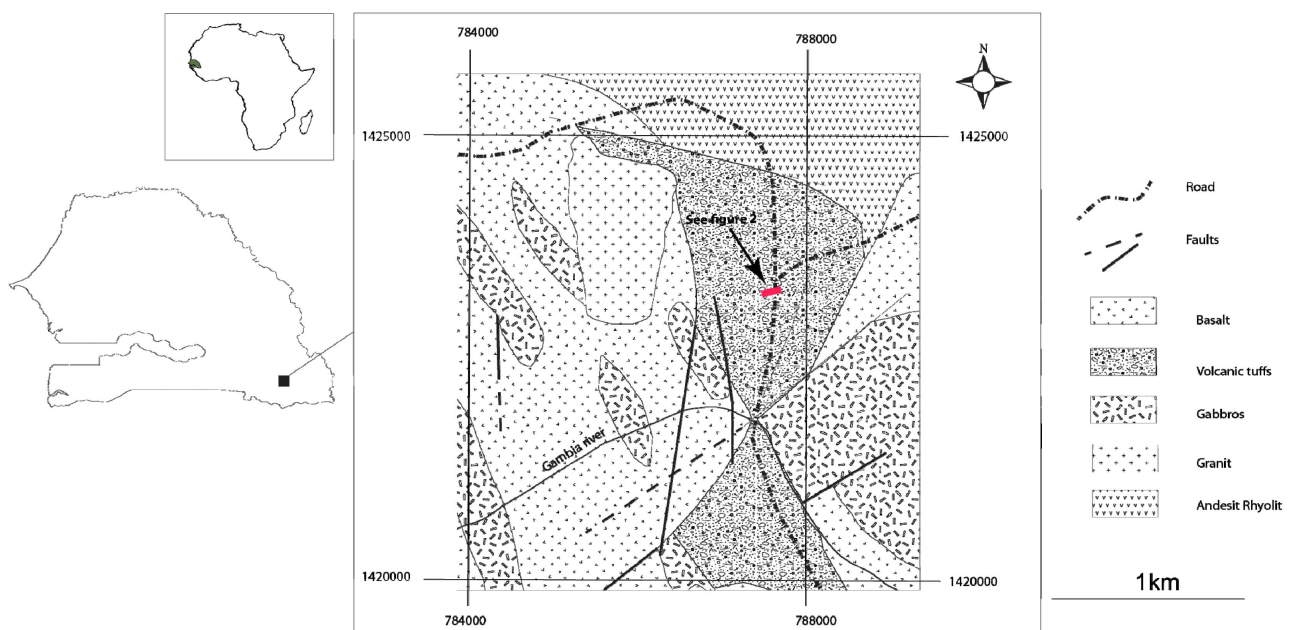


Figure 1. Geological context of the volcanic tuffs. We can see.

A cross section oriented ENE-WSW (**Figure 2**) shows volcanic tuffs of 50m of thick, over bedded by metasediment and lava flow. All these formations are metamorphosed under green schist-facies conditions [3] [4] [5] [6] [8] [15] [36]. The volcanic tuffs are exposed along the road on several kilometres (**Figures 1-3**).

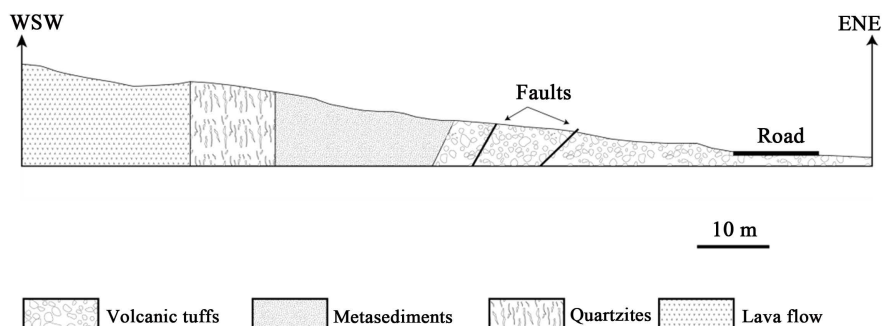


Figure 2. Geological profile on **Figure 1** showing the context of taking place of the volcanic tuffs.

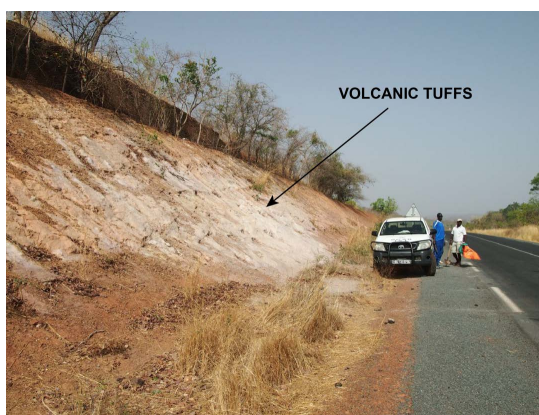


Figure 3. Outcrop of the volcanic tuffs on the side of the road. The volcanic tuffs are stripped to build the road.

3. Material and Method

3.1. Material

Clinker, gypsum and volcanic tuffs are the main components used in this study.

Clinker

Clinker or Portland Cement Clinker obtained by burning calcareous and clayey materials.

Gypsum

Gypsum is added to clinker as a set regulator. It is hydrated calcium sulphate in chemical form and plays a very important role in controlling the rate of hardening of the cement.

Portland cement (PC)

Portland cement obtained by pulverizing gypsum (5%) and clinker (95%) (**Figure 4**).

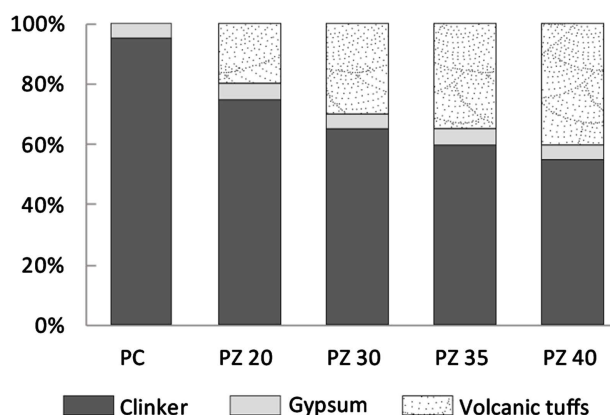


Figure 4. Percentage of constituents of the cements. PC: Portland cement, PZ: Pozzolanic cement.

Volcanic tuffs

Samples of volcanic tuffs are obtained from a deposit located in Mako (**Figure 3**), the Kedougou district of Senegal-Oriental (Senegal). Representative samples amounting to a total of 100 kg were collected from.

Pozzolanic cements (PZ)

Four categories of cements are manufactured according to formulations defined on **Figure 4**.

Cements are obtained grinding clinker, gypsum and volcanic tuffs.

3.2. Method

3.2.1. Chemical Analysis

Chemical analysis is carried out on clinker, gypsum, volcanic tuffs and cements to determine major elements composition. For each element a homogeneous laboratory sample is crushed and analysed according to [34]. The chemical analysis is an alkali fusion followed by a hydrochloric acid attack. Silica is quantified by gravimetry method. Oxides like SiO_2 , Al_2O_3 , CaO , MgO , Fe_2O_3 and Al_2O_3 are quantified by complexometric titration. The loss on ignition (LOI) is determined by calcinations.

3.2.2. Physical Analysis

The volcanic tuffs are analysed with X-ray diffraction to determine minerals and amorphous or vitreous phase. Pozzolanic activity is proportional to the vitreous phase in the cement [13] [30].

The specific surface is measured only on the cements and the slightly crushed volcanic tuffs. The activity of a natural pozzolan, which is essentially determined by the reactive silica content, is also closely controlled by its specific surface area, chemical and mineralogical composition [1] [31] [40] [43].

Mechanical tests are the best method to evaluate the pozzolanic activity of cements. The tests are realized on standardized prismatic mortar bars ($4 * 4 * 16$ cm). The composition of mortar is:

- 1350 g of standardized European sand (CEN EN 196 1),

- 450 g of cement,
- 225 g of water.

The homogeneous mortars are conserved in mould for 24 hours in humid atmosphere.

After that, mortar bars are extract from mould and kept inside water at 20°C.

Tests of compressive strength of mortar bars are realized at 2, 7, 14, 28 and 90 days after conservation inside water.

4. Result and Discuss

4.1. Specific Surface of Volcanic Tuffs

The specific surface of volcanic tuffs is 8895 cm²/g. This shows that the volcanic tuffs are very fine. According to Largent (1975), the potential pozzolanic activity of matter depends on a high specific surface.

4.2. Chemical Composition of Constituents

Insoluble residue (IR) is a non-cementing material which is present in Portland cement. This residue material affects the properties of cement, especially its compressive strength [29]. Insoluble residue is not measured in the gypsum and volcanic tuffs. But in these constituents the proportion of IR is very important.

In the volcanic tuffs the silica content is 61.63% (Table 1) greater than 45%. That gives them a potential pozzolanic activity [30] [38]. So, these natural pozzolans content a high of SiO₂ + Al₂O₃ (78.64%) but a low content of MgO and SO₃, then it can exhibit a high pozzolanic activity [1].

For the CaO, SiO₂ and Al₂O₃ the position of volcanic tuffs of Mako on Ternary Keil-Rankin diagram ([14]; [25]) is between volcanic glass and ashes (Figure 5).

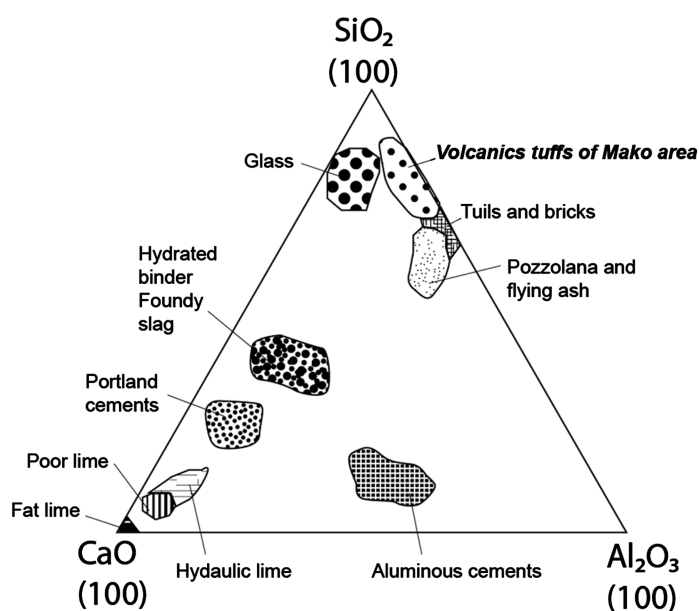


Figure 5. Position of Mako volcanic tuffs on Ternary Keil-Rankin diagram for the CaO-SiO₂-Al₂O₃.

Table 1. Chemical composition of volcanic tuffs and gypsum.

	LOI	SiO ₂	SO ₃	CaO	MgO	Fe ₂ O ₃	Al ₂ O ₃	Total
Volcanic tuffs	5.58	61.63	-	1.23	0.51	11.71	17.01	97.67
Gypsum	25.85	6.08	48.02	15.69	1.31	0.60	0.65	98.2

IR: Insoluble residue. LOI: Loss on ignition.

The difference between the tenors in lime and silica of volcanic tuffs is 67.31%.

In the clinker the percentage of IR is 0.09% (**Table 2**). So, the measurements of free lime and C₃S mineral are respectively 0.3 d 57.74%. This confirms the good quality of the clinker.

Volcanic tuffs are natural rocks of volcanic origin and composed of silica and alumina oxides but almost no lime. Therefore, they cannot develop hydraulic properties in the absence of hydrated lime.

Hydrated lime or material that can release it during its hydration (e.g. Portland cement) is then required to activate the natural pozzolans as a binding material [13].

The activity of a natural pozzolan, which is essentially determined by the reactive silica content, is also closely controlled by its specific surface area, chemical and mineralogical composition [29].

4.3. X-Ray Diffraction of Volcanic Tuffs

The result of X-Ray Diffraction shows the presence of quartz and other weathering minerals like kaolinite, muscovite, montmorillonite, muscovite (**Figure 6**). The quartz is very abundant. The hematite is also present. An important amorphous phase (A) gives hopes a potential pozzolanic activity by the volcanic tuffs. Because the amorphous phase could be potentially reactive with Ca(OH)₂ of cement [13]. So, according to [30], the pozzolanic activity of matter is proportional of the present a morphous phase. Therefore the amorphous phase in these volcanic tuffs could be altered due to these ancient ages.

4.4. Time of Grinding and Fineness of the Cements

The cements are made by referring to the **Figure 4**. Grinding of the cements is executed at the same granulometry (**Figure 7**). That's why the time of grinding of the cements is inversely proportional to the percentage of addition of volcanic tuffs (**Table 3**). With the addition of 40% of volcanic tuff I, this time decreases of 50% comparatively to Portland cement.

4.5. Specific Surface of Cements

For the specific surface, the pozzolanic cements values higher than the one of Portland cements (**Table 4**). This fact shows the degree of fineness of the volcanic tuffs. The specific surface is proportional to the addition of volcanic tuffs.

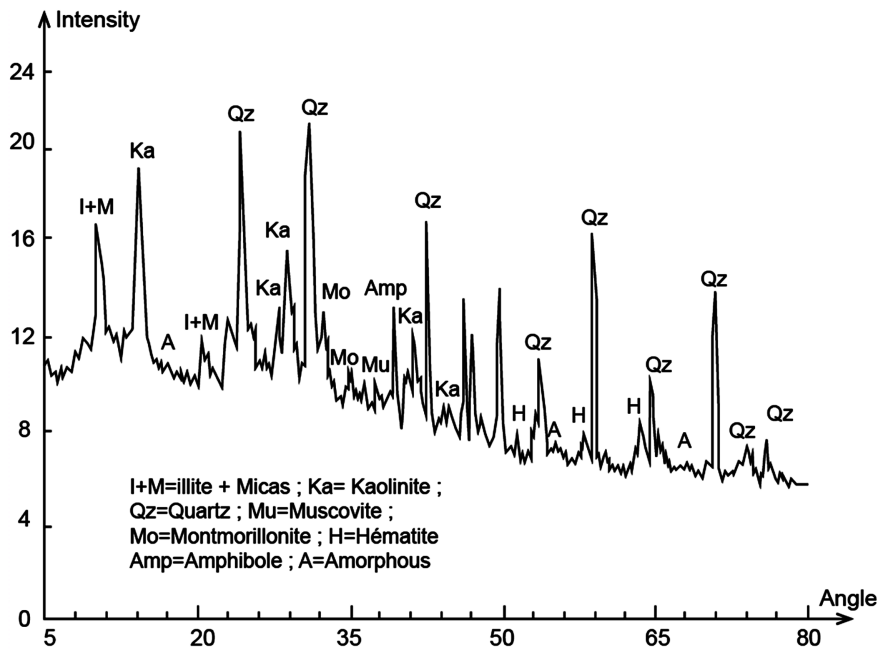


Figure 6. X-ray diagram of volcanic tuff of Mako area.

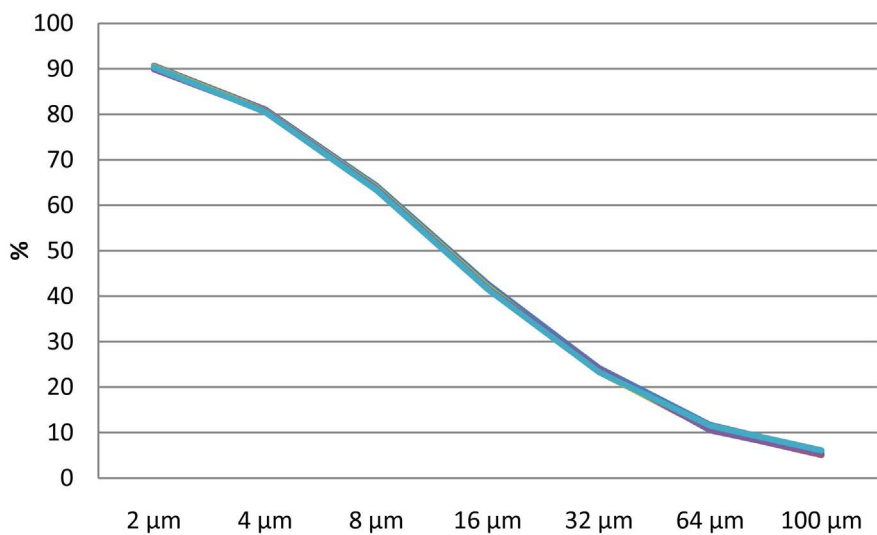


Figure 7. Fineness of cements. Cements are grinded at the same granulometry to avoid the influence of the fineness on compression strength.

Table 2. Chemical composition of the clinker.

	LOI	IR	SiO ₂	SO ₃	CaO	MgO	Fe ₂ O ₃	Al ₂ O ₃	CaOf	C ₃ S	Total
Clinker	0.41	0.09	21.05	1.46	64.65	3.45	3.15	4.55	0.30	57.74	99.32

IR: Insoluble residue, LOI: Loss on ignition, CaOf: free lime.

Table 3. Time of grinding of the cements.

Cements	PC	PZ 20	PZ 30	PZ 35	PZ 40
Time of grinding (min)	60	36	34	32	30

Table 4. Specific surface of cements.

Cements	Specific surface (cm ² /g)
PC	4212
PZ20	5435
PZ30	5472
PZ35	5551
PZ40	6005

4.6. Chemical Composition of Cements

Chemical constituents like SiO₂, Fe₂O₃ and Al₂O₃ increase proportionately with the addition of volcanic tuffs in blended cements (Table 5). But sulphate and loss on ignition contents are respectively lower than 3.5% and 5% required for a blended cement [1].

The measurement of the CaOf and C₃S in the clinker is respectively 0.2% and 47.26%. Then potential reactive silica of volcanic tuffs could associate with CaOf of clinker. These pozzolanic reactions lead to the formation of additional hydrate minerals (C-S-H) with binding properties [2].

4.7. Mechanical Performance of Blended Cements

Mechanical performances at 2, 7, 14, 28 and 90 days age of mortars are illustrated in Table 6 and Figure 8. Generally, the compressive strength of cements increases with time. It is closely controlled by the addition of volcanic tuffs to the PC. We can deduce that the hydration of blended cements continues until 90 days. Which may due to the presence of new hydrated minerals formed by reaction between reactive silica from volcanic tuffs and free lime from clinker.

A consistent reduction in the compressive strength and rate of strength development of mortars is observed as the amount of the volcanic tuffs in the blended cement increased (Table 6 and Figure 8). The compressive strength of all mortars is higher than 16 and 32 N/mm² respectively at 7 and 28 days. Then, in reference on NF EN 197-1 these cements with addition of volcanic tuffs are pozzolanic cement belong to the class CEM IV/BP 32.5.

Silicate minerals including feldspar, mica, hornblende, pyroxene and quartz or olivine present in volcanic rocks can easily undergo alteration to form secondary mineral phases such as clays, zeolites, calcite and various amphiboles [28]. The contribution of these secondary minerals to the pozzolanic activity of the volcanic tuffs is demonstrated by compressive strength growth.

Generally natural pozzolans include increased workability, decreased permeability increased resistance to sulphate attack, improved resistance to thermal cracking and increased ultimate strength and durability of concrete [9] [27] [40].

On that experience the volcanic tuffs are used directly without any pre-treatment. Therefore, it would be interesting to see the enhancing of the pozzolanic activity of these old volcanic tuffs pre-treating by thermal or chemical method. The

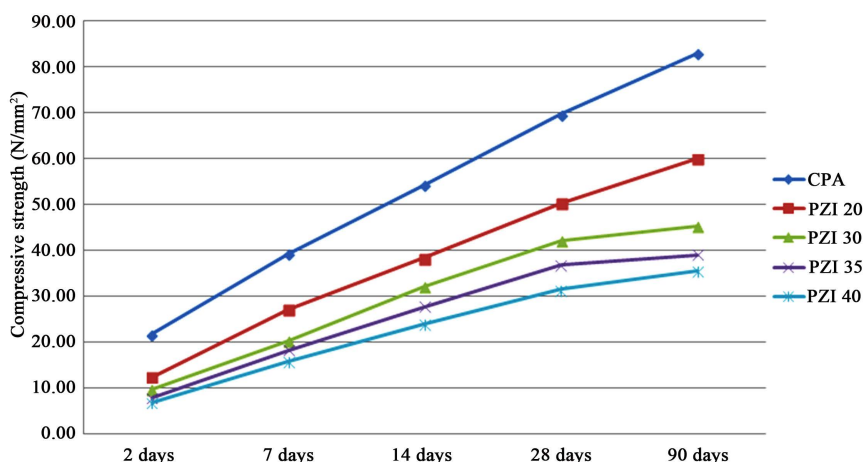


Figure 8. Compressive strength of cements.

Table 5. Chemical constituents of blended cements.

Cements	LOI	IR	SiO ₂	SO ₃	CaO	MgO	Fe ₂ O ₃	Al ₂ O ₃	Total
PC	1.72	0.32	21.06	3.64	61.54	3.62	3.23	3.77	98.9
PZ20	2.53	6.85	32	3.21	39.17	2.58	4.92	7.01	98.27
PZ30	2.6	9.41	37.13	2.63	32.13	2.23	5.12	7.23	98.48
PZ35	2.9	11.2	39.12	2.6	27.23	2.1	6.31	7.32	98.78
PZ40	3.2	13.11	41.21	2.59	23.32	2.08	6.52	7.82	99.85

(IR: insoluble residue, LOI: Loss on ignition, CaO: free lime).

Table 6. Compressive strength of cements (N/mm²).

Cements	Days in water				
	2 days	7 days	14 days	28 days	90 days
PC	21.8	39.2	54.2	69.7	82.9
PZI 20	12.5	27.1	38.4	50.4	60.0
PZI 30	9.7	20.3	32.1	42.2	45.2
PZI 35	7.9	18.3	27.8	36.8	39.1
PZI 40	7.0	15.9	24.1	31.5	35.5

thermal method consists in heating the material at 800°C - 900°C before the addition and grinding with the PC. The chemical method [42] is to activate the pozzolanic reaction with chemical activators such as Na₂SO₄ and CaCl₂.

5. Conclusions

For the first time, the volcanic tuffs of Mako area in Senegal-Oriental are used to the pozzolanic activity. They are altered but they have physical and chemical characteristics of pozzolans. The time of grinding to obtain pozzolanic cements decreases with the addition of volcanic tuffs, significantly reducing the costs. So, the addition of volcanic tuffs could reduce the production of clinker, which may

significantly reduce CO₂ emissions in the atmosphere. The pozzolanic activity of the volcanic tuffs of Mako area has been shown by the compressive strength which increases until 90 days of conservation in water. In fact, the active silica from the volcanic tuffs reacts with the free lime of clinker to produce new hydrated minerals which participate in the increasing of the compressive strength.

For perspectives, the pozzolanic activity of the volcanic tuffs of Mako area could be improved by thermal method or chemical method using Na₂SO₄ or CaCl₂.

Acknowledgements

The authors thank SOCOCIM Industry for allowing us to realize chemical and mechanical test of the raw materials and cements and its financial support.

Conflicts of Interest

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

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